# REMOVAL OF CHROMIUM AND PHENOL FROM SINGLE AND BINARY SIMULATED SYNTHETIC TANNERY WASTE WATER

**Ph.D. THESIS**

*by*

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**ROORKEE - 247 667 (INDIA)**
**MARCH, 2016**

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A THESIS

*Submitted in partial fulfilment of the*
*requirements for the award of the degree*
*of*

DOCTOR OF PHILOSOPHY

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# INDIAN INSTITUTE OF TECHNOLOGY ROORKEE ROORKEE

## CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"REMOVAL OF CHROMIUM AND PHENOL FROM SINGLE AND BINARY SIMULATED SYNTHETIC TANNERY WASTE WATER"** in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy and submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from July, 2012 to March, 2016 under the supervision of Dr. Chandrajit Balomajumder, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee India.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

**(Ankur Gupta)**

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

**Date:** March……. , 2016 (CHANDRAJIT BALOMAJUMDER)
Supervisor

The Ph.D. Viva-Voce Examination of **Mr. ANKUR GUPTA**,
Research Scholar, has been held on ………………

**Chairman, SRC** **External Examiner**

This is to certify that the student has made all the corrections in the thesis

**Supervisor** **Head of the Department**

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″Sever the ignorant doubt in your heart with the sword of self-knowledge. Observe your discipline. Arise **″.**

***-Bhagwat Geeta***

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# ABSTRACT

With the increase in industrialization worldwide, industries such as electroplating, leather tanning, textile, paints and pigments discharge toxic effluent, which contains Cr(VI) and organic matter like phenol (Gupta et al. 2015; Song et al. 2009). Both chromium and phenol are used in tanneries in the tanning process for the manufacturing of leather (Munz et al. 2009; Srivastava et al. 2007). Simultaneous removal of Cr(VI) and phenol is a matter of concern for the industries such as tanneries, photographic-film production, preservation of wood, manufacturing of car, petroleum refining and agricultural production because Cr(VI) and organic pollutants like Phenol, naphthalene are discharged simultaneously from the waste effluent of these industries. Two stable oxidation states of chromium such as trivalent [Cr(III)] & hexavalent [Cr(VI)] are found in the environment. Cr(VI) is in the form of chromate ($CrO_4^{2-}$) or dichromate ($Cr_2O_7^{2-}$) ions while Cr(III) is in the form of oxides, hydroxides or sulphates and less mobile than Cr(VI) but it can be oxidized to Cr(VI) (Thinh et al. 2013). Cr(III) is hazardous to the plants and living beings only at higher concentration and less toxic to animals or living beings while Cr(VI) is mutagenic and carcinogenic to the living organism. Cr(VI) enters into the human body causes epigastric pain, nausea, vomiting, severe diarrhea, corrosion of the skin, respiratory tract and lung carcinoma. Hence, removal of Cr(VI) from industrial effluents becomes necessary before its discharge to main water sources. Among the various harmful and toxic organic compounds like dyes, pesticides and fluorine, phenol is most toxic to the environment. Phenol is a weak biodegradable and toxic aromatic compound and consumption of phenol causes various diseases such as gastrointestinal disorder, lung damage, liver disease, kidney disease, heart attack and finally death of living beings (Chaudhary et al. 2014). WHO (world health organization) sets the maximum permissible limit for Cr(VI) and phenol as 0.05 and 1 mg/L, respectively (Vlyssides et al. 1997; Chaudhary et al. 2014). Various methods are developed for the removal of toxic metals and organic compounds from waste effluent such as oxidation-reduction (Dittert et al. 2014), electro coagulation (Hamdan et al. 2014), reverse osmosis (Lin et al. 2014), evaporation (Sun et al. 2011), ion exchange (Cavaco et al. 2015), photocatalytic oxidation (Gupta et al. 2012; Saleh et al. 2012), elecrokinetic remediation (Sawadaa et al. 2004) etc. But these methods are associated with various disadvantages such as high energy and chemical requirements, low efficiency and generate large amount of sludge (Ahmaruzzaman et al. 2011). Therefore there is a need for the development of method which overcomes theses problems. Biological treatment of toxic metal and organic compounds from wastewater is a new emerging technology, does not produced

secondary waste and cost effective but yet to be established and commercialized (Dash et al. 2008). Biosorption of toxic pollutant using agricultural waste material is a low cost technology, high selectivity and efficiency of removal of pollutant used for the removal of heavy metal and organic compounds from industrial wastewater (Uluozlu et al. 2008). Various methods are used for the analysis of Cr(VI) and phenol such as on-line flame atomic absorption spectrophotometry, UV spectrometric method, inductively coupled plasma mass spectrometry (ICP-MS) (Saracoglu et al. 2002; Sadaf et al. 2014). In the present study, single component and binary synthetic simulated wastewater was prepared in the laboratory. The residual concentration of Cr(VI) and phenol of these water samples were analyzed through the UV spectrophotometer (HACH DR 5000). The 1, 5 diphenyl carbazide method at a wavelength (λ) of 540 nm was used for analysis of Cr(VI) and 4 amino antipyrene method at wavelength of 510 nm was used for the analysis of phenol. The work has been divided into four sections, namely (i) application of adsorption and simultaneous adsorption and bioaccumulation of Cr(VI) and simultaneous adsorption and biodegradation of phenol from single and binary solution, (ii) application of continuous reactor system for simultaneous removal of Cr(VI) and phenol (iii) application of phytoremediation using water hyacinth.

*i) Application of adsorptive system for single and multicomponent system:* Agricultural waste products such as tea waste (TW), Rice husk (RH), Bagasse (BG), Bagasse fly ash (BFA), Distillery sludge (DS), Neem leaves (NL), Fe treated tea waste (Fe TW) and Fe treated rice husk (Fe RH) and granular activated carbon (GAC) were selected as adsorbents for adsorption studies for the removal of Cr(VI) and phenol from single component synthetic simulated solution. GAC is used in the present study as control since it has been widely used in the removal of number of heavy metals from the effluent of industrial wastewater, reported in literature. The best adsorbent selected from single component solution for the removal of Cr(VI) and phenol were used for the simultaneous removal of Cr(VI) and phenol from binary solution. For characterization proximate, ultimate, SEM-EDX, FTIR and BET surface area, were performed. The surface modifications of the selected adsorbents by iron impregnation were performed in order to increase the capacity of the adsorbents for the removal of Cr(VI) and phenol from single component and binary solution. Optimization of process parameters viz. pH, contact-time, temperature, adsorbent dosage and initial concentration were performed. Tea waste, Rice husk, Fe treated tea waste, Fe treated rice husk and GAC were proved to be best adsorbent out of all above adsorbents used for the adsorption studies for the removal of Cr(VI) and phenol from single component and binary solution. Single and multicomponent adsorption isotherm models such as Langmuir, Freundlich, Temkin, Redlich, Non modified Langmuir, Modified Langmuir, Extended Langmuir, Extended Freundlich, Non modified Redlich Peterson, Modified Redlich Peterson were applied to the experimental data for the prediction of the adsorption capacity of Cr(VI) and phenol from single and binary solution. The parameters obtained from single component solution were used for the estimation of multicomponent adsorption isotherm parameters. The interactive effect such as synergist and antagonistic was determined for the multicomponent system for simultaneous removal of Cr(VI) and phenol. RSM (Response surface methodology) using Box Behnkin design was also applied to the best adsorbent among binary component system to know the interactive effect of process parameters such as pH, adsorbent dose and contact time and initial concentration of Cr(VI) and phenol. To know the kinetics of adsorption of Cr(VI) and phenol from single and binary solution onto the surface of various adsorbents kinetic models such as pseudo first order, pseudo second order and intra particle diffusion model were applied. The thermodynamic study was carried out for both single and multicomponent system, which showed the feasible and spontaneous nature of the sorption of Cr(VI) and phenol species onto the selected adsorbents.

*ii) Application of SAB system for single and multicomponent system:* Two bacterial strain (*Escherichia* coli MTCC No. 5041) and (*Bacillus* sp. MTCC No. 3166) was purchased from MTCC Chandigarh and NCIM pune, India, respectively. The bacterium *Escherichia* coli and *Bacillus* sp. was acclimatized to the various concentrations of Cr(VI) and phenol using single and binary synthetic simulated solution prepared in the laboratory. Monod and Haldane kinetics models are used to explain the kinetics of Cr(VI) reduction and Phenol degradation for single component solution. The sum of kinetic model was applied to the binary system for the estimation of interaction parameters for Cr(VI) and phenol. The Bacterial strain *Eischerichia coli* was capable of removing Cr(VI) while *Bacillus* sp. was capable of removing both Cr(VI) and phenol from both single and binary solution. SAB studies were performed in batch reactor under optimum conditions of temperature and pH by immobilizing the bacterium onto the surface of best adsorbent (GAC, TW and RH) selected from batch adsorption studies for single component system and (TW) for multiocomponent system.

*iii) Application of continuous reactor system for simultaneous removal of Cr(VI) and phenol:* The continuous reactor study was carried out for simultaneous removal of Cr(VI) and phenol by packing best adsorbent tea waste biomass selected from batch adsorption study in the packed bed column. Various kinetic models such as Adams Bohart, Wolborska and Yoon nelson were applied to the experimental data. The bacterium used in SAB study such as *Bacillus* sp. and *Escherichia coli* was also immobilized onto the surface of adsorbent bed in packed bed reactor for the simultaneous removal of Cr(VI) and phenol from synthetic simulated waste water prepared in the laboratory. The simultaneous removal of Cr(VI) and phenol from real industrial waste water is also a need of the demand of process industries therefore simultaneous removal from the discharge of effluent of various industries such as tannery, electroplating, pulp and paper is also required. The 99 % removal of Cr(VI) and phenol was obtained at initial concentration of 2000 mg/L of Cr(VI) and 1000 mg/L of phenol by immobilizing bacterial species onto the surface of packed bed. RTD (residence time distribution study) was also carried out to know the deviation from ideal plug flow behaviour of the reactor. The flow model of real reactor is usually lies somewhere between plug flow and mixed flow. The reason for the deviation from the ideal condition is the recycling of the fluid or the creation of stagnant region or channeling of fluid in the reactor. Therefore, the determination of fluid velocity distribution is important for the economic design of the reactor. Consequently, for the velocity distribution better understanding of fluid particles within the reactor to study the distribution of the residence time (RTD) is important because it determines the way in which an individual molecule passes into a reactor.

*iii) Application of phytoremediation for removal of Cr(VI) and phenol from single and binary solution*: Phytoremediation is an alternative technology to remove Cr(VI) and phenol species in contaminated water and soil. In this study the assessment and mechanism for Cr(VI) and phenol species uptake and accumulation in water hyacinth was conducted under optimized hydroponic system. The aquatic macrophyte such as water hyacinth (*Eichhornia crassipes*) was used for the uptake of two important pollutants Cr(VI) and phenol from single and binary solution. Artificial photosynthesis chamber was used for the growth of plant at 30 ºC and 60% relative humidity. Experiments were carried out at four concentrations 5, 10, 15 and 20 mg/L of Cr(VI) and 10, 20, 30, and 40 mg/L of phenol in both single and binary mixtures of Cr(VI) and phenol, respectively. The FTIR and EDX analysis was carried out to confirm the uptake of Cr(VI) and phenol. The uptake of Cr(VI) was found more in the presence of phenol which shows the synergistic effect for the removal of Cr(VI). It could be because phenol was used as carbon or carbohydrate energy source by the plant at more stressed condition. In case of both single and binary solution, toxic effect was observed at 20 mg/L of Cr(VI). The toxic effect on the plant was determined by estimating chlorophyll, protein and sugar content before and after uptake of Cr(VI) and phenol form single and binary solution. Michaelis-Menten kinetic was applied by calculating the chlorophyll content at different concentration of Cr(VI) and phenol in single and binary solution to determine the kinetic behaviour of the plant for different growth stages of water hyacinth plant. The residual concentration of Cr(VI) and phenol and chlorophyll content  was determined using UV spectrophotometer.


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# ABBREVIATIONS AND NOTATIONS

## ABBREVIATIONS

| | |
|---|---|
| AAS | Atomic absorption spectroscopy |
| ANOVA | Analysis of variance |
| ARE | Average relative error |
| BG | Bagasse |
| BFA | Bagasse fly ash |
| BET | Brunauer-Emmett-Teller |
| BCF | Bioconcentration factor |
| CC | Central composite |
| CPCB | Central pollution control board |
| CV | Coefficient of variation |
| DS | Distillery sludge |
| DNA | Deoxyribonucleic acid |
| DF | Degree of freedom |
| DOE | Design of experiments |
| EDX | Energy dispersive X-ray |
| EPA | Environmental protection agency |
| Fe TW | Fe treated tea waste |
| Fe RH | Fe treated rice husk |
| FTIR | Fourier transform infrared spectroscopy |
| GAC | Granular activated carbon |
| MCL | Maximum contaminated level |
| MPSD | Marquardt’s percent standard deviation |
| NB | Nutrient broth |
| NL | Neem leaves |
| N | Number of observations in the experimental isotherm |
| OD | Optical density |
| P | Number of parameters |
| RH | Rice husk |
| RSM | Response surface methodology |
| SAB | Simultaneous adsorption and bioaccumulation |
| SEM | Scanning electron microscopy |
| RMSE | Root mean squares of error |
| RGR | Relative growth rate |

| | |
|---|---|
| Std. Dev | Standard deviation |
| USEPA | United States Environmental Protection Agency |
| TW | Tea waste |
| WHO | World Health Organization |
| XRD | X-ray diffraction |

# NOTATIONS

| | |
|---|---|
| $C_o, C_i$ | Initial concentration of adsorbate in solution, mg/l |
| $C_e$ | Equilibrium liquid phase concentration, mg/l |
| $C_t$ | Equilibrium liquid phase concentration after time t, mg/l |
| $C_{ei}$ | Concentration of $i^{th}$ component in the binary mixture at equilibrium (mg $L^{1}$) |
| $C_i / C_o$ | Normalized concentration |
| $S$ | Substrate concentration |
| $a_R$ | Constant of Redlich-Peterson isotherm, l/mg |
| $q_e$ | Equilibrium adsorption capacity, mg/g |
| $q_t$ | Equilibrium adsorption capacity after time t, mg/g |
| $q_{max}$ | Maximum adsorption capacity of adsorbent, mg/g |
| $q_{e,i}$ | Amount of $i^{th}$ component adsorbed per gram of adsorbent at equilibrium (mg $g^{-1}$) |
| $q_{e,i}^{exp}$ | Experimental specific uptake (mg $g^{-1}$) |
| $q_{e,i}^{cal}$ | Calculated specific uptake (mg $g^{-1}$) |
| $q_{i,total}$ | Total amount of component ‘i’ adsorbed by the column, mg |
| $q_o$ | Equilibrium metal sorption, (mg/g) |
| $Q_{mix}$ | adsorption capacity of one adsorbate in mixture(mg $g^{-1}$) |
| $Q_o$ | adsorption capacity of one adsorbate when present alone(mg $g^{-1}$) |
| $Q_{o,i}$ | Constant in modified Langmuir model for $i^{th}$ component (mg $g^{-1}$) |
| Q | Volumetric flow rate (mL/min) |
| $k_1$ | Pseudo 1st order rate constant, $min^{-1}$ |
| $k_2$ | Pseudo-second-order rate constant, g/mg.min |
| $K_{id}$ | Intra-particle diffusion rate constant, mg/g $min^{1/2}$ |
| $K_R$ | R-P isotherm constant, l/mg |
| $K_F$ | Freundlich constant, l/mg |
| $K_{F,i}$ | Constant in extended freundlich constant for $i^{th}$ component (mg $g^{-1}$)/(mg $L^{-1})^{1/n}$ |

| | |
|---|---|
| $K_c$ | Equilibrium constant (amount of adsorbate on adsorbent/amount of adsorbate in solution), |
| $k_{AB}$ | Kinetic constant (L/ mg min) |
| $k_{Th}$ | Thomas rate constant, (mL $mg^{-1}$ $min^{-1}$) |
| $k_{YN}$ | Rate constant ($min^{-1}$) |
| $K_S$ | Half velocity constant, or saturation constant, or Monod constant (g/L) |
| $K_i$ | Haldane inhibitory constant |
| $m_{i,total}$ | Total amount of component ‘i’ sent to the column, mg |
| $1/n$ | Mono-component (non-competitive) Freundlich heterogeneity factor of the single component, dimensionless |
| $K_L$ | Langmuir adsorption constant, L/mg |
| $B$ | Temkin adsorption constant, L/mg |
| $b_i$ | Langmuir constants for individual components |
| $\eta_i$ | Correction factor for ‘i’ component. |
| A | Temkin isotherm constant |
| $K_{RP}$ | Redlich Peterson isotherm constant (L $g^{-1}$) |
| $E$ | Mean free energy of sorption per molecule of the sorbate, kJ/mol |
| $T$ | Temperature, $^oC$ or $K$ |
| $^oC$ | Degree Celsius |
| $t$ | Time, min or hour |
| E | Exit age distribution, $time^{-1}$ |
| $\tau$ | Time required for 50 % breakthrough (min) |
| $t_{total}$ | Total flow time, (min) |
| $U_0$ | Superficial velocity (m/ min) |
| $V$ | Volume of the solution, L |
| $V_{eff}$ | Effluent Volume, (mL) |
| $W$ | Mass of the adsorbent, g/L |
| $R^2$ | Correlation coefficients |
| $k$ | Rate constant, $min^{-1}$ |
| $R$ | Universal gas constant, 8.314 J/mol K |
| $R_L$ | Separation factor |
| $q_{e,cal}$ | Calculated value of solid phase concentration of adsorbate at equilibrium, mg/g |
| $q_{e,\exp}$ | Experimental value of solid phase concentration of adsorbate at equilibrium, mg/g |
| $f$ | Response function |
| $Y$ | Response (% Removal) |

| | |
|---|---|
| $X_n$ | Number of factors (in RSM study) |
| $c_p$ | Number of central points |
| $x_1, x_2 \ldots\ldots, x_k$ | Variables |
| $x_i$ | Coded value of the *i*th variable |
| $X_i$ | Uncoded value of the *i*th test variable |
| $X_{min}$ | Lowest limits of the $i^{th}$ variable |
| $X_{max}$ | Highest limits of the $i^{th}$ variable |
| $X$ | Mass of packing material in the column |
| $x_i$, $y_i$, $z_i$ | Constant in extended freundlich model for the $i^{th}$ component |
| R | Universal gas constant  8.31541 J/(mol K) |
| $D$ | Axial diffusion coefficient ($m^2$/min) |
| *Chl a and b* | *Chlorophyll a and b* |
| $V_{max}$ | maximum rate of arsenic uptake by wheat plant, µg/g h |
| Z | Height of the column (m) |
| M | Units of tracer introduced (g or moles) |
| $N_o$ | Saturation concentration of column (mg/L) |

# GREEK LETTERS

| | |
|---|---|
| $\alpha_o$ | Intercept coefficient |
| $\alpha_i$ | Linear coefficients |
| $\alpha_{ii}$ | quadratic coefficients |
| $\alpha_{ij}$ | Interaction term |
| $\beta$ | Exponent ($0< \beta <1$) (in Redlich-Peterson isotherm) |
| $\beta_a$ | Kinetic coefficient of external mass transfer ($min^{-1}$) |
| $\beta_0$ | External mass transfer coefficient with negligible D ($min^{-1}$) |
| $\Delta S^o$ | Entropy change of adsorption, kJ/mol.K |
| $\Delta H^o$ | Enthalpy change of adsorption, kJ/mol |
| $\Delta G^o$ | Gibbs free energy of adsorption, kJ/mol |
| $\rho_L$ | Density, $kg/m^3$ |
| µ | Specific growth rate $h^{-1}$ |
| $\mu_m$ | Maximum specific growth rate, ($h^{-1}$) |
| $\mu_L$ | Liquid viscosity, kg/m.s |

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# *Chapter – I*

# INTRODUCTION

## 1.1 General

Industrial pollution is a potential threat affecting the water bodies, soil and air, which ultimately affects the whole ecosystem. Due to urbanization and modernization there is an increase in the number of industries. The non-biodegradable heavy metals and organic compounds released from various industries entered into a water stream. These toxic pollutants not only cause water pollution by entering in rivers, lakes, oceans and other surface water bodies, but also cause air, soil and other types of pollution (Dasgupta et al. 2015). Natural water resources are mostly contaminated with various heavy metals like Cr(VI) and toxic organic matters like phenol. Therefore, the treatment of waste effluent containing heavy metals and organic compounds is required. The wastewater containing various heavy metals such as As, Zn, Cu, Ni, Pb, Cd and Cr and organic compounds such as phenol, naphthalene and trichloroethylene discharged from various chemical industries contaminate the ground water. Among these heavy metals and organic compounds, pollution caused by chromium (Cr) and phenol ($C_6H_5OH$) is of considerable concern because these are used in several industries such as electroplating, leather tanning, textile, paints and pigments, paper, wood preservation and car manufacturing units and highly toxic (Song et al. 2013; Lin et al. 2009; Garg et al. 2013; Gunasundari et al. 2013; Reddy et al. 2011). Both chromium and phenol is found in high concentrations in tannery in the range of 200-1000 mg/L and 100-500 mg/L, respectively. The US Environmental protection agency (US EPA) recommends the maximum permissible limit for the discharge of Cr(VI) and phenol from industrial waste water as 0.05 mg/L and 1 mg/L, respectively (Tziotzios et al. 2008). Chromium occurs in aqueous system in two oxidation states trivalent [$Cr^{3+}$ and $CrOH^{2+}$] and hexavalent [$HCrO_4^-$ and $Cr_2O_7^{2-}$] out of which hexavalent chromium is most toxic, carcinogenic and mutagenic to the living organism (Garg et al. 2009; Park et al. 2011). Trivalent, Cr(III) is oxidized to hexavalent, Cr(VI) which is more mobile and toxic. Cr(VI) entered into the human body causes respiratory tract and lung carcinoma, epigastric pain, vomiting, nausea, corrosion of the skin and severe diarrhoea. Among the various harmful and toxic organic compounds like dyes, pesticides and fluorine, phenol is most toxic to the environment (Pilli et al. 2014). Phenol is toxic aromatic organic compound and weak biodegradable pollutant. Exposure of phenol causes gastrointestinal disorder, lung damage, liver damage, kidney damage, heart attack and finally can lead to death (Chaudhary et al.

2014). Hence, removal of Cr(VI) and phenol from industrial effluents become necessary before its discharge in to main water stream. The traditional methods used for the removal of Cr(VI) and phenol from industrial wastewater are chemical reduction, reduction followed by chemical precipitation, adsorption on activated carbon (Agarwal et al. 2013), solvent extraction (Yang et al. 2006), reverse osmosis (Lin et al. 2014), oxidation-reduction (Dittert et al. 2014), electro-coagulation (Hamdan et al. 2014), evaporation (Sun et al. 2011), ion exchange (Cavaco et al. 2007), photocatalytic oxidation (Gupta et al. 2012; Saleh et al. 2012), electrokinetic remediation (Sawadaa et al. 2004; Reddy et al. 2003), catalyst and phytoremediation (Alkorta et al. 2001; Fritioff et al. 2003) but these processes are expensive, non-economic, high energy consumption and discharge of secondary waste which again pollute the water bodies. Biosorption is a low cost technology used for the removal of heavy metals and organic compounds from industrial waste water (Uluozlu et al. 2008; Garg et al. 2004; Ahmad et al. 2009). In comparison to these conventional treatment methods, biosorption is ecofriendly, cost effective, has high efficiency and selectivity and easy removal of heavy metals can be obtained (Bhatti et al. 2014). Nowadays with the advances in biotechnology, the use of microorganisms comes out with an alternative method for the removal of heavy metals and organic compounds. The bio-removal of heavy metals and organic compounds is ecofriendly and have the potential for the complete removal of heavy metals and toxic organic compounds, respectively under aerobic and anaerobic conditions and cheaper in comparison to others conventional methods (Habibi et al. 2013). Combination of adsorption and biological methods i.e. the simultaneous adsorption and bioaccumulation of Cr(VI) and simultaneous adsorption and biodegradation of phenol offers certain benefits being highly cost effective and involving less or no generation of secondary waste. As toxic pollutant is completely consumed by the microbes therefore these methods are not associated with the problem of production of secondary waste generation (Zahoor et al. 2009). The concept of zero waste is the conversion of waste product of industries into the value added products (Singh et al. 2011; Kuila et al. 2014; Babu et al. 2010). But in industries, large amount of waste effluent is produced containing high concentration of Cr(VI) and phenol therefore for the need of the demand of process industries continuous simultaneous removal of Cr(VI) and phenol is required. Thus, for this purpose a continuous-flow packed bed column is required for the full-scale biosorption of pollutant Cr(VI) and phenol. Continuous bioreactor have certain advantages over others conventional treatment technologies such as high percentage removal of pollutant, convenient to operate and can be easily scaled up from laboratory pilot plant to industrial scale (Caravelli et al. 2009). Therefore, technology developed in batch process can be applied in continuous column reactor. The water harvesting in industries is important for the economic point of view (Khan et al. 2008; Sherif et al. 1999). The treated effluent discharged from various industries often does not meet the prescribed limits by the regulatory agencies and contaminates the fresh water bodies of the industrial region. Moreover phytoremediation of toxic pollutant using aquatic macrophyte at the discharge site overcomes these problems in aqueous phase (Speranza et al. 2007). Aquatic macrophytes are free-floating plants having large hairy roots and can easily grow in polluted wastewater (Mishra et al. 2009). It can grow very fast, having high pollutant uptake capacity and constant relatively growth rate (Maine et al. 2001).

## 1.2 Problem Identification

Availability of drinking water free from toxic heavy metals and organic compounds is worldwide concerned. There are several industries such as electroplating, tannery, textile, paper, paints and pigments, wood preservation, car manufacturing which discharged Cr(VI) and phenol simultaneously from waste effluent. Therefore treatment of waste effluent discharge by these industries containing heavy metal and organic compound is necessary. Till date there are no proven technologies available for the efficient simultaneous removal of Cr(VI) and phenol from waste water. Available technologies in literature are non-conventional and costly and cannot be affordable for the rural areas. Therefore there is a need of development of technology which is cost effective and environment friendly. These methods have several problems such as high energy and chemical requirements, low efficiency and produce a large amount of sludge (Ahmaruzzaman et al. 2011). Among these methods adsorption of heavy metals and organic compounds onto the surface of granular activated carbon (GAC) and carbon nanotube material is conventional method, but not cost effective (Dash et al. 2008; Salam et al. 2014; Saleh et al. 2012; Saleh et al. 2014; Gupta et al. 2011). Development of activated carbon using various low cost biosorbent is also well known technique for adsorption of heavy metals and organic compounds (Gupta et al. 1997). Biological treatment is a cost effective technology but due to its low efficiency for the removal of heavy metal and organic compound need to be established and commercialized (Ahmaruzzaman et al. 2011). Biosorption using low cost biosorbent or using the waste product of industries such as fly ash, sludge, bagasse, pressmud for the adsorption of toxic pollutant is a low cost technology used for the removal of heavy metal and organic compound from industrial waste water (Uluozlu et al. 2008). In comparison to other conventional treatment method adsorption of heavy metal and organic compound using low cost biosorbent is ecofriendly, cost effective, high efficient and selective and thus easy removal of toxic pollutant can be obtained (Bhatti et al. 2014). Phytoremediation of heavy metals and organic compounds at the discharged site of toxic pollutant for various industries is also necessary to meet the permissible limit. Most of these technologies explained above are not only expensive but cannot bring down the contamination level below the regulatory level set by various environmental agencies. Some of the technologies are not attractive for the regeneration of the system, poor efficiencies, secondary sludge disposal problems, expensive operating and initial cost, not affordable and not accessible to contaminated water bodies. Therefore for the industrial application of these technologies it is required that these are cost effective, high efficiency of removal, regeneration of the system can be obtained. Therefore continuous treatment of the pollutant in continuous reactor is essential for the efficient treatment of industrial waste water. With the view of above, following objectives have been framed.

## 1.3 Objectives of the present study

Due to rapid industrialization there is a negative consequence on the environment, which affects from human beings to even flora and fauna. Effluents discharged from the various industries contaminate ground water, surface water and other sources of drinking water. Therefore the treatment of toxic pollutants is essential. In the present work simultaneous removal of Cr(VI) and phenol from industrial waste water using single and binary synthetic simulated waste water containing Cr(VI) and Phenol (2:1) based on industrial waste water composition was carried out. Based on extensive literature review following objectives have been laid down:

1. Estimation/ and surface modification of the best adsorbent for the maximum individual and simultaneous removal of Cr(VI) and phenol from single and binary synthetic simulated waste water in batch process.
2. Simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol using consortium culture of *Escherichia coli* and *Bacillus* sp. in SBB (Simultaneous bioaccumulation and biodegradation) batch reactor.
3. Continuous study for simultaneous removal of chromium and phenol from synthetic simulated binary waste water in continuous flow packed bed reactor (PBCFR).
4. Extension of present study for the treatment of real industrial wastewater.
5. Phytoremediation of Cr(VI) and phenol from single and binary solution in artificial photosynthesis chamber using aquatic macrophyte water hyacinth (*Eichhornia crassipes*).

## 1.4 Organization of Thesis

The present thesis has been divided into the following chapters for the easy understanding of the subject matter. The present thesis is organized as follows:

### Chapter 1: Introduction

This chapter deals with the importance of topic, health effect, treatment technologies available, problem identification and objectives of the work.

### Chapter 2: Literature Reviews

This chapter deals with the review of all possible literature, published for the remediation of chromium and phenol from synthetic waste water, industrial waste water, solid waste and from soil using various methods such as adsorption, bio removal, SAB (simultaneous adsorption and bioaccumulation of chromium and biodegradation of phenol), continuous reactor study and phytoremediation.

### Chapter 3: Experimental setup and Instrumentation

This chapter deals with the experimental set up; equipment / instrument used for the present study.

### Chapter 4: Experimental Program

This chapter deals with the details of experiments conducted during the present work in sequential order.

### Chapter 5: Results and Discussions

This chapter describes the results and discussion part in brief as follows:

1. **Batch adsorption study:** Bath adsorption study has been carried out to investigate the adsorption capacity of various biosorbent for the simultaneous adsorption of Cr(VI) and phenol. The adsorption capacity of various biosorbent was also compared with reference to conventional adsorbent such as GAC (Granular activated carbon). Various single and multicomponent adsorption isotherm models were applied to the

experimental data to observe the nature of adsorption weather it is chemisorption or physiosorption. Kinetics of adsorption was also studied by applying the various kinetic models. Thermodynamic study was also carried out to investigate the feasible and spontaneous nature of the adsorption process.

2. **Bio-removal of Cr(VI) and phenol:** Bio-removal of Cr(VI) and phenol is an emerging technology for the bioremediation of Cr(VI) and phenol. In the present study two bacterium namely *Escherichia* coli and *Bacillus* sp. is proved to be potential bacterium for the removal of Cr(VI) and phenol. It was observed that Escherichia coli was able to consume Cr(VI) while Bacillus sp. can consume both Cr(VI) and phenol. Therefore consortium culture of both Cr(VI) and phenol was also used for the simultaneous bioaccumulation of Cr(VI) and biodegradation of phenol.

3. **SAB (Simultaneous adsorption and bioaccumulation of Cr(VI) and biodegradation of phenol):** The best biosorbent obtained from the batch adsorption study as described in section 1 was used for the SAB study. The bacterium Escherichia coli and bacillus sp. as described in section 2 was immobilized on to the surface of biosrobent. The advantage of using the SAB study is that there is no need for the regeneration of biosorbent as Cr(VI) and phenol adsorbed onto the surface of biosorbent is consumed by the bacterium Escherichia coli and Bacillus sp. The disadvantage of adsorption process is that after equilibrium condition when all the active sites are filled then saturation condition is reached and at this condition there is no adsorption of Cr(VI) and phenol. This disadvantage is overcome by SAB process as the toxic pollutant adsorbed in to the vacant sites of biosorbent is simultaneous consumed by bacterium therefore there is no limitations of active sites for the adsorption of pollutant.

4. **Continuous study:** Due to the need of the demand of process industries the continuous removal of Cr(VI) and phenol is required. The waste effluent containing Cr(VI) and phenol is discharged by various industries such as electroplating, pulp and paper, textile, wood preservation, automobiles and tannery. Out of which tannery industries discharge high concentrations of Cr(VI) and phenol. These industries discharge Cr(VI) and phenol in large quantities due to which continuous reactor is required for the continuous removal of Cr(VI) and phenol. Therefore the technology developed in the batch adsorption and SAB study is applied in continuous packed bed column. The

continuous reactor is capable of treating high concentration of Cr(VI) and phenol upto1000 mg/L.

5. **Phytoremediation study:** The waste effluent discharged by various industries does not meet the limit of the regulatory agencies. Therefore these have adverse effects onto the flora and fauna. It was observed that various macrophytes are grown easily at the discharge sites of various industries and river containing various heavy metals and organic compounds. Therefore in the present study the uptake capacity of aquatic macrophyte water hyacinth is tested for the removal of Cr(VI) and phenol. The toxic effects such as reduction in sugar, protein and chlorophyll contents of water hyacinth after uptake of Cr(VI) and phenol was also studied. The advantages of using phytoremediation study is its applicability for the uptake of Cr(VI) and phenol from soil.

### Chapter 6: Conclusion

This chapter deals with the detailed conclusion of the present study as described above.


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# CHAPTER-2

# LITERATURE REVIEW

## 2.0 Motivation

Industrial waste water vis-à-vis contaminated surface and ground water contain surface and ground water contain a large number of impurities. Before this removal, its chemistry, interaction with each other, and characterization are required to known along with the available treatment/removal technologies. These motivate the review of the literatures and inclusion of this chapter in the thesis. Ultimately, this formulates the objectives.

## 2.1 Introduction

There are various industries such as tanneries, photographic-film production, preservation of wood, manufacturing of car, petroleum refining and agricultural production, electroplating industries which discharge Cr(VI) and phenol as major pollutants (Saracoglu et al. 2002; Sadaf et al. 2014). Out of which tannery waste characteristically consists of complex mixture of both organic and inorganic pollutants such as Cr(VI) and phenol and releases high concentration of chromium and phenol in surrounding water bodies. In the tanneries, chemical processes such as tanning are used for the conversion of animal hides and skin into leather and related products (Bini et al. 2008; Katsifas et al. 2004). For one kilogram of hides processed, 30 litres of effluent is produced and the total quantity of effluent discharged by Indian industries is about 50,000 $m^3$/day (Midha et al. 2008). Leather and tanning industries cause a severe hazardous impact on water bodies, terrestrial and atmospheric systems due to its toxic chemical constituents, high oxygen demand and discolouration capacities (Song et al. 2000; Song et al. 2003). Tannery wastewater comprises of various pollutants such as chromium and phenol, which are more toxic than other pollutants. Therefore, it is essential to study the toxic nature and characterization of such wastewater and identification of various potential remediation technologies. There are various physico-chemicals, biological and combinations of various methods are available for the treatment of tannery wastewater (Mwinyihija 2007).

Various treatment technologies have been developed in recent years for the treatment of industrial wastewater comprising toxic metal ions and organic pollutants in order to improve the amount and quality of the treated wastewater discharged from various industries (Gunda et al.

2014; Sarkar et al. 2015). Although various physico-chemical treatment methods such as chemical precipitation, coagulation-flocculation, adsorption, flotation, ion exchange and membrane filtration are developed for the removal of heavy metal ions and organic compounds from industrial waste water, all these processes have their advantages and disadvantages in application such as production of secondary waste, high cost and sludge disposal. In recent years based on environmental and economic point of view, there is a need for the development of agro-based adsorbents to replace the conventional adsorbents (Chandra et al. 2015). Various physical and chemical properties of Cr(VI) and phenol is given in table 2.1.1 and table 2.1.2, respectively.

**Table 2.1.1: Properties of Cr(VI) [EPA, 2002]**

| **Property** | **Information** |
|---|---|
| Molecular weight | 0.051996 kg/mol |
| and Atomic number | 24 |
| Colour | Silver grey |
| Physical state | Lustrous, brittle, hard metal |
| Density | 7190 kg/m$^3$ at 293.15 K |
| Melting point | 2180.15 K |
| Boiling point | 2945.15 K |
| Ionic radius | 0.063 nm |
| Electro negativity | 1.59 |

**Table 2.1.2: Properties of Phenol [EPA, 2002]**

| **Property** | **Information** |
|---|---|
| Molecular weight | 0.094111 kg/mol |
| Colour | Colourless to pink |
| Physical state | Crystalline solid, liquid (8% $H_2O$ by wt) |
| Density | 1054.5 kg/m$^3$ at 293.15 K |
| Melting point | 314.13 K |
| Boiling point | 454.85 K |
| Odour | Distinct aromatic, somewhat sickening sweet |
| Solubility | a) In water at 298.15 K – 8.28 ×10$^4$ mg/L<br>b) Somewhat soluble in water and ethanol, very soluble in ether, miscible with acetone |

**2.2 Properties and major sources of Chromium:** Chromium is most commonly found in two oxidation state Cr(III) and Cr(VI) in the environment. Chromium is in a group of 6 elements with atomic number 24. It is hard, brittle, steel grey colour metal. Chromium is extracted from the chromite ore ($FeCr_2O_4$) which is iron chromium oxide and is the chief source of chromium. Environmental sources of chromium are cement dust, rocks, asbestos lining erosion, tobacco smoke and contaminated landfill. Cr(III) is nontoxic or toxic at higher concentration and immobile however it can be oxidized to Cr(VI) form which is mobile and more toxic in nature (Dakiky et al. 2002). Cr(VI) persists in the form of chromate and dichromate anions as $CrO_4^{2-}$ and $Cr_2O_7^{2-}$ under strong oxidizing conditions (Turan et al. 2007). In seawater, the concentration of chromium is found to be 0.6 ppb. The surface water concentration of chromium is estimated as 1 ppb. The degree of immobilization of chromium and rather successful proposed treatments depend on the general chemical processes acting on all systems in the subsoil (Hamadi et al. 2001). These processes include complex formation, surface sorption and precipitation. Chromium is entered into the natural bodies of water from process industries such as electroplating, leather tanning, cement industries, steel industries, photography, textile, pulp and paper, aluminium operation conversion coatings, steel manufacturing, spinning, weaving, paints, dyes, paper, ink, metal cleaning and fertilizer industries, imaging and wood preservation caused environmental problems and public health severe (Ackerley et al. 2004; Rengaraj et al. 2001). Among all these industries, the tannery wastewater contains very high concentration of chromium therefore the treatment of wastewater discharged through these industries is essential. Typical concentration of chromium discharged from various industries is given in table 2.2.

**Table 2.2: typical concentrations of chromium in various industrial wastewaters**

| Industry | Cr(VI) concentration (mg/L) | Reference |
|---|---|---|
| Hardware factory | 60.0 | Xu et al. 2005 |
| Chrome tanning plant | 3.7 | Gupta at al., 1999 |
| Electroplating plant | 215-3860 | Kongsricharoern et al. 1995 |
| Tannery plant | 1500-4000 | Balasubramanian et al. 1999 |

**2.3 Properties and major sources of phenol:** Among the listed priority pollutants according to the US Environmental Protection Agency (US EPA), phenol is a crystalline, colourles substance, possesses a characteristic odour and is soluble in water and organic solvents. It is extracted from coal tar and is formed by high quantities of plant cumene transformation. It can also be obtained by reacting chlorobenzene and sodium hydroxide, oxidation of toluene and synthesis from benzene and propylene. Hydroxybenzene (phenol) is also produced due to chemical reactions occurring in the atmosphere in condensed water vapour which form clouds during the natural processes such as biosynthesis in plants or decomposition of organic matter (Garg et al. 2013; Mukherjee et al. 2007). These components also penetrate the ecosystem through the drainage of industrial sewage and municipal water to the surface water. In recent years the phenol concentration is rapidly increasing in the environment which is a matter of serious concern as the toxic influence of phenols and its derivatives cause histopathological changes, mutagenicity and carcinogenicity (Phenols-sources and toxicity). According to Michalowicz and Duda 2007 (Phenols-sources and toxicity), exposure of phenol increased daily from 10-240 mg per person caused diarrhoea, dark urine, mouth sores, pain in the mouth. Therefore, treatment of phenol is mandatory before discharging phenol containing industrial effluent into the water bodies (Verma et al. 2006; Aksu et al. 2001).

Phenol is a soluble and volatile compound due to which it is generally found in surface water or ground water. Phenol is introduced into the surface water from industrial effluents of refineries, gasoline, coal tar, disinfectant, rubber proofing, textile, steel, pharmaceutical, petrochemical industries, plastic industries, agricultural run-offs, explosive manufacture, chemical spills and wood preservation plants (Rengaraj et al., 2002; Selvin et al. 2001). Other sources are household insecticide, plasticizers, lawn chemicals, consumer products, fiberglass units and related metallurgical operations. A typical concentration of phenol released by various industries is given in table 2.3.

**Table 2.3: Typical concentrations of Phenol in various industrial wastewaters**

| Industry | Concentration (mg/L) |
|---|---|
| Steel | 500-1000 |
| Petroleum refinery | 40-200 |
| Coal conversion | 1700-17000 |
| Textile | 100-200 |
| Petrochemical | 100-2200 |
| Leather | 4.4-5 |
| Paper and pulp | 22 |
| Phenolic resin | 1600 |

**2.4 Maximum permissible limits of chromium:** According to the guidelines recommended by WHO (World Health Organization) the maximum permissible limit of total chromium and Cr(VI) in drinking water is 2 mg/L and 0.05 mg/L, respectively. According to the US environmental protection agency the maximum permissible limit of chromium for the safe discharge is 0.1 mg/L for industrial waste effluent containing chromium (Karthikeyan et al. 2005; Vlyssides et al. 1997).

### 2.5 Maximum permissible limits of Phenol

The Ministry of Environment and Forest (MOEF), India and United States Environmental Protection Agency, (USEPA) constrained phenol as the toxic pollutant and its permissible limit for the safe discharge according to USEPA is below 0.05 mg/L (Tziotzios et al. 2008). The maximum permissible limit for the industrial effluent safe discharge is 1 mg/L. The World Health Organization (WHO) constrained the limit of phenol in drinking water is 0.001 mg/L (Chaudhary et al. 2014).

### 2.6 Industrial Sources of Cr(VI) and Phenol

Both Cr(VI) and phenol are found in waste effluent of a number of industries where they are either used or are generated as waste. The table 2.6 given below shows the few industries that discharge both Cr(VI) and phenol as effluents along with the standards of their discharge as per the Environment (Protection) rules, 1986 and Ministry of Environment and Forests. Simultaneous removal of Cr(VI) and phenol is a matter of concern because Cr(VI) and organic pollutants such as Phenol, naphthalene are discharged simultaneously from industrial effluent of tanneries, photographic-film production, preservation of wood, manufacturing of car, paints, paper, textile, petroleum refining and agricultural production (Song et al. 2009; Munz et al. 2009; Srivastava et al. 2007; Debadatta et al. 2012).

Table 2.6: Typical concentrations of effluent of various industries containing Cr(VI) and phenol

| **S. No.** | **Reference** | **Parameters** | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | BOD (mg/L) | COD (mg/L) | TSS (mg/L) | TDS (mg/L) | Sulfate (mg/L) | Phosphate (mg/L) | Potassium (mg/L) | Chloride (mg/L) | Total Nitrogen (mg/L) | TOC (mg/L) | Phenolic compounds (mg/L) | Total chromium (mg/L)) |
| 1. | chandra et al. 2009 | 8.3 ± 0.2 | 3650 ± 132 | 14216 ± 406 | 90.92 ± 4.2 | 113.12 ± 11.01 | 1519.9 ± 26.5 | 432.14 ± 10.06 | 256.26 ± 9.36 | 37.98 ± 5.02 | 287.92 ± 24.5 | | 9.38 ± 0.9 | 38.32 ± 3.24 |
| 2. | Costa et al. 2008 | 4 | - | - | - | - | - | - | - | 787 | - | 1005 | 47.3 | 49.8 |
| 3. | El-Sherif et al. 2013 | 3.28 | Zero | 4200 | 1564 | - | - | 5.5 | - | - | - | - | - | 1750 |
| 4. | Murugananthan et al. 2004 | 7.09 | 2250 | 4417 | 5080 | 10214 | 2400 | - | - | - | - | - | - | 44.6 |
| 5. | Vlyssides et al. 1997 | - | 210-4300 | 180-27000 | 925-36000 | - | 1-500 | - | - | 1500-28000 | 90-630 | - | 0.4-100 | 3-350 |
| 6. | Reemtsma et al. 1997 | - | - | - | - | - | - | - | - | - | - | - | 54 | 95 ± 55 |
| 7. | Ganesh et al. 2006 | - | - | 4800± 350 | 2820 ± 140 | - | - | - | - | - | 225 ±18 | - | - | - |
| 8. | Chandra et al. 2011 | 8.5 ± 0.17 | 2933 ± 126 | 12,466 ± 321 | 60,180 ± 246 | - | 6.65 ± 1.12 | 1.48 ± 0.23 | - | - | 578 ± 63 | - | 225 ±18 | 38.90 ± 13.16 |
| 9. | Rose et al. 2013 | 8.2 | - | - | - | - | 364 | 19 | - | 4048 | - | - | - | - |
| 10. | Tammaro et al. 2014 | 7.5 | - | 1186 | 758 | - | 570 | < 0.5 | - | 218 | 6.8 | - | 15.14 | 48.874 |
| 11. | Pandey et al. 2000 | 8.2 | 389 | 1300 | 11 | 72 | 1825 | 0.03 | - | 2800 | 147 | 235 | - | 14 |
| 12. | Houshyar et al. 2012 | 3.7 | - | 5470 | 1213 | 86, 700 | 15, 378 | 1.73 | - | - | - | - | - | 6900 |
| 13. | Costa et al. 2010 | 2.4 ± 0.1 | - | 2370 ± 30 | - | - | - | - | - | - | - | 756 ± 6 | 73 ± 2 | - |
| 14. | Anjali et al. 2014 | 7-8.5 | 1200-2700 | 3000-6000 | 2000-3000 | 10,000-21,000 | 1000-3000 | - | - | 6000-9500 | 250-400 | - | - | 60-75 |
| 15. | Elongovan et al. 2009 | 4.2 | - | 32 | - | - | - | - | - | - | - | - | - | 180.1 |
| 16. | Sahu et al. 2009 | 2.5 | 2200 | 4400 | - | - | 12000 | - | - | - | - | - | - | 4570 |
| 17. | Tammaro et al. 2014 | 7.5 | - | 1186 | 758 | - | 6800 | - | - | 2380 | - | 820 | - | 48.874 |

## 2.7 Various removal technologies for Cr(VI) and phenol

Various physic-chemical techniques employed for the removal of chromium and phenol include chemical precipitation, coagulation-flocculation, flotation, membrane filtration, reverse osmosis, ion exchange, adsorption on activated carbon, liquid extraction, and electrochemical treatment techniques, simultaneous adsorption and bioaccumulation, simultaneous adsorption and biodegradation, continuous packed bed reactor and phytoremediation. The brief descriptions of these methods are given in table 2.7. In general, unlike biological system, physic-chemical treatment methods have several advantages like easy to operate, high removal efficiency and can accommodate variable input loads, temperature and flows such as seasonal flows and complex discharge. In addition, the physic-chemical treatment systems require less space and installation cost (Kurniawan et al. 2006). The advantages and disadvantages of various treatment techniques are given in table 2.7.

Table 2.7 Advantages and disadvantages of various removal techniques

| Techniques | Material used | Advantages | Disadvantages |
|---|---|---|---|
| Adsorption | Activated carbon | 1. The most effective adsorbent; very high surface area<br>2. Porous sorbent; high capacity and high rate of adsorption<br>3. Fast kinetics; a high quality treated effluent is obtained | 1. Expensive; the higher the quality; the greater the cost<br>2. Performance is dependent on the type of carbon used<br>3. Requires complexing agents to improve its removal performance; nonselective; ineffective for disperse<br>4. High reactivation cost; reactivation results in the loss of carbon |
| | Chitosan | 1. Low cost natural polymer; environment friendly<br>2. Extremely cost effective; outstanding metal binding capacities; high efficiencies and selectivity in detoxifying both very dilute or concentrated solutions; excellent diffusion properties high quality treated effluent is obtained<br>3. Easy regeneration if required | 1. Nonporous sorbent; the solvent capacity depends on the origin of the polysaccharide and the degree of N-acetylation<br>2. Variability in the bead characteristics; pH dependence<br>3. Requires chemical modification to improve its performance |
| | Biosorbent | 1. Low cost; cost effective at low concentration<br>2. Less biological sludge | 1. Sensitivity to operating conditions like pH and ionic strength |

| | | | |
|---|---|---|---|
| | | production and optimal use of chemicals<br>3. Regeneration of bisorbents; no additional nutrient requirements; possibility of metal recovery | 2. Sensitivity to the presence of organic or inorganic ligands<br>3. Requirements of large amounts of biosorbent; replacement after 5-10 sorption-desorption cycles |
| | Inorganic membrane | 1. High chemical stability; high thermal stability<br>2. Less space requirement | 1. High cost; low surface<br>2. Membrane fouling |
| Filtration | Polymeric membrane | 1. Less pace requirement | 1. Low chemical and thermal stability<br>2. Membrane fouling |
| | Liquid membrane | 1. High selectivity; high diffusion rate<br>2. No sludge generation; less time consuming<br>3. Low energy demand | 1. Instability of SLM due to the loss of membrane liquid in to the aqueous phases; Emulsion swelling in ELM<br>2. Not all metal ion exchange resin is suitable for metal removal<br>3. High capital cost; requires tight operation and maintenance<br>4. Feed concentration must be monitored closely |
| | Reverse osmosis | 1. Recover concentrated metal salt solution for reuse. | 1. High priced equipment and/or expensive monitoring system<br>2. High energy requirement and sludge generation |
| Ion exchange | Membrane electrolysis | 1. Energy efficient<br>2. Low maintenance | 1. Solution concentration must be monitored<br>2. Solution heating encouraged to maximize efficiency |
| Electrochemical treatment | Electrochemical precipitation | 1. No additional chemical reagents required<br>2. High selectivity<br>3. Low cost | 1. Production of dendrite<br>2. Loose or spongy deposit<br>3. Production of sludge |
| Phytoremediation | Macrophytes | 1. The cost of the phytoremediation process is lower than that of the traditional processes<br>2. Easily monitoring of the plants<br>3. The pollutant cam be recovered by the plants<br>4. This process is not harmful or least harmful to the environment | 1. Phytoremediation of pollutant depends upon the surface area and the depth of the roots of the plants<br>2. This process is very slow in comparison to others traditional processes<br>3. The complete remediation of the pollutant is not possible by these methods<br>4. Survival of the plants is not possible at the higher level of toxic pollutant. |

### *2.7.1 Ion exchange Techniques*

In ion exchange process, there is a reversible exchange of metal ions between the solid and liquid phases. The insoluble substance (resin) is used for the removal of metal ions from an electrolytic solution without any morphological change of the resin. Among all the physicochemical treatment methods developed for the removal of heavy metal ions from industrial wastewater, ion exchange is an important method and becomes very popular in the recent years (Dabrowski et al. 2004).

### *2.7.2 Membrane filtration techniques*

Membrane filtration technique is a conventional method for the treatment of industrial wastewater. In this treatment method various types of membrane such as inorganic, polymeric and liquid membrane are used for the removal of heavy metal ions such as Cr(VI) (Kimura et al. 2002).

### *2.7.3 Electrochemical treatment techniques*

Electrochemical treatment techniques are mostly employed for the treatment of industrial wastewater because various industries produce non-biodegradable toxic waste and can be treated by a costly physicochemical pre-treatment method (Akbal et al. 2011).

### *2.7.4 Chemical reduction*

It is Conventional method for reduction of $Cr^{+6}$ to $Cr^{+3}$ with a suitable reducing agent. The most popular reducing agents for the reduction of Cr(VI) are sulphur dioxide gas and sodium metabisulfite. Alternative reducing agents includes sodium hydrosulfite, ferrous sulphate and iron or steel scrap. The efficiency of the reduction reaction is dependent on pH and mostly pH 2.0-3.0 is used for the reduction of Cr(VI) (Aravindhan et al. 2004).

### *2.7.5 Adsorption techniques*

Adsorption is the process where molecules or particles bind to a surface normally by covalent or van der waal’s forces and filling the pores in a solid. In adsorption, substance is bound at an interface of solid and fluid phases. Adsorption processes have been used since 1950s but these processes are been expanding recently due to new design of the systems and the development of new adsorbents. Adsorption processes are used on large-scale for solvent concentrations in the range of 10 to 10,000 mg/L. The solute removed from the liquid phase is called as adsorbate and adsorbent is solid phase in the process (Benjamin et al. 1981). Adsorption processes offers a complementary technique to available method. The adsorption can be used in purification, extraction and depollution. Physisorption is not specific and bound by weak forces between molecules. The adsorbed molecules are free to move over the surface and do not accumulate at a particular site on the solid surface (Sawyer et al. 1994). Chemical adsorption (chemisorption) is based on electrostatic chemical bond between molecules (Macaskie et al. 1998). Adsorption of an organic adsorbate occurs onto a non-polar adsorbent like carboneous material from polar solvent i.e. water in wastewater treatment. Non polar compounds are adsorbed more strongly to non-polar adsorbents by hydrophobic bonding therefore, are adsorb onto carbon more strongly (Banat et al. 2000).

Adsorbent is usually porous material on which compounds to be removed (adsorbate) diffuse and retained by some attractive forces on surface. The mostly used adsorbents for pollution control applications are as follows:

#### *2.7.5.1 Activated carbon*

Adsorption is a process in which substance is transferred from the liquid phase to the solid phase and bound there by physical and/or chemical forces. Adsorption onto the surface of activated carbon for wastewater containing heavy metals has become one of the alternative treatment techniques because of its large surface area and high adsorption capacity (Agarwal et al. 2013).

#### *2.7.5.2 Zeolites (Molecular Sieves)*

These are crystalline in nature with uniformity in pores of diameter. They have been largely used to remove moisture from exhaust streams, for separation of hydrocarbons in refinery and for removal of nitrogen oxide compounds from air. The separation of gases is based on molecular size and shape (Han et al. 2009).

#### *2.7.5.3 Synthetic Polymers*

They are formed from long chain polymers by cross linking. They have robust micro porous structure and high adsorption capacities for selective compound. They can be regenerated more rapidly and easily than activated carbon. It is also been used for gas streams containing high water vapour concentrations (>50 % relative humidity) because they are less prone to water vapour. Its main limitation is high cost (Serizawa et al. 1998).

### *2.7.5.4 Silica Gel*

Silica gels are made by adding sulphuric acid to sodium silicate resulting in formation of a jelly-like precipitant known as “gel”. This precipitant is then dried, roasted and different grades are produced. They are used preferentially for removal of moisture from exhaust streams. Silica gels are not effective above 500 °F (260 °C) temperatures (Chiron et al. 1998).

### *2.7.5.5 Biosorbent*

Biosorption is an emerging technology that uses biological materials for removing heavy metals from wastewater by adsorption. In the process of biosorption heavy metals and organic compounds are accumulated through metabolically mediated or physico-chemical pathways from wastewater. There is several mechanisms such as ion exchange, precipitation, chelation, sorption by physical forces and metals ion entrapment in inter and intra fibrillar capillaries, spaces of the structural lignin and polysaccharide networks for the adsorption of pollutants through biosorption. The biosorption process have several advantages over conventional treatment methods such as high efficiency, low cost, minimization of biological and/or chemical sludge regeneration of biosorbent, no additional nutrient requirement and the possibility of metal recovery (Elangovan et al. 2008).

## 2.8 Biological Treatment

Heavy metals can be easily remediated by the microbes but phenolic compounds have similar structure to herbicides and pesticides which are generally resistant to biodegradation, thus it is difficult to remove them by biological processes (Rengaraj et al. 2001). However, biochemical ways can be applied for phenol removal from wastewater (Galiatsatou et al. 2002). This method requires the action and use of living microorganisms. The microorganisms that can be used for biological treatment method must have the ability to utilize waste material and converting them into simple compounds by natural metabolism (Ghosh et al. 2014; Jeswani et al. 2012). Adsorption processes can be incorporated with the conventional biological treatment (Zulfiqar et al. 2011). The waste is carefully mixed with adsorbent, microorganisms and nutrients as required. The organic material is degraded in biological method, while inorganic materials can be taken up as in adsorption (Nathanson, 1997). Higher biological degradation of phenol concentrations has been reported in literature (Metcalf and Eddy, 2003).

### *2.8.1 Bioaccumulation and Biodegradation pathway of Cr(VI) and phenol*

In the last few decades biological treatment has been emerged as a cost effective and environment friendly method for the removal of Cr(VI) and phenol. Microbial detoxification of wastewater is advantageous in comparison to other conventional treatment technologies due to its in-situ treatment, complete detoxification and its natural nontoxic by-products (Gurbuz et al. 2004). Biological treatment can be applicable under various situations including in situ, aerobic and anaerobic, active and passive and suspended and attached growth system. Various researches reported that bacteria, fungi and yeast are capable of utilizing heavy metals and organic compounds. Some of the chromium removal bacteria are *Pseudomonas* sp. (Gopalan et al. 1994), *Escherichia coli* (Shen et al. 1995), *Bacillus* sp. (Chirwa et al. 1997), *Acinetobacter haemolytius* (Zakaria et al. 2008), *Bacillus coagulans* (Philip et al. 1998), *Acinetobacter* (Dermou et al. 2005), *Provindencia* sp. (Thacker et al. 2006), *Anacystis nidulans* (Khattar et al. 2007), *Arthrobacter* sp. (Cordoba et al. 2008), *Candida* sp. (F. de Maria G et al. 2009), *Arthrobacter viscosus* (Pazos et al. 2010), *Bacillus subtilis* (Sundar et al. 2011) and phenol reducing microorganism *Bacillus stearothermophilus* (Gurujeyalakshmi et al. 1989), *Pseudomonas putida* (Allsop et al. 1993), *Pseudomonas flurorescens* (Torres et al. 1998), *Acinetobacter* sp. (Hao et al. 2002), *Rhodococcus erythropolis* (Prieto et al. 2002), *Acinetobacter* sp. PCP3 (Srivastava et al. 2007), *Pseudomonas putida Migula* (Yun-guo et al. 2008), *Bacillus cereus* MTCC 9817 (Banerjee et al. 2011), *Bacillus* sp. (Djokic et al. 2013).

***2.8.1.1 Biodegradation pathway of phenol:*** Both aerobic and anaerobic microorganisms are capable of degrading phenol. The mechanism of aerobic degradation pathway is more advanced and well-studied than anaerobic degradation pathway.

#### 2.8.1.1.1 Aerobic biodegradation of phenol

The aerobic degradation pathway of phenol is shown in Fig. 2.8.1.1. The first step of aerobic biodegradation of phenol is the hydroxylation of phenol at ortho-position yielding a molecule of catechol (1, 2- dihydroxybenzene) catalyzed by the enzyme hydroxylase and requiring a reduced pyridine nucleotide ($NADH_2$). The type of micro-organism determines the breakdown of catechol thus formed depends on as either ortho - or meta-cleavage pathway can be followed. The critical step towards the biodegradation of phenol is achieved by dioxygenase-catalysed reactions which is the destruction and fission of the benzoid ring. The aromatic ring is breakdown between the catechol hydroxyls by a catechol 1,2 - dioxygenase (intradio fission, i.e. carbon bond between two hydroxyl groups) in the ortho-or β-ketoadipate pathway. The resulting cis, cis muconate is further metabolized via β-ketoadipate to Krebs cycleintermediates following the action of successive enzymes namely, lactonizing enzyme, isomerase, 3-oxoadipate eno-lactonase, transferase, acyltransferase and thiolase.

In the meta cleavage pathway, the fission of benzoid ring is catalyzed by the enzyme catechol 2, 3- dioxygenase, adjacent to the two hydroxyl groups of catechol (extradiol fission, i.e, between one of the hydroxyl groups and a non-hydroxylated carbon) transforms catechol to 2-hydroxymuconic semialdehyde. This compound is metabolized further to the intermediates of the krebs cycle via set of the following enzymes: dehydrogenase, decarboxylase, 2-keto-4-pentenoate hydratase, aldolase and thiolase. The micro-organisms which follow aerobic pathway for phenol utilization are *Acinetobacter calococeticus, pseudomonas sp. and* Bacillus *sp.* Ortho-pathway is the preferred productive pathway for the organism as it is very less energy consuming. Some micro-organisms utilizing *ortho*- and *meta*-pathway for biodegradation of phenol are Streptomyces setonii, *Acinetobacter calcoaceticus, pseudomonas sp.* ETS1001, *Trichosporoncutaneum*, *candida tropicalis* etc and *pseudomonas putida* U, *Pseudomonas aeruginosa* T1, *Pseudomonas sp.* CF 600, *Pseudomonaspickettii* PKO 1, *Ralstoniaeutropha*, *Bacillus stearothermophilus* etc. respectively (Nelson et al. 1987; Nair et al. 2008).

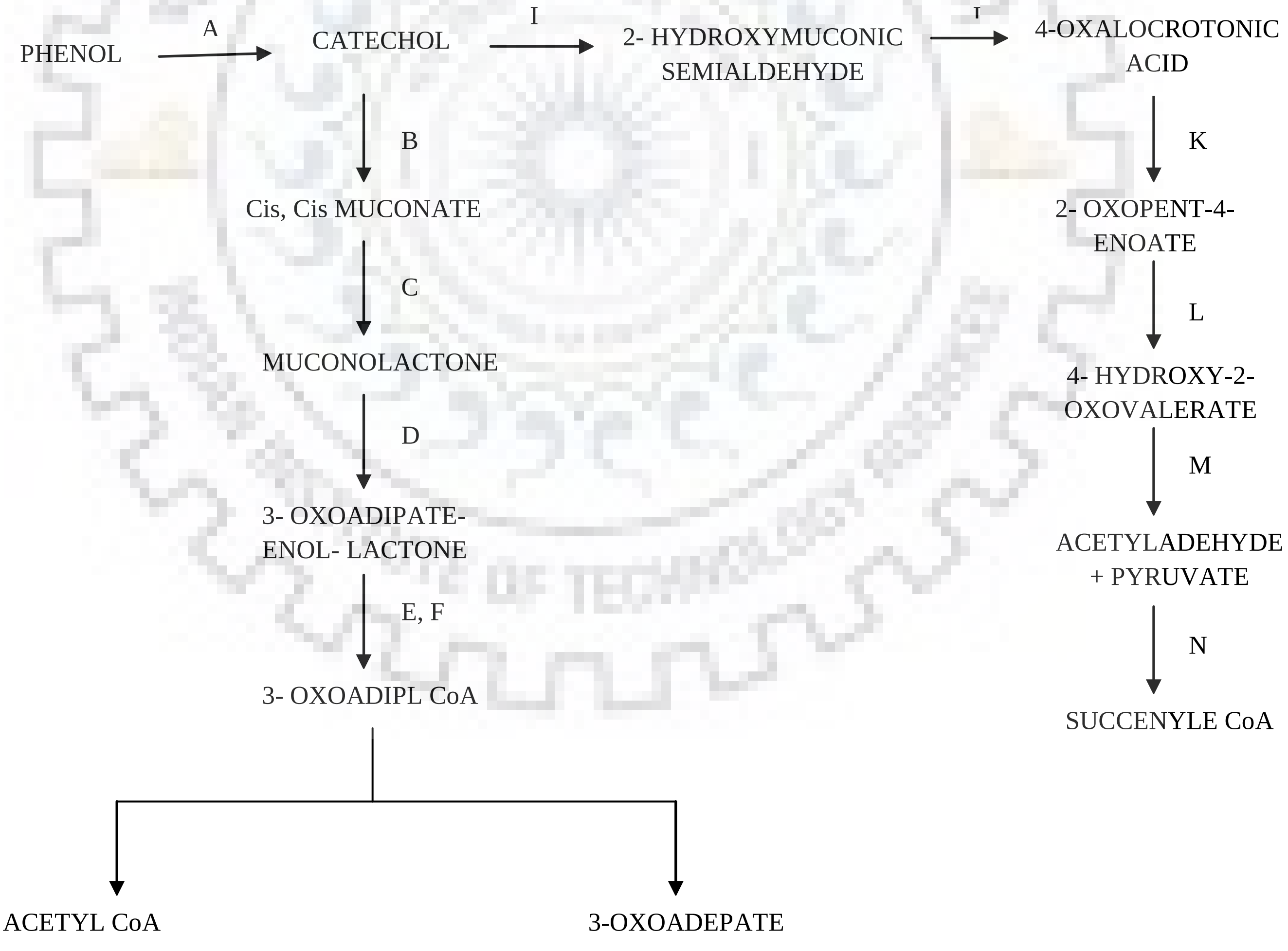

**Fig. 2.8.1.1.1 Aerobic pathway for phenol degradation**

### *2.8.1.1.2 Anaerobic biodegradation of phenol*

Mechanism of anaerobic biodegradation of phenol is less advanced than that of aerobic biodegradation, the former is considered to be analogous with the anaerobic benzoate pathway proposed for *Paracoccus dentrificans* (Schie and Young, 2000). The pathway of biodegradation of phenol in the absence of oxygen has been reported to vary for methanogenic, nitrate-reducing, sulfate-reducing and iron-reducing conditions. Anaerobic phenol degradation is best understood in the facultative anaerobic dentrifier *Thauera aromatica*. Anaerobic degradation of phenol is initiated by phosphorylation and carboxylation in the para-position catalysed by phenyl phosphate synthase and phenyl phosphate carboxylase respectively (Fig. 2.8.1.1.2). The product thus formed, 4-hydroxy benzoate (OHB) is further converted to the central intermediate benzoyl-coenzyme A (CoA) by the activities of 4-OHB-CoA ligase and 4-hydroxybenzoyl-CoA reductase (Hasan et al. 2015).

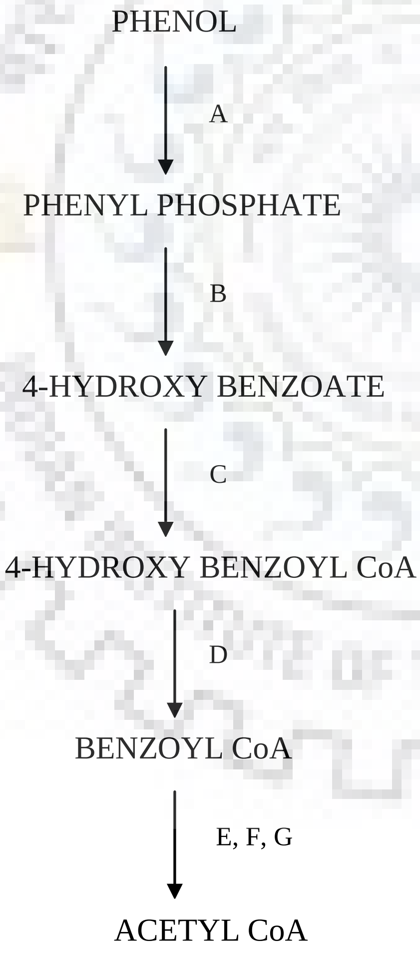

**Fig. 2.8.1.1.2 Anaerobic pathway for phenol degradation**

### 2.8.2 Bioaccumulation pathway of Cr(VI) reduction:

Microorganisms through various oxidation-reduction reactions obtain their energy for metabolism of heavy metals. The transfer of electron is the driving force for all the microbial processes. Some of the (CRB) Cr(VI) resistant bacteria reduces the Cr(VI) to Cr(III). The reduction of Cr(VI) to Cr(III) is governed by some of bacteria as a defence mechanism because Cr(III) is less or no toxic to the bacterium and environment (Wang et al. 1997; Tebo et al. 1998).

There are two metabolic pathways of Cr(VI) reduction:

(i) direct enzymatic reduction, and

(ii) Indirect reduction

It is difficult to distinguish between enzymatic and non-enzymatic Cr(VI) reduction. The direct enzymatic reduction is due to the reduction of Cr(VI) by the metal reductase system. Indirect reduction of Cr(VI) depends upon the conditions provided by bacterium such as bacterial metabolites or the redox potential.

#### *2.8.2.1 Direct Enzymatic Reduction of Cr(VI)*

There are various ways of Cr(VI) reduction by the bacterium and it is unclear whether it is reduced in the cytoplasm or the periplasm or through transfer of electrons or both (Arnold et al. 1988). There are various chromium reducing bacteria (CRB) which reduces the chromium through soluble enzyme systems or the membrane-bound system (Bae et al. 2000; Clark et al. 1994). *Enterobacter cloacae* HO1 bacterium shows the membrane-associated chromate reductase activity as insoluble form of reduced chromate precipitates was observed onto surface of cell. In the presence of ascorbate reduced phenazine meth sulfate (PMS) as electron donor, right-side-out membrane vesicles of *Enterobacter cloacae* HO1 observed high chromate reduction (Wang et al. 1989). (Bopp et al. 1983) Enzymatic reduction of Cr(VI) was associated with the membrane that mediated the transfer of electrons from NADH to chromate. The chromate reductase activity in case of *Shewanella putrefaciens* MR-1 is done with the anaerobically grown cytoplasmic membrane (106). Formate and NADH served as an electron donors for the microbial reduction of Cr(VI). In case of *Pseudomonas putida*, NADPH (L-lactase) employed as an electron donor for the reduction of Cr(VI). Study conducted by Shen and Wang suggested that the reduction of Cr(VI) by *Escherichia coli* was due to the presence of soluble chromate reductase. Cr(VI) reduction in another gram negative bacteria, in case of *Pseudomonas* sp. the reduction of Cr(VI) is mediated by a soluble enzyme contained in cytoplasm (Shen et al. 1993). The NADH worked as electron donor for the chromate reduction in *Bacillus coagulans* (Phillip et al. 1998). The metabolic pathway for the reduction of Cr(VI) is shown in Fig. 2.8.2.1.

### 2.8.2.2 Bacterially Mediated Indirect Reduction of Cr(VI)

#### *2.8.2.2.1 Redox potential-pH*

The pH and redox conditions of bacterial cultures were changed due to the formation of metabolites and changes in various biochemical reactions. These changes indirectly affect the growth of microorganisms. Various authors reported that the low pH and redox potential condition favours the reduction of Cr(VI) (Daulton et al. 2001).

#### *2.8.2.2.2 Fe (III)-mediated reduction of Cr(VI)*

Fe (III) is employed as terminal electron acceptor and donor for the reduction of Cr(VI) by various microorganisms. The stoichiometry of the Fe(III) mediated reduction of Cr(VI) is given below:

$$3\ \mathrm{Fe(II)} + \mathrm{Cr(VI)} \rightarrow 3\mathrm{Fe(III)} + \mathrm{Cr(III)}$$

The reduction of Cr(VI) by iron-reducing bacterium was first reported by (Wielinga et al. 2001).

***2.8.2.2.3 Embden-Meyerhof-Parnas pathway for reduction of Cr(VI):*** The Embden-Meyerhof-Parnas proposed the glycolytic pathway for the reduction of Cr(VI). According to this pathway, the oxidation of one mole of glucose yields two moles of pyruvate, two moles of NADH and two ATP molecules. The pyruvate formed by the oxidation of glucose is further decarboxylated to acetyl CoA, $CO_2$, and $H_2$ using pyruvate-ferredoxin oxidoreductase and hydrogenase. The acetyl CoA formed further reduced via two routes. A part of it is condensed to form acetoacetyl-CoA, which is further reduced to β-hydroxybutyryl-CoA using one of the two NADHs. The β-hydroxybutyryl-CoA is reduced to butyryl-CoA using the second NADH. CoASH is displaced by inorganic phosphate and butyryl phosphate donates phosphoryl group to ADP and produce ATP and butyrate. Some aetyl CoA is also converted to acetate via acetyl - P in a reaction that yields an additional ATP. Twice as much ATP is generated per acetate produced as opposed to butyrate (Romano et al. 1996).

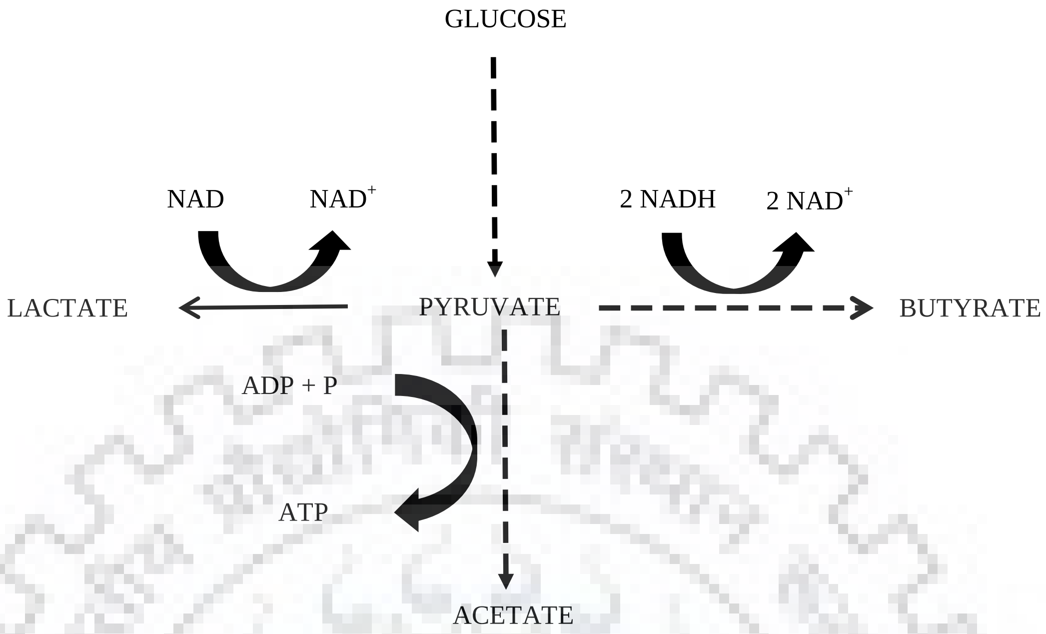

Fig. 2.8.2.1 Metabolic pathway for Cr(VI) reduction

### 2.9 Continuous Packed bed reactor or immobilized bacterium bioreactor

The continuous flow processes are generally operated in packed bed fluidized bed CSTR adsorption system. They may be operated either in the up flow columns or in down flow column mode. Spent adsorbent may be periodically withdrawn from the bottom. In bio column adsorptive reactor a thin layer of bacteria (biolayer) is formed onto the surface of adsorbent bed which functioned as a unit of biofiltration for bioaccumulation of toxic contaminants. Biological reactions occurring in the column may also function as filter bed retaining suspended solids entering with the feed. Laboratory or pilot plant studies on specific waste water to be treated should be carried out. The variables to be examined include type of adsorbent, liquid feed rate, solute concentration in feed and height of adsorbent bed (Mondal et al. 2008).

### 2.10 Phytoremediation system

This process has the capability to convert contaminated wastewater or ground water to usable form by plants. In the process of phytoremediation, the plants remove, transfer, stabilize or destruct contaminants from soil and ground water by the uptake or transpiration of contaminated water (Smolyakov et al. 2012; Alkorta et al. 2001). Plants take nutrients through roots, volatilize water through leaves and form a transformation system to metabolize organic compounds and heavy metals (Dhir et al. 2011). Plants consume large amount of toxic elements and nutrients out of which only small amounts of toxic elements are harmful or they affect the plants only at higher concentration (Mongkhonsin et al. 2011). Phytoremediation process is the use of specialized plants to clean up contaminated soil and ground water (Wolverton et al. 1978). Those sites, where the contaminants are spread within the root zone of plants, are best-suited sites for the use of phytoremediation (Augustynowicz et al. 2010).

There is a continuous increase in contaminated substances from various industry, social and agricultural activities due to careless disposal of these toxic substances on the land areas, surface water and ground water. These toxic pollutants eg. metals and organic contaminants causes major effects on natural resources and environment viz. plants and animals. The industrial wastewater is then used for the agricultural purposes and the presence of toxic pollutants in water affects the fertility of land. In various developing countries around 900,000 hectares of agriculture land is processed by the industrial wastewater. Various processes for treating the waste water is introduced for example biological, physical and chemical but they are very costly and only applicable for the small amount of wastewater (Rezania et al. 2015; Rezania et al. 2014). Hence, an alternative process for wastewater treatment is introduced i.e phytoremediation, which is a plant-based technology, which uses various plants for the treatment of wastewater and removes the toxic pollutants from wastewater (Mant et al. 2006; Hozhina et al. 2001). This treatment process is relatively cheap and considered to be the most suitable option for various countries. Phytoremediation can be used together with constructed wet lands and natural wet lands. For phytoremediation, various plant species have been identified which can grow in different environmental conditions (Malik et al. 2007; Mishra et al. 2014).

### 2.10.1 Applications of Phytoremediation

#### *2.10.1.1 In-situ phytoremediation*

In this method, live plants are used with the contaminated surface water for the phytoremediation process. Through this process, the contaminated material is not removed by the phytoremediation. In this mechanism, the toxic pollutants consumed by the plants get accumulated in the plant biomass and no transpiration of toxic pollutants takes place. The plants after recovery or uptake of the toxic pollutants were harvested from the site for the disposal. Requirement for the in-situ approach is that the contaminants present in wastewater must be physically accessible to the roots of plants. The in-situ approach is least expensive strategy for phytoremediation (Zhenga et al. 2007).

### *2.10.1.2 In-vivo phytoremediation*

In this process, the live plants are grown in wastewater for the remediation of toxic pollutants. For surfaces where the toxic pollutant is not physically permeable to the roots of the plants, In-vivo phytoremediation is applied. The contaminants are extracted by mechanical methods and then exposed to the plants selected for phytoremediation of toxic pollutants in temporary treatment area. This approach is more expensive than other approaches. Treatment can be done at the site of contaminants or at another site (Zhao et al. 2014).

### *2.10.1.3 In-vitro phytoremediation*

In this methodology, the components of live plants i.e. extracted enzymes are used for phytoremediation. In this approach the plants extract pollutants from contaminated site using enzyme mechanism. This approach is also used for temporary contaminated treatment area by transferring the plants from toxic pollutant site. Theoretically, this approach is the most expensive method due to the costs of preparation of plant enzymes but some plants can produce enzyme under stress condition, which reduce the cost of process. The time during which the enzyme remains active for breakdown of contaminants is another important factor for considering this approach (Maine et al. 2001).

## 2.10.2 Mechanisms of Phytoremediation

Some of the factors given below affect the uptake and distribution of pollutants within living plants (Meagher et al. 2000):

a) Physical and chemical characteristics of the toxic pollutants such as solubility in water, vapour pressure, molecular weight and octanol-water partition coefficient.

b) Environmental conditions such as pH, temperature, organic matter and soil moisture content.

c) Characteristics of plant biomass such as type of root, shoot and leaf of the plants system and type of enzymes.

The various mechanisms used by plants for phytoremediation are and shown in Fig. 2.10.2:

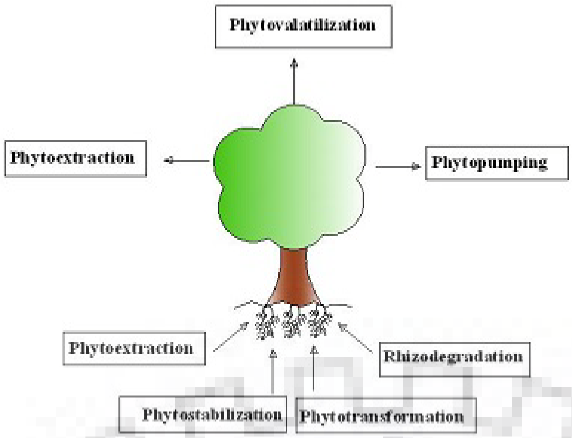

Fig. 2.10.2 Mechanism of Phytoremediation

### *2.10.2.1 Phytoextraction*

Phytoextraction is also known as phytoaccumulation can be defined as the uptake of pollutants from wastewater by live plant in the root. This mechanism occurs when the contaminants taken by the plants are not completely degraded or consumed by the plants, resulting in an accumulation of the pollutants in different parts of the plant. Some of the aquatic macrophytes are hyperaccumulators which absorb huge amount of pollutants in comparison to other plants. Therefore the plants after uptake of toxic pollutants are either incinerated or sent to recycle the metals. The level of contaminants in the plants down to the allowable limits before the disposal of the plant. After the incineration of toxic pollutants the ash must be disposed off in a hazardous waste landfill. The volume of ash should not exceed more than 10 % of the volume of contaminated soil used for the experimentation. The process of phytoextraction removes various toxic heavy metals such as Chromium, Nickel, Zinc, Arsenic and Copper metals.

### *2.10.2.2 Phytopumping*

In phytopumping, plants can be utilized to minimize or remove migration of the contaminants. In this mechanism, the plants are functioned as the organic pumps for the uptake of large volumes of the toxic wastewater through transpiration process. The migration of contaminants in ground water is reduced after this mechanism. This mechanism can only be used for the plants, which are capable of pumping out large volumes of water. This property of plants can provide an inexpensive alternative option to the mechanical pumping system for contaminated ground water in shallow aquifers (Sridhar et al. 2011).

### *2.10.2.3 Phytostabilization*

This mechanism is used to minimize the migration of pollutants in soil through the uptake and accumulation by the roots, the roots adsorption or precipitation within the root zone of plants. The roots of the plants have the ability to alter the environmental conditions of the soil, ie, pH and moisture content of the soil. This process uses this ability of plants. The contaminant mobility, migration to groundwater or air and the bioavailability of entry into the food chain is reduced during this process. By this technique a vegetation cover at sites where natural vegetation is lacking due to high metal concentration in surface of soils or physical disturbances to materials at the surface is re-establish (Priya et al. 2014).

### *2.10.2.4 Phytotransformation*

Phytotransformation process is also known as phytodegradation. Phytotrasformation is the breakdown of contaminants through metabolic processes of plants or the external breakdown of contaminants through the release of enzymes. This process also relates to the absorption of contaminants with subsequent breakdown, mineralization or metabolized by the plant through various internal enzymatic reactions and metabolic processes (Sharmin et al. 2012).

### *2.10.2.5 Phytovolatilization*

Phytovolatilization is a process in which plants convert a contaminant into a volatile form by volatilization process from the plants either from the leaf, stomata or stems of plants and then removing the contaminants from the soil or water at a contaminated site (Quinones et al. 2009).

### *2.10.2.6 Rhizodegradation*

Rhizodegradation process is a biological treatment of contaminants by improving fungal and bacterial activity in the rhizosphere of some vascular plants. In the rhizosphere, the microbial density and activity of the root is decreased. The geochemical environment in the rhizosphere be moderated by plants and provides the ideal conditions for bacteria and fungi to grow and degrade organic pollutants. The litter of plant and exudates of root provides nutrients that reduce or eliminate the need for costly additives fertilizer. The plants root penetrates the soils, provide the zones of aeration, and stimulate aerobic biodegradation. Some molecules, which are released by root, die back and exudation resembles common contaminants and used as substrates (Ontanon et al. 2014)

**2.11 Mathematical model:** The experimental data obtained by carrying out various experiments fitted to various kinetic and isotherm model for single and binary synthetic simulated waste water.

The amount of Cr(VI) and phenol adsorbed per unit mass of the adsorbent (mg/g) was calculated by using the following equation (Mohan et al. 2006):

$$q_t = (C_i - C_e) \times V/W \qquad (2.1)$$

Where $C_i$ and $C_e$ are the initial and equilibrium concentrations of Cr(VI) and phenol (mg/L), respectively, $V$ is the volume of the working solutions of Cr(VI) and phenol (mL), and $W$ is the weight of adsorbent (g).

The percentage removal of Cr(VI) and phenol was calculated using the following equation (Alebrahim et al. 2015):

$$\%\ \text{Removal of Cr(VI) and phenol} = (C_i - C_f)/C_i * 100 \qquad (2.2)$$

Where $C_i$ and $C_f$ are the initial and final concentrations of Cr(VI) and phenol present for the adsorption process.

### 2.11.1 Equilibrium Isotherm study

At definite intervals of time, percentage removal of Cr(VI) and phenol becomes constant due to equilibrium established between adsorbate and adsorbent. Therefore, maximum adsorption capacity (mg/g) of the adsorbent was reached. Therefore, at the equilibrium condition there is no change in the amount of the pollutant adsorbed and amount of pollutant remaining in the solution. At equilibrium, the amount of material adsorbed onto the surface of the adsorbent is estimated using Equation 2.3 (Allen et al. 2004; Sarin et al. 2006). The advantages and disadvantages of various equilibrium adsorption isotherm models are given in table 2.11.1.

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (2.3)$$

Where $q_e$= Uptake capacity of the adsorbent at equilibrium (mg/g)

$C_0$= Initial Concentration of the pollutant (mg/L)

$C_e$= Concentration of pollutant at equilibrium (mg/L)

V= Volume of the solution (L)

$W$= Weight of adsorbent (g)

The single component models used in this present study are

- Langmuir Isotherm
- Freundlich Isotherm
- Redlich Peterson isotherm
- Temkin isotherm

### *2.11.1.1 Langmuir Isotherm:*

The Langmuir isotherm is the model describes the monolayer chemisorption onto the identical sites of homogeneous surface of adsorbent. Basic assumptions of Langmuir isotherms are:

- Adsorption can be due to weak vander wall forces (physiosorption) or chemical bonding between adsorbate and adsorbent (chemisorption).
- One active site of adsorbent can adsorb only one adsorbate molecule (monolayer adsorption)
- Constant heat of adsorption for surface molecule
- The interaction between the adsorbate molecules is negligible.

Basic Langmuir isotherm equation

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{2.4}$$

Where $q_e$= Equilibrium monolayer uptake (mg/g)

$q_{max}$= Maximum adsorption capacity (mg/g)

$K_L$= Langmuir Constant

$C_e$= Equilibrium concentration of pollutant (mg/L)

Langmuir constant ‘$K_L$’ also shows the favourability of adsorption by determination of dimensionless separation factor $R_L$ which is estimated by equation 3 (Shen et al. 2009; Liu et al. 2009).

$$R_L = {}^{1}\!/_{(1 + K_L C_0)} \quad (2.5)$$

The nature of adsorption is indicated as

$R_L > 1$ (Unfavourable)

$R_L < 1$ (Favourable)

$R_L = 0$ (irreversible) (Kumar et al. 2011).

*2.11.1.2 Freundlich isotherm:*

The Freundlich adsorption isotherm model represents the adsorption for both multilayer adsorption and heterogeneous adsorption. Freundlich adsorption isotherm model follows the assumption that there is multiple numbers of vacant adsorption sites onto the surface of the adsorbent but all the sets behave in accordance to Langmuir isotherm (Fonseca-Correa et al. 2013).

The basic equation for Freundlich isotherm is given by equation 2.6.

$$q_e = K_F C_e^{1/n} \quad (2.6)$$

Where $K_F$ and n are the constant for Freundlich isotherm and $K_F$ shows the adsorption capacity and 1/n is the measure of reaction’s intensity, favourable adsorption conditions exist when $n>1$.

*2.11.1.3 Redlich Peterson isotherm:* Redlich Peterson isotherm is the hybrid of Langmuir and freundlich isotherm. There is a liner dependence of the concentration onto the adsorption capacity in the numerator while the adsorption capacity depends exponentially in the denominator of the model. Therefore the value of β should be less than 1 otherwise Redlich Peterson model tends towards the Langmuir adsorption isotherm model. If the value of β tends to zero, the Redlich Peterson model approaches towards the Freundlich isotherm model. The equation of the Redlich Peterson model is given below (Yousef et al. 2011):

$$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta}} \quad (2.7)$$

$K_{RP}$ Redlich Peterson isotherm constant (L $g^{-1}$)

$a_{RP}$ Redlich Peterson isotherm constant (L $mmol^{-1})^{\beta}$

β Redlich Peterson isotherm exponent.

*2.11.1.4 Temkin isotherm model:* Temkin adsorption isotherm model depends on the assumptions that the heat of adsorption of all the molecules decreases linearly rather than logarithmic with coverage (Gupta et al. 2009).

$$q_e = \frac{RT}{b} \ln (aC_e) \qquad (2.8)$$

Where $C_e$ equilibrium concentration,

R is the universal gas constant (8.314 J/mol/K),

T absolute temperature K,

a Temkin isotherm constant,

b Temkin constant.

### ***2.11.2 Multicomponent Adsorption Isotherm:***

Single component adsorption isotherms cannot be used for the estimation of the adsorption capacity when more than one component is present in the waste water. Therefore, for the multicomponent adsorption isotherms are required to be used for the binary solution because one component present in the solution can provide the competition to another component for the adsorption onto the same active site. The multicomponent adsorption isotherms employed in this study are Non-modified Langmuir, Modified Langmuir, Extended Langmuir, Extended Freundlich, Competitive non-modified Redlich Peterson and Competitive modified Redlich Peterson adsorption isotherm models. The constants of the multicomponent adsorption isotherms were calculated with the help of single component model adsorption isotherm modelling of the individual component (Wurster et al. 2000; Kumar et al. 2011; Nouri et al. 2007).

**Table 2.11.1** Advantages and disadvantages of various equilibrium adsorption isotherm models

| Isotherm model | Functional Equation | Assumptions | Advantages | Disadvantages |
|---|---|---|---|---|
| Langmuir | $q_e = q_{\max}\frac{K_L C_e}{1+K_L C_e}$<br>where,<br>$C_e$= Equiibrium concentration<br>$K_L$= Sorption equilibrium constant<br>$q_{\max}$= maximum adsorption capacity | 1. Metal ions are chemically adsorbed at a fixed number of well-defined sites<br>2. Monolayer adsorption<br>3. All site are energetically equivalent<br>4. No interaction between adsorbate atoms or molecules. | Valid over wide range of concentration due to finite saturation limit and Henry law. | Valid under low pressure conditions only, based on monolayer assumption |
| Freundlich | $q_e = K_F\, C_e^{1/n}$<br>$C_e$= Equiibrium concentration<br>$K_F$= adsorption capacity<br>n = adsorption affinity | 1. Freundlich isotherm made no such assumptions and derived his equations empirically.<br>2. In fact Freundlich isotherm equation is derived from Langmuir isotherm equation assuming that there exist multiple sites on surface of adsorbent with each site behaving as per Langmuir isotherm. | Simple expressions has surface heterogeneity parameter | It fails at higher pressure, does not have Henry law and no saturation limit |
| Temkin | $q_e = \frac{KT}{b} \ln{(aC_e)}$<br>$C_e$= Equiibrium concentration<br>R = gas constant<br>T = absolute Temperature<br>a = Temkin Isotherm constant<br>b = temkin constant in relation to heat of sorption | The decline in heat of sorption as a function of temperature is linear rather than logarithmic. | Simple expression | Not applicable over wide range of concentration |
| Redlich peterson | $q_e = \frac{K_{RP} C_e}{1+a_{RP} C_e^{\beta}}$<br>$C_e$= Equiibrium concentration<br>$K_{RP}, a_{RP}$ and β are Redlich Paterson's parameters | Redlich Peterson isotherm is a combination of Langmuir and Freundlich isotherm. At low concentration its behaviour approaches toward Henry law while at higher as freundlich isotherm | Capable to represent adsorption equilibrium over wide concentration range | At the unit value of β it behaves as langmuir isotherm. |

### *2.11.2.1 Non Modified Langmuir Isotherm:*

The general equation for Non-modified Langmuir Isotherm is given by equation 2.9 (Kumar et al. 2011; Nouri et al. 2002; Aksu et al. 2002; Agarwal et al. 2013).

$$q_{e,i} = Q_{o,i} b_i C_{e,i} / \left(1+\sum_{j=1}^{N} b_j\, C_{e,j}\right) \qquad (2.9)$$

Where $q_{e,i}$= Equilibrium monolayer capacity for *i* component, (mg/g)

$Q_{0,i}$ and $b_i$are the Langmuir constants for individual components.

$C_{e,i}$= Equilibrium concentration for the '$i$' component (mg/L)

### *2.11.2.2 Modified Langmuir Isotherm*

The general equation for Modified Langmuir isotherm is given by equation 2.10 (Kumar et al. 2011; Nouri et al. 2002; Aksu et al. 2002; Agarwal et. al. 2013).

$$q_{e,i} = (Q_{o,i} b_i C_{e,i} / n_j) / \left(1 + \sum_{j=1}^{N} b_j\, (C_{e,j} / n_j)\right) \qquad (2.10)$$

Where $\eta_i$= Correction factor for '$i$' component.

### *2.11.2.3 Extended Langmuir Isotherm*

The general equation for extended Langmuir isotherm is given by equation 2.11 (Agarwal et. al. 2013; Levan et al. 1981).

$$q_{e,i} = Q_{o,i} b_i C_{e,i} / \left(1 + \sum_{j=1}^{N} b_j\, C_{e,j}\right) \qquad (2.11)$$

### *2.11.2.4 Extended Freundlich Isotherm:*

The equation of extended Freundlich isotherm is given by equation 2.12 and equation 2.13 (Mckay et al. 1991; Azizian et al. 2007; Al-Asheh et al. 2003).

$$q_{e,i} = \left(K_{F,i} C_{e,i}^{\frac{1}{n_i + x_i}}\right) / \left(C_{e,i}^{x_i} + y_i\, C_{e,j} Z_i\right) \qquad (2.12)$$

$$q_{e,j} = \left(K_{F,j} C_{e,j}^{\frac{1}{n_j + x_j}}\right) / \left(C_{e,j}^{x_j} + y_j\, C_{e,i} Z_j\right) \qquad (2.13)$$

Where $K_{F,i}$= Freundlich isotherm constant for 'i' component

$x_i$ , $y_i$, $z_i$ = Freundlich constants for ‘i’ component

#### 2.11.2.5 Competitive Non Modified Redlich Peterson model:

$$q_{e_i} = \frac{K_{RP_i} C_{eq_i}}{1+\sum_{j=1}^{N} a_{RP_j} C_{eq_j}^{\beta_j}} \tag{2.14}$$

#### 2.11.2.6 Competitive Modified Redlich Peterson model

$$q_{eq_i} = \frac{K_{RP_i}\frac{C_{eq_i}}{n_i}}{1+\sum_{j=1}^{N} a_{RP_j}\left[\frac{C_{eq_j}}{n_j}\right]^{\beta_j}} \tag{2.15}$$

## 2.12 Statistical optimization of process parameters using Response Surface Methodology (RSM)

In this methodology, design expert software (8.0.7) is used for the optimization of process parameters using Box-behnken design of response surface methodology. RSM is a technique in which changes can be made simultaneously in more than one input variables for the optimization of responses or output variables by developing an empirical model using mathematical and statistical analysis (Liyana-Pathirana et al. 2005). A number of experimental runs suggested by the design expert were used for the optimization of responses. Development of experimental design i.e. design of experiments (DoE) which is a particular combination of experimental runs called level and ranges is first step in RSM. Then the responses either are presented graphically, as three-dimensional space or contour plots that helps to predict the response surface shapes. Contours curves are response plotted in the $x_i$, $x_j$ plane while other parameters are kept constant (Liyana-Pathirana et al. 2005; Tripathi et al. 2012).

### 2.12.1 Experimental Design

The coded values of the process parameters were determined by the following equation (Rajasimman et al. 2009; Satapathy et al. 2014; De Sales et al. 2013).

$$x_i = \frac{X_i - X_o}{\Delta x} \tag{2.16}$$

Where $x_i$ is the coded value of the $i^{th}$ variable, $X_i$ is the uncoded value of the $i^{th}$ test variable and $X_0$ is the uncoded value of the *i*th test variable at centre point. Where $x_i$ is the dimensionless coded value, $X_i$ is the natural value; $X_{min}$ and $X_{max}$ are the lowest and the highest limits of the $i^{th}$ variable, respectively. The independent variables are coded as (±1), 0 is the centre point and the axial points are located at (±α). Y denotes the variance of the predicted response and X is the distance between design centre and point (Myer et al. 2001; Clarke et al. 1997).

### *2.12.2 Modelling and Statistical Analysis*

The experimental data was analysed using Design Expert software version 8.0.7 (STAT-EASE Inc., Minneapolis, USA) statistical software, which develops a polynomial equation by RSM for predicting the responses as a variable functions. The experimental data was validated for two responses of adsorption process; percentage removal efficiency ($Y_1$) and adsorption capacity ($Y_2$). Each response developed the model by correlating the four variables using second-degree polynomial Eq. (2.17) (Zainudin et al. 2005).

$$Y_i = \alpha_o + \sum_{i=1}^{n} \alpha_i x_i + \left(\sum \alpha_{ii} x_i\right)^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \alpha_{ij} x_i x_j \qquad (2.17)$$

Where $Y_i$ is the predicted response, $\alpha_i$ is the linear coefficients, $\alpha_o$ is the intercept coefficient, $\alpha_{ii}$ is the quadratic coefficients, $\alpha_{ij}$ is the interaction term and $x_i$, $x_j$ are the coded values of variables. The multiple regression analysis technique in the RSM was utilized to determine the model coefficient and experimental error and to justify the suitability of model. The analysis of variance (ANOVA) was included to judge the adequacy of model. Some model terms, which may be insignificant, can be neglected and the model with fewer terms was selected for good expression of the experimental data. The final model generated the responses in terms of graphical representations of the parameter shown by contour plots that gave their relative influence and an optimum parameter combination.

## 2.13 Kinetic Models

The kinetic studies for the simultaneous adsorption of Cr(VI) and phenol were carried out using contact time data of batch experiments. The models considered are generally pseudo first order, pseudo second order and intraparticle diffusion (Agarwal et. al. 2013; Ho et al. 1999; Lagergren 1898). The kinetic models used in the present study are given below:

Pseudo first order kinetics nonlinear model:

$$q_t = q_e(1 - \exp(-k_1 t)) \qquad (2.18)$$

Pseudo first order kinetics linear model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (2.19)$$

Pseudo second order kinetics nonlinear model:

$$q_t = {k_2 q_e^2 t}\Big/{(1 + k_2 q_e t)} \qquad (2.20)$$

Pseudo second order kinetics linear model

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2.23)$$

Intraparticle diffusion kinetics nonlinear model:

$$q_t = k_{id} t^{0.5} \qquad (2.24)$$

Intraparticle diffusion kinetics linear model:

$$q_t = k_{id} t^{1/2} + I \qquad (2.25)$$

Where, $k_1$= Rate constant for pseudo first order kinetic model ($h^{-1}$)

$k_2$ = Rate constant for pseudo second order kinetic model (mg $g^{-1}$ $h^{-1}$)

**2.14 Error Functions:**

The error functions ARE (Average relative error) and MPSD (Marquardt's percent standard deviation) were used to estimate the fit between experimental and predicted value for both kinetic models. The equation for ARE and MPSD error function is given below (Ho et al. 1999; Foo et al. 2010; Kumar et al. 2008; Mane et al. 2007):

$$\mathrm{ARE}\ \% = 100/\mathrm{N} \times \sqrt[2]{\sum\left(\frac{\mathrm{q_{e,i}^{exp}} - \mathrm{q_{e,i}^{cal}}}{\mathrm{q_{e,i}^{exp}}}\right)^2} \qquad (2.26)$$

Where N= number of observations

$$\mathrm{MPSD} = 100 \times \sqrt{\frac{1}{\mathrm{N-P}} \sum_{\mathrm{i=1}}^{\mathrm{n}} \left(\frac{\mathrm{q_{e,i}^{exp}} - \mathrm{q_{e,i}^{cal}}}{\mathrm{q_{e,i}^{exp}}}\right)^2} \qquad (2.27)$$

$q_e$ Specific uptake of adsorbent at equilibrium (mg $g^{-1}$ of adsorbent)

MPSD Marquardt's percent standard deviation,

ARE Average Relative Error,

$q_{e,i}^{exp}$ Experimental specific uptake (mg $g^{-1}$),

$q_{e,i}^{cal}$ Calculated specific uptake (mg $g^{-1}$),

N number of observations in the experimental isotherm,

P number of parameters in the regression model

### 2.15 Thermodynamic study

The experimental data obtained for the simultaneous removal of Cr(VI) and phenol were examined for the calculation of thermodynamic properties of Cr(VI) and phenol adsorption onto the surface of various adsorbents. The thermodynamic properties such as Gibbs free energy ($\Delta G_o$), enthalpy ($\Delta H^o$) and entropy changes ($\Delta S_o$) were determined for the adsorption of Cr(VI) and phenol by various adsorbents.

A plot of ln $K_c$ vs 1/T is drawn to calculate the value of $\Delta H^o$, $\Delta S_o$ and $\Delta G_o$ from the slope and intercept of the following equations (Kumar et al. 2008; Srihari et al. 2008; Lee et al. 2001)

$$\ln K_c = \frac{-\Delta H^o}{RT} + \frac{\Delta S_o}{R} \quad (2.28)$$

$$\Delta G_o = -R\,T \ln K_C \quad (2.29)$$

### 2.16 Mathematical description of Column reactor:

The curve obtained by plotting normalized concentration ($C/C_0$) versus time or effluent volume is called the breakthrough curve and is further utilized for estimation of percentage removal or the column capacity of the packed bed reactor (Aksu et. al. 2004; Sarin et al. 2006; Ghorai et al. 2004).

Where $C_0$= Inlet concentration (mg/L)

C= Outlet concentration (mg/L)

$$V_{eff} = Qt_{total} \tag{2.30}$$

Where $V_{eff}$= Effluent Volume, (mL)

$Q$ = Volumetric flow rate, (mL/min)

$t_{total}$ = Total flow time, (min)

Percentage removal of a particular pollutant can be calculated by equation 2.31.

$$Removal\ \%,_i = \frac{q_{i,total}}{m_{i,total}} \times 100 \tag{2.31}$$

Where $q_{i,total}$ = Total amount of component 'i' adsorbed by the column, mg

$m_{i,total}$ = Total amount of component 'i' sent to the column, mg

$$q_{i,total} = QA_i \tag{2.32}$$

$$m_{i,total} = C_0\ Qt_{i,total} \tag{2.33}$$

Where $A_i$ = Area under the curve plotted between normalized concentration and time for component 'i'.

Maximum column capacity can be estimated by equation 2.34.

$$q_{eq,i} = \frac{q_{i,total}}{X} \tag{2.34}$$

Where X = Mass of packing material in the column.

$q_{eq,i}$ = Equilibrium capacity for component 'i'

## 2.17 Kinetic Models

The dynamic behavior of the packed bed reactor is determined by different kinetic models (Trepanier et al. 2009).

### *2.17.1 Adams Bohart Model:*

This model assumes that adsorption rate is directly proportional to the adsorbate and adsorbent's residual capacity. The model works better for $C/C_0 < 0.15$ (Singh et al. 2012).

The general equation of this model is

$$ln\frac{C}{C_0} = k_{AB}C_0t - k_{AB}N_0\frac{Z}{U_0} \qquad (2.35)$$

Where $k_{AB}$ is the kinetic constant (L/ mg min), $U_o$ is the superficial velocity (m/ min) and Z is the height of the column (m) and $N_o$ is the saturation concentration of column (mg/L)

A graph is plotted between $\ln(C/C_0)$ and time (t) which gives a slope equal to $k_{AB}C_0$ and an intercept equal to $k_{AB}N_0\frac{Z}{U_0}$.

### *2.17.2 Wolborska Model:*

In the present work Wolborska model was used (equation 2.36) (Chen et al. 2012; Singh et al. 2009)

$$ln\frac{C}{C_0} = \frac{\beta_a C_0}{N_0}t - \frac{\beta_a Z}{U_0} \qquad (2.36)$$

Where $\beta_a = \frac{U_0^2}{2D}(\sqrt{1 + \frac{4\beta_0 D}{U_0^2}} - 1)$ (2.37)

$\beta_a$= Kinetic coefficient of external mass transfer ($min^{-1}$)

D = Axial diffusion coefficient ($m^2/min$)

$\beta_0$= External mass transfer coefficient with negligible D ($min^{-1}$)

If $k_{AB} = \frac{\beta_a}{N_0}$ then Wolborska solution is equivalent to Adams-Bohart relation.

Where $\beta_a$ is the Kinetic coefficient of external mass transfer ($min^{-1}$), D is the axial diffusion coefficient ($m^2$ $min^{-1}$) and $\beta_0$ is the external mass transfer coefficient with negligible D ($min^{-1}$).

### *2.17.3 Thomas Model:*

Thomas model assumes the kinetics to be second order without any axial dispersion along with Langmuir kinetics for adsorption. The general equation of the model is:

$$\frac{C}{C_0} = \frac{1}{1+\exp\left(\frac{k_{Th}}{Q}(q_0 X - C_0 V_{eff})\right)} \qquad (2.38)$$

The equation can be linear as given below:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{Th} q_0 X}{Q} - k_{Th} C_0 t \qquad (2.39)$$

X = Weight of the biomass packed in the column (g).

$q_o$ = equilibrium metal sorption (mg $g^{-1}$).

$k_{\mathrm{Th}}$ is the Thomas rate constant (mL $mg^{-1}$ $min^{-1}$)

The equation is linearized and the plot of ln[(C/$C_0$)-1] versus time is utilized for the estimation of $k_{Th}$ i.e. Thomas constant and $q_0$ (Preetha et al. 2007).

*2.17.4 Yoon and Nelson Model*

The major assumption of this model is that the rate of adsorption is directly proportional to the probability of adsorbate adsorption (Park et al. 2006; Yoon et al. 1984). The equation of this model is

$$ln\frac{C}{C_0 - C} = k_{YN} t - \tau k_{YN} \qquad (2.40)$$

Where $k_{YN}$= Rate constant ($min^{-1}$)

$\tau$ = Time required for 50 % breakthrough (min)

A plot of ln C/($C_0$-C) versus time gives $k_{YN}$ i.e. rate constant ($min^{1}$) from slope and $\tau$ i.e. 50 % breakthrough time (min) from intercept.

*2.17.5 Mass Transfer Zone Estimation:*

The mass transfer zone is the length of the reactor where the actual mass transfer takes place. It is estimated as

$$MTZ = \left(1 - \frac{T_v}{T_c}\right) Z \qquad (2.41)$$

Where $T_v = \int_0^{T_{bp}} \left(1 - \frac{C}{C_0}\right) dt \qquad (2.42)$

$$T_c = \int_0^{\infty} \left(1 - \frac{C}{C_0}\right) dt \qquad (2.43)$$

The rate of movement of mass transfer zone (RMTZ) can be calculated as

$$RMTZ = \frac{MTZ \times Q}{V_{0.9} - V_{0.2}} \tag{2.44}$$

Where $V_{0.9}$ and $V_{0.2}$ are volume of effluent at 90% breakthrough and 20% breakthrough, respectively.

### 2.18 Residence Time Distribution (RTD) Studies

The residence time distribution or RTD studies are carried out to visualize the flow pattern of a packed bed reactor to avoid stagnant region or channelling of the fluid. RTD studies are carried out using a tracer which is easily detectable, is non-reactive to the carrier fluid, there is not much density difference with the tracer and the carrying fluid and it should not get adsorbed or absorbed by the packing material or the walls of the reactor (Levenspeil et al. 1970).

#### *2.18.1 E-curve:*

All fluid elements in the reactor do not take the same time to appear in the outlet stream. The study of different time duration taken by different fluid element is called exit age studies and the curve thus obtained between exit age and time is called E-curve or exit age distribution curve (Saravanathamizhan et al. 2008).

$$\int_0^\infty E dt = 1 \tag{2.45}$$

Where E(t)dt = fraction of material in exit stream with ages between (t, t+dt)

E= exit age distribution, time$^{-1}$

#### *2.18.2 F-curve:*

The fluid element that have age less than any time ‘$t_1$’ is represented by F($t_1$), which is also called fluid fraction’s “cumulative distribution” (Xi et al. 2015).

$$\int_0^{t_1} E dt = F(t_1) \tag{2.46}$$

Mean value of the E-Curve or the mean residence time can be calculated as

$$t_m = \frac{\int_0^\infty tE(t)dt}{\int_0^\infty E(t)dt} \tag{2.47}$$

For constant density systems mean residence time is calculated as

$$\tau = V/Q \tag{2.48}$$

Where $V$ = working volume of the reactor, $m^3$ or mL

$Q$ = volumetric flow rate of the fluid, $m^3$/min or mL/min

M = units of tracer introduced (g or moles)

E-curve can be estimated from the C-curve as

$$E = \frac{C_{pulse}}{M/_{Q}} \tag{2.49}$$

$$E_\theta = \tau E = \frac{V}{M}C \tag{2.50}$$

$$\theta = \frac{t}{\tau} \tag{2.51}$$

Spread of the E-curve can be measured by estimation of variance ($\sigma^2$), It has the unit of $time^2$

$$\sigma^2 = \frac{\int_0^\infty (t-t_m)^2 C dt}{\int_0^\infty C dt} = \frac{\int_0^\infty t^2 C dt}{\int_0^\infty C dt} - t_m^2 \tag{2.52}$$

***2.18.3 Dispersion Model:***

Further to characterize the flow pattern of the reactor a term of dispersion number (D/uL) is defined as per dispersion model. If dispersion number is 0 the flow is more towards plug flow and if the dispersion number is infinity the flow is more towards mixed flow. D/uL is estimated by equation 2.53 (Valderrama et al. 1986)

$$\sigma_\theta^2 = 2(\frac{D}{uL}) \tag{2.53}$$

There is presence of low dispersion when dispersion number is less than 0.05, presence of moderate dispersion when dispersion number is between 0.05 and 0.25 and there is the presence of high dispersion when dispersion number is greater than 0.25 (Levenspiel et al. 1970).

### 2.19 Kinetic models used in Phytoremediation study

***2.19.1 Relative growth rate (RGR):*** The relative growth rate of the plant is calculated by following equation (Maine et al. 2001; Gomez et al. 2011)

$$RGR = \frac{W_2 - W_1}{T_2 - T_1} \tag{2.54}$$

$W_1$ = Weight of the plant at time $T_1$

$W_2$ = weight of the plant at time $T_2$

***2.19.2 Bio concentration factor (BCF):*** Bio concentration factor (BCF) of the pollutant in the root of the plant was calculated as given by equation 2.55 (Tejeda et al. 2010; Singh et al. 2008; Chen et al. 2010).

$$BCF = \frac{C_{org}}{C_w} \tag{2.55}$$

$C_{org}$ = Concentration of the heavy metals in the root of plant

$C_w$ = Concentration of heavy metal in synthetic waste water

BCF was calculated to determine the ability of water hyacinth for the accumulation of heavy metal Cr(VI).

### 2.20 Michelis Menton kinetic models:

Michelis menton kinetics model was applied for the simultaneous removal of Cr(VI) and phenol through phytoremediation and bioremediation using equilibrium experimental data. The specific growth rate ($h^{-1}$) was calculated as per the following equation (Huertas et al. 2010; Littlejohns et al. 2008; Tekerlekopoulou et al. 2013; Trigueros et al. 2010).

$$\mu = \frac{\ln(OD_2/OD_1)}{(t_2 - t_1)} \tag{2.56}$$

$OD_2$ = optical density at time $t_2$

$OD_1$ = optical density at time $t_1$

$t_2$= exponential phase time

$t_1$ = lag phase time

#### *2.20.1 Monod Kinetic model:*

If Cr(VI) and phenol is considered as non-inhibitory compound. Thus Monod non inhibitory kinetic model was applied to the experimental data for the estimation of model parameters $\mu_m$ and $K_s$ (Golicnik et al. 2011; Kaur et al. 2012). The linearized form of the Monod kinetic model is given below which is also known as line weaver Burk plot (Srivastava et al. 1998; Arya et al. 2006).

$$\frac{1}{\mu} = \frac{1}{\mu_m} + \frac{K_S}{\mu_m}\frac{1}{S} \tag{2.57}$$

When S >>$K_S$,

$K_S$ is the half velocity constant, or saturation constant, or Monod constant (g/L), S substrate concentration, $\mu_m$ maximum specific growth rate ($h^{-1}$). Values of $\mu_m$ and $K_s$ can be evaluated from 1/μ versus1/S plot (supposing S = $S_o$ at the start of exponential growth) returns a straight line with a y–axis intercept of $1/\mu_m$ and a slope of $K_s/\mu_m$.

### *2.20.2 Haldane kinetic model:*

If the Cr(VI) and phenol was considered as an inhibitory compound for a single substrate solution, then the Haldane inhibitory kinetic model was applied to the experimental data for the estimation of Haldane inhibitory constant $K_i$ (Gopinath et al. 2011).

$$\mu = \frac{\mu_{max} S_L}{K_s + S_L + \frac{S_L^2}{K_i}} \tag{2.58}$$

### *2.20.3 Sum kinetic model:*

For the binary solution of Cr(VI) and phenol, the interaction parameters were determined according to the sum kinetic model for binary inhibitory substrates (Juang et al. 2006; Abuhamed et al. 2004).

$$\mu = \frac{\mu_{max,1} S_{1L}}{K_{S,1} + S_{1L} + I_{2,1} S_{2L} + \frac{S_{1L}^2}{K_{1i}}} + \frac{\mu_{max,2} S_{2L}}{K_{s,2} + S_{2L} + I_{1,2} S_{1,L} + \frac{S_{2L}^2}{K_{2i}}} \tag{2.59}$$

**2.21 Work done on removal of chromium by batch adsorption method:** The extensive literature survey was carried out for the simultaneous removal of Cr(VI) from single component synthetic solution using adsorption. Table 2.21 shows the adsorption study carried out by various researchers for the removal of Cr(VI).

**(1) Li et al. (2015):** They used nanosized chitosan fibres for the removal of chromium (VI). Batch shake flask experiment was performed to investigate the adsorption capacity of chitosan fibres. The maximum adsorption capacity of chitosan fibres was found to be 131.58 mg/g. XPS (X-ray photoelectron spectrometry), SEM and FTIR were performed to confirm the adsorption of Cr(VI) ions. Various equilibrium adsorption isotherms and kinetic models were applied to experimental data to estimate the behaviour of Cr(VI) adsorption onto the surface of chitosan fibres.

**(2) Mthombeni et al. (2015):** They investigated the adsorption of Cr(VI) onto the surface of magnetic natural zeolite-polymer composite. The surface morphology, functional groups present onto the surface of zeolite polymer, composition of various elements present and structure were obtained by FE-SEM, FTIR, EDX and XRD respectively. At an initial concentration of 300 mg/L, pH 2 and Temperature 45 $^{o}$C, 99.99% removal of Cr(VI) was obtained. The adsorption capacity of zeolite polymer composite was found to be increased from 344.83 - 434.78 mg/g with increasing temperature from 25-45 $^{o}$C according to Langmuir adsorption isotherm.

**(3) Mani et al. (2015):** In this investigation an efficient visible active C-doped $TiO_2$ nanomaterial was developed for the simultaneous removal of Cr(VI) and phenol. XRD and TEM were performed to estimate the physical properties of nanomaterial. BET surface area was performed which shows the high surface area 290 $m^2$/g. Photo catalytic removal of Cr(VI) and phenol was performed which indicated that it is potential nanomaterial for the simultaneous removal of Cr(VI) and phenol.

**(4) Zhang et al. (2014):** adsorption characteristic of HCB/$TiO_2$ prepared from sol gel method was investigated for the adsorption of Cr(VI). Various characterization methods such as XRD, TEM was carried out to confirm the deposition of $TiO_2$ onto the surface of HCB. The effect of various parameters such as pH, adsorbent dose, contact time, initial concentration of Cr(VI) were estimated onto the percentage removal of Cr(VI) using batch adsorption experiment. In the acidic medium, the maximum adsorption capacity of HCB/$TiO_2$ was found to be 27.33 mg/g. Mathematical and thermodynamic modelling of such equilibrium adsorption isotherm were applied to the experimental data.

**(5) Marjanovic et al. (2013):** Adsorption of Cr(VI) from synthetic aqueous solution of Cr(VI) onto the surface of amine-functionalized natural and acid-activated sepiolites was investigated. The point of zero charge was estimated to optimise the effect of pH. The maximum percentage removal of Cr(VI) was found to be decreased with increasing the pH of the aqueous solution and it was found to be maximum at pH 2. The maximum adsorption capacity was found to be 60 mg/g. Freundlich adsorption isotherm, Pseudo second order model was agreed well with experimental data. Thermodynamic modelling of the experimental data reveals that adsorption process was spontaneous in nature.

**(6) Gładysz-Płaska et al. (2012):** In this study natural red clay modified by HDTMA (hexadecyl trimethyl ammonium bromide) was used to study the simultaneous adsorption of Cr(VI) and phenol from synthetic binary aqueous solution. The equilibrium condition was reached after 5 h for Cr(VI) and after 6 h for phenol. The pH corresponding to the maximum adsorption of Cr(VI) and phenol was 4-6.5. The maximum adsorption capacity of Red clay at pH 5.5 was found to be 0.086 mmol/g for Cr(VI) and 0.012 mmol/g for phenol. The adsorption characteristic of Cr(VI) and phenol was measured by XRD and FTIR of red clay before and after the adsorption of Cr(VI) and phenol. First order kinetic model was fitted to the experimental data for the simultaneous adsorption of Cr(VI) and phenol onto the surface of red clay modified by HDTMA.

**(7) Albadarin et al. (2012):** In this study industrial waste water from a major aerospace manufacturing facility containing Cr(VI) was used for the treatment. The raw dolomite as adsorbent was used for the batch adsorption experiments. The effect of initial concentration of Cr(VI), quantity of adsorbent, temperature, particle size and speed (rpm) was investigated onto the percentage removal of Cr(VI). Maximum percentage removal was obtained at pH 2.0. Kinetic, thermodynamic and adsorption isotherm modelling were applied onto the experimental data. From kinetic study it was evident that with an adsorbent dose of 1 g/L, 96 h contact time was sufficient for attaining equilibrium. Adsorption studies were carried out at an initial concentration range of 5–50 mg/L. It was observed that the Freundlich isotherm model best described the equilibrium adsorption. Pseudo second order model follows the kinetic process of adsorption. Thermodynamic study reveals that the process is spontaneous and exothermic in nature.

**(8) Jain et al. (2010):** In this study adsorption of Cr(VI) ions was carried out from aqueous solution by sulphuric acid treated sunflower waste. Sunflower plant head and stem waste were used for the adsorption of Cr(VI) namely SHC (Sunflower plant head) and SSC (Sunflower stem waste) respectively. FTIR, SEM, BET surface area and EDX were used for the characterization of adsorbent. The effect of various process parameters such as pH, temperature, initial metal ion concentration, adsorbent dosage and contact time were studied onto the percentage removal of Cr(VI). The maximum percentage removal was obtained at optimum conditions of pH 2, contact time of 2 h, adsorbent dosage 4.0 g/L, initial concentration 250 mg/L, temperature 25 $^{o}$C, and at 180 rpm. The Adsorption isotherms such as Freundlich, Langmuir and D–R isotherm models were applied to the experimental data for the mathematical description of the equilibrium condition. The experimental data were fitted well to the Langmuir isotherm and calculated maximum adsorption capacities were found to be 53.76 mg/g and 56.49 mg/g for SHC and SSC, respectively.

**(9) Bhatnagar et al. (2010):** They claimed that adsorption using activated carbon is one of the best water treatment technologies worldwide. Activated carbon is a universal adsorbent for the removal of heavy metals and organic compounds from industrial wastewater. But due to the higher cost of activated carbon in comparison to other cheap bio sorbents it cannot be used in industrial scale applications. Therefore, there is a need for the development of effective biosorbent comparable to activated carbon. They investigates that the use of agricultural waste materials as adsorbents is attractive because of their low cost, thus contributing to environmental protection. In this review a wide range of low-cost adsorbents prepared using waste material were compiled and their adsorption capacities for the removal of various heavy metals and organic compounds were presented.

**(10) Acharya et al. (2009):** In this study, the activated carbon was prepared from tamarind wood and activated with zinc chloride for the adsorption of Cr(VI). Batch adsorption studies were carried out in the range of 10-50 mg/L of initial concentration of Cr(VI) and 10-50 $^{o}$C temperature. Adsorption isotherm such as Langmuir and Freundlich were applied to the experimental data. Both Freundlich isotherm and the Langmuir isotherm were well described the adsorption capacity 28.019 mg/g which was in good agreement with experimental adsorption capacity. Kinetics of adsorption was studied by applying various kinetic models, which shows that pseudo-second order kinetic model was fitted well with experimental data. Boyd plot shows that the external mass transfer was the rate limiting step in the adsorption process. Thermodynamic study was carried out to know the feasibility of adsorption process which was spontaneous and endothermic in nature.

**(11) Kumar et al. (2009):** They prepared activated carbon prepared from non-usable Bael fruit shell (BS) for the removal of Cr(VI) from aqueous synthetic solution. The effect of various batch adsorption study process parameters such as pH, contact time, initial concentration and adsorbent dosage were studied onto the percentage removal. The maximum percentage removal chromium from aqueous solution was found at pH 2.0 and at a contact time of 240 min. The adsorption isotherm models such as Langmuir and Freundlich agreed well with experimental data. The adsorption capacity calculated according to Langmuir equation was found to be 17.27 mg/g. The pseudo-second-order chemisorptions kinetic model well defines the adsorption kinetic. The scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectrometer (FT-IR) analysis were carried out to confirm the adsorption of Cr(VI) onto the adsorbent surface. Activation of adsorbent surface with phosphoric acid improved the pores available for adsorption and played an important role in adsorption.

**(12) Levankumar et al. (2009):** In this work the adsorption of hexavalent chromium onto the surface of *Ocimumamericanum* L. Seed pods from aqueous solution was studied. The optimum process parameters such as pH and shaker speed were found to be 1.5 and 121 rpm. The equilibrium adsorption data agreed well with Langmuir adsorption isotherm. The maximum chromium adsorption capacity according to Langmuir isotherm was found to be 83.33 mg/g. The batch experiments were carried out at concentrations of 100 mg/L, 150 mg/L and 200 mg/L chromium solution. The optimum adsorbent dosage was found to be 8 g dry seed pods/L. The 100% removal was observed at all initial concentrations studied. The equilibrium condition was achieved in less than 120 min for all the three concentrations. The adsorption kinetic data was fitted well with first and second order kinetic models.

**(13) Yun-guo et al. (2008):** In this study consortium culture of *Bacillus* sp. and *Pseudomonas Putida Migula* (CCTCC AB92019) was used for the simultaneous reduction of Cr(VI) and biodegradation of phenol. Phenol was used as the sole carbon source by *Bacillus* sp. for the biodegradation of phenol and metabolites formed during biodegradation of phenol was used by *Pseudomonas Putida Migula* for the reduction of Cr(VI). The maximum percentage removal of Cr(VI) at an initial concentration of 15 mg/L was observed in the presence of phenol at an initial concentration of 150 mg/L. It was observed that amount of Cr(VI) reduced and biodegradation of phenol was found to be more than that of stoichiometrically mass balance of Cr(VI) and phenol.

**(14) Bhattacharya et al. (2008):** In this study different low-cost adsorbents was used for the removal of Cr(VI). Various adsorbents such as clarified sludge a steel industry waste material, rice husk ash, activated alumina, fuller’s earth, fly ash, saw dust and neem bark were used for the removal of chromium. The effect of pH, adsorbent dose, initial Cr(VI) concentration and contact time onto the percentage removal were studied. The adsorption process was highly dependent on pH. The maximum percentage removal of Cr(VI) was found between pH 2-3. Kinetic studies were carried out to describe the rate of adsorption of Cr(VI) which shows that pseudo second order kinetic model best fitted with experimental data. Langmuir and Freundlich adsorption isotherms were applied to the experimental data and their constants were evaluated. The thermodynamic study was conducted which shows that the process was spontaneous in nature. Out of different adsorbent clarifier sludge was more effective among those selected for the removal of Cr(VI) from aqueous solution.

**(15) Mohan et al. (2006):** They investigated that hexavalent chromium Cr(VI) is a well-known, highly toxic metal, considered a priority pollutant. Various industries include leather tanning, cooling tower blow down, plating, electroplating, anodizing baths, rinse waters, etc discharge Cr(VI) as waste effluent. The most common method used for the removal of Cr(VI) was conversion of hexavalent to its trivalent form in acid (pH∼2.0).After conversion, precipitation of Cr(III) was carried out by increasing the pH to ∼9.0–10.0 using lime. In this study an extensive review was carried out for the removal of chromium using various technologies and their advantage and disadvantages were reported.

**(16) Sankararama krishnan et al. (2006):** They studied the suitability of a novel cross linked, chemically modified chitosan as highly efficient adsorbent for the removal of toxic chromium(VI). The adsorption process was found to be both pH and concentration dependent and maximum percentage removal was found at pH 3. The pseudo-second-order kinetics constant for CMCB and CMCF were found to be 2.037 and 4.639 g/mg/min, respectively. The experimental data followed the Langmuir isotherm model with maximum capacities of 625 mg/g and 256.4 mg/g for CMCF and CMCB respectively.

**(17) Quintelas et al. (2006):** They studied the removal of chromium and organic compounds (chlorophenol, phenol and o-cresol) using a biofilm of *Arthrobacter* viscous supported on granular activated carbon. The potential of *Arthrobacter* viscous supported on granular activated carbon for removal of Cr(VI) and phenol was estimated from both single and in combination of Cr(VI) and phenol. The optimum adsorption of Cr(VI) and phenol was observed at an initial concentration of 100 mg/L Cr(VI) and 60 mg/L phenol, respectively. The adsorption of chromium and organic compound after 15 h of experiment were observed in the following order:

Phenol > chlorophenol > o-cresol >Cr(VI)

The maximum value of biosorption capacity of organic compound was 9.94 mg/g phenol, 9.70 mg/g chlorophenol and 13.99 mg/g o-cresol.

**(18) Aksu et al. (2001):** In this study competitive biosorption of Cr(VI) and phenol both from single and binary solution of Cr(VI) and phenol were studied using dried anaerobic activated sludge. The influence of pH, single and dual concentration of Cr(VI) and phenol in synthetic solution on equilibrium uptake were studied. Single and multicomponent adsorption isotherm modelling were applied onto the experimental data and non-linear regression method was used to solve the model for parameters estimation. They claim that dried anaerobic activated sludge is potential biosorbent for simultaneous removal of Cr(VI) and phenol.

**(19) Nkhalambayausi-Chirwa et al. (2000):** In this study bioreactor consists of consortium culture of *Pseudomonas putida* and *Escherichia coli* was used for the simultaneous Cr(VI) reduction and biodegradation of phenol. Maximum percentage removal of Cr(VI) and phenol was found to be under loading of 5-21 mg/L/d of Cr(VI) and 840-3350 mg/l/d of phenol.

**2.22 Work done on removal of phenol by batch adsorption method:** The brief literature review for the simultaneous removal of Cr(VI) and phenol from single component solution was carried out. Table 2.22 shows the literature survey of the study conducted by various researchers for the adsorption of phenol from single component solution.

**1. Han et al. (2015):** In this study a series of CNT@MIL- 68(Al) composites with different carbon nanotubes (CNTs) loadings were synthesized in the laboratory for the adsorption of phenol. The adsorptive properties of CNT composites was characterised by SEM, TEM, PXRD, TGA and $N_2$ adsorption. Adding appropriate amount of carbon nanotubes in the series improve the BET surface area and adsorption capacity up to 187.7 %. Regeneration of the composites also performed which show that it can be easily regenerated for at least five cycles.

**2. Hank et al. (2014):** In this investigation, potential of F400 carbon and bentonite for adsorption of phenol were studied. Langmuir, Freundlich and Temkin adsorption isotherm model were fitted well to the experimental data. A full factorial design using response surface methodology was used for the optimization of parameters. F400 activated carbon shows negative results while bentonite was potential biosorbent for the removal of phenol.

**3. Pacurariu et al. (2013):** In this study two polymers styrene-co-divenylbenzene $P_1$(functionalized with amino-phosphinic acid groups) and $P_2$ (functionalized with carboxylic acid groups) were synthesized for the adsorption of two pollutants phenol and p-chlorophenol from aqueous solutions. The adsorptive properties of this polymer were compared with commercially available XAD-4 resins.

## Table 2.21 Various Adsorbents used for the adsorption of Cr(VI) in literature

| S. NO | Authors | Bioadsorbent | Initial Cr conc. | Temp (°C) | pH | Time (hr) | Adsorbent dose (g/l) | Removal efficiency (%) | Adsorption capacity mg/g |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Mthombeni et al. 2015 | MZ-PPy composite | 300 | 45 | 2 | 24 | 15 | 99.99 | 434.78 |
| 2 | Daraei et al. 2014 | eggshell membrane | 5 | 20 | 3.54 | 1.96 | 35.40 | 81.47 | 107.77 |
| 3 | Marjanovic et al. 2013 | amine-functionalized composite | 10 | 25 | 2 | 24 | 10 | 99.99 | 60 |
| 4 | Demiral et al. 2012 | Activated carbon from olive bagasse | 100 | 30 | 2 | - | 15 | 88 | - |
| 5 | Mohan et al. 2011 | Oak wood char, oak bark chars | 100 | 45 | 2 | 48 | 10 | - | 4.93, 7.51 |
| 6 | Hadjmohammadi et al. 2011 | Pine needle powder | 50 | Room temp | 3 | 0.75 | 1 | - | 40 |
| 7 | Sartape et al. 2010 | Wood apple shell | 90 | 37 | 2 | 3 | 0.5 | 98.05 | 13.74 |
| 8 | Vinodhini et al. 2009 | Mango sawdust | 150 | 28 | 2 | 6 | 2 | - | 37.73 |
| 9 | Vinodhini et al. 2009 | Neem sawdust | 150 | 28 | 2 | 6 | 2 | - | 58.82 |
| 10 | Bhattacharya et al. 2008 | Clarified sludge | 50 | 30 | 3 | 2 | 10 | 97.4 | 26.31 |
| 11 | Bhattacharya et al. 2008 | Rice husk ash | 50 | 30 | 3 | 2 | 10 | 94.8 | 25.64 |
| 12 | Bhattacharya et al. 2008 | Activated alumina | 50 | 30 | 3 | 2 | 10 | 93.8 | 25.57 |
| 13 | Bhattacharya et al. 2008 | Fuller;s earth | 50 | 30 | 3 | 2 | 10 | 88.5 | 23.58 |
| 15 | Bhattacharya et al. 2008 | Fly ash | 50 | 30 | 3 | 2 | 10 | 89.2 | 23.86 |
| 16 | Bhattacharya et al. 2007 | Saw dust | 50 | 30 | 3 | 2 | 10 | 86.5 | 20.70 |
| 17 | Tahir et al. 2007 | Bentonite clay | 100 | - | 2.5 | 0.25 | 10 | 93 | 49.75 |
| 18 | Vankateswarlu et al. 2007 | Neam leaf powder | 75 | Room temp | 7.4 | 5 | 2 | 96 | 7.43 |
| 19 | Garg et al. 2007 | Sugarcane bagasse, maize corn cob, jjatropha oil cake | 500 | 25 | 2 | 1 | 20 | 92<br>62<br>97 | - |
| 20 | Babu et al. 2007 | Neem leaves | 700 | 30 | 1 | 67 | 10 | - | 62.97 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 21 | Mohan et al. 2006 | Coconut shell fibers | 100 | 25 | 5 | 0.1 | 80 | 48 | 12.2 |
| 22 | Sarin et al. 2006 | Eucalyptus bark | 250 | 32 | 2 | 5 | 99 | 24 | 45 |
| 23 | Baral et al. 2006 | Treated sawdust of sal tree | 40 | 30 | 3.5 | 1 | 0.1 | - | 9.55 |
| 24 | Babu et al. 2006 | Tamrind seeds | 50 | 30 | 7 | - | 10 | - | 11.08 |
| 25 | Karthikeyan et al. 2005 | Heveabrasiliensis sawdust activated carbon | 200 | 30 | 2 | 5 | 1 | - | 44.05 |
| 26 | Oliveira et al. 2005 | Raw rice bran | 75 | 25 | 2 | 1.5 | 10 | - | 0.15 |
| 27 | Garg et al. 2004 | Formaldehyde treated saw dust Indian rosewood | 100 | 26 | 3 | 4 | 3 | 62.2 | - |
| 28 | Acar-Malkoc et al. 2004 | Beech sawdust | 200 | 25 | 1 | 1.33 | 10 | 100 | 16.13 |
| 29 | Bishnoi et al. 2004 | Formaldehyde treated rice husk | 10 | - | 2 | 1 | - | 88.88 | - |
| 30 | Gupta et al. 2004 | Bagasse fly ash | 20 | 30 | 5 | 1 | 10 | 98 | - |
| 31 | Farajzadeh et al. 2004 | White bran | 20 | 25 | 5 | - | 80 | 89 | 93 |
| 32 | Hu et al. 2003 | Activated Carbon (GA-3) | 200 | - | 3.2 | 72 | 2 | 74.7 | 57.7 |
| 33 | Hu et al. 2003 | Activate carbon (SHT) | 200 | - | 3.2 | 72 | 2 | 63.1 | 48.7 |
| 34 | Selvaraj et al. 2003 | Distillery sludge | 10 | - | 3 | 1.75 | 0.35 | 82 | 5.7 |
| 35 | Dakikky et al. 2002 | Wool | 100 | 30 | 2 | 2 | 8 | 70 | 8.66 |
| 36 | Rajeshwari sivaraj et al. 2002 | Activated parthenium carbon | 100 | Room temp. | 3.2 | 1 | 10 | 63.75 | - |
| 37 | M. Rao et al. 2002 | Pretreated bagasse with NaOH and $CH_3COOH$ | 100 | - | - | - | - | 90, 67 | - |
| 38 | Dakiky et al. 2002 | Almond | 100 | 30 | 2 | 2 | 8 | 23.5 | 10 |
| 39 | Dakiky et al. 2002 | Cactus | 100 | 30 | 2 | 2 | 8 | 19.8 | 7.08 |
| 40 | Dakiky et al. 2002 | Coal | 100 | 30 | 2 | 2 | 8 | 23.6 | 6.78 |
| 41 | Daneshvar et al. 2002 | Soy cake | 50 | 25 | 1 | 1 | 0.75 | - | 0.28 |
| 42 | Dakiky et al. 2002 | Olive cake | 100 | 30 | 2 | 2 | 8 | 47.1 | 33.44 |
| 43 | Dakiky et al. 2002 | Pine needlws | 100 | 30 | 2 | 2 | 8 | 42.9 | 21.50 |
| 44 | Dakiky et al. 2002 | Saw dust | 100 | 30 | 2 | 2 | 8 | 53.5 | 15.82 |
| 45 | Selvi et al. 2001 | Coconut tree sawdust | 20 | 30 | 3 | 3 | 4 | - | 3.60 |
| 46 | Gardea-torresday et al. 2000 | Oat biomass | 100 | 30 | 2 | 2 | 30 | 80 | - |
| 47 | Namasivayam et al. 1995 | Biogas residual slurry | 40 | 30 | 2 | - | 4 | - | 5.87 |
| 48 | Sharma et al. 1994 | Saw dust | 1000 | 25 | 2 | 24 | 4 | - | 39.7 |

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|---|---|---|---|---|---|---|---|---|---|---|
| 49 | Sharma et al. 1994 | Sugarcane bagasse | 500 | 25 | 2 | 24 | 4 | - | 13.4 |
| 50 | Sharma et al. 1994 | Sugar beet pulp | 500 | 25 | 2 | 24 | 4 | - | 17.2 |
| 51 | Tan et al. 1993 | Palm pressed fibres | 5 | Room temp | 2 | 2 | 10 | - | 15 |
| 52 | Orban et al. 1993 | Agricultural waste | 5 | Room temp | - | 2 | 3 | 93 | 1.55 |
| 53 | Namasivayam et al. 1993 | Fe(III)/Cr(III) hydroxide | 10 | - | 5.6 | 3 | 10 | - | 1.43 |
| 54 | Orban et al. 1993 | Walnut Shell | 5 | Room temp. | - | 2 | 0.1 | 80 | 1.33 |
| 55 | Alaerts et al. 1989 | Coconut based activated shell carbon | 20 | - | 2.5 | - | - | - | 2 |
| 56 | Hunag et al. 1977 | Coconut husk fibers | - | - | 2.05 | - | - | - | 29 |

**4. Lu et al. (2012):** This study investigated the ability of aerobic microorganism *Bacillus amyloliquefaciens* strain WJDB-1 for utilizing carbon from phenol. It was isolated and identified based on physical, biochemical characteristics, and morphology and 16S r DNA sequence analysis. The alginate–chitosan–alginate microcapsules formed by immobilization on isolate was capable of degrading 200 mg/L of phenol within 36 h. Microbial cells immobilized in alginate–chitosan–alginate microcapsules were superior than free suspended ones on account of loading. The optimal conditions for preparation of microcapsules to achieve higher phenol degradation by adjusting the sodium alginate, chitosan and calcium chloride concentrations. This strain was found to be capable for the phenol removal from wastewater.

**5. Yousef et al. (2011):** Authors have investigated the use of zeolitic tuff for the phenol removal in a batch adsorption. The adsorption studies were performed using zeolite. The pseudo-second-order model was followed by the adsorption process. The Freundlich was best-fitted adsorption isotherm model for 25–45 °C temperature. From the Langmuir model, maximum adsorption capacity of zeolite were 35, 29, 28 and 23 mg/g at 25, 35, 45 and 55 °C temperature respectively. It was estimated thermodynamically that the process is physisorption and enthalpy $\Delta H° = -10.2$ kJ/mol.

**6. Beker et al. (2010):** In this study activated carbon was prepared from Cherry stone and activated with KOH and $ZnCl_2$ for the removal of phenol from aqueous solution. Comparative study on the phenol removal was examined by using activated carbon and two polymeric adsorbents containing styrene–divinyl benzene. Equilibrium studies were conducted with initial concentration ($C_O$) of 30 mg/l, 6–9 pH and 30 °C temperature. The cherry stone based activated carbon was activated using $ZnCl_2$ and KOH were used at different chemical ratios for better porosity. Polymeric sorbents and commercial activated carbon had low adsorption than activated carbons for phenol removal.

**7. Aravindhan et al. (2009):** This work showed the use of *Caulerpascal pelliformis*, a biosorbent, for phenol removal from the effluent of tanning industry. Biosorption using algal biomass was judged by investigating the effects of $C_0$, temperature, initial pH ($pH_0$) and contact time. Biosorption isotherm and kinetics were described by Langmuir and pseudo second order model, respectively, which confirmed the monolayer biosorption. The maximum uptake was found to be 20 mg/g for 87% removal efficiency at $pH_0$ of 6.0. A Boyd plot showed that the external mass transfer was the slowest step and thermodynamic studies confirmed that the biosorption process was exothermic. The average effective diffusion coefficient ($k_D$) was found to be $1.44 \times 10^{-9}$ $cm^2/s$. This method was effective for the removal of phenol at optimized parameters for the treatment of waste effluent.

**8. Tan et al. (2008):** In this study, activated carbon was produced from coconut husk and activated it by KOH and $CO_2$ treatment. The effects of variables such as temperature for activation of $CO_2$, time and ratio of KOH to char impregnation on the 2,4,6-trichlorophenol (2,4,6-TCP) uptake and yield of activated carbon were studied. The central composite design (CCD) was used and two quadratic models were developed. From the analysis of variance (ANOVA), the most influencing factor on response was detected. The optimized parameters for preparation of activated carbon were calculated by maximizing both the responses. The responses as predicted from the models were in good agreement with the experimental values. The optimum conditions were found to be 750 °C of $CO_2$ activation temperature, 2.29 h of $CO_2$ time and 2.91 impregnation ratio and 191.73 mg/g of uptake and 20.16 % of yield.

**9. Mukherjee et al. (2007):** Here a comparison was made of three adsorbents materials, bagasse ash activated carbon and wood charcoal for removal of phenol. The two initial concentrations of 50 mg/L and 30 mg/L and adsorbent dose of 50 g/L were used in batch experiments. The study on solution pH, EDTA concentrations, anions and adsorbent dosage effects were also evaluated. Desorption tests were also carried out in this work. Experimental results showed that 98%, 90% and 90% removal efficiencies were achieved for phenol–Activated carbon, phenol–wood charcoal and phenol–bagasse ash adsorption systems respectively. First order kinetic and Freundlich isotherm model were found to be best fitted. Removal of phenol increased on decreasing pH of adsorption system. However, opposite effects by chloride ion is shown on bagasse ash. The film diffusion may be controlling the adsorption of phenol shown by diffusion coefficient.

**10. Sarkar et al. (2006):** This study evaluated the ability of fly ash for the adsorption of some phenolic pollutants and the effects of different operating variables such as initial concentrations, agitation time, speed, dose, particle size, solution pH and temperature. The work showed that the molecular size, solute concentration and molecules of the solute affected the solute removal. The adsorption was characterized by the surface of fly ash and pH has very important role. It is because of the solutes ionizing capacity and the fly ash zero point charge. The process is favorable and spontaneous shown by isotherm parameter and the Gibbs energy change. The leaching experiment was also carried out which indicated that the adsorbed solutes did not release from fly ash.

**11. Srivastava et al. (2006):** The research evaluated the ability of carbon rich bagasse FA, commercial grade and laboratory grade activated carbon for the adsorption of phenol. Experimental parameters like initial pH, initial concentrations, time and adsorbent dose were studied in batch studies. Adsorption isotherms were studied by varying initial concentration from 75 to 300 mg/L with adsorption rate on activated carbon-commercial grade being the highest followed by that on rich bagasse FA and activated carbon laboratory grade. The maximum percentage removal of phenol was obtained at optimum conditions of pH 6.5, adsorbent dose 10 g/L and equilibrium time 5 h. The $k_D$ of phenol was determined to be $10^{-10}$ $m^2/s$. Redlich–Peterson isotherm best described the experimental data for all the adsorbents. The thermodynamic parameters $\Delta H°$ and $\Delta S°$ for bagasse FA were determined as 0.5 MJ/kg and 1.8 MJ/kg K respectively. Bagasse FA showed better adsorption and could be utilized as adsorbent due to the silica, alumina and high carbon content.

**12. Tor et al. (2006):** This work was carried out on phenol removal using red mud. This research was performed to remove the phenol by using neutralized red mud in batch study. Maximum removal of phenol was obtained in a pH range from 1–9 and 10 h of equilibrium time. The adsorption data was studied and Freundlich isotherm model represented the measured adsorption data. The study showed that the heterogeneous adsorption. Influence of anions was studied showing an increase in chloride dosage did not affect the removal efficiency of phenol than nitrate and sulfate. This is accounted for the selectivity toward nitrate and sulfate ions by red mud.

**13. Mohanty et al. (2005):** This paper studied the *Terminalia Arjuna*, agricultural waste for the preparation of activated carbon from and its modification using zinc chloride under four different activation atmospheres. The pore structure of carbon was changed at different activation atmosphere. The optimal experimental conditions for the maximum removal of 93 % were achieved at 1 h of time and temperature of 500 °C. The BET surface area and micro pore volume obtained as 1260 $m^2/g$ and 0.560 $cm^3/g$, respectively. The maximum phenol removal was 93% at optimized conditions. Optimized conditions were pH 3.5, adsorbent dose of 10 g/l and initial concentration 100 mg/l. The batch adsorption tests indicate that the activated carbon derived from *Terminalia Arjuna* nut had a markable adsorption characteristic for phenol removal.

**14. Roostaei et al. (2004):** Phenol adsorption was studied using adsorbents like activated alumina, silica-gel, zeolites and activated carbon. Silica-gel and activated alumina had low phenol removal however zeolite-Y showed the highest removal. Activated carbon reached its saturation capacity after 10 days period during the phenol adsorption. Adsorption capacity of zeolite was decreased with increase in temperature thus system being exothermic.

**15. Annadurai et al. (2002):** Phenol biodegradation was carried out using *Pseudomonas putida* (ATCC 31800) and activated sludge. Temperature, pH, $(NH_4)_2SO_4$ and glucose were used as experimental variables. RSM was used on Box–Behnken model to evaluate the factors on phenol degradation. Second-order polynomial regression equation was developed that gave the $F$-value as 3605.45 and $R^2$-value of 0.9997 and the maximum degradation of phenol was 80.1%.

**2.23 Work done on removal of chromium by continuous method:** An extensive literature was reviewed for the simultaneous removal of Cr(VI) and phenol in continuous column. Table 2.23 shows the work carried out by various researchers for the continuous removal of Cr(VI) and phenol.

**1. Sahinkaya et al. (2012):** In this study, batch experiments were carried out for the abiotic reduction of Cr(VI) with elemental sulphur in the absence of biomass. These experiments were carried out in an anaerobic reactor for the microbial reduction of Cr(VI) using all required micro and macro nutrients for the growth of microbes, 5 g elemental sulphur and 2 mg/L Cr (VI). The continuous reactor was operated at 30 $^oC$ for 24 h. The stoichiometry of reduction of Cr(VI) to hydrogen sulphide was evaluated. The continuous reactor was consisting of 150 mL serum bottles filled with 100 mg/L Cr(VI) aqueous solution in distilled water and covered with rubber septa and aluminium caps. For the anaerobic reduction of Cr(VI) oxygen was removed by passing $N_2$ gas for 5 minutes to the serum bottles.

**2. Carmona et al. (2012):** Removal of Cr (III) and Cr(VI), two oxidation states of chromium were studied. The removal of Cr(VI) and Cr(III) were carried out in continuous reactor consisting of *Saccharomyces cerevissae* immobilized on residual pumice. The residual pumice was used as biosorbent due to its low cost and mechanical resistance. Breakthrough curve was drawn for the removal of Cr(VI) and Cr(III) with time. Furthermore, the upgradation of biosorbent immobilization on the mechanical support was carried out using redistribution system through the column length for the better contact between the adsorbate and adsorbent through the continuous reactor. The breakthrough curves were drawn for the study of percentage removal of chromium with time.

The continuous reactor was consists of a PVC column of 4.3 cm diameter and 140 cm length, mechanical support was residual pumice, with a void fraction of 0.67, diameter 0.53 cm and redistribution particles diameters were 0.3 cm.

**3. Kumar et al. (2011):** In this study immobilized trichodermavirirde biomass as adsorbent was used in continuous reactor for the removal of toxic heavy metals. Both real waste water of electroplating industry and synthetic waste water consisting of Cr(VI), Ni(II) and Zn(II) were passed through the reactor for the removal of toxic pollutant. The effects of continuous reactor process parameters such as bed-depth, flow rate and initial concentration of metal ions were studied.

**4. Ferro-Orozco et al. (2011):** In this study the removal of Cr (VI) was carried out using mixture of activated sludge (AS) and powdered activated carbon. The effect of initial concentration of Cr(VI) and powdered activated carbon were investigated onto the growth kinetics of activated sludge. The synergistic or antagonistic effect of combining the PAC with activated sludge was determined. The Cr(VI) was reduced to less toxic form Cr (III) and then adsorbed onto the surface of powdered activated carbon. The process parameters, which also affect the microbial Cr (VI) reduction, were also studied. It is concluded that the biological reduction of Cr(VI) is associated with the phase of cell multiplication when no substrate limitation of carbon and nitrogen source.

**5. Wang et al. (2011):** In this study the simultaneous Cr (VI) reduction and phenol degradation were carried out in a fixed-film bioreactor. The packed bed was immobilized with consortium culture of phenol degrading bacteria *Pseudomonas putida DMP-1* and Cr (VI) reducing bacteria *Escherichia coli ATCC 33456*. The reactor column was 20 cm long and 3.8 cm internal diameter and it was constructed from pyrex glass. The various influent feed flow rates (IFR) of 104.7, 221, 419 and 140 mL/d were studied together with a high recycle rate (300 X 104.7 mL/d) for the complete mix conditions.

**Table 2.22: Various Adsorbents used for the adsorption of phenol in literature**

| ***Source*** | ***$C_0$ (mg/l)*** | ***Adsorbent dose(g/l)*** | ***Adsorption capacity (mg/g)*** | ***Removal (%)*** | ***pH*** | ***Temperature ($^{o}$C)*** | ***Time (h)*** | ***Reference*** |
|---|---|---|---|---|---|---|---|---|
| CNT@MIL-68(Al) composites | 1000 | 10 | 109.90 | 99.99 | 7 | 30 | 24 | Han et al. 2015 |
| Bentonite | 20 | 8 | 17.35 | 99.99 | 8 | 30 | 1 | Hank et al. 2014 |
| styrene-co-divinyl benzene | 102 | 6 | 89.67 | 98.65 | 6.5 | 25 | 24 | Pacurariu et al. 2013 |
| Modified fly ash | 30-80 | 20 | - | 61.3 | 9 | 30 | 2 | Allinor et al., 2012 |
| Activated carbon from tobacco residues | 12 | 4 | 6 | 92 | 7 | 20 | 1 | Kilic et al., 2011 |
| Cherry stone based activated carbon by using $ZnCl_2$ and KOH | 25 | 0.5 | - | 94 | 6.5 and 9 | 30 | 24 | Beker et al., 2010 |
| CuO impregnated activated carbon | 1000 | 1 | - | 98 | 7 | 80 | 2 | Liou et al., 2009 |
| Chemically modified Micro alga | 10-150 | - | 20 | 87 | 6 | 30 | 6 | Aravindhan et al., 2009 |
| Activated phosphate rock | 200 | 0.2-1 | 38.34 | 93 | 8 | 20 | 3 | Alzaydien et al., 2009 |
| Bentonite modified with cetyltrimethyl ammonium bromide | 100 | 333 | - | 63 | 9 | 25 | 1 | Senturk et al., 2009 |
| Activated carbon prepared from biomass (rotten sawdust) | 25-200 | 0.2 | 149.25 | - | 3-10 | 30 | 24 | Hameed et al. 2008 |
| Granular activated carbon | 200 | 0.5 | 350 | 98 | 5.7 | 30 | 24 | Sulaymon et al., 2008 |
| Hexadiaminetrimethyl Br on fly ash Zeolite | 50 | 2 | - | 58.5 | 7 | 25 | 24 | Kamble et al., 2008 |
| Granular activated carbon | 207 | - | 1.481 | 89 | 8.5 | 20 | 24 | Vazquez et al., 2007 |
| Sugarcane bagasse fly ash | 200 | 10 | 23.832 | - | 6.5 | 30 | 5 | Srivastava et al., 2006 |
| Activated carbon commercial grade | 200 | 10 | 30.2187 | - | 6.5 | 30 | 5 | Srivastava et al., 2006 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Activated carbon laboratory grade | 200 | 10 | 24.6458 | - | 6.5 | 30 | 5 | Srivastava et al., 2006 |
| Neutralised red mud | 5-200 | 8 | - | - | 6 | 25 | 10 | Tor et al., 2006 |
| Fe/active carbon | 100 | - | - | 90 | 3 | 50 | 20-25 | Zazo et al., 2006 |
| Commercial activated carbon | 200 | 0.5-9 | 49.72 | 94 | - | 20 | 2 | Ozkaya et al., 2006 |
| Amberlite | 100 | 1.5 | 316.8 | - | 8 | - | 48 | Carmona et al., 2006 |
| Resin | 100 | 1 | 207.7 | - | 7 | 25 | - | Pan et al., 2005 |
| Activated carbon treated with $H_3PO_4$ | 1000 | 10 | 142.8 | - | 6 | 25 | 72 | Ahmaruzzaman et al., 2005 |
| Residual Coal treated with $H_3PO_4$ | 1000 | 10 | 142.8 | - | 6 | 25 | 72 | Ahmaruzzaman et al., 2005 |
| Samla coal | 1000 | 10 | 13.3 | - | 6 | 25 | 72 | Ahmaruzzaman et al., 2005 |
| Activated carbon with zinc chloride activation | 100 | - | - | 93 | 3.5 | 25 | 5 | Mohanty et al., 2005 |
| Sawdust | 500 | 30 | - | 25.38 | 6 | 30 | 6-8 | Jadhav et al., 2004 |
| Polymerized sawdust | 500 | 30 | - | 38.48 | 6 | 30 | 6-8 | Jadhav et al., 2004 |
| Saw dust carbon | 500 | 30 | - | 35 | 6 | 30 | 6-8 | Jadhav et al., 2004 |
| FA | 500 | 5 | - | 97 | 7 | 22 | 24 | Nollet et al., 2003 |
| Cetyltrimethyl ammonium bromide/Al Bentonite | 100 | - | 9.9 | - | 2-8 | 25 | 24 | Al-Asheh et al., 2003 |
| Activated carbon with $TiO_2$ | 0.05 | 0.3 | - | 75 | - | 700 | 6 | Tryba et al., 2003 |
| Activated carbon with palm seed coat | 10-60 | 2 | 18.3 | 90 | 6.2 | 27±1 | 24 | Rengaraj et al., 2002 |
| Modified bentonite | 200 | 10 | 34 | 90 | 7 | 25 | 1 | Shen, 2002 |
| *Pseudomonas putida* | 50 | - | - | 80.1 | 7 | 30 | - | Annadurai et al., 2002 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Bentonite | 250 and 500 | 2.5 | 1 | - | 5 | 20 | 48 | Banat et al., 2000 |
| Fly ash | 25-500 | 0.5 | 27.9 | - | 8 | 25 | 24 | Aksu et al. 1999 |
| Peat | 1000 | - | - | 46.1 | 4-5 | 21 | 16 | Viraraghavan et al., 1998 |
| FA | 1000 | - | - | 41.6 | 4-5 | 21 | 5 | Viraraghavan et al., 1998 |
| Bentonite | 1000 | - | - | 42.5 | 4-5 | 21 | 16 | Viraraghavan et al., 1998 |
| Dried activated sludge | 25-500 | 0.5 | 91.1 | - | 8 | 25 | 24 | Aksu et al. 1998 |
| FA | 100 | - | 67 | 43 | - | 20 | - | Akgerman et al., 1996 |

**6. Calereo et al. (2009):** Removal of trivalent chromium from aqueous solution was studied in a fixed bed continuous reactor packed with olives stone as adsorbent. The effect of various process parameters such as inlet concentration of chromium (mg/L), feed flow rate (mL/h) and bed height (cm) were estimated. Various kinetic models such as Bohart-adams, Thomas and Yans model have been applied and compared with experimental breakthrough curve. The Adams-Bohart model describes the initial part of the breakthrough curve. It was observed that the bed height was an important parameter for the designing of fixed bed column.

**7. Kumar et al. (2009):** They studied the removal of Cr(VI) in fixed bed reactor packed with short chain polymer, polyaniline synthesized on the surface of jute fiber (PANI- jute) from synthetic solution. The influence of various process parameters such as influent pH, column bed depth, influent Cr(VI) concentration and influent flow rate were investigated onto the performance of fixed bed reactor. The BDST kinetic model equation was best described the experimental breakthrough curve. Adsorption rate constant and dynamic bed capacity at 10 % breakthrough were calculated as 0.01 l/mg/h and 1069.46 mg/L, respectively.

**8. Elangovan et al. (2009):** They carried out the research for the estimation of performance of various bioreactors under different operating conditions for the COD and hexavalent chromium removal. The Aerobic suspended growth system, Aerobic attached growth system and Anoxic attached growth system were studied in the continuous reactor using both fabricated synthetic and real industrial waste water. The bacterial strain *Arthrobacter rhombi RE* (MTCC 7048) a Cr(VI) reducing microorganism was isolated from chromium contaminated soil. This bacterial strain was used for the removal of COD and Cr(VI) in continuous reactor. Experiments were carried out for the estimation of bio kinetic parameters for both aerobic and anoxic system. The biokinetic parameters for aeorobic system were as follows:

$\mu_{max}$ = 2.34/d, $K_s$ = 190 mg/L as COD, $K_i$ = 3.8 mg/L of Cr (VI), $Y_T$ = 0.377. The biokinetic parameters for anoxic system were $\mu_{max}$ = 0.57/d, $K_s$ = 710 mg/L as COD, $K_i$ = 8.77 mg/L of Cr (VI), $Y_T$ = 0.13.

**9. Ramirez C. et al. (2007):** This study investigated the removal of trivalent chromium Cr(III) and hexavalent chromium Cr(VI) in continuous biosorption column packed with residual brewer *saccharomyces cerevisiae* immobilized on volcanic rock. The continuous column has dimensions of diameter of 45 cm and a length of 140 cm, working flow rate 15 mL/min. Breakthrough curves were used to study the yeast biosorption behaviour in the process. The aim of this study is to investigate the biosorption of chromium using *saccharomyces cerevisiae* as supported on volcanic rock as biosorbent bed in continuous reactor. The behaviour of the experimental breakthrough curves was analysed for each one of the stable oxidation states of chromium using the two parameters (dose-response) mathematical model.

**10. Quintelas et al. (2006):** They investigated the simultaneous removal of chromium and organic compounds (chlorophenol, phenol and o-cresol) from aqueous solution in a continuous reactor packed with a biofilm of *Arthrobacter viscous* supported on granular activated carbon. The synthetic aqueous solution consists of initial phenol concentration of 100 mg/L, initial concentration of chromium 60 mg/L. The adsorption capacity of phenol, chlorophenol and o-cresol were found to be 9.94, 9.70 and 13.99 mg/g respectively. In terms of percentage removal after 15 h of experiment the affinity order was as follows:

Phenol> chlorophenol> o-cresol> Cr (VI)

In this study an innovative process for the simultaneous removal of heavy metals and organic compounds was developed. The influence of process parameters such as initial concentrations of the metal and organic compound (mg/L) and the competition between heavy metals and organic compounds were analysed and the adsorption capacity and percentage removal were quantified.

**11. Pant et al. (2005):** They used the eucalyptus bark as adsorbent in the continuous packed bed reactor for the adsorption of hexavalent chromium. The thermodynamic parameters were estimated as ΔS 100.97 J/mol/K, ΔH 24 KJ/mol and ΔG 0.737 KJ/mol. Surface properties of adsorbent bed were characterized by SEM (Scanning electron microscope), X-ray diffraction technique (XRD) and infrared technique. They studied the effect of fixed bed column height, flow rate, initial chromium concentration on the performance of breakthrough curve.

**12. Gupta et al. (2004):** They used the fly ash as biosorbent obtained from the sugar industry for the removal of two important pollutants lead and chromium. The simultaneous removal of these two metal ions was carried out in continuous flow reactor at a flow rate of 0.5 mL/min made of a pyrex-glass tube (30 x 2 cm). The manometer was attached to the right hand side of the column by the two pressure points for the monitoring of introduction of air into the reactor. Wire mesh 250 BS (British standard size) gauge was set at pressure points to prevent entry of adsorbent particles at these points. The upper end of the reactor was covered with a cover for the removal of air bubbles. The natural flow of wastewater was maintained by connecting a head tank to the upper most part of the reactor from which the flow rate of wastewater was regulated by a valve. The stop-per point at the lower end of the column also regulated the flow of wastewater. The supporting medium glass wool was packed in continuous reactor by hydraulic filling. The weighted adsorbent material was washed with deionized water and soaks it in for 12 h before packing in continuous column. The column was kept as such whole night after packing for the settlement of adsorbent. The flow rate is varied to achieve maximum absorption of lead and chromium in this column manufactured.

**13. Nkhalambayausi-Chirwa et al. (2001):** In this study simultaneous Cr(VI) reduction and phenol degradation was carried out by a consortium culture of phenol-degrading bacteria and *Escherichia coli* 33456 in a continuous reactor operation under loadings of 5-21 mg/L-day and 840-3350 mg phenol/L-day in a fixed bed reactor. The continuous flow reactor was packed with chitosan as an adsorbent as it is biodegradable, biocompatible, nontoxic biopolymer and it is effective heavy metals absorber due to the presence of functional amino group. The chemical stability of chitosan adsorbent bed can be reinforced using crosslinking agents such as glutaraldehyde, apichlorohydrin and diglycidyl ether. In this study a mathematical model equation was developed for simulating the performance of simultaneous adsorption and bio reduction and biodegradation of Cr(VI) and phenol, respectively. The surface diffusivity of Cr (VI) was determined in a chitosan adsorbent bead using a batch kinetic test. The bio-kinetic parameters of *Escherichia coli* 33456 were determined using batch kinetic tests. The fluxes of Cr(VI) was evaluated in to biofilm and chitosan bead by numerical modelling. The experimental results were compared and model simulation of adsorption and bio reduction for Cr(VI) with respect to process mechanisms was carried out. The comparison of Cr(VI) reduction and Cr(III) production by *E. coli* 334565 attached on chitosan beads was analysed.

**2.24 Study on phytoremediation for simultaneous removal of Cr(VI) and Phenol:** Various plant species used for the accumulation of heavy metals is given in table 2.24.1 and uptake capacity of various plants for the accumulation of pollutant is given in table 2.24.2.

**1. Oves et al. (2013):** They performed a study on bacterial strain *Pseudomonas aeruginosa* OSG 41. This bacterial strain was isolated from the heavy metal contaminated water. This wastewater was irrigated to rhizospheric soil of mustard crop. The bacterial strain isolated from waste water can tolerated the chromium concentration up to 18000 µg/mL and consumed it by 100% at pH 6-8 after 120 h incubation at 30-40 $^{\circ}$C. The present study demonstrates that the bio-inoculants effectively decreased the toxicity of hexavalent chromium Cr(VI) to chickpea plants and simultaneously increased the biological and chemical characteristics of chickpea plant.

## Table 2.23: Literature review on continuous removal of Cr(VI) and phenol

| S. No | Author | Reactor mode | Types microbes | Operating conditions | Cr(VI) conc. mg/L | Cr(VI) reduction (%) | Initial organic substrate conc. | % organic substrate removal | Specific Cr(VI) reduction rate |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Chirwa et al., 1997 | Attached system fixed film bioreactors | *Bacillus* sp. | 24 | 100 | 99.8 | Glucose = 5 mg/l | 99.98 | 87 g/m$^3$/h |
| 2 | Kim et al., 1998 | Aeorobic | Enticed microorganism of leachate contaminant | - | 50 | - | - | - | 1.476 mg/g/h |
| 3. | Phillip et al., 1998 | Aeorobic | *Bacillus coagulans* | - | 104 | - | - | - | 1.09 mg/g/h |
| 4 | Philip et al., 1999 | Fed batch reactor (immobilized in polyaerylamide gel) | *Bacillus coagulans* | 24 | 26 | 100 | Yeqast extract = 5 mg/l | 99.98 | 1.08 g/m$^3$/h |
| 5 | Wanner et al., 1990 | Suspended system activated sludge process | Mixed microbes | 23 | 2 | 60 | TOC = 320 mg/l | 90 | - |
| 6 | Gopalan et al., 1994 | Banch scale continuous stirred tank | *Pseudomonas* sp. | 72 | 32 | 88 | COD = 5700 mg/l | 40 | 0.82 mg/gMLSS/h |
| 7. | Shen et al., 1995 | Two stage bioreactor (first stage – Aeorobic) | *Escherichia coli* ATCC-33456 | 5.1 | 1.54 | 99.4 | Glucose = 3 g/l | 99.8 | 0.12 mg/(10$^{10}$) of cell/day |
|  |  | Second stage – anaerobic |  | 5.1 | 11.7 | 62.7 | Glucose = 3 g/l | 99.8 | - |
| 8 | Chirwa et al., 1997 | Aerated packed bed | *Bacillus* sp. | - | 10-200 | 99.99 | - | - | - |
| 9 | Zakaria et al., 1997 | Packed bed | *Acinetobacterhaemolytius* | - | 15 | 97 |  | - | - |
| 10 | Stasinakis et al., 2004 | Aeorobic | Mixed microbe | 20 | 3 | 42 | COD = 300 mg/l | ➢ 90 | 0.014 mg/gMLSS/h |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Anoxic-aeorobic | Mixed microbe | 20 | 3 | 84 | COD = 300 mg/ | ➢ 90 | 0.027 mg/gMLSS/h |
| | | Anaerobic-anoxic aeorobic | Mixed microbe | 20 | 3 | 80 | COD = 300 mg/ | ➢ 90 | 0.025 mg/gMLSS/h |
| 11 | Elangovan et al., 2009 | Suspended growth system | *Arthrobacter Rhombi* | 24 | 20 | 99.6 | COD = 300 mg/ | 90-95 | 0.29 mg/gMLSS/h |
| 12 | Chirwa et al., 2001 | Fixed film coculture bioreactor | Phenol degrading bacteria-P. putidaand Cr(VI) reducing bacteria E. Coli | 24 | 20 | 97.6 | Phenol = 800 mg/l | 97.4 | 0.83 g/m$^3$/h |
| 13 | Dermou et al., 2005 | Aeorobic trickling filter | Acinetobacter | sp. SBR operation (24 h) with recirculation (40 min) | 30 | 100 | Organic carbon = 390 mg/l | 69.23 | 13 g/m$^3$/h |
| 14 | Krishna et al., 2005 | Packed bed bioreactor (facultative anaerobic conditions) | Enriched microbes | 8 | 10 | 90 | Nutrients medium eith 5 g/l of molasses | 59 | 6.6 g/m$^3$/h |
| 15 | Brunet et al., 2006 | Pilot bioreactor | sulphur-reducing organism, desulphmicrobiumnorvegium mixed microbes | 7 | 20 | 99 | COD = 400 mg/l | 20 | 2.2 g/m$^3$/h |
| 16 | Dermou et al., 2007 | Pilot scale trickling filter | Mixed microbes | SBR operation mode with recirculation 48 HRT | 5 | 62 | TOC = 400 mg/l | 20 | 16.62 g/m$^3$/h |
| 17 | Khattar et al., 2007 | Packed with immobilized cells | Anacystisnidulans | 48 | 1.56 | 85.92 | Medium/inidazale-HCL buffer | - | - |
| 18 | Zakaria et al., 2007 | Packed bed bioreactor | Acinetobacterhaemolytius | 4.58 | 15 | 96 | Glucose = 4.95 g/l | - | - |
| 19 | Dermou et al., 2008 | Pilot scale trickling filter | Mixed bacterial | Volumetric flow rate of 900 ml/min | 5.5 | 99.6 | TOC = 200 mg/l | - | 20 g/m$^3$/h |

|  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| 20 | Tziotzios et., 2008 | Pilot scale packed bed reactor | Mixed bacterial culture | 3.3 | 5.5 | 100 | Phenol = 1500 mg/l | 50 | 258 g/m$^3$/h |
| 21 | Cordoba et al., 2008 | Packed bed reactor under SBR recirculating mode | Arthrobacter sp. | Under SBR recirculating mode (27.5 h) | 30 | 100 | Glucose = 10 g/l | - | 0.9 g/m$^3$/h |
| 22 | Elangovan et al., 2009 | Packed bed reactor | Arthrobacter | 24 | 20 | 99.4 | Glucose = 3000 mg/l | 92-96 | 0.83 g/m$^3$/h |
|  |  | Packed bed reactor | Arthrobacter rhombi – RE – anoxic | 24 | 20 | 99.8 | COD = 3000 mg/l | 50-55 | 0.82 g/m$^3$/h |
| 23 | Barros et al., 2004 | Continuous reactor packed with adsorbent zeolite NaX | - | 5 | 3 | - | - | - | - |
| 24 | Jimenez et al., 2009 | Draft – tube airlift | Candida sp. | - | 78 | 99 | - | - | - |
| 25 | Pazos et al., 2010 | Zeolite packed column | Arthrobacterviscosus | - | 100 | 100 | - | - | - |
| 26 | Elangovan et al.,2009 | Aeorobic attached growth | Arthrobacter rhombi – RE | - | 18-36 | 50-98 | - | - | - |
|  |  | Anoxic attached growth |  | - | 18-36 | 50-98 | - | - | - |
|  |  | Aeorobic activated sludge |  | - | 0.5-5 | 37-45 | - | - | - |
| 27 | Lee et al., 2008 | Sand column | Indigenous consortium | - | 12 | 39.1-63.6 | - | - | - |
| 28 | Stasinakis et al., 2003 | Denitrifying hydrogen based membrane biofilm | Mixed culture biofilm | - | 0.25-10 | 45-63 | - | - | - |
| 29 | Chang et al., 2007 | Sulfidogenic two stage packed bed reactor system | Mixed sulphate reducers | - | 225-352.5 | 100 | - | - | - |
| 30 | Smith et al., 2000 | Sulfidogenic batch reactor | Sulphate reducing bacterium | - | 26 | 88 | - | - | - |
| 31 | Sahinkaya et | Sulphur reducing | Mixed sulphate reducers | - | 5-50 | 100 | - | - | - |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | al., 2012 | packed bed reactor | | | | | | | | |
| 32 | Middleton et al., 2003 | Aeorobic and denitrifying conditions | S. oneidensis MR-1 | - | 26 | - | - | - | | 0.78 mg/g/h |
| 33 | Thacker et al., 2006 | Aeorobic | provindencia sp. | - | 100 | - | - | - | | 13.02 mg/g/h |
| 34 | Caravelli et al., 2008 | Aeorobic | Sphaerotilusnatans | - | 80 | - | - | - | | 0.355 mg/g/h |
| 35 | Bae et al., 2000 | Aeorobic-ATCC 60 | E. coli ATCC | - | 10 | - | - | - | | 0.31 mg/g/h |
| | | ATCC 57 | E. coli ATCC | - | 10 | - | - | - | | 0.71 mg/g/h |
| | | NB | E. coli ATCC | - | 10 | - | - | - | | 0.33 mg/g/h |
| | | LB | E. coli ATCC | - | 10 | - | - | - | | 0.66 mg/g/h |
| 36 | Carmona et al., 2012 | Packed bed reactor | Saccharomyces cerevisiae | 5 | 300 | 60 | - | - | | - |

**2. Dhir et al. (2011):** Conducted a study of phytoremediation on *Salvinia Natans*, a fast growing free-floating aquatic weed was chosen for the study of removal of heavy metals Cr, Fe, Ni, Cu, Pb and Cd ranged between 6 and 9 mg/g dry wt., while the accumulation of heavy metals Co, Zn and Mn to the leaves of the plant was 4 mgg$^{-1}$ dry wt. The accumulation of heavy metals in the different parts of the plant affects the physiological status of plants. Photosystem II activity was observed to decreases when the plant was exposed to Ni, Co, Cd, Pb, Zn and Cu, while Photosystem I activity was observed to increase under heavy metal stress in comparison to control. Studies suggested that *Salvinia Natans* possess efficient photosynthetic mechanism to withstand heavy metal stress.

**3. Wani et al. (2010):** In this study the toxic effect of chromium was investigated on to the plant and microbial diversity. The chickpea plant for the phytoremediation of chromium. The rhizobacteria *Bacillus species* PSB10 which enhance the growth of the plant and also helps in the reduction of Cr(VI) was grown into the root of the plant. The bacterium *Bacillus species* PSB10 significantly increased the growth of plant, nodulation, chlorophyll content, leghaemoglobin, seed yield protein contents of chickpea plant. The experiments were carried out using sandy loam soil of composition (0.4% organic carbon, 0.75 g/kg kjeldahl N, 16 mg/kg olsen P, pH 7.2 and 0.44 mg/g WHC, 10.81 µg/g Ni, 19.21µg/g Zn). The chickpea seeds (var.avradhi) were sterlized (70 % ethanol, 3 min 3% sodium hypochlorite, 3 min), rinsed six times with sterile water and then dried in shade. The plant was exposed to the different concentrations of chromium. It was reported that the *Bacillus* PB10 improved the growth of the plant and was capable of remediation of chromium from the chromium-contaminated sites.

**4. Baumann et al. (2009):** In this study experiments were carried out to investigate the effects of various heavy metals such as, Copper (Cu), Chromium (Cr), Zinc (Zn), Cadmium (Cd) and lead (Pb) on photosynthetic activity of plant was measured as pulse amplitude modulation (PAM). The chlorophyll fluorescence yield was observed in seven species of green, red and brown macro algae in 14 days period. The 10 µmol/L of Cr and Zn reduced the chlorophyll fluorescence of all the species in 4 days, and 10 µmol/L of Cu and Cd reduced the fluorescence of some species. However fluorescence yield of all the plant species were not affected by 10 µmol/L of Pb. Metals was generally accumulate the heavy metals in the following order of Cu > Pb > Zn > Cr > Cd.

**5. Xu et al. (2009):** carried out a study to investigate the capacity of freshwater green alga Monoraphidium convolutum for the removal of multifaceted Cr(VI) toxicity. Photosynthesis activity and growth-survival scores were investigated. The exponential growth rate at (5.78±0.29) division/day until 8th day was found to be with linear increasing chlorophyll a/protein ratios (CHLa/PROT) throughout the period. Cultures of M. convolutum were exposed for 5 days to Cr(VI) concentrations from 0 to 100 mg/L showing that CHLa/PROT ratios were sensibly affected, in agreement to the calculated LC50,48h (5.38±0.72) mg/L from the concentration-response curve of cell mortality after 48 h. Plant physiology, photosynthesis and biochemical data suggested that the GSH-dependent antioxidant system is capable to sustain M. Convolutum viability through efficient photosynthesis activity and adequate antioxidant responses up to Cr(VI) concentrations of 1.0 mg/L, when redox unbalances were first evidenced.

**6. Magateli et al. (2009):** carried out experiments to examine the effects of toxic heavy metals such as cadmium (Cd), copper (Cu) and zinc (Zn) onto the aquatic macrophyte Lemnagibba were determined under controlled conditions. The percentage removal of heavy metals from the growth medium was followed. The results showed that the three heavy metals affected the growth of the plant.

**7. Garbisu et al. (2001):** In this study phytoextraction of heavy metals was carried out for the removal of various heavy metals from the soil. The phytoextraction of heavy metals from soil is a cost effective technology that represents the largest economic opportunities for the phytoremediation of heavy metals due to the need of the demands of process industries. The problems associated with safe discharge of toxic pollutant to the environment are a great challenge for the process industries. Phytoremediation improves the metal-contaminated soil and offers a competitive advantage of plant based remediation technology. The characteristic of ideal plants for the phytoremediation of heavy metals is given below:

- Can tolerate the high level of toxicity
- Can accumulate the high concentration of heavy metals
- The growth of the plant should be rapid
- The high biomass should be produced by the plants
- Should have large hairy root system

**8. Vajpayee et al. (2000):** In this study the uptake of chromium metal is investigated by the aquatic water plant European water lily of Nymphae alba L of family Nymphaeaceae grown at various level of Cr(VI) ranging from 1-200 µm accumulated chromium in concentration and duration-dependent manner. The accumulation of chromium by Nymphae alba L follows the following order:

Roots > leaves > Rhizomes

They investigated the 93% uptake of chromium by this plant. The plant has their own self defence mechanism to negotiate the effects caused by the uptake of heavy metals. The production of δ-amino levulinic acid (ALA) and δ-amino levulinic dehydratase (ALAD), Nitrate reductase (NR), improves the total chlorophyll and protein contents of plant after the uptake of toxic pollutant.

**9. Chaney et al. 1997:** The mechanism of uptake of pollutant through plant was studied. Phytoextraction: the plants were used for the removal of toxic pollutants from contaminated soil. The toxic pollutants were accumulated by the plants through the transportation system and concentrate the contaminant (metals or organics) from the soil into the above-ground shoots. Roots or seedlings of the plant were utilized for the absorption of toxic pollutants from aqueous wastewater stream. If the root absorbs the toxic pollutant then it called rhizofiltration or if seedlings absorbed the toxic metal then it called blastofiltration. The roots or seedlings of the plant in toxic aerated wastewater absorb, precipitate and concentrate pollutant from the waste effluent.

Table 2.24.1 Various Plant species used for the accumulation of toxic pollutants

| **Common name** | **Scientific name** | **Trace elements** | **References** |
|---|---|---|---|
| Lesser Bulrush | *Typha angustifolia* | Cd, Pb, Cr, Ni, Zn, Cu | Chandra et al. 2004; Demirezen et al. 2004 |
| Bulrush | *Typha latifolia* | Cr, As, Zn, Pb, Cd, Cu. Ni | Ye et al. 1997; Ye et al. 1998; Hozhina et al. 2001; Blute et al. 2004; P. Chandra et al. 2004; Deng et al. 2004; Pratas et al. 2007; Sasmaz et al. 2008. |
| Waterweed/pondweed | *Elodea Canadensis* | As, Pb, Cr, Zn, Cu, Cd | Mayes et al. 1977; Mal et al. 2002; Fritioff et al. 2003; Robinson et al. 2005; Dogan et al. 2009. |
| Brazilian waterweed | *Veronica aquatic* | As | Robinson et al. 2005 |
| Water-milfoil | *Myriophyllum spicatum* | Co, Cr, Cu, Pb, Zn, Ni | Keskinkan et al. 2003; Chandra et al. 2004; Lesage et al. 2007 |
| Fragrant water lily | *Nymphaea odorata* | Cr | Chandra and Kulshreshtha, 2004 |
| Pickerelweed | *Pontederia cordata* | | |
| Tape grass/eel grass | *Vallisneria spiralis* | Hg | Gupta and Chandra, 1998 |

|  |  |  |  |
|---|---|---|---|
| Wild celery | *Vallisneria Americana* | Cr | Chandra and Kulshreshtha, 2004 |
| – | *Nymphaea spontanea* | Cr(VI) | Choo et al. 2006 |
| Shichito matgrass | *Cyperus malaccensis Lam.* | Pb, Zn, Cu, Cd | Deng et al., 2004 |
| Swamp rice grass | *Leersia hexandra Swartz.* |  |  |
| Burma reed | *Neyraudia reynaudiana* |  |  |
| Flagroot | *Acorus calamus L.* |  |  |
| – | *Eleocharis valleculosa* |  |  |
| Water pepper | *Polygonum hydropiper* | As | Robinson et al. 2005 |
| Reed canary grass | *Phalaris arundinacea L.* | Pb, Zn, Cu, Cd | Deng et al. 2004 |
| – | *Equisetum ramosisti Desf.* |  |  |
| Soft rush | *Juncus effusus L.* |  |  |
| – | *Polypogon fugax Steud.* |  |  |
| – | *Egeria densa* | As | Robinson et al. 2005 |
| Alligatorweed | *Althernanthera philoxeroides* | As, Pb | Elayan, 1999 |
| Water lettuce | *Pistia stratiotes* | As, Cr, Pb, Ag, Cd, Cu, Hg, Ni, Zn | Maine et al. 2004; Miretzky et al. 2004; Espinoza-Quinones et al. 2008; Espinoza-Quinones et al. 2009 |
| Floating pondweed | *Potamogeton natans* | Zn, Cu, Cd, Pb | Fritioff and Greger, 2003; Fritioff and Greger, 2006 |
| Willow moss | *Fontinalis antipyretica* | Cu, Zn | Goncalves and Boaventura, 1998; Martins and Boaventura, 2002 |
| Needle spikerush | *Eleocharis acicularis* | As, In, Ag, Pb, Cu, Cd, Zn, Sb, Ni, Mg | Ha et al., 2009a; Ha et al., 2009b; Ha et al., 2011 |
| Rigid hornwort | *Ceratophyllum demersum* | As, Pb, Zn, Cu | Keskinkan et al., 2004; Robinson et al., 2005 |
| Watercress | *Lepidium sativum L.* | As | Robinson et al., 2003 |
| – | *Najas indica* | Pb | Singh et al., 2010 |
| Watercresses | *Nasturtium officinale* | Cu, Zn, Ni | Kara, 2005 |
| Curly waterweed | *Lagarosiphon major* | As | Robinson et al., 2005 |
| Duckweed | *Lemna gibba L.* | As, U, Zn | Fritioff and Greger, 2003; Mkandawire et al., 2004a,b; Mkandawire and Dudel, 2005 |
| Lesser duckweed | *Lemna minor L.* | As, Zn, Cu, Hg | Fritioff and Greger, 2003, Kara, 2004; Miretzky et al., 2004; Robinson et al., |

| | | | |
|---|---|---|---|
| | | | 2005; Alvarado et al., 2008; Mishra et al., 2008 |
| Star duckweed | *Lemna trisulca L.* | Zn | Huebert and Shay, 1992 |
| Water hyacinth | *Eichhornia crassipes* | As, Fe, Cu, Zn, Pb, Cd, Cr, Ni, Hg | Wolverton and McDonald, 1978; Muramoto and Oki, 1983; Delgado et al., 1993; Vesk et al., 1999; Cordes et al., 2000; Chandra and Kulshreshtha 2004; Odjegba and Fasidi 2007; Alvarado et al., 2008; Espinoza-Quiñones et al., 2008; Mishra et al., 2008; Dixit and Dhote, 2010 |
| Water-starwort | *Callitriche cophocarpa* | Cr(VI) | Augustynowicz et al., 2010 |
| Petries starwort | *Callitriche petriei* | As | Robinson et al., 2005 |
| Common reed | *Phragmites australis* | Cr, Cu, Ni, Pb, S, V, Zn, Cd | Deng et al., 2004; Ghassemzadeh et al. 2008; Baldantoni et al. 2009 |
| Butterfly fern | *Salvinia rotundifolia* | Pb(II) | Banerjee and Sarker, 1997; Dhir, 2009. |
| | *Salvinia natans* | As, Ni, Cu, Hg(II) | Sen and Mondal, 1987; Sen and Mondal, 1990; Sen and Bhattacharyya, 1993; Rahman et al., 2008c |
| | *Salvinia minima* | As, Pb, Cd, Cr | Olguin et al. 2003; Hoffmann et al. 2004; Sanchez-Galvan et al., 2008 |
| | *Salvinia herzogii* | Cd, Cr | Maine et al. 2004; Sune et al. 2007 |
| Eared watermoss | *Salvinia auriculata* | Zn, Hg, Cr | Molisani et al., 2006; Espinoza-Quiñones et al. 2008; Wolff et al. 2009 |
| Greater duckweed | *Spirodela intermedia* | Cu, Zn, Mn,Cr, Pb | Miretzky et al. (2004) |
| | *Spirodela polyrhiza L.* | As, Hg | Rahman et al., 2007; Mishra et al., 2008; Rahman et al., 2008b |
| Indian/sacred lotus | *Nelymbium speciosum* | Cr, Cu, Ba, Ti, Co, Pb | Vardanyan and Ingole, 2006 |
| | *Ludwigia perennis L.* | | |
| Arrowhead | *Sagittaria sagittiflia L.* | | |
| – | *Nymphoides ceristatum* | | |
| Shoreline seapurslane | *Sasuvium portulacastrum L.* | | |
| – | *Nymphae stellate* | | |
| Water spinach | *Ipomoea aquatic* | As, Cd, Pb, Hg, Cu, | Lee et al., 1991; Gothberg |

| | | | |
|---|---|---|---|
| | | Zn | et al., 2002; Gothberg et al., 2004; Hu et al., 2008; Wang et al., 2008 |
| Eelgrass/eelweed | *Vallisneria spiralis L.* | Cu, Cd, Hg | Rai and Tripathi, 2009; Wang et al. 2010 |
| Esthwaite waterweed | *Hydrilla verticillata* | As, Pb, Zn, Cr | Lee et al., 1991; Dixit and Dhote, 2010 |
| Mosquito fern | *Azolla caroliniana* | As, Hg, Cd | Zhang et al., 2008 |
| Water fern | *Azolla filiculoides* | | Rahman et al., 2008a; Rai, 2008; Zhang et al., 2008; Rai and Tripathi, 2009 |
| Water velvet | *Azolla pinnata* | | |
| Elephant’s ear | *Colocasia esculenta* | Cd, Cu, Pb, Zn | Cardwell et al., 2002 |
| Umbrella sedge | *Cyperus eragrostis* | | |
| Spike rush | *Eleocharis equisitina* | | |
| Parrot’s feather | *Myriophyllum aquaticum* | | |
| Miriophyllum | *Myriophyllum propinquum* | As | Robinson et al., 2005 |
| Water lily | *Nymphaea violacea* | Cd, Cu, Pb, Zn | Cardwell et al., 2002 |
| | *Nymphaea aurora* | Cd | Schor-Fumbarov et al., 2003 |
| Marshwort | *Nymphoides germinate* | Cd, Cu, Pb, Zn | Cardwell et al., 2002 |
| Knotweeds | *Persicaria attenuatum* | | |
| – | *Persicaria orientalis* | | |
| – | *Persicaria subsessilis* | | |
| – | *Potamogeton orchreatus* | As | Robinson et al., 2005 |
| Willow smartweed | *Persicaria lapathifolium* | Cd, Cu, Pb, Zn | Cardwell et al., 2002 |
| – | *Potamogeton javanicus* | | |
| Fennel pondweed | *Potamogeton pectinatus* | Cd, Pb, Cr, Ni, Zn, Cu | Demirezen and Aksoy, 2004 |
| Curled dock | *Rumex crispus* | Cd, Cu, Pb, Zn | Cardwell et al., 2002 |
| River clubrush | *Schoenoplectus validus* | | |
| Cumbungi | *Typha domingensis* | | |
| Cumbung | *Typha orientalis* | | |
| Lesser Bulrush | *Typha angustifolia* | Cd, Pb, Cr, Ni, Zn, Cu | Chandra and Kulshreshtha, 2004; Demirezen and Aksoy, 2004 |

Table 2.24.2: Uptake capacity (mg/g) of various plant species used for the accumulation of toxic pollutants

| common name of plant | Scientific name of plant | Uptake of metals | Initial concentration (mg/l) | Exposure Time days | pH | % Removal | Uptake capacity $q_e$ (mg/g) | Reference |
|---|---|---|---|---|---|---|---|---|
| Wild radish | Raphanussativus L | Cr | 360, 630, 900, 1170, 1440 | 28 | Neutral | 20.18, 23.42, 30.80, 33.13, 49.48 | | Sayantan et al., 2013 |
| potatoes, carrots and onions | Daucuscarrota, Allium cepa, Solanum tuberosum | Ni, Cr | 0-250 | 180 | | | | Stasinos et al., 2013 |
| Garden snail | Helix aspersa | Pt, Cr | | 56 | | | $19 \times 10^{-3}$ | Eybe et al., 2013 |
| Chickpea | Cicer arietinum L | Cr | 1800 | 5 | 6-8 | | .1085 | Oves et al., 2013 |
| Water velvet, duckweed | Azolla pinnata and Lemna minor | Fe, Mn, Cu, Zn, Ni, Pb, Cr and Cd | 0.18 | 7 | 6.2 | 77.7 | 78.89 | Bharti et al., 2012 |
| Wand riverhemp | Sesbania virgate | Cu, Cr, Zn | 50-116 mg/kg | 30 days | 6 | | 0.0023-0.0028 | Branziniet al., 2012 |
| Sea Purslane | Halimione portulacoides | Cr(VI) | 0 -30 | 7 | 1 | 60 | | Duarte et al., 2012 |
| Pond weed aquatic macrophyte | Potamogeton pusillus | Cr, Cu | 864, 1728, 3456, 6935 | 5, 10 or 15 | 7.5 | 28-56 | | Monferran et al., 2012 |
| Pea | Pisum sativum, | Cr(VI) | 20 -2000 | 28 | 7.8 | 55 | | Rodriguez et al., 2012 |
| Marine algae | Laminaria digitata | Cr(III) | 250 | | 4 | | 42 | Dittert et al., 2012 |
| Indian mustard | Brassica juncea | Se and Mo | | | | | | Schiavon et al., 2012 |
| Green algae | Micrasterias | Cr | 0.18 | 21 | 6 | 78 | | Volland et al., 2012 |
| Green alga | Monoraphidium convolutum | Cr(VI) | 0-100 | 5 | 7.4 | 82 | | Takami et al., 2012 |
| Chinese silver grass | Miscanthus sinensis | Cr | 0, 9, 18, 36, 54, 90, 135, 180 | 3 | 5.8 | | 1.308 | Sharmin et al., 2012 |
| Giant reed | Arundo donaxL | As, Cd and Pb | | | | | | Miao et al., 2012 |
| Amazon sword plant, Undulate cryptocoryne | Echinodorusamazinocus and Cryptocoryneundulata | Fe, Cu, Zn, Cr, Ni, Mg, Mn, Ca | 5-20 | 7 | 7.4 | | 6.8 | Sapci et al., 2012 |

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|---|---|---|---|---|---|---|---|---|
| Sambung nyawa batik | Gynura pseudochina | Cr, Cu, Zn, Fe | 100 | 14 | 6 |  | 0.8231 ± 0.005 | Mongkhonsin et al., 2011 |
| Red marine algae | Pterocladia capillacea | Cr | 5-100 |  | 7 | 80-85 | 66 | El Nemr et al., 2011 |
| Mushroom | Cucumis utillissimus | Cr(VI) | 0, 50, 100, 150 µg/g | 30 | 6.7 ± 0.02 | 83.05 | 5.6 ± 0.1 | Sinam et al., 2011 |
| Krambe | Crambe abyssinica | Cr | 0, 9, 18, 27, 36, 45 | 10 |  |  |  | Zulfiqar et al., 2011 |
| Gramineae | Leersia hexandra Swartz | Cr(III) | 54 | 20 | 5.5 |  | 2.131 ± 0.166 | Liu et al., 2011 |
| Floating water moss | Salvinia natans | Cr | 15 | 10 | 4.5-5 | 56.8 | 0.932 | Dhir et al., 2011 |
| Cord grass | Spartina argentinensis | Cr | 0-3600 | 30 | 6.8 | 53 | 15.1 | Redondo-Gomez et al., 2011 |
| water-starwort aquatic macrophyte | Callitriche cophocarpa Sendtn | Cr(VI) | 9-126 | 21 | 6.6 |  | 1 | Augustynowicz et al., 2010 |
| Water spinach | Ipomonea aquatic | Cr(III) | 10 | 14 | 6 |  | 13.217 | Chen et al., 2010 |
| Smooth Mesquite | Prosopis laevigata | Cr(VI), Cd(II) | 0-612 | 50 | 360, 612 |  | 5.035, 8.09 | Buendia-Gonzalez et al., 2010 |
| Rice paddy | Oryza sativa L. | Cr(VI) | 2.5, 5, 10, 25, 50, 75, 100 and 200 | 30 | 6-6.5 | 75 |  | Sundaramoorthy et al., 2010 |
| Floating fern | Salvinia minima | Cr |  |  |  |  |  | Prado et al., 2010 |
| Chickpea | Cicer arietinum L | Cr | 67.5 mg/kg | 90 | 7 |  |  | Ahmad Wani et al., 2010 |
| Barbados nut | Jatropha curcas L | As, Cr and Zn | 0, 25, 50, 100, 250 , 500 mg $kg^{-1}$ | 12 months | 7.0 ± 0.5 |  | 0.0312 ± 0.0022 | Yadav et al., 2009 |
| Water hyacinth | Eichhornia crassipes | Cr, Zn | 1, 5,10,20 | 11 | 8.3 ± 0.20 | 84 | 0.10, 1.13, 1.41, 1.71 | Mishra et al., 2009 |
| Water Hyacinth | Eicchornia crassipes | Cr | 1-50 | 23 | 3.5 - 5.5 |  | 4.93 | Espinoza-Quinones et al., 2009 |
| Spurge, Mullein, Tragacanth | Euphorbia macroclada(EU), Verbascum cheiranthifolium(VR), and Astragalus gummifer(AS) | Sr |  |  |  |  |  | Sasmaz et al., 2009 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Poacea | Saccharum officinarum L | Cr | | | | | | Xia et al., 2009 |
| Marine macroalgae | Ulva intestinalis | Cu, Cr, Zn, Cd, Pb | | | | | | Baumann et al., 2009 |
| Green onion, moonlight ferns | Allium fistulosum, Pteris cretica cv Mayii | Pb, As | | | | | | Cho et al., 2009 |
| Fat duckweed | Lemna gibba | Cd, Cu and Zn | | | | | | Megateli et al., 2009 |
| Eelgrass | Zostera marina | Cr | | 14 | | | | Mascaro et al., 2009 |
| Aquatic macrophytes | L. minor, S. polyrhiza, C. aquatica, C. palustris and E. Canadensis | Cr | | | | | | Dosnon-Olette et al., 2009 |
| Aquatic macrophyte | Salvinia auriculata, Pistia stratiotes and Eichhornia crassipes | Cr(VI) | 0.1-5 | 27 | 3.5-5.1 | | | Espinoza-Quinonesa et al., 2009 |
| Thorn apple | Datura innoxia | Cr(VI) and Cr(III) | 0, 9, 18, 180, 360 | 7 | | | 0.57 | Vernay et al., 2008 |
| Sunflower | Helianthus annus | Cr | 20, 40, 60 mg/kg | 7 | 6.75 | | 0.00011 | Andaleeb et al., 2008 |
| Sunflower | Helianthus annus | Cr, Ni, Fe, Cd, As | 30 | 28 | | 4.88 | | January et al., 2008 |
| Hankow willows | Salix matsudana Koidz | Cr(VI), Cr(III) | 1.92 | | | 78 | 0.00095 | Yu et al., 2008 |
| Green Amaranth | Amaranthus viridis | Cr | 0.18, 1.8, 18 | 20 | 5.5 | 4.6, 16.8, 62 | | Liu et al., 2008 |
| Chinese brake | Pteris vittata | Cd, As | | | | | | Xiyuan et al., 2008 |
| Basket willow | Salix | Cr | | | | | | Quaggiotti et al., 2007 |
| Perennial ryegrass | Lolium perenne | Cr | 0-90 | 15 | | | 2.45 | Vernay et al., 2007 |
| kiwifruit pollen | Actinidia deliciosa | Cr | 2880- 13500 | | 7.4 | | | Speranza et al., 2007 |
| Green algae | Chlamydomonas reinhardtii | Cr | | | | | | Rodriguez et al., 2007 |
| Green algae | Gelidium | Cr, Zn | 100 | 11.8 ± 0.5 | 5.3 | | 18 | Vilar et al., 2007 |
| Green alga | Ulva lactuca | Cr | 5-100 | | 1 | 92 | 10.61 | El-Sikaily et al., 2007 |
| Gramineae | Leersia hexandra Swartz | Cr | 10 | 15 | 6 | 58.5 | 2.978 | Zhang et al., 2007 |
| Genipapo or Huito | Genipa americanaL | Cr | 30 | 34 | - | - | - | Barbosa et al., 2007 |
| Aquatic | Salvinia herzogii and | Cr | 1, 2, 4 and 6 | 1, 2, 5, | 6.87 | 33 | | Sune et al., 2007 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| macrophytes | Pistia stratiotes | | | 14, 31 | | | | |
| Water lily | Nymphaea spontanea | Cr | 10 | 7 | 6 | | 2.119 | Choo et al., 2006 |
| Water hyacinth | Eichhornia crassipes | Cr, Zn | | | | | | Mishra et al., 2006 |
| Giant Chinese silver grass | Miscanthus | Cr | 50-200 | 36 | 7.5 | 90-95 | | Arduini et al., 2006 |
| Fungi | Aspergillus sp. | Cr | 500 | 3 | 6 | 70 | | Srivastava et al., 2006 |
| elephant grass | Penisetum purpureum | Cr | 10 and 20 mg Cr dm$^{-3}$. | 1 | | 97–99.6% | | Mant et al., 2006 |
| Water cabbage | Pistia stratiotes L | Cr | 0, 1.8, 7.2, 28.8 | 2 | 7.5 | | | Sinha et al., 2005 |
| Spinach | Spinacea oleracea L | Cr, Fe | | | | | | Sinha et al., 2005 |
| Paddy rice | Oryza sativa Linnaeus | Cr | | | | | | Bhattacharyya et al., 2005 |
| Mustard | Brassica juncea cv | Cr(VI) | 0.036, 0.036, 0.36 | 15 | Neutral | | 0.075, 0.41, 0.897 | Pandey et al., 2005 |
| Watermoss, water cabbage | Salvinia herzogii, Pistia stratiotes | Cr | 1, 2, 4, 6 | 30-35 | 6.87 | 92.8 | 6.20 | Maine et al., 2004 |
| aquarium watermoss, duckmeat | Salvinia and Spirodela | Cr, Ni | | | | | | Srivastav et al., 2004 |
| Field bindweed | Convolvulus arvensis L | Cd, Cr and Cu | 20 | 15 | 5.8 ± 0.2 | | 2.1 | Gardea-Torresdey et al., 2004 |
| Mosquito fern | Azolla caroliniana | Hg(II), Cr(III), Cr(VI) | 0.1, 0.5 and 1.0. | 12 | | 74 | 71 to 964 mg kg$^{-1}$ dm | Bennicelli et al., 2004 |
| Yeast | Pichia guilliermondii | Cr | 90 | 3 | 5.5 | | 0.4–0.9 | Ksheminska et al., 2003 |
| Watermelon | Citrullus | Cr | 9, 18, 36 | 24 | 6.8 | | 0.0039 | Dube et al., 2003 |
| Cabbage | Brassica oleracea | Cr | 90 | 42 | | | 19.549 | Pandey et al., 2003 |
| Basket willow | Salix | Pb, Zn and Cu | | | | | | Pulford et al., 2003 |
| Sunflower | Helianthus annus | Cd, Cr, Ni | 150 | 28 | | 75 | 0.03 | Cheng et al., 2001 |
| Epiphytic alga | Pleurococcus sp. | Cr | | | | | | Cervantes et al., 2001 |
| Willd | Salvinia minima | Cr | 1-2 | 14 | 6.5 | | | Nichols et al., 2000 |
| Wild grass | Echinochloa colona | Cr | 1.25 | 10 | 6.8 | | 3 | Rout et al., 2000 |
| White water lily | Nymphaea alba L | Cr | | | | | | Vajpayee et al., 2000 |
| Cauliflower | Brassica oleracea | Cr, Co, Cu | 90 | 56 | | | 0.00099 | Chatterjee et al., 2000 |
| Pondweed | Elodea Canadensis | Cr, Ni | 150, 800, 2.09 | 1 | | | 0.0008-0.00084 | Kanhkonen et al., 1998 |
| Paddy | Oryza sativa | Cr(III) | 0.09-4.5 | 120 | 7.5-8.2 | 90 | 0.00241 | Mishra et al., 1997 |

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  | and Cr(VI) |  |  |  |  |  |  |
| Wheat plant | Triticum aestivum | Cr |  |  |  |  |  | Kleiman et al., 1997 |
| Maize | Zea mays | Cr | 0.5-25 | 10 | 7.2-7.8 |  | 0.0754 | Mishra et al., 1995 |
| Duckweed | Lemna minor | Cu, Cr(III) |  |  |  |  |  | Abdel Wahaab et al., 1995 |
| Floating heart | Limnanthemum cristatum Griseb | Cr |  |  |  |  |  | Chandra et al., 1992 |

**2.25 Detailed objectives:** Based on the extensive literature review following detailed objectives have been formulated

1. Preparation of single and binary synthetic, simulated solution of Cr(VI) and phenol.
2. To analyze the Cr(VI) and phenol in UV spectrophotometer using 1,5 diphenyl carabazide colorimetric method for Cr(VI) and 4 amino antipyrene method for phenol.
3. To select the best adsorbents such as agricultural waste products or waste product of industries (Granular activated carbon, Tea waste, Rice husk, Bagasse, Bagasse fly ash, Distillery sludge, Neem Leaves, Fe treated tea waste and Fe treated rice husk) for the maximum removal of Cr(VI) and phenol.
4. To study the effect of process parameters such as initial concentration of Cr(VI), initial concentration of phenol, pH, temperature, adsorbent dosage and contact time for the individual and simultaneous removal of Cr(VI) and phenol using batch reactor.
5. Characterization of biosorbents such as FTIR, FE SEM, EDX, BET surface area before and after adsorption of Cr(VI) and phenol from single and binary solution.
6. Study of various single and multicomponent adsorption isotherms, kinetics and thermodynamic models for the removal of Cr(VI) and phenol from single and binary solution.
7. Statistical optimization of process parameters to study the interactive effects using Box behnkim design of response surface methodology.
8. Acclimatization of bacterium *Escherichia coli* NCIM No. 5051 for the removal of Cr(VI) and *Bacillus* sp. MTCC No. 3166 for the removal of Cr(VI) and phenol from single and binary solution.
9. Simultaneous reduction of Cr(VI) and biodegradation of phenol using consortium culture of *Escherichia coli* and *Bacillus* sp.
10. Michelis Menton kinetics for the simultaneous reduction of Cr(VI) and biodegradation of phenol using *Bacillus* sp.
11. SAB (Simultaneous adsorption and bioaccumulation) study to investigate the efficiency of immobilized *Escherichia coli* bacterium onto the surface of best biosorbent for the removal of Cr(VI) and simultaneous adsorption and bioaccumulation and biodegradation study by immobilizing *Bacillus* sp. onto the surface of best biosorbent for the removal of Cr(VI) and phenol from single and binary solution. The simultaneous adsorption and bioaccumulation

of Cr(VI) with biodegradation of phenol by immobilizing consortium culture of *Bacillus* sp. and *Escherichia coli* onto the surface of tea waste biomass was also carried out.

12. To study the various single and multicomponent adsorption isotherm models and kinetic models for the SAB study for the removal of Cr(VI) and phenol.
13. Continuous study for the simultaneous removal of Cr(VI) and phenol from synthetic binary solution in packed bed reactor.
14. Continuous SAB study in packed bed reactor by immobilizing mixed culture of *Bacillus* sp. and *Escherichia coli* onto the surface of packed bed for the simultaneous removal of Cr(VI) and phenol from synthetic binary solution.
15. To study the effect of important parameters namely flow rate, bed height, DO and pH for the simultaneous removal of Cr(VI) and phenol in packed bed reactor.
16. Study of various Kinetic model for the simultaneous removal of Cr(VI) and phenol in packed bed reactor.
17. Mass transfer study for the simultaneous removal of Cr(VI) and phenol in packed bed reactor for the estimation of pseudo first order rate constant.
18. RTD (Residence time distribution study) for the removal of Cr(VI) and phenol in packed bed reactor.
19. Phytoremediation of Cr(VI) and phenol from single and binary solution in artificial phytoremediation chamber using aquatic macrophyte water hyacinth (*Eichhornia crassipes*).
20. To analyze the accumulation of Cr(VI) and phenol in the different part of water hyacinth such as root, stem and leaves.
21. Characterization of different part of plant before and after uptake of Cr(VI) and phenol from single and binary solution to confirm the removal.
22. Michelis Menton kinetics was applied onto the chlorophyll content for the simultaneous removal of Cr(VI) and phenol using water hyacinth.

**2.26 Conclusion:** Though large volume of work have been done for the removal of chromium and phenol individually from synthetic and industrial waste water but there is a lack of knowledge for the simultaneous removal of chromium and phenol from industrial waste water.

## *Chapter – III*

# EXPERIMENTAL SETUP AND INSTRUMENTATION

### 3.0 Motivation

This chapter deals with the Experimental setup and instrumentation used for the simultaneous removal of Cr(VI) and phenol from synthetic simulated single and binary solution by adsorption, bioaccumulation of Cr(VI) using *Escherichia coli* and *Bacillus* sp., biodegradation of phenol using *Bacillus* sp., simultaneous adsorption and bioaccumulation of Cr(VI), simultaneous adsorption and biodegradation of phenol, continuous column reactor and phytoremediation. Further, the experimental design, range of experimental parameters, details of setups and analytical instruments used in the present study are described in this chapter.

### 3.1 Preparation of single and binary solution of Cr(VI) and phenol

In the present study Potassium dichromate ($K_2Cr_2O_7$) salt was used for the preparation of synthetic solution of Cr(VI) and phenol crystal ($C_6H_5OH$) in liquid phase was used for the preparation of synthetic solution of phenol. Also the binary solution of Cr(VI) and phenol (2:1) (v/v) was prepared for the simultaneous removal of Cr(VI) and phenol according to the tannery waste water composition. All the chemicals were of analytical grade and solutions were prepared by milli-Q water (Q- $H_2O$, Millipore Crop. with resistivity of 18.2 MΩcm). Stock solutions of Cr (VI) and phenol were prepared by dissolving known amount of phenol and potassium dichromate in 1 L of distilled water. To avoid photo-oxidation of phenol, stock solution was stored in a brown glass bottle (Aggarwal et al. 2013). Various initial concentrations of test solutions of phenol and Cr (VI) were prepared by diluting their respective stock solutions. For multicomponent test, a solution of phenol and Cr(VI) was prepared by diluting their respective stock solution and mixing them in the desired proportion. The method for the preparation of single and binary simulated synthetic solution of chromium and phenol is given in appendix B1.

**3.2 Analysis methods for Cr(VI) and phenol:** Analysis of Cr(VI) and phenol was carried out according to American standard method [APHA] For the analysis of Cr(VI) and phenol in filtrate UV spectrophotometer made of HACH (model No: DR 5000) was used. For the analysis of Cr(VI), 100 mL of filtrate was reacted with a diphenyl carbazide solution and $H_2SO_4$ and let them stand for 10 min for full colour development and its absorbance was taken at 540 nm. The residual concentration of phenol in the filtrate was determined by mixing 100 mL phenol sample with buffer solution of ammonium chloride (pH 8), of 4-amino antipyrine (20.8 mM) and of potassium ferricyanide (83.4 mM) and let them stand for 15 min for full colour development and its absorbance was taken at 510 nm (Ontanon et al. 2014). The methods for the determination of residual concentrations of Cr(VI) and phenol is given in appendix B2 and appendix B3.

### 3.3 Selection of Adsorbents

All the adsorbents were selected based on their carbon and nitrogen content. All the adsorbents selected for the present study contain either carbon or nitrogen or both according to the ultimate and proximate analysis. The surface area ($m^2/g$) of all the adsorbents were investigated by BET surface area. This may help in further decreasing the operational cost of the process.

### 3.4 Adsorbent and their preparation

Nine types of industrial and agricultural waste products were used as adsorbents. GAC, tea waste, rice husk, bagasse, bagasse fly ash, distillery sludge, Fe treated tea waste and Fe treated rice husk were taken as adsorbents is given in Fig. 3.1. All the adsorbents are waste product of industrial and agricultural industry and are cheap and easily available all over India. These adsorbent were sieved into fractions of 0.5- 1, 1- 1.5, 1.5-2, 2-4 and 4-5 mm particle sizes and used in the present study. The adsorbents were then washed several times with distilled water and dried in hot air oven at 50 $^{\circ}$C for 2 h to completely remove moisture, cooled to room temperature and then stored in airtight glass bottles.

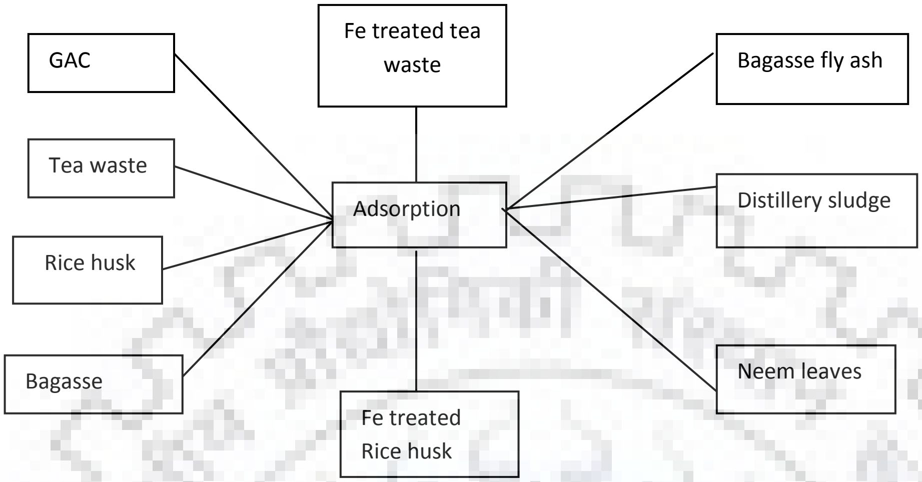

**Fig. 3.1: Various adsorbents used in the present study**

**3.5 Batch adsorption studies:** The batch adsorption studies were carried out for the removal of Cr(VI) and phenol from single and binary component solution. The process parameters such as pH, temperature (ºC), adsorbent dose (mg/g), contact time (h), initial concentration of Cr(VI) (mg/L), initial concentration of phenol (mg/L) were optimized. For the optimization of process parameters the parameters that was optimized was varied while others, parameters were kept constant as shown in table 4.2, table 4.3 and table 4.4 for single component solution of Cr(VI), single component solution of phenol, binary solution of Cr(VI) and phenol, respectively. The synthetic simulated single and binary solutions of Cr(VI) and phenol were prepared in the laboratory. For the co-adsorption of Cr(VI) and phenol the concentrations of Cr(VI) and phenol were taken in (2:1) ratio. The working volume for single component adsorption was 50 mL while for the simultaneous co-adsorption of Cr(VI) and phenol was taken as 100 mL. The flat bottom round flasks of working volume 250 mL were used for the experimentation. The experiments were carried out in incubator cum shaker as shown in Fig. 3.2 at desired temperature and 120 rpm shaking speed. The sample was filtered using whatman filter paper and filtrate was analysed in UV spectrophotometer (HACH DR 5500). The 1,5 diphenyl carabazide and 4 aminoantipyrene methods were used for the analysis of Cr(VI) and phenol, respectively.

***3.5.1 Instrumentation and control:*** The agitation speed and temperature of the incubator were controlled by rpm controller and thermostat, respectively. The pH of the sample was maintained constant at different interval of time by pH meter.

***3.5.2 Limitation of the set up:*** There is the change in shape and size of the batch reactor, fluctuation of temperature in incubator shake when the samples were taken at different intervals of time. The change in pH with time can also lead to the error in the experimentation.

**3.6 Bioremoval of Cr(VI) and phenol:** The bio-removal of Cr(VI) and phenol were carried out using two bacterial strain *Escherichia coli* (NCIM NO. 5041) and *Bacillus* sp. (MTCC NO. 3166). The bacterial strain *Escherichia coli* was capable of reducing Cr(VI) from single substrate solution while *Bacillus* sp. can accumulate Cr(VI) and degrade phenol in both single and binary substrate solution of Cr(VI) and phenol. All the experiments were carried out in laminar flow unit as shown in Fig. 3.3.

### *3.6.1 Sterilization of glassware's used for the biological removal of Cr(VI) and phenol*

All the glassware's used in the bacteriological studies were properly sterilized. Conical flasks, Petri dishes and test tubes were properly washed with lab wash and rinsed with distilled water for several times, dried in an oven at a temperature of 200 °C and cotton plugged. These glassware's along with the solid and liquid medium were sterilized in an autoclave at 15 Pascal for 20 min. Transfer of bacteria and media were done in laminar hood over the flame of spirit lamp.

### *3.6.2 Cell Growth Analysis*

Bacterial growth was measured by measuring optical density at 600 nm using UV-Vis spectrophotometer (HACH model DR 5500).

### *3.6.3 Biomass Concentration Analysis*

The dry weight of cells was determined as follows:

The samples containing different amounts of biomass were centrifuged at 12000 rpm for 15 min after which the supernatant was decanted and the cell pellet was dried by inverting it on paper towel until the medium was drained out. After that the pellet was washed with ethanol for several times to dehydrate the pellet and then dried in the oven at 50°C for 5-10 min. The dry cell weight was measured and the calibration curve was plotted between optical density and biomass concentration per litre.

***3.6.4: Instrumentation and control:*** The control of temperature and pressure of autoclave and the time of UV light passed to the laminar airflow unit.

***3.6.5 Limitation of set up:*** The proper sterilization of all the glassware's used for the experimentation and proper cleaning of the laminar airflow chamber is required to avoid the contamination.

**3.7 Simultaneous adsorption and accumulation of Cr(VI) and biodegradation of phenol:** The simultaneous adsorption, bioaccumulation of Cr(VI) and biodegradation of phenol were conducted by immobilizing the bacterium *Escherichia coli* and *Bacillus* sp. onto the surface of various adsorbents (Granular activated carbon, Tea waste and Rice husk). The experiments were carried out in incubator cum shaker at 37 $^{o}$C. For the optimization of process parameters the parameters that was optimized was varied while others, parameters were kept constant as shown in table 4.21, table 4.22 and table 4.23 for single substrate solution of Cr(VI), single substrate solution of phenol, binary substrate solution of Cr(VI) and phenol, respectively. The residual concentrations of Cr(VI) and phenol in single and binary substrate solution was measured before centrifuging at 10,000 rpm for 10 min in UV spectrophotometer by 1, 5 diphenyl carbazide and 4, aminoantipyrene method respectively.

### 3.8 Simultaneous Removal of Cr(VI) and phenol in Column Reactor

All the experiments for the simultaneous removal of Cr(VI) and phenol from synthetic simulated wastewater were conducted in column reactor. The photographic image and line diagram of continuous column reactor along with the accessories has been shown in Fig. 3.8.1 and Fig. 3.8.2, respectively. The whole set up consisted of column reactor, mixing chamber fitted with stirrer, feed tank, peristaltic pump, rotameter, water filter unit, compressor, probe ports for temperature, pH, D.O., pressure gauge, drainage line, level indicators and sampling ports $P_1$ to $P_5$ with valves attached at various portion of connecting lines.

The material of construction of the bio- column reactor, feed tank, mixing vessel and connecting lines was stainless steel. The reactor assembly was a close circuit unit. The column reactor had a working height of 100 cm, an internal diameter of 8 cm and a net volume of 5.03 L. It was equipped with five equidistant ports of 1.25 cm diameter for collecting liquid samples along the height of the reactor. The top and the bottom portions were connected with the main column by two flange joints, supported on stainless steel screen (mesh no: 16 BSS, width aperture: 1.00 mm). The reactor was filled with pre-treated tea waste biomass. For the experiment of simultaneous biodegradation and adsorption process a bio-layer of *Escherichia coli* and *Bacillus* sp. was immobilized on adsorbent bed in the column reactor. An appropriate amount of potassium dichromate and phenol were dissolved in 1 L of double distilled water to prepare a binary solution of 2000 mg/L of Cr(VI) and 1000 mg/L of phenol (2:1).

Fig 3.8.1 Photograph of Continuous column reactor

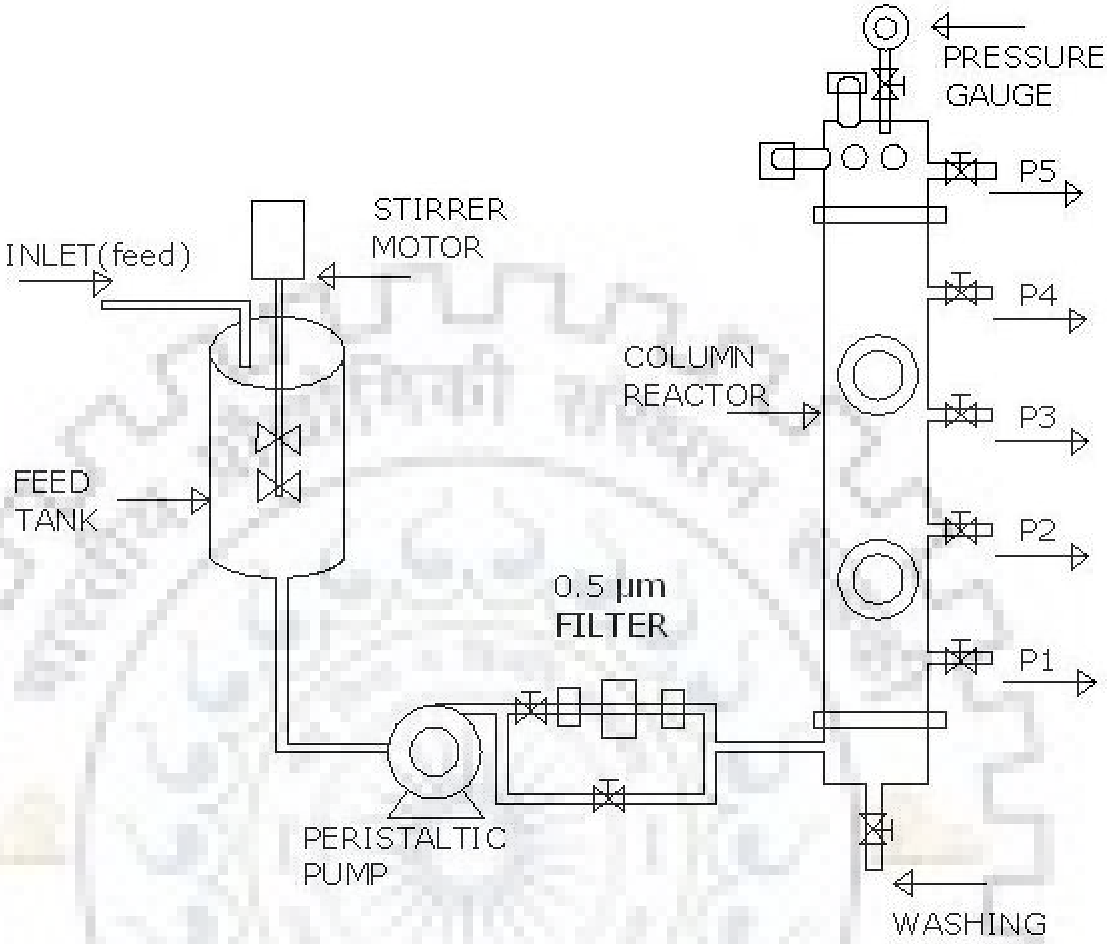

Fig. 3.8.2 Line diagram of continuous column reactor

### *3.8.1 Instrumentation and control*

Liquid flow rate was controlled and calibrated by peristaltic pump (PP- 20) procured from Miclins India, Chennai. pH meter and D.O meter were used to measure the pH and D.O of the effluent samples respectively in mixing tanks as well as at the outlet of reactor.

### *3.8.2 Limitation of the set-up*

Measuring instruments like pH meter, D.O meter were table top type. Therefore, the cross checking of the data collected from these instruments was essential. To insert the probes of the pH and D.O meter at the outlet of the reactor, a dead volume of around 300 mL had to be created.

## 3.9 Analytical instruments used in the present study

A number of analytical instruments used in the present study are UV-Vis Spectrophotometer, Fourier Transform Infrared spectrophotometer (FT-IR), BET Surface area analyzer, Fe-SEM Analysis. The photograph of analytical instrument used in the present study is given in Fig. 3.9.

## 3.10 Auxiliary Equipment's used in the Present Investigation

Auxiliary equipment used in the present study were orbital cum incubator shaker, hot air oven, laminar airflow unit, pH meter, dissolved oxygen meter, muffle furnace, centrifuge, autoclave, water bath, Milli-Q water unit and weighing balance etc. The photographic image of Auxiliary Equipment's used in the present study is shown in Fig. 3.10.

## 3.11 Calibration of Measuring Instruments

Calibration of instruments is very essential to get reliable data in the experiments. The procedure for the calibration of pH meter, D.O. meter and instruments used for the experimentation is given below:

### *3.11.1 Calibration of pH Meter*

Calibration of pH meter was done using pH buffers as per the instruction manual provided by the manufacturer.

### *3.11.2 Calibration of D.O. Meter*

Calibration of D.O meter was done using sodium thiosulphite solution as per the instruction manual provided by the manufacturer.

### *3.11.3 Calibration of Experimental Setup*

For batch experiments the temperature of incubator cum shaker was calibrated with the help of a pre-calibrated thermometer. For column study, variable speed peristaltic pump and rotameters required calibration before the start-up of experiments in column reactor. The rotameters were purchased with calibration certificate. Calibration of the peristaltic pump (Model PP-20) was done according to the instruction manual provided by Miclins India Ltd.

(a) Spectrophotometer (HACH DR 5000)

(b) Fe-SEM QUANTA 200 FEG (FEI Netherlands)

(c) FTIR Spectrometer (Thermo Model AVATR 370)

(d) BET Surface Area Analyzer

**Figure 3.9:** Photographic images of analytical instruments used in the present investigation


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(a) Research Centrifuge REMI

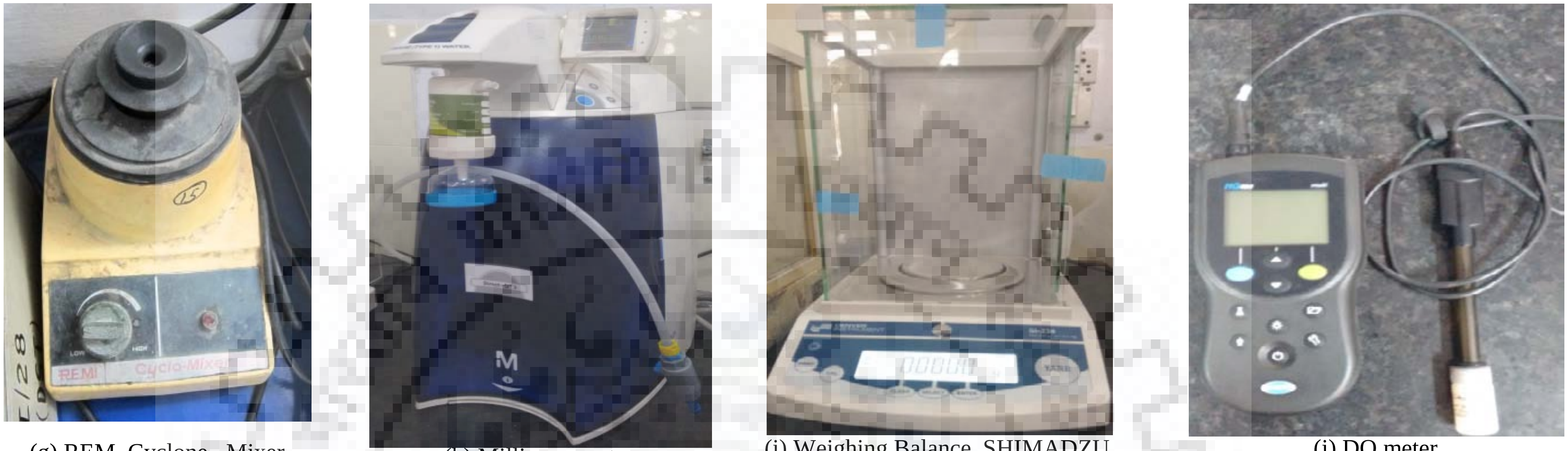
(b) Muffle Furnace

(c) Orbital Shaker Cum Incubator

(d) Hot Air oven

(e) Autoclave, Rivotek

(f) Laminar Air Flow Unit, Researcher Equipment



(g) REM  Cyclone , Mixer

(h) Milli pore water

(i) Weighing Balance, SHIMADZU, Japan

(j) DO meter

(k) pH meter (Toschon Pvt. Ltd., India)

(l) Peristaltic pump

**Figure 3.10** Photographic images of some auxiliary instruments used during the present investigation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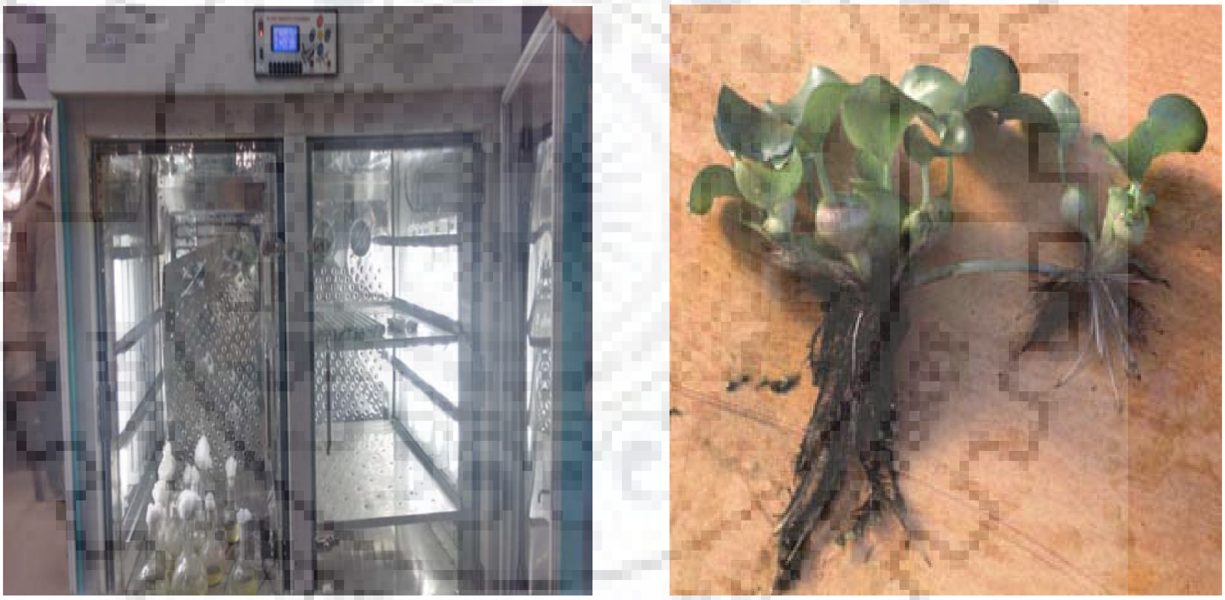
**3.12 Artificial Photosynthesis chamber:** The artificial photosynthesis chamber was used for the growth of aquatic macrophyte water hyacinth collected from solani river Roorkee. The plant was exposed to the toxic pollutant Cr(VI) and phenol in single and binary substrate solution. The temperature, relative humidity and light intensity can be controlled in chamber. The Photographic image of plant growth chamber and water hyacinth is shown in Fig. 3.12. The plants were grown in 500 mL container made of polypropylene in nutrient Hoagland solution.

***3.12.1 Instrumentation and control:*** The maintenance of 24 h light and dark cycle, temperature, pressure and relative humidity is required.

***3.12.2 Limitation of the set up:*** The maintain of concentration of oxygen in the chamber for the photosynthesis is required.



(a) Plant growth chamber

(b) Water hyacinth palnt

Fig. 3.12 Photographic image of plant growth chamber and water hyacinth plant

**3.13 Concluding remarks:** This chapter is concerned with the understanding of the experimental set up formulated and the calibration of various instruments used for the experimentation.

## *Chapter – IV*

# EXPERIMENTAL PROCEDURE

### 4.0 GENERAL

Based on the extensive literature review, aims and objectives an extensive research program for simultaneous removal of Cr(VI) and phenol from binary wastewater through various methods such as Adsorption, Biological study, SAB system, Continuous system, Continuous bioreactor system and phytoremediation has been made. This chapter deals with the materials and methods of Cr(VI) and phenol removal, and the experimental procedures adopted to carry out the present work.

### 4.1 Design of Experiments

Experimental program is essential to meet the objectives of every research work. For the present study, it is given in Fig. 4.1.1. A total  2003 numbers of experiments as detailed in annexure A-1 to A-43 were carried out for the removal of Cr(VI) and phenol from synthetic single and binary solution by adsorption, bioaccumulation of Cr(VI), biodegradation of phenol, simultaneous adsorption and bioaccumulation, simultaneous adsorption and biodegradation, continuous reactor and phytoremediation. Adsorptive removal of Cr(VI) from single component solution of Cr(VI) has been performed with pre-treated agricultural and industrial waste adsorbents like Granular activated carbon (GAC), Tea waste (TW) rice husk (RH), Bagasse (BG), Bagasse fly ash (BFA), Distillery sludge (DS), Neem leaves (NL), Iron treated tea waste (Fe TW) and Iron treated rice husk (Fe RH) (Annexure A.1 to A.9). Similarly, for single component solution of phenol for various adsorbents (GAC, TW, RH, BG, BFA, DS, NL, Fe TW and Fe RH) is given in Annexure from A.10 to A.18, respectively. According to the experimental results of  adsorption of Cr(VI) and phenol from single component solution the adsorbent tea waste (TW), Rice husk (RH), Fe treated tea waste (Fe TW) and Fe treated rice husk (Fe RH) were selected for the simultaneous adsorption of Cr(VI) and phenol from binary solution (Annexure from A.19 to A.23). Biological removal of Cr(VI) and phenol were carried out using bacterium *Escherichia* coli and Bacillus sp. from single and binary substrate solution of Cr(VI) and phenol is given in Annexure A.24 to A.29, respectively. The bacterium *Escherichia coli* was capable of removing Cr(VI) from single substrate solution while *Bacillus* sp. was found to be having the ability of both reducing the Cr(VI) and biodegrading the phenol. The simultaneous reduction and biodegradation of phenol was also carried out in binary substrate solution of Cr(VI) and phenol. However, bioaccumulation and bio-degradation of Cr(VI) and phenol supplemented with adsorption has been performed in batch reactor, as well as in column reactor for removing Cr(VI) and phenol from single and binary simulated waste water. The biosorbent TW, RH and GAC were used as support for the immobilization of bacterium *Escherichia coli* and *Bacillus* sp. in single substrate solution and TW for simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol. Experimental data for simultaneous adsorption and bioaccumulation of Cr(VI) from single substrate solution is given in Annexure A.30 to A.35 and for simultaneous adsorption and biodegradation of phenol is given in Annexure A.36 to A.38. The experimental data for simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol is given in Annexure A.39. Tea waste biomass as adsorbent was selected as packed bed in continuous reactor for the simultaneous adsorption of Cr(VI) and phenol is given in Annexure A.40. Consortium culture of *Escherichia coli* and *Bacillus* sp. was immobilized onto the surface of packed bed for the simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol is given in Annexure A.41. Phytoremediation studies have been performed in artificial photosynthesis chamber using aquatic macrophyte water hyacinth for single and binary substrate solution is given in Annexure A.42 and A.43 respectively. The Cr(VI) and phenol analysis, preparation of single and binary waste water of Cr(VI) and phenol and preparation and characterization of adsorbents, calibration of measuring instruments and set-up, design of experiments, experimental procedure and data recording for adsorptive removal, bioaccumulation and biodegradation of Cr(VI) and phenol from simulated waste water have been discussed in this chapter. The summary of Experiment carried out is given in table 4.1

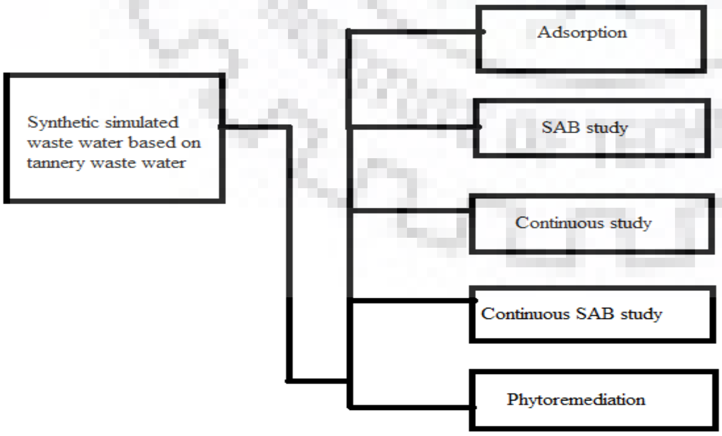


**Figure 4.1.1:** Experimental program for simultaneous removal of Cr(VI) and phenol from contaminated water using various treatment methods

Table 4.1 Summary of various experiments conducted in the present study

| Process | Raw material (Adsorbent/Bacteria) | Batch study | Column study | Phytoremediation study using aquatic macrophyte water hyacinth (*Eichhorniacrassipes*) |
|---|---|---|---|---|
| Adsorption study for removal of Cr(VI) and phenol from single component solution | Granular activated carbon (GAC) | 1 | | |
| | Tea waste (TW) | 2 | | |
| | Rice husk (RH) | 3 | | |
| | Bagasse (BG) | 4 | | |
| | Bagasse fly ash (BFA) | 5 | | |
| | Neem Leaves (NL) | 6 | | |
| | Distillery sludge (DS) | 7 | | |
| | Fe treated tea waste (Fe TW) | 8 | | |
| | Fe treated Rice husk (Fe RH) | 9 | | |
| Co-adsorptive study for the removal of Cr(VI) and phenol from binary solution | GAC | 10 | | |
| | TW | 11 | 27 | 29 |
| | RH | 12 | | |
| | Fe TW | 13 | | |
| | Fe RH | 14 | | |
| Bio removal of Cr(VI) and phenol | *Escherichia coli* NCIM NO. 5051 used for the reduction of Cr(VI) | 15 | | |
| | *Bacillus* sp. MTCC No. 3166 used was used for both reduction of Cr(VI) and biodegradation of phenol from single and binary substrate solution | 16 | | |
| Simultaneous adsorption and bioaccumulation of Cr(VI) study using single component synthetic waste water | *Escherichia coli* immobilized GAC | 17 | | |
| | *Escherichia coli* immobilized TW | 18 | | |
| | *Escherichia coli immobilized RH* | 19 | | |
| | *Bacillus* sp. immobilized GAC | 20 | | |
| | *Bacillus* sp. immobilized TW | 21 | | |
| | *Bacillus* sp.immobilized RH | 22 | | |
| Simultaneous adsorption and biodegradation of phenol using single component solution of phenol | *Bacillus* sp. immobilized GAC | 23 | | |
| | *Bacillus* sp. immobilized TW | 24 | | |
| | *Bacillus* sp.immobilized RH | 25 | | |
| Simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol from synthetic binary solution | Consortium culture of Escherichia coli and Bacillus sp. immobilized on tea waste biomass | 26 | 28 | |

## 4.2 BATCH ADSORPTION STUDY

### 4.2.1 Adsorbents and their preparation method

The adsorbents used in the present study for the removal of Cr(VI) and phenol were Sugar and Distillery industrial wastes, namely, Bagasse (BG), Bagasse fly ash (BFA), Distillery sludge (DS), and agricultural waste include tea waste (TW), rice husk (RH), Neem leaves (NL). These adsorbents are cheap and easily available across the country. In the present investigation, they were collected from local industries and local place.

**i)** **Granular activated carbon (GAC):** GAC was purchased from HIMEDIA. It was crushed in rotatory crusher to the desired particle size. After crushing it was washed with distilled water in triplicates and then dried in hot air oven at 50 °C.

**ii)** **Tea waste biomass (TW):** Tea waste biomass was collected from a local tea shop, Roorkee, India. Tea waste was boiled for 30 min for the removal of soluble matter, dirt and coloured components. After boiling, tea waste biomass was washed with distilled water in triplicate and then dried in hot air oven at 50 ºC for 12 h. When all the moisture and volatile material was removed from tea waste biomass it was sieved to obtain a constant particle size 1.5-2.0 mm.

**iii)** **Rice husk (RH):** Rice husk was obtained from local rice husk crusher machine Roorkee, INDIA. Initially, the grime content of Rice husk was removed by washing with hot water (65$^{o}$C), treating with 0.1 N HCl for 5 h in 1:2 ratio of liquid-solid. The Rice husk was washed repeatedly with double distilled water. After washing, it was dried in natural air for 4-5 hours and then dried in oven for about 24 hrs at 50$^{o}$C to remove the moisture content. Subsequently, the dried sorbents were grounded, sieved (range 0.5 mm to 4 mm) and stored in containers at room temperature. This pretreatment improves the ions presence onto the surface of adsorbents for better adsorption of Cr(VI) and phenol ions by electrostatic force.

**iv)** **Bagasse (BG):** Bagasse was collected from a local sugar-cane crushing plant and the pith was removed from it. After removing the pith from the bagasse, it was boiled with distilled water at 100 °C for 30 min for the removal of dirt and soluble sugar from it and then dried at 50 °C in hot air oven for 24 h and then finally grounded and sieved to the desired particle size.

**v)** **Bagasse Fly ash (BFA):** Bagasse fly ash was obtained from a sugar refinery at Modinagar, Uttar Pradesh, India. The bagasse fly ash was treated with hydrogen peroxide ($H_2O_2$) (0.1 w/v) at 60°C for 24 h to oxidize the adhering organic matter. After 24 h of operation resulting material was separated by the help of vacuum filter assembly. Residual material was then washed with distilled water in triplicate, dried at 50 °C and stored in a vacuum desiccator. The adsorbent was powdered, ground and sieved to the desired particle size before use.

**vi)** **Distillery sludge (DS):** Waste distillery sludge was collected from Modi sugar & distillery in Modinagar, Uttarpradesh, India. All samples were dried overnight in an oven at 105 °C both before and after pretreatment, which provided a biomass source of extended shelf life. Biosorbent was physically modified by heating (heated up to 50 °C in an electric oven for 24 h), boiling (100 g biosorbent/150 mLwater) and autoclaving (at 115 °C for 1 h). The pretreated biosorbent was washed with double distilled water (DDW) in triplicate and filtered through whatman filter paper until a pH 7±0.1 was attained. The resulting biomass was oven dried for 48 h to constant weight. The dried samples were grounded with a laboratory grinder and passed through laboratory vibro-sieving machine to obtain the uniform particle size.

**vii)** **Neem leaves (NL):** Neem leaves were obtained from the IIT Roorkee campus. It was cleaned with doubled distilled water to remove the dirt adhering on to the surface in triplicate. After washing it was dried in sun light for 6 h. It was treated with 0.1 N HCl for 24 h in order to remove the lignin content of the leaves and then again washed and dried in hot air oven at 40 °C. Neem leaves obtained after drying in hot air oven was sieved to the desired particles size.

**4.2.2 Surface modification of biosorbent/ impregnation of metal ions onto the surface:** The surface of biosorbent was modified to improve the percentage removal of Cr(VI) and phenol from both single and binary synthetic simulated waste water. As both Cr(VI) and phenol are present in the form of negatively charged ions in synthetic solution therefore it was modified by impregnating the positively charged ions onto the surface of adsorbent (Wielinga et al.2000).

**i) Fe treated Rice husk:** 2 g of rice husk was added to 8 mL of 2 M $FeSO_4{\cdot}7H_2O$ solution in 500 mL conical flask and then kept on stirring plate at 105 $^oC$. 0.1 M of NaOH was added drop wise to the solution with the help of burette fitted to conical flask to increase the pH 4-5 so that iron is precipitated. This process was carried out continuously for 3-4 h. Upon cooling the rice husk was covered with a thick layer of orange colour iron oxide. Then rice husk was washed with distilled water to remove extra quantity of iron precipitate which was not impregnated onto the rice husk surface. Finally, these Fe treated rice husk was dried in an oven at 50 $^oC$ for 2 h and then sieved to obtain homogeneous particle size.

**ii) Fe treated tea waste biomass:** 5 g of tea waste biomass was added to 50 mL solution of 2 M $FeSO_4{\cdot}7H_2O$ in 500 mL conical flask. The conical flask was kept on a magnetic stirring plate at $100^oC$. 0.1 M of NaOH was added drop wise to the solution by burette fitted to a conical flask to increase the pH 4-5 so that iron was impregnated onto the surface of tea waste biomass. This process was carried out continuously for 3-4 h. Upon cooling the tea waste biomass was covered with a thick layer of orange colour iron oxide. Then tea waste biomass was washed with distilled water to remove extra quantity of iron precipitate which was not impregnated onto the surface of tea waste biomass. Finally, these Fe treated tea waste biomass was dried in an oven at 50 $^oC$ for 2 h and then sieved to obtain homogeneous particle size (Nethaji et al. 2013).

### 4.2.3 Characterization of adsorbents

The physicochemical characterization of the surface of adsorbents was carried out by proximate analysis and ultimate analysis using standard procedures. Surface area and pore volume of the adsorbents analyzed by BET (Burnauer-Emmett-Teller) method. The morphology of the surface of adsorbents was determined using the scanning electron microscope (LEO 435 VP, England) operating with SE1 detector. For SEM analysis, the adsorbents samples coated with gold (Au) to provide conductivity. Electron dispersive spectroscopy (EDX) analysis was carried out to determine elemental composition of the adsorbents using the FE-SEM (QUANTA 200 FEG). The various functional groups available on the surface of adsorbents were identified using a FTIR spectrophotometer (Nicolet Avtar 370, USA) equipped with EZ-OMNIC software. The instrument operates with a CsI beam splitter and a DTGS-CsI detector. The adsorbent were prepared using potassium bromide (KBr) disc method. The sludge samples first grounded in an agate mortar to fine powder. This powder was mixed with KBr in a mass ratio of 100:1. This mixture underwent through vacuuming and pressing under high pressure in a pellet press obtaining a thin translucent pellet. A referential pellet for recording the background was made from pure KBr. Spectra obtained by subjecting the prepared pellet samples to a frequency ranging from 5000-400 $cm^{-1}$ scanned at the rate of 16 nm/s.

### 4.2.3.1 Physical and chemical properties of adsorbent

***4.2.3.1.1 BET (Brunauer–Emmett–Teller) surface area:*** The (BET) surface area ($m^2/g$) and bulk density (g/L) of various adsorbents were calculated using surface area analyser ASAP 2010 Micrometrics, USA) (Chattopadhyaya et al. 2006).

#### *4.2.3.1.2 Proximate analysis*

The moisture present in adsorbents (GAC, TW, RH, BG, BFA, DS, NL, Fe TW and Fe RH) was calculated by taking 3 g of adsorbent. These adsorbents were kept in oven at a high temperature of 105 $^oC$ for 1 h. Later on heating it was well ventilated and weighted (Branzini et al. 2012). Result was obtained in the form of difference in weight of adsorbent, shown in table 5.1.1, following formula was used to calculate the moisture contents present in adsorbent.

$$X = \frac{w_i - w_f}{w_i}$$

$w_i$ = Initial weight of adsorbent

$w_f$ = Final weight of adsorbent

X = moisture content (wt %)

#### *4.2.3.1.3 Volatile material*

The volatile material present in adsorbents (GAC, TW, RH, BG, BFA, DS, NL, Fe TW and Fe RH) was calculated by taking 1 g of raw material. These adsorbent were kept in oven at a high temperature of 750 °C for 7 min. After heating, it was well ventilated and weighted (Babu et al. 2008). Result was obtained in the form of difference in weight of adsorbent, shown in table 5.1.1, following formula was used to calculate the volatile contents present in the adsorbent.

$$\mathrm{X} = \frac{\mathrm{w_i} - \mathrm{w_f}}{\mathrm{w_i}}$$

$\mathrm{w_i}$ = weight of adsorbent initially

$\mathrm{w_f}$ = weight of adsorbent after heating

X = Volatile contents

### *4.2.3.1.4 Ultimate analysis:*

The C(%), H(%) and N(%) contents present in adsorbent (GAC, TW, RH, BG, BFA, DS, NL, Fe TW and Fe RH) were calculated by ultimate analysis as given in table 5.1.1. Ultimate analyses were carried out by taking 1 g of adsorbent and keep it in hot air oven at a high temperature of 450 °C for 1 h (Acar et al. 2004). Fixed carbon was calculated by deducting from 100 the sum of the moisture content, volatile matter and ash, expressed as percent.

### 4.2.4 Experimental program for batch adsorption study

Batch experiments were carried out for the simultaneous removal of Cr(VI) and phenol removal from single and binary simulated synthetic waste water. Fig. 4.2.4 shows the complete sequence of the experiments performed for the removal of Cr(VI) and phenol.

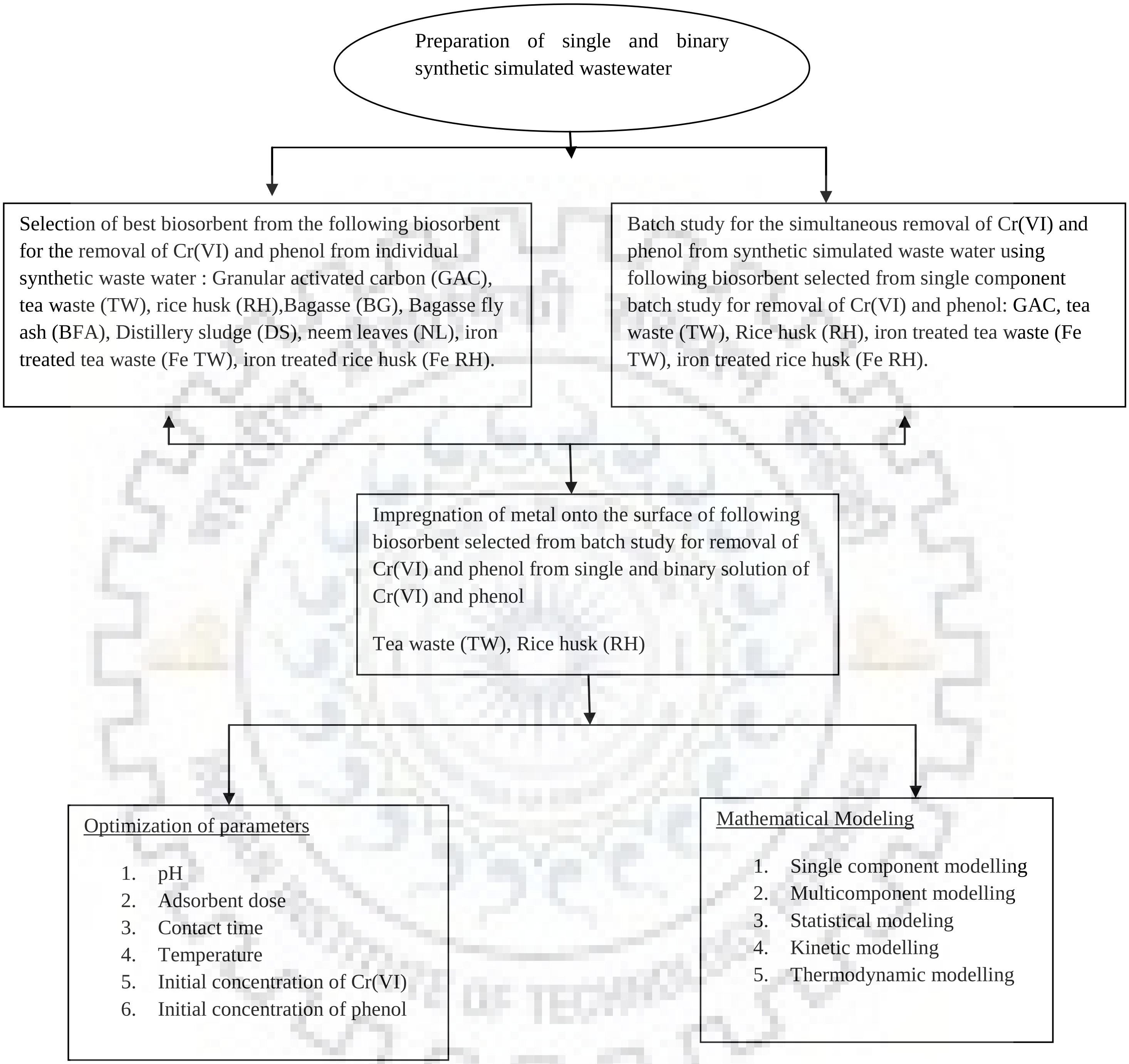


**Fig. 4.2.4:** Schematic block diagram of batch experimentation for Cr(VI) and phenol removal by adsorption using various adsorbents

### 4.2.5 Batch experiments for removal of Cr(VI) and phenol

The batch adsorption studies were carried out to evaluate the effect of various parameters onto the percentage removal of Cr(VI) and phenol. The batch adsorption experiments were carried out in 250 ml round bottom flasks. The required amount of various adsorbent were added in 50 ml of individual and binary synthetic simulated solution of Cr(VI) and phenol. The flasks were agitated in thermostatically orbital shaker at 120 rpm (Kamsonlian et al. 2012 b). The effect of pH, contact time, adsorbent dose, initial concentration of Cr(VI), initial concentration of phenol, temperature were studied by varying one parameter and keeping others constant to determine the removal efficiency of Cr(VI) and phenol in single and binary solution of Cr(VI) and phenol using various adsorbent. The desired pH of the single and binary solution of Cr(VI) and phenol was maintained using 1 N NaOH and 1 N HCl by the help of pH meter. The effect of various operating parameters, viz. pH, adsorbent dose, initial concentration of Cr(VI), initial concentration of phenol, temperature and contact time were studied. To investigate the effect of various process parameters such as pH, temperature, adsorbent dose, contact time, initial concentration the range of operating parameters for single component solution of Cr(VI), single component solution of phenol, simultaneous adsorption of Cr(VI) and phenol from binary solution is given in table 4.2, table 4.3 and table 4.4, respectively. These experimental data is used for thermodynamic, equilibrium isotherm and kinetic modelling.

#### 4.2.5.1 Batch adsorption studies onto the removal of Cr(VI) and phenol at various pH for single and binary solution:

The effect of pH onto the adsorption of Cr(VI) and phenol in the range 2-10 was investigated using single and binary synthetic simulated waste water. All the experiments were carried out in thrice and average values were reported in Annexure. The Run numbers for various adsorbents (GAC, TW, RH, BG, BFA, DS, NL, Fe TW and Fe RH) for the adsorption of Cr(VI) and phenol associated with single component solution of Cr(VI), single component solution of phenol and binary solution of Cr(VI) and phenol is given in table 4.5, table 4.10 and table 4.15 respectively.

### 4.2.5.2 Batch adsorption studies onto the removal of Cr(VI) and phenol at various Temperature ($^oC$) for single and binary solution:

The effect of varying temperature ($^oC$) from 10 -50 was carried out for various adsorbents for single component solution of Cr(VI), single component solution of phenol and batch adsorption studies for the simultaneous removal of Cr(VI) and phenol from binary solution is given in table 4.6, table 4.11 and table 4.16, respectively. The results of these experimental runs were also used for thermodynamic modelling of the adsorption process with each adsorbent using Linearized Van't Hoff equations.

### 4.2.5.3 Batch adsorption studies onto the removal of Cr(VI) and phenol at various adsorbent dose (mg/g) for single and binary solution:

The batch experiments were carried out to investigate the effect of adsorbent dose (mg/g) for the adsorption of Cr(VI) and phenol for single and binary synthetic simulated solution onto the surface of various adsorbents. The experimental data associated with the effect of adsorbent dose for the single component solution of Cr(VI), single component solution of phenol and binary solution of Cr(VI) and phenol is given in table 4.7, table 4.12 and table 4.17, respectively.

### 4.2.5.4 Batch adsorption studies onto the removal of Cr(VI) and phenol at various contact time(h) for single and binary solution:

The effect of contact time was carried out for the investigation equilibrium condition where driving force becomes zero i.e., the concentration gradation between adsorbent surface and synthetic solution of Cr(VI) and phenol becomes zero. In order to evaluate the effect of contact time the samples were taken at various intervals of time and the residual concentration was analysed until it becomes constant. All the experiments were conducted thrice and average results have been reported in table 4.8, table 4.13 and table 4.18 for single component solution of Cr(VI), single component solution of phenol and binary solution of Cr(VI) and phenol, respectively. The results of these experimental runs were also used for kinetic modelling of the adsorption process with each adsorbent using pseudo-first order, pseudo-second order and intraparticle diffusion model.

#### 4.2.5.5 Batch adsorption studies onto the removal of Cr(VI) and phenol at various initial concentration (mg/L) for single and binary solution:

In the present work, batch adsorption studies for various adsorbents to evaluate the effect of initial concentrations, 100-400 mg/L for single component solution of Cr(VI) and phenol. The batch adsorption studies for the co adsorption of Cr(VI) and phenol in binary synthetic simulated solution (2:1) were carried out in the range of 100-500 mg/L of Cr(VI) and 50-250 mg/L of phenol according to the composition of industrial waste water. The experimental data generated for the investigation of the effect of initial concentration was used for the equilibrium isotherm modelling is given in table 4.9, table 4.14 and table 4.19, respectively.

**Table 4.2: Range of operating parameters for adsorption studies of Cr(VI) from single component solution**

| Experiment | Operating Parameters | | | | |
|---|---|---|---|---|---|
| | pH | Temp. ($^oC$) | Dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h |
| | | | **Granular activated carbon (GAC)** | | |
| Effect of pH | **2-10** | 30 | 4 | 100 | 1.5 |
| Effect of Temperature ($^oC$) | 2 | **10-50** | 4 | 100 | 1.5 |
| Effect of adsorbent dose (g/L) | 2 | 30 | **2-5.2** | 100 | 1.5 |
| Effect of Initial concentration (mg/L) | 2 | 30 | 4 | **100-400** | 1.5 |
| Effect of contact time (h) | 2 | 30 | 4 | 100 | **0.25-3** |
| | | | **Tea waste (TW)** | | |
| Effect of pH | **2-10** | 30 | 8 | 100 | 1.75 |
| Effect of Temperature ($^oC$) | 2 | **10-50** | 8 | 100 | 1.75 |
| Effect of adsorbent dose (g/L) | 2 | 30 | **2-14** | 100 | 1.75 |
| Effect of Initial concentration (mg/L) | 2 | 30 | 8 | **100-400** | 1.75 |
| Effect of contact time (h) | 2 | 30 | 8 | 100 | **0.25-2** |
| | | | **Rice husk (RH)** | | |
| Effect of pH | **2-10** | 30 | 40 | 100 | 10 |
| Effect of Temperature ($^oC$) | 2 | **10-50** | 40 | 100 | 10 |
| Effect of adsorbent dose (g/L) | 2 | 30 | **5-50** | 100 | 10 |
| Effect of Initial concentration (mg/L) | 2 | 30 | 40 | **100-400** | 10 |
| Effect of contact time (h) | 2 | 30 | 40 | 100 | **1-12** |
| | | | | | |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| **Bagasse (BG)** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 40 | 100 | 6 |
| Effect of Temperature ($^oC$) | 2 | **10-50** | 40 | 100 | 6 |
| Effect of adsorbent dose (g/L) | 2 | 30 | **4-48** | 100 | 6 |
| Effect of Initial concentration (mg/L) | 2 | 30 | 40 | **100-400** | 6 |
| Effect of contact time (h) | 2 | 30 | 40 | 100 | **0.5-6.5** |
| **Bagasse Fly ash** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 45 | 100 | 20 |
| Effect of Temperature ($^oC$) | 2 | **10-50** | 45 | 100 | 20 |
| Effect of adsorbent dose (g/L) | 2 | 30 | **5-50** | 100 | 20 |
| Effect of Initial concentration (mg/L) | 2 | 30 | 45 | **100-400** | 20 |
| Effect of contact time (h) | 2 | 30 | 45 | 100 | **1-21** |
| **Distillery sludge** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 26 | 100 | 11 |
| Effect of Temperature ($^oC$) | 2 | **10-50** | 26 | 100 | 11 |
| Effect of adsorbent dose (g/L) | 2 | 30 | **10-30** | 100 | 11 |
| Effect of Initial concentration (mg/L) | 2 | 30 | 26 | **100-400** | 11 |
| Effect of contact time (h) | 2 | 30 | 26 | 100 | **1-12** |
| **Neem leaves (NL)** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 20 | 100 | 22 |
| Effect of Temperature ($^oC$) | 2 | **10-50** | 20 | 100 | 22 |
| Effect of adsorbent dose (g/L) | 2 | 30 | **5-40** | 100 | 22 |
| Effect of Initial concentration (mg/L) | 2 | 30 | 20 | **100-400** | 22 |
| Effect of contact time (h) | 2 | 30 | 20 | 100 | **2-24** |
| **Fe treated tea waste (Fe TW)** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 6 | 100 | 2 |
| Effect of Temperature ($^oC$) | 2 | **10-50** | 6 | 100 | 2 |
| Effect of adsorbent dose (g/L) | 2 | 30 | **1-8** | 100 | 2 |
| Effect of Initial concentration (mg/L) | 2 | 30 | 6 | **100-400** | 2 |
| Effect of contact time (h) | 2 | 30 | 6 | 100 | **0.2-2.5** |
| **Fe treated Rice husk (Fe RH)** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 28 | 100 | 7.5 |
| Effect of Temperature ($^oC$) | 2 | **10-50** | 28 | 100 | 7.5 |
| Effect of adsorbent dose (g/L) | 2 | 30 | **4-32** | 100 | 7.5 |
| Effect of Initial | 2 | 30 | 28 | **100-400** | 7.5 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| concentration (mg/L) |  |  |  |  |  |
| Effect of contact time (h) | 2 | 30 | 28 | 100 | **0.5-8** |

**Table 4.3: Range of operating parameters for adsorption studies of phenol from single component solution**

| Experiment | Operating Parameters |  |  |  |  |
|---|---|---|---|---|---|
|  | pH | Temp. ($^{o}$C) | Dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h |
| **Granular activated carbon (GAC)** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 16 | 100 | 12 |
| Effect of Temperature ($^{o}$C) | 7 | **10-50** | 16 | 100 | 12 |
| Effect of adsorbent dose (g/L) | 7 | 30 | **4-32** | 100 | 12 |
| Effect of Initial concentration (mg/L) | 7 | 30 | 16 | **100-400** | 12 |
| Effect of contact time (h) | 7 | 30 | 16 | 100 | **1-15** |
| **Tea waste (TW)** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 40 | 100 | 20 |
| Effect of Temperature ($^{o}$C) | 7 | **10-50** | 40 | 100 | 20 |
| Effect of adsorbent dose (g/L) | 7 | 30 | **5-50** | 100 | 20 |
| Effect of Initial concentration (mg/L) | 7 | 30 | 40 | **100-400** | 20 |
| Effect of contact time (h) | 7 | 30 | 40 | 100 | **2-24** |
| **Rice husk (RH)** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 35 | 100 | 26 |
| Effect of Temperature ($^{o}$C) | 7 | **10-50** | 35 | 100 | 26 |
| Effect of adsorbent dose (g/L) | 7 | 30 | **5-45** | 100 | 26 |
| Effect of Initial concentration (mg/L) | 7 | 30 | 35 | **100-400** | 26 |
| Effect of contact time (h) | 7 | 30 | 35 | 100 | **2-28** |
| **Bagasse (BG)** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 45 | 100 | 20 |
| Effect of Temperature ($^{o}$C) | 7 | **10-50** | 45 | 100 | 20 |
| Effect of adsorbent dose (g/L) | 7 | 30 | **5-60** | 100 | 20 |
| Effect of Initial concentration (mg/L) | 7 | 30 | 45 | **100-400** | 20 |
| Effect of contact time (h) | 7 | 30 | 45 | 100 | **2-24** |
| **Bagasse Fly ash** |  |  |  |  |  |
| Effect of pH | **2-10** | 30 | 40 | 100 | 26 |
| Effect of Temperature ($^{o}$C) | 8 | **10-50** | 40 | 100 | 26 |
| Effect of adsorbent dose | 8 | 30 | **5-50** | 100 | 26 |

| | | | | | |
|---|---|---|---|---|---|
| (g/L) | | | | | |
| Effect of Initial concentration (mg/L) | 8 | 30 | 40 | **100-400** | 26 |
| Effect of contact time (h) | 8 | 30 | 40 | 100 | **2-30** |
| **Distillery sludge** | | | | | |
| Effect of pH | **2-10** | 30 | 45 | 100 | 28 |
| Effect of Temperature ($^o$C) | 7 | **10-50** | 45 | 100 | 28 |
| Effect of adsorbent dose (g/L) | 7 | 30 | **5-60** | 100 | 28 |
| Effect of Initial concentration (mg/L) | 7 | 30 | 45 | **100-400** | 28 |
| Effect of contact time (h) | 7 | 30 | 45 | 100 | **2-32** |
| **Neem leaves (NL)** | | | | | |
| Effect of pH | **2-10** | 30 | 40 | 100 | 30 |
| Effect of Temperature ($^o$C) | 7 | **10-50** | 40 | 100 | 30 |
| Effect of adsorbent dose (g/L) | 7 | 30 | **5-50** | 100 | 30 |
| Effect of Initial concentration (mg/L) | 7 | 30 | 40 | **100-400** | 30 |
| Effect of contact time (h) | 7 | 30 | 40 | 100 | **2-32** |
| **Fe treated tea waste (Fe TW)** | | | | | |
| Effect of pH | **2-10** | 30 | 25 | 100 | 18 |
| Effect of Temperature ($^o$C) | 8 | **10-50** | 25 | 100 | 18 |
| Effect of adsorbent dose (g/L) | 8 | 30 | **5-40** | 100 | 18 |
| Effect of Initial concentration (mg/L) | 8 | 30 | 25 | **100-400** | 18 |
| Effect of contact time (h) | 8 | 30 | 25 | 100 | **2-22** |
| **Fe treated Rice husk (Fe RH)** | | | | | |
| Effect of pH | **2-10** | 30 | 24 | 100 | 22 |
| Effect of Temperature ($^o$C) | 8 | **10-50** | 24 | 100 | 22 |
| Effect of adsorbent dose (g/L) | 8 | 30 | **2-32** | 100 | 22 |
| Effect of Initial concentration (mg/L) | 8 | 30 | 24 | **100-400** | 22 |
| Effect of contact time (h) | 8 | 30 | 24 | 100 | **2-24** |

**Table 4.4: Range of operating parameters for simultaneous co-adsorption of Cr(VI) and phenol from binary solution**

| Experiment | | Operating Parameters | | | | | |
|---|---|---|---|---|---|---|---|
| | pH | Temp. ($^{o}$C) | Dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time h Cr(VI) | Contact time h Phenol |
| **Granular activated carbon (GAC)** | | | | | | | |
| Effect of pH | **2-10** | 30 | 10.50 | 100 | 50 | 3.5 | 3.5 |
| Effect of Temperature ($^{o}$C) | 5 | **10-50** | 10.50 | 100 | 50 | 3.5 | 3.5 |
| Effect of adsorbent dose (g/L) | 5 | 30 | **1.5-12** | 100 | 50 | 3.5 | 3.5 |
| Effect of Initial concentration (mg/L) | 5 | 30 | 10.50 | **100-400** | **50-200** | 3.5 | 3.5 |
| Effect of contact time (h) | 5 | 30 | 10.50 | 100 | 50 | **0.5-4.5** | **0.5-4.5** |
| **Tea waste (TW)** | | | | | | | |
| Effect of pH | **2-10** | 30 | 15 | 100 | 50 | 12 | 24 |
| Effect of Temperature ($^{o}$C) | 7 | **10-50** | 15 | 100 | 50 | 12 | 24 |
| Effect of adsorbent dose (g/L) | 7 | 30 | **2.5-20** | 100 | 50 | 12 | 24 |
| Effect of Initial concentration (mg/L) | 7 | 30 | 15 | **100-400** | **50-200** | 12 | 24 |
| Effect of contact time (h) | 7 | 30 | 15 | 100 | 50 | **2-26** | **2-26** |
| **Rice husk (RH)** | | | | | | | |
| Effect of pH | **2-10** | 30 | 20 | 100 | 50 | 12 | 12 |
| Effect of Temperature ($^{o}$C) | 5 | **10-50** | 20 | 100 | 50 | 12 | 12 |
| Effect of adsorbent dose (g/L) | 5 | 30 | **2-24** | 100 | 50 | 12 | 12 |
| Effect of Initial concentration (mg/L) | 5 | 30 | 20 | **100-400** | **50-200** | 12 | 12 |
| Effect of contact time (h) | 5 | 30 | 20 | 100 | 50 | **1-17** | **1-17** |
| **Fe treated tea waste (Fe TW)** | | | | | | | |
| Effect of pH | **2-10** | 30 | 15 | 100 | 50 | 10 | 15 |
| Effect of Temperature ($^{o}$C) | 2 | **10-50** | 15 | 100 | 50 | 10 | 15 |
| Effect of adsorbent dose (g/L) | 2 | 30 | **2.5-20** | 100 | 50 | 10 | 15 |
| Effect of Initial concentration (mg/L) | 2 | 30 | 15 | **100-400** | **50-200** | 10 | 15 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Effect of contact time (h) | 2 | 30 | 15 | 100 | 50 | **1-17** | **1-17** |
| **Fe treated Rice husk (Fe RH)** | | | | | | | |
| Effect of pH | **2-10** | 30 | 9 | 100 | 50 | 10 | 10 |
| Effect of Temperature ($^oC$) | 5 | **10-50** | 9 | 100 | 50 | 10 | 10 |
| Effect of adsorbent dose (g/L) | 5 | 30 | **2-16** | 100 | 50 | 10 | 10 |
| Effect of Initial concentration (mg/L) | 5 | 30 | 9 | **100-400** | **50-200** | 10 | 10 |
| Effect of contact time (h) | 5 | 30 | 9 | 100 | 50 | **1-14** | **1-14** |

**Table 4.5: Run numbers of experiments conducted to study the effect of varying pH on to the removal of Cr(VI) from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.1 | 1-9 |
| TW | A.2 | 43-51 |
| RH | A.3 | 80-88 |
| BG | A.4 | 123-131 |
| BFA | A.5 | 167-175 |
| DS | A.6 | 209-217 |
| NL | A.7 | 253-261 |
| Fe TW | A.8 | 294-302 |
| Fe RH | A.9 | 333-341 |

**Table 4.6: Run numbers of experiments conducted to study the effect of varying pH onto the removal of phenol from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.10 | 371-379 |
| TW | A.11 | 415-423 |
| RH | A.12 | 458-466 |
| BG | A.13 | 503-511 |
| BFA | A.14 | 548-556 |
| DS | A.15 | 594-602 |
| NL | A.16 | 643-651 |
| Fe TW | A.17 | 690-698 |
| Fe RH | A.18 | 730-738 |

**Table 4.7: Run numbers of experiments conducted to study the effect of varying pH on to the simultaneous removal of Cr(VI) and phenol from binary solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.19 | 771-778 |
| TW | A.20 | 808-815 |
| RH | A.21 | 849-856 |
| Fe TW | A.22 | 898-905 |
| Fe RH | A.23 | 943-950 |

**Table 4.8: Run numbers of experiments conducted to study the effect of varying Temperature (°C) on to the removal of Cr(VI) from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.1 | 10-14 |
| TW | A.2 | 52-56 |
| RH | A.3 | 89-93 |
| BG | A.4 | 132-136 |
| BFA | A.5 | 176-180 |
| DS | A.6 | 218-222 |
| NL | A.7 | 262-266 |
| Fe TW | A.8 | 303-307 |
| Fe RH | A.9 | 343-346 |

**Table 4.9: Run numbers of experiments conducted to study the effect of varying Temperature (°C) on to the removal of phenol from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.10 | 380-384 |
| TW | A.11 | 424-428 |
| RH | A.12 | 467-471 |
| BG | A.13 | 512-516 |
| BFA | A.14 | 557-561 |
| DS | A.15 | 603-607 |
| NL | A.16 | 652-656 |
| Fe TW | A.17 | 699-703 |
| Fe RH | A.18 | 739-743 |

**Table 4.10: Run numbers of experiments conducted to study the effect of varying temperature (ºC) on to the simultaneous removal of Cr(VI) and phenol from binary solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.19 | 779-783 |
| TW | A.20 | 816-820 |
| RH | A.21 | 857-861 |
| Fe TW | A.22 | 906-910 |
| Fe RH | A.23 | 951-955 |

**Table 4.11: Run numbers of experiments conducted to study the effect of varying adsorbent dose (g/L) on to the removal of Cr(VI) from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.1 | 15-23 |
| TW | A.2 | 57-64 |
| RH | A.3 | 94-103 |
| BG | A.4 | 137-146 |
| BFA | A.5 | 181-190 |
| DS | A.6 | 223-233 |
| NL | A.7 | 267-274 |
| Fe TW | A.8 | 308-315 |
| Fe RH | A.9 | 347-354 |

**Table 4.12: Run numbers of experiments conducted to study the effect of varying adsorbent dose (g/L) on to the removal of phenol from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.10 | 385-392 |
| TW | A.11 | 429-438 |
| RH | A.12 | 472-481 |
| BG | A.13 | 517-528 |
| BFA | A.14 | 562-571 |
| DS | A.15 | 608-619 |
| NL | A.16 | 657-666 |
| Fe TW | A.17 | 704-711 |
| Fe RH | A.18 | 744-751 |

**Table 4.13: Run numbers of experiments conducted to study the effect of varying adsorbent dose (mg/g) on to the simultaneous removal of Cr(VI) and phenol from binary solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.19 | 784-791 |
| TW | A.20 | 821-828 |
| RH | A.21 | 862-873 |
| Fe TW | A.22 | 911-918 |
| Fe RH | A.23 | 956-963 |

**Table 4.14: Run numbers of experiments conducted to study the effect of varying contact time h on to the removal of Cr(VI) from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.1 | 31-42 |
| TW | A.2 | 72-79 |
| RH | A.3 | 111-122 |
| BG | A.4 | 154-166 |
| BFA | A.5 | 198-208 |
| DS | A.6 | 241-252 |
| NL | A.7 | 282-293 |
| Fe TW | A.8 | 323-332 |
| Fe RH | A.9 | 362-370 |

**Table 4.15: Run numbers of experiments conducted to study the effect of varying contact time h on to the removal of phenol from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.10 | 400-414 |
| TW | A.11 | 446-457 |
| RH | A.12 | 489-502 |
| BG | A.13 | 536-547 |
| BFA | A.14 | 579-593 |
| DS | A.15 | 627-642 |
| NL | A.16 | 674-689 |
| Fe TW | A.17 | 719-729 |
| Fe RH | A.18 | 759-770 |

**Table 4.16: Run numbers of experiments conducted to study the effect of varying contact time (h) on to the simultaneous removal of Cr(VI) and phenol from binary solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.19 | 799-807 |
| TW | A.20 | 836-848 |
| RH | A.21 | 881-897 |
| Fe TW | A.22 | 926-942 |
| Fe RH | A.23 | 971-984 |

**Table 4.17: Run numbers of experiments conducted to study the effect of varying initial concentration (mg/L) on to the removal of Cr(VI) from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.1 | 24-30 |
| TW | A.2 | 65-71 |
| RH | A.3 | 104-110 |
| BG | A.4 | 147-153 |
| BFA | A.5 | 191-197 |
| DS | A.6 | 234-240 |
| NL | A.7 | 275-281 |
| Fe TW | A.8 | 316-322 |
| Fe RH | A.9 | 355-361 |

**Table 4.18: Run numbers of experiments conducted to study the effect of varying initial concentration (mg/L) on to the removal of phenol from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.10 | 393-399 |
| TW | A.11 | 439-445 |
| RH | A.12 | 482-488 |
| BG | A.13 | 529-535 |
| BFA | A.14 | 572-578 |
| DS | A.15 | 620-626 |
| NL | A.16 | 667-673 |
| Fe TW | A.17 | 712-718 |
| Fe RH | A.18 | 752-758 |

**Table 4.19: Run numbers of experiments conducted to study the effect of varying initial concentration (mg/L) on to the simultaneous removal of Cr(VI) and phenol from binary solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| GAC | A.19 | 792-798 |
| TW | A.20 | 829-835 |
| RH | A.21 | 874-880 |
| Fe TW | A.22 | 919-925 |
| Fe RH | A.23 | 964-970 |

**4.2.5.6 Analysis of Cr(VI) and Phenol in filtrate:** After a fixed interval of time an appropriate volume of samples was withdrawn from shaker and filtered using standard whatman filter paper (Cat No. 1001 125). Thereafter concentration of Cr (VI) and phenol in the filtrate was analysed.

For the analysis of Cr(VI) and phenol in filtrate UV spectrophotometer made of Hach (model No: DR 5000) was used. For the analysis of Cr(VI) 10 mL of filtrate was reacted with a 200 µL diphenyl carbazide solution and 500 µL $H_2SO_4$ and let them stand for 10 min for full colour development and its absorbance was taken at 540 nm. The residual concentration of phenol in the filtrate was determined by mixing 100 mL phenol sample with 700 mL of sodium bicarbonate (pH 8), 100 mL of 4-amino antipyrine (20.8 mM) and 100 mL of potassium ferricyanide (83.4 mM) and let them stand for full colour development and its absorbance was taken at 510 nm (Ontanon et al. 2014).

## 4.3 BIOLOGICAL STUDY

Two bacterial strains namely *Escherichia coli* (NCIM No. 5041) and *Bacillus* sp.(MTCC No. 3166) were purchased from NCIM Pune and MTCC Chandigarh, and used for the study of bioaccumulation and biodegradation of Cr(VI) and phenol. *Escherichia coli* was used for the reduction of Cr(VI) and *Bacillus* sp. was used for the both reduction of Cr(VI) and biodegradation of phenol in both individual and combined solution of Cr(VI) and phenol. Batch experiments on the adsorption and bioaccumulation of Cr(VI) and adsorption and biodegradation of phenol were carried out using bacterial strain *Escherichia coli* and *Bacillus* sp., which was immobilized on suitable biosorbent. Initially the experiments were designed to acclimatize the bacterial strain to grow on higher Cr(VI) and phenol concentrations. This process adapts the micro-organism to utilize Cr(VI) for bioaccumulation and phenol for biodegradation in their metabolic activity and hence accumulate and degrade the Cr(VI) and phenol species. The operating parameters were also optimized through these experiments.

**4.3.1 Bioaccumulation of Cr(VI) and biodegradation of phenol in single and binary substrate solution:** Experiments were carried out for the bioaccumulation of Cr(VI) using bacterium *Escherichia coli* and *Bacillus* sp. and biodegradation of phenol by *Bacillus* sp. in single substrate solution. The consortium culture of *Escherichia coli* and *Bacillus* sp. was used for the simultaneous reduction of Cr(VI) and biodegradation of phenol. The experimental data associated with bioaccumulation of Cr(VI) and biodegradation of phenol is given in table 4.20. Table 4.20 comprises of Annexure A.24 growth curve of *Bacillus* sp. for the single substrate solution of Cr(VI) and phenol, annexure A.25 growth curve for *Escherichia coli* for the single substrate solution of Cr(VI), A.26 growth curve for the pure culture of *Bacillus* sp. and consortium culture of *Escherichia coli* and *Bacillus* sp. for the simultaneous reduction of Cr(VI) and biodegradation of phenol, annexure A.27 growth curve for the acclimatization of *Bacillus* sp. to the different concentrations of Cr(VI) and phenol in single substrate solution, annexure A.28 growth curve for the acclimatization of *Escherichia coli* to the different concentrations of Cr(VI) in single substrate solution, annexure A.29 growth curve for the acclimatization of pure culture of *Bacillus* sp. and consortium culture of *Escherichia coli* and *Bacillus* sp. to the different concentrations of Cr(VI) and phenol (1:2) ratio for the simultaneous reduction of Cr(VI) and biodegradation of phenol.

#### 4.3.1.1 Bacteria Plating

The bacterial strain purchased from MTCC Chandigarh and NCIM Pune was revived in Nutrient broth medium. After obtaining maximum growth of bacterium it was stored in agar plates in the nutrient medium and kept in a deep freezer at very low temperature of 4 ºC. The plating procedure is as follows:

1. The Nutrient broth medium was prepared by adding 2g agar to 50 mL of Millipore water containing media components as required.
2. The nutrient agar solution was autoclaved at 121 $^0$C at 14.7 psi for 21 min.
3. The sterilized nutrient agar solution was cooled for some time and then it was poured in the plates in UV chamber in the presence of spirit lamp to avoid contamination.
4. When the agar plates were solidified it was covered and kept overnight without disturbing.
5. A loop of bacteria was taken in the inoculation loop from the cultured nutrient medium and inoculated on the agar plates.
6. The plates were then incubated in an incubator at 37$^0$C for 24 h.
7. After 24 h, colonies of bacteria started to grow on the nutrient plates.
8. Then the cultured plates were stored at 4 $^{\circ}$C for further use.

#### 4.3.1.2 Study on growth of bacteria

The freeze-dried culture of bacterial strain (*Escherichia coli* MTCC No. 5041) and (*Bacillus* sp. MTCC No. 3166) was purchased from MTCC Chandigarh and NCIM Pune, respectively. The *Escherichia coli* was grown in both L.B. (Luria-Bertani) media and N.B. (Nutrient broth) media to examine the growth and percentage removal of Cr(VI). A L.B. medium ATCC 57 consist of ($K_2HPO_4$ 7.0 g, $KH_2PO_4$ 3.0 g, glycerol 5.0 g, $(NH_4)_2SO_4$ 1.5 g, L-lysine 0.1 g, $MgSO_4$ 0.1 g, $CaCl_2$ 0.01 g, and $FeSO_4.7H_2O$ 0.5 mg in 1 L of distilled water, pH 7.0) and N.B. media (Beef extract 1.0 g/L, Yeast extract 2.0 g/L, Peptone 5.0 g/L, NaCl 5.0 g/L and Agar 15.0 g/L at pH 7) was used for the growth of microorganism (Bae et al. 2000). The L.B. media shows the higher percentage removal of Cr(VI) for *Escherichia coli*. *Bacillus* sp. was also cultured in both N.B and L.B media to study the growth of microorganism. For *Bacillus* sp. N.B medium (Beef extract 1.0 g, yeast extract 2.0 g, peptone 5.0 g, NaCl 5.0 g, Agar 15 g in 1 L of distilled water, pH 7) shows the maximum growth of bacterium. The culture was inoculated in 100 ml of media in 250 ml of conical flask and then incubated in an incubator shaker with agitation speed of 120 rpm at 37 °C. The conical flask containing growth medium was steam sterilized in autoclave at 121±1°C for 20 minutes at a pressure of 15 psi. All the batch experiments were carried out in properly cleaned UV chamber and all the glass wares used for the batch experiments were autoclaved to avoid the contamination. The growth of the bacterium (*Escherichia coli* and *Bacillus* sp.) was measured in UV spectrophotometer at 600 nm, at the time interval of 1 to 60 hours of incubation.

#### 4.3.1.3 Study on growth of bacterium (*Escherichia coli)* in presence of Cr(VI) and its maximum tolerance limit

In this study, batch experiments were carried out to determine the effect of presence of Cr(VI) on the growth of *Escherichia coli* and maximum tolerance limit towards Cr(VI). This bacterium cell was acclimatized to the Cr(VI) environment by growing the bacterial strain in minimal media. The bacterial strain of *Escherichia coli* was acclimatized to the different concentration of Cr(VI) ranging from 5-100 mg/L in different 250 mL conical flasks and agitated in an incubator shaker at 120 rpm and 37 °C.

### 4.3.1.4 Study on growth of bacterium (*Bacillus sp.*) in presence of Cr(VI) and phenol and its maximum tolerance limit

In this study, batch experiments were carried out to determine the effect of presence of Cr(VI) and phenol onto the growth of *Bacillus* sp. and maximum tolerance limit towards Cr(VI) and phenol in single and binary solution of Cr(VI) and phenol. This bacterium cell was acclimatized to the toxic Cr(VI) and phenol environment by growing the bacterial strain agitated in minimal media. The bacterium *Bacillus sp.* was acclimatized to the different concentration of Cr(VI) and phenol ranging from 5-100 mg/L in different 250 mL conical flasks and in an incubator shaker at 120 rpm and 37 °C.

**Table 4.20: Run numbers of experiments conducted for the bioremediation of Cr(VI) and phenol using bacterium *Bacillus* sp. and *Escherichia coli***

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| Growth curve of *Bacillus* sp. MTCC No 3166 for single substrate solution of Cr(VI) and phenol | A.24 | 985-1003 |
| Growth curve of *Escherichia coli* MTCC No 5041 for single substrate solution of Cr(VI) | A.25 | 1004-1023 |
| Growth curve of pure culture of Bacillus sp. and consortium culture of *Escherichia coli* and *Bacillus* sp. for the simultaneous reduction of Cr(VI) and biodegradation of phenol from binary substrate solution | A.26 | 1024-1043 |

| | | |
|---|---|---|
| Growth curve for the acclimatization of *Bacillus*sp. to the various concentrations of Cr(VI) and phenol in single substrate solution | A.27 | 1044-1138 |
| Growth curve for the acclimatization of *Escherichia coli* to the various concentrations of Cr(VI) for single substrate solution | A.28 | 1139-1233 |
| Growth curve for the acclimatization of pure culture of *Bacillus* sp. and consortium culture of *Escherichia coli* and *Bacillus* sp. to the various concentrations of Cr(VI) and phenol for binary substrate solution of Cr(VI) and phenol | A.29 | 1234-1328 |

### 4.3.2 Batch Studies on Simultaneous adsorption and bioaccumulation of Cr(VI) and biodegradation of Phenol:

Experiments for simultaneous adsorption and bioaccumulation of Cr(VI) and biodegradation of phenol were carried out in 250 mL flat bottom flask in a 100 mL solution by immobilizing bacterium *Bacillus sp.* and *Escherichia coli* onto the surface of adsorbent selected from batch study which provides the maximum simultaneous percentage removal of Cr(VI) and phenol. The simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol were also carried out by immobilizing consortium culture of *Bacillus* sp. and *Escherichia coli* onto the surface of tea waste. The concentrations of Cr(VI) and phenol in binary solution was taken in (2:1) ratio which was as same as in batch study for the simultaneous removal of Cr(VI) and phenol.

Different concentrations of Cr(VI) and phenol were taken in the range of 100-500 mg/L and 50-250 mg/L respectively. The flasks were placed further in the incubator and orbital shaker at 37 °C at an rpm of 120 for the maximum time until percentage removal of Cr(VI) and phenol becomes constant. After 60 h the samples were collected and they were first filtered by Whatman filter paper (Cat No 1001 125) to filter out the adsorbent. The filtrate was then collected and centrifuged at 10000 rpm in a centrifuge. The supernatant was then collected and analysed for phenol and cyanide concentration by colorimetric methods.

#### 4.3.2.1 Experimental program

Experiments were carried out for biological removal of Cr(VI) and phenol from both single and binary synthetic solution of Cr(VI) and phenol (Fig. 4.3.2.1). This illustrates the complete sequence of the experiments performed for Cr(VI) and phenol removal by SAB process in the batch studies.

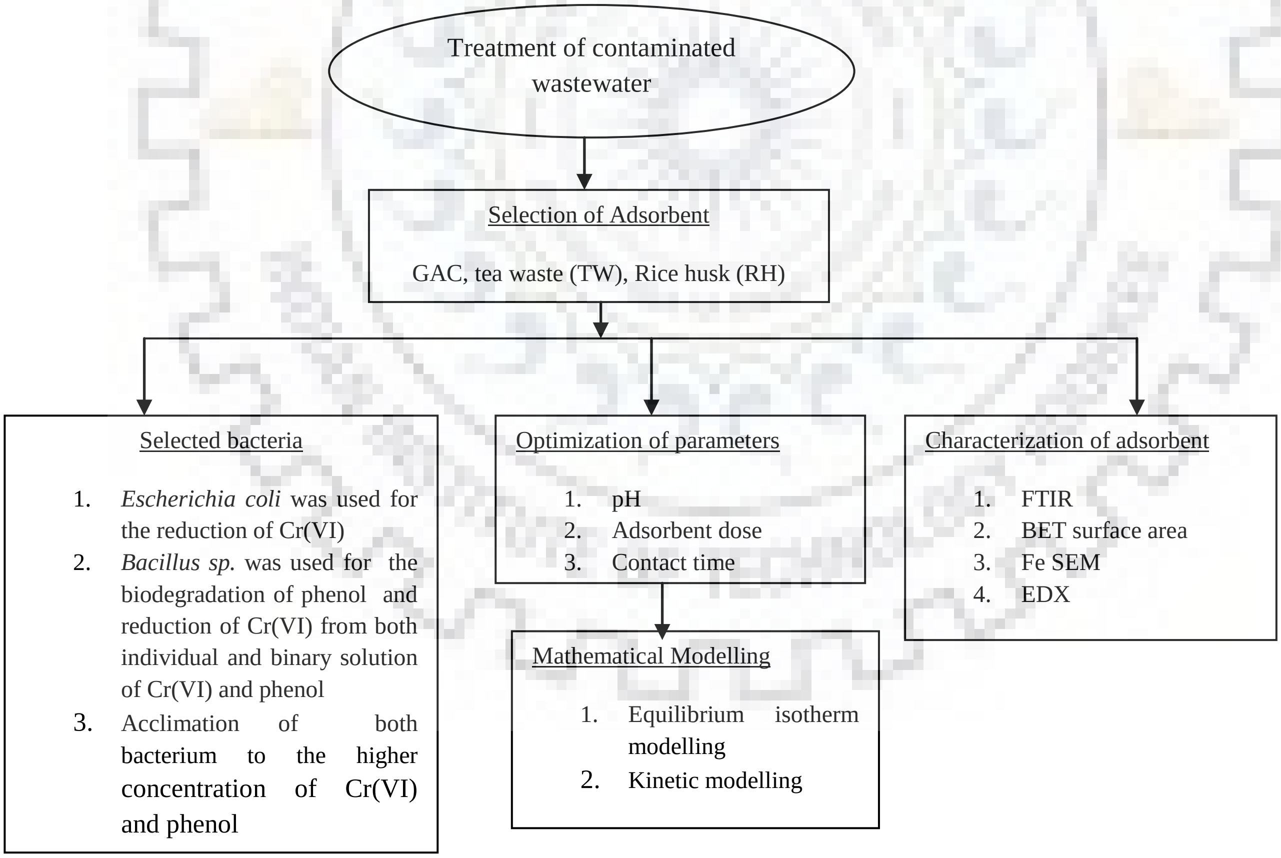


**Figure 4.3.2.1:** Schematic block diagram of batch experimentation on biological removal of Cr(VI) and phenol in SAB system

#### 4.3.2.2 Study on bio-removal of Cr(VI) by adsorption and by bioaccumulation

Experiments were carried out for the removal of Cr(VI) using *Escherichia coli* and *Bacillus* sp. in a batch reactor. The selected adsorbents from single component batch adsorption study, which provides the maximum percentage removal of Cr(VI) were added to the bacterial strain as supporting media for bacterial immobilization to study the effect of initial concentration of Cr(VI) onto the percentage removal of Cr(VI) by *Escherichia coli* and *Bacillus* sp. in simultaneous adsorption and bioaccumulation system. For this study pH and temperature was maintained at 7 and 37°C, respectively, according to the literature. Equilibrium parameters were evaluated from the experimental data.

#### 4.3.2.3 Study on bio-removal of phenol by adsorption and by biodegradation

Similar experiments were carried out for the removal of phenol using *Bacillus sp.* isolated from tannery wastewater (MTCC No. 3166) in a batch reactor. The best biosorbent obtained from batch study, which gives maximum percentage removal of phenol, were added to the bacterial strain as supporting media for bacterial immobilization. This is done to study the effect of initial concentration of phenol onto the percentage removal of phenol by *Bacillus* sp. in simultaneous adsorption and bioaccumulation system. For this study pH and temperature was maintained at 7 and 37 °C, respectively, according to the literature. Equilibrium parameters were evaluated from the experimental data.

#### 4.3.2.4 Study on simultaneous bio-removal of Cr(VI) and phenol by adsorption and bioaccumulation of Cr(VI) and biodegradation of phenol

Based upon the single component SAB study for the removal of Cr(VI) and phenol simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol was carried out using consortium culture of *Escherichia coli* and *Bacillus* sp. immobilized onto the surface of tea waste for the same range of operating parameters pH 7 and temperature 37°C.

#### 4.3.2.5 Range of operating parameters

Experiments were carried out to study the removal of Cr(VI) and phenol using Bacillus sp. and Escherichia coli immobilized on to the surface of various adsorbents (GAC, TW and RH). Effect of various process parameters such as adsorbent dose, contact time, initial concentration at constant pH 7 and temperature 37 $^{o}$C were evaluated. The range of operating parameters associated with simultaneous adsorption and bioaccumulation of Cr(VI) in single component solution, simultaneous adsorption and biodegradation of phenol in single component solution and simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol is given in table 4.21, table 4.22 and table 4.23, respectively. Adsorbent was steam sterilized before adding to the medium. At the end of experimental run, sample was withdrawn and centrifuged at 8000 g for 10 min and the supernatant was analyzed for Cr(VI) and phenol by colorimetric method 1, 5 diphenyl carbazide and 4 aminoantipyrene method, respectively.

**Table 4.21: Range of operating parameters for simultaneous adsorption and bioaccumulation of Cr(VI) from single substrate solution**

| Experiment | Operating parameters | | |
|---|---|---|---|
| | Dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h |
| ***Escherichia coli* supported GAC** | | | |
| Effect of adsorbent dose (g/L) | **1.5-17.5** | 100 | 60 |
| Effect of Initial concentration (mg/L) | 12.5 | **100-500** | 60 |
| Effect of contact time (h) | 12.5 | 100 | **6-66** |
| ***Bacillus* sp. supported GAC** | | | |
| Effect of adsorbent dose (g/L) | **1.5-17.5** | 100 | 72 |
| Effect of Initial concentration (mg/L) | 12.5 | **100-500** | 72 |
| Effect of contact time (h) | 12.5 | 100 | **6-84** |
| ***Escherichia coli* supported TW** | | | |
| Effect of adsorbent dose (g/L) | **1.5-10** | 100 | 30 |
| Effect of Initial concentration (mg/L) | 5 | **100-500** | 30 |
| Effect of contact time (h) | 5 | 100 | **3-36** |
| ***Bacillus* sp. supported TW** | | | |
| Effect of adsorbent dose (g/L) | **1.0-10** | 100 | 60 |
| Effect of Initial concentration (mg/L) | 7 | **100-500** | 60 |
| Effect of contact time (h) | 7 | 100 | **6-66** |
| ***Escherichia coli* supported RH** | | | |
| Effect of adsorbent dose (g/L) | **2.5-15** | 100 | 60 |
| Effect of Initial concentration (mg/L) | 12.5 | **100-500** | 60 |
| Effect of contact time (h) | 12.5 | 100 | **6-66** |
| ***Bacillus* sp. supported RH** | | | |
| Effect of adsorbent dose (g/L) | **1.25-12.5** | 100 | 48 |
| Effect of Initial concentration (mg/L) | 10 | **100-500** | 48 |
| Effect of contact time (h) | 10 | 100 | **6-60** |

**Table 4.22: Range of operating parameters for simultaneous adsorption and bioaccumulation of Cr(VI) from single substrate solution**

| Experiment | Operating parameters | | |
|---|---|---|---|
| | Dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h |
| ***Bacillus* sp. supported GAC** | | | |
| Effect of adsorbent dose (g/L) | **0.5-6.0** | 100 | 13 |
| Effect of Initial concentration (mg/L) | 4.5 | **100-500** | 72 |
| Effect of contact time (h) | 4.5 | 100 | **1-14** |
| ***Bacillus* sp. supported TW** | | | |
| Effect of adsorbent dose (g/L) | **1.25-11.25** | 100 | 36 |
| Effect of Initial concentration (mg/L) | 8.75 | **100-500** | 60 |
| Effect of contact time (h) | 8.75 | 100 | **3-39** |
| ***Bacillus* sp. supported RH** | | | |
| Effect of adsorbent dose (g/L) | **1.25-11.25** | 100 | 39 |
| Effect of Initial concentration (mg/L) | 7.5 | **100-500** | 48 |
| Effect of contact time (h) | 7.5 | 100 | **3-42** |

**Table 4.23: Range of operating parameters for simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol from binary substrate solution**

| Experiment | Operating parameters | | | | |
|---|---|---|---|---|---|
| | Dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time h Cr(VI) | Contact time h Phenol |
| ***Escherichia coli* and *Bacillus* sp. supported TW** | | | | | |
| Effect of adsorbent dose (g/L) | **1.25-10** | 100 | 50 | 24 | 45 |
| Effect of Initial concentration (mg/L) | 7.5 | **100-500** | **50-250** | 24 | 45 |
| Effect of contact time (h) | 7.5 | 100 | 50 | **3-51** | **3-51** |

#### *4.3.2.5.1 Studies on to the effect of varying adsorbent dose (mg/g) for simultaneous adsorption and bioaccumulation of Cr(VI) and biodegradation of phenol in single and binary synthetic simulated waste water*

The batch experiments were carried out to investigate the effect of adsorbent dose (mg/g) for the immobilization of bacterium *Escherichia coli* and *Bacillus* sp. for the simultaneous adsorption and bioaccumulation of Cr(VI) and biodegradation of phenol in single and binary synthetic simulated solution. The experimental data associated with the effect of adsorbent dose for the single component solution of Cr(VI), single component solution of phenol and binary solution of Cr(VI) and phenol is given in table 4.24, table 4.27 and table 4.30, respectively.

#### ***4.3.2.5.2 Studies on to the effect of varying contact time (h) for simultaneous adsorption and bioaccumulation of Cr(VI) and biodegradation of phenol in single and binary synthetic simulated waste water***

In the present work, studies on the effect of varying agitation time on SAB of Cr(VI) and phenol were carried out. For each adsorbent experiment were carried out in 250 mL flat bottom round flask with working volume of 200 mL. The flasks were agitated for 6, 12, 18, 24, 30, 36, 42, 48, 54, 60, 66, 72, 84 and 90 h. All the experiments were carried out thrice and average values were reported. The run No.s associated with simultaneous adsorption and bioaccumulation of Cr(VI), simultaneous adsorption and biodegradation of phenol, simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol is given in table 4.25, table 4.28 and table 4.31, respectively.

#### ***4.3.2.5.3 Studies onto the effect of varying initial concentration (mg/L) for simultaneous adsorption and bioaccumulation of Cr(VI) and biodegradation of phenol in single and binary synthetic simulated waste water***

In the present work, studies on the effect of varying initial concentration of Cr(VI) and phenol in the range 100-500 mg/L of Cr(VI) and 50-250 mg/L of phenol according to the composition of industrial waste water as they are discharged in (2:1) ratio from tannery waste water. For each adsorbent five experimental runs were carried out. The Run No.s associated with simultaneous adsorption and bioaccumulation of Cr(VI), simultaneous adsorption and biodegradation of phenol, simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol is given in table 4.26, table 4.29 and table 4.32 respectively. All the experiments were repeated thrice and average results have been reported in annexure A.36 to A. 39.

**Table 4.24: Run numbers of experiments conducted to study the effect of varying adsorbent dose (g/L) on to simultaneous adsorption and bioaccumulation of Cr(VI) from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| *Escherichia coli* immobilized GAC | A.30 | 1329-1342 |
| *Bacillus* sp. immobilized GAC | A.31 | 1363-1375 |
| *Escherichia coli* immobilized TW | A.32 | 1399-1406 |
| *Bacillus* sp. immobilized TW | A.33 | 1428-1437 |
| *Escherichia coli* immobilized RH | A.34 | 1458-1469 |
| *Bacillus* sp. immobilized RH | A.35 | 1490-1499 |

**Table 4.25: Run numbers of experiments conducted to study the effect of varying adsorbent dose (g/L) on to simultaneous adsorption and biodegradation of phenol from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| *Bacillus* sp. immobilized GAC | A.36 | 1519-1528 |
| *Bacillus* sp. immobilized TW | A.37 | 1546-1554 |
| *Bacillus* sp. immobilized RH | A.38 | 1577-1585 |

**Table 4.26: Run numbers of experiments conducted to study the effect of varying adsorbent dose (mg/g) on to the simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol from binary solution using consortium culture of *Escherichia coli* and *Bacillus* sp.**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| *Bacillus* sp. immobilized TW | A.39 | 1609-1616 |

**Table 4.27: Run numbers of experiments conducted to study the effect of varying contact time h on to simultaneous adsorption and bioaccumulation of Cr(VI) from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| *Escherichia coli* immobilized GAC | A.30 | 1352-1362 |
| *Bacillus* sp. immobilized GAC | A.31 | 1385-1398 |
| *Escherichia coli* immobilized TW | A.32 | 1416-1427 |
| *Bacillus* sp. immobilized TW | A.33 | 1447-1457 |
| *Escherichia coli* immobilized RH | A.34 | 1479-1489 |
| *Bacillus* sp. immobilized RH | A.35 | 1509-1518 |

**Table 4.28: Run numbers of experiments conducted to study the effect of varying contact time h on to simultaneous adsorption and biodegradation of phenol from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| *Bacillus* sp. immobilized GAC | A.36 | 1538-1545 |
| *Bacillus* sp. immobilized TW | A.37 | 1564-1576 |
| *Bacillus* sp. immobilized RH | A.38 | 1595-1608 |

**Table 4.29: Run numbers of experiments conducted to study the effect of varying contact time (h) on to the simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol from binary solution using consortium culture of *Escherichia coli* and *Bacillus* sp.**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| *Bacillus* sp. immobilized TW | A.39 | 1626-1642 |

**Table 4.30: Run numbers of experiments conducted to study the effect of varying initial concentration (mg/L) on to the simultaneous adsorption and bioaccumulation of Cr(VI) from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| *Escherichia coli* immobilized GAC | A.30 | 1343-1351 |
| *Bacillus* sp. immobilized GAC | A.31 | 1376-1384 |
| *Escherichia coli* immobilized TW | A.32 | 1407-1415 |
| *Bacillus* sp. immobilized TW | A.33 | 1438-1446 |
| *Escherichia coli* immobilized RH | A.34 | 1470-1478 |
| *Bacillus* sp. immobilized RH | A.35 | 1500-1508 |

**Table 4.31: Run numbers of experiments conducted to study the effect of varying initial concentration (mg/L) on to the simultaneous adsorption and biodegradation of phenol from single component solution by various adsorbents**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| *Bacillus* sp. immobilized GAC | A.36 | 1529-1537 |
| *Bacillus* sp. immobilized TW | A.37 | 1555-1563 |
| *Bacillus* sp. immobilized RH | A.38 | 1586-1594 |

**Table 4.32: Run numbers of experiments conducted to study the effect of varying initial concentration (mg/L) on to the simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol from binary solution using consortium culture of *Escherichia coli* and *Bacillus* sp.**

| Adsorbent (s) | Table No. (s) | Run No. (s) |
|---|---|---|
| *Bacillus* sp. immobilized TW | A.39 | 1617-1625 |

**4.4 Continuous study for simultaneous removal of Cr(VI) and Phenol:** Experiments were carried out in continuous column reactor for the removal of Cr(VI) and phenol from synthetic simulated waste water. The parameters studied were Empty Bed contact time (EBCT) and bed height. The change in pH and DO with time were also carried out. The experimental setup consists of an inlet feed tank, cylindrical reactor and a peristaltic pump. Workload of the column was 2.9 L calculated experimentally. There are four sampling ports in the same distance of 12.5 cm. The wastewater flow was controlled by a peristaltic pump of series PP, PP-20-EX. EBCT (empty bed contact time) is manually adjusted to 4 h in the peristaltic pump. The volume flow rate was 5.46 mL/min at an EBCT of 4 h. Tea biomass was packed in the column. The binary synthetic solution of 100 mg/L of Cr(VI) and 50 mg/L of phenol was passed through the reactor. Samples were collected after every 5 minutes from the port and the residual concentration of Cr(VI) and phenol was analyzed by the colorimetric method using a UV-Vis spectrophotometer.

Kinetic modelling of experimental data using various kinetic models was also executed. The continuous column was packed with tea waste biomass for carrying out experiments. The Run No.s for the simultaneous removal of Cr(VI) and phenol in continuous column is given in table 4.33. The experimental data of continuous column reactor at different flow rate (mL/min) and bed height (cm) for various intervals of time is given in annexure A.40 used for the kinetic modelling.

### 4.4.1. Simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation phenol in continuous column reactor:

The column reactor packed with tea waste was immobilized with consortium culture of *Escherichia coli* and *Bacillus* sp. The close circuit assembly was sterilized with steam at 121 ºC and 15-psi pressure for 30 min. The 5 L stock solution of Cr(VI) and phenol (2:1) ratio was filled in feed tank of reactor for the experimentation. Firstly, the nutrient solution was filled in the feed tank and passed to the packed bed column through peristaltic pump for the conditioning of the adsorbent bed. After conditioning the consortium culture of *Escherichia coli* and *Bacillus* sp. grown in the nutrient medium was passed to the packed bed column. The solution was kept inside the column for the growth of bacterium onto the surface of tea waste biomass packed bed. After 3 days the bacterium *Escherichia coli* and *Bacillus* sp. was immobilized or stabilized onto the surface of adsorbent bed. After immobilization synthetic simulated (2:1) of Cr(VI) and phenol was passed to the column for the simultaneous reduction of Cr(VI) and biodegradation of phenol. The Run No.s for the simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol in continuous column is given in table 4.33. The experimental data of continuous column reactor at different flow rate (mL/min) and bed height (cm) for various intervals of time is given in annexure A.41 used for the mass transfer modelling.

**Table 4.33: Run Nos. of experiments conducted for the simultaneous removal of Cr(VI) and phenol in continuous reactor**

| Packed bed column | Table No. (s) | Run No. (s) |
|---|---|---|
| Tea waste biomass | A.40 | 1643-1761 |
| Tea waste biomass immobilized with consortium culture of *Escherichia coli* and *Bacillus* sp. | A.41 | 1762-1876 |

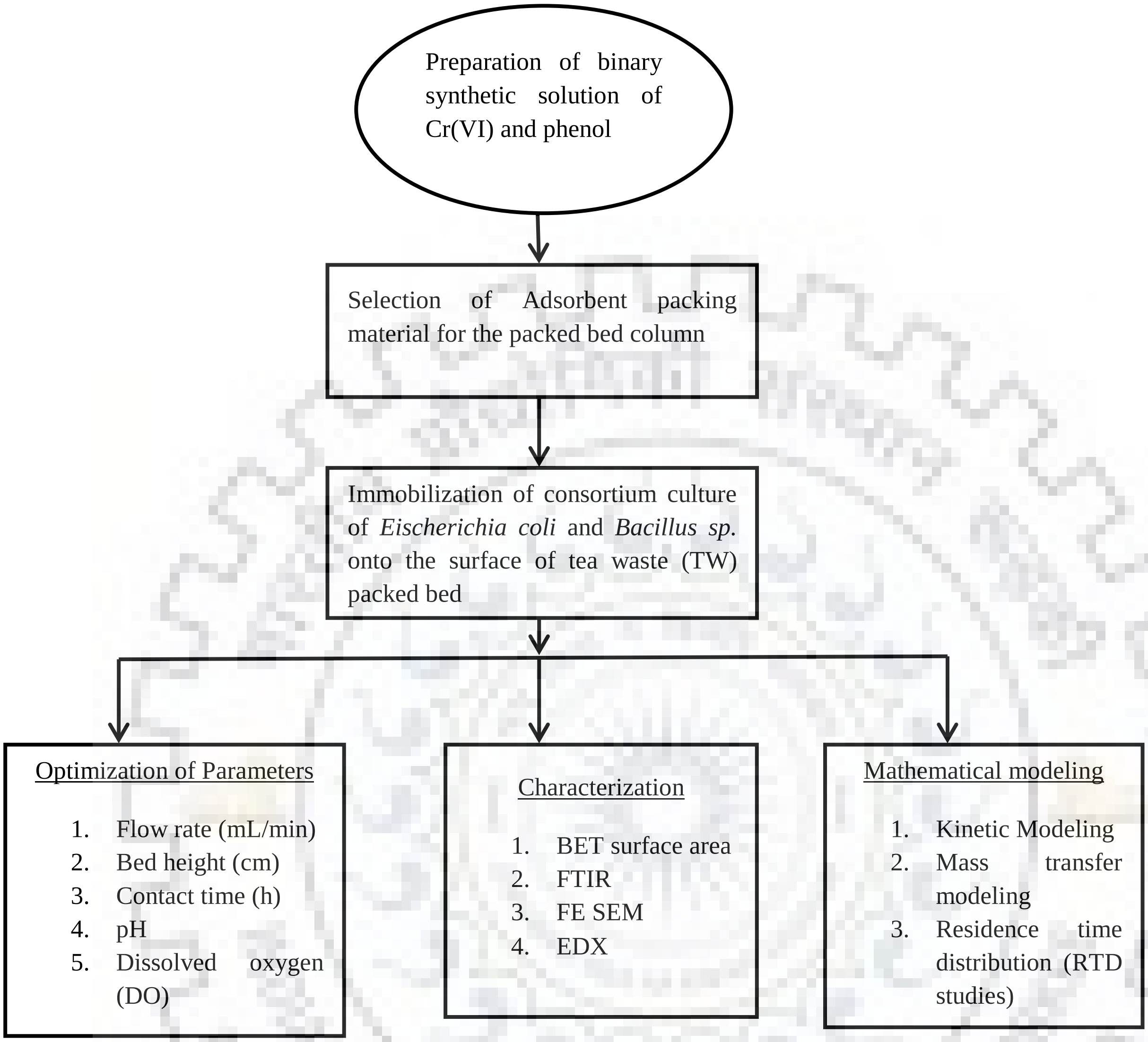


Figure 4.4.1: Schematic block diagram of batch experimental on biological removal of Cr(VI) and phenol in Continuous reactor system.

## 4.5 PHYTOREMEDIATION OF Cr(VI) AND PHENOL BY WATER HYACINTH

### 4.5.1 Experimental program

The complete sequence of the experiments performed for phytoremediation of Cr(VI) and phenol species using water hyacinth plants in the batch studies from single and binary solution of Cr(VI) and phenol has been depicted in Fig. 3.8.1.

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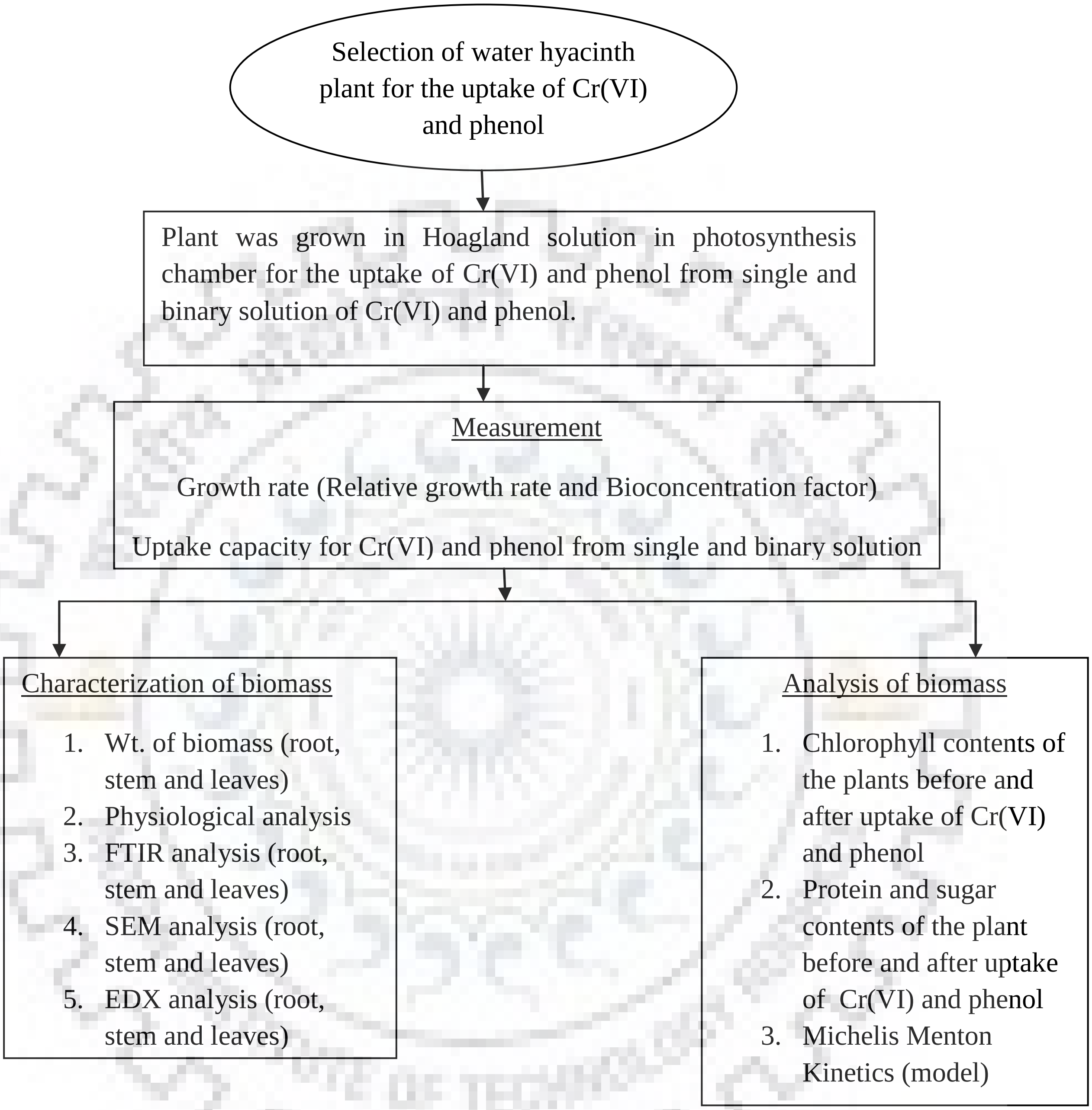

**Figure 3.8.1:** Schematic block diagram for phytoremediation of Cr(VI) and phenol using water hyacinth from single and binary solution of Cr(VI) and phenol

### 4.5.2 Plant growth in phytoremediation chamber experiment:

Samples of water hyacinth were collected from Solani River Roorkee, India from the stagnant water body and clean with distilled water to remove dirt and soluble substances. All the plants used for the experimentation were of the same size and 4-5 weeks old. After washing these plants were dried using tissue paper and weigh the initial weight of the plants. 3% Hoagland nutrient solution (g/l) (($K_2SO_4$ 7.66, $MgSO_4$ 12, $KH_2PO_4$ 1.7, KCl 0.4, $Ca(NO_3)_2$ 23.62, $H_3BO_3$ 0.12, $MnSO_4$ 0.06, $CuSO_4$ 0.10 and $NH_4$molybdate 0.05), Fe-EDTA 36.6 g/l and $ZnSO_4$ 287.54 g/l (Geng et al., 2005).) was used for the growth of water hyacinth in the phytoremediation chamber under controlled conditions (30 ± 1 ºC, 45 µmol $m^{-2}s^{-1}$ photon flux intensity, 60% relative humidity). Water hyacinth plants were grown in 2 L pots containing 1 L Hoagland nutrient solution kept in phytoremediation chamber. Single and binary component stock solution of Cr(VI) and phenol were prepared by adding an adequate quantity of Cr(VI) and phenol in distilled water (Quinones et al. 2009). The binary solution contained Cr(VI) and phenol in (1:2) ratio. Using a stock solution of Cr(VI) and phenol desired initial concentrations was prepared by diluting their respective stock solution. Water hyacinth was grown at different concentrations of 5-20 mg/L of Cr(VI) and 10-40 mg/L of phenol both in single and binary solution of Cr(VI) and phenol respectively. The plants were grown under phytoremediation chamber with a photoperiod of 12 h (light period) and 12 h of darkness cycles. The nutrient solution was refilled once every week and aerated continuously (Baldwin and Butcher, 2007). The PVC pots were arranged daily during the growth period of plants. After every 6 days, sampling test was carried out to measure the amount of Cr(VI) and phenol concentration in the solution, along with the growth rate of plant parts (like shoot length and root length).

The water level was decreased due to uptake and evaporation was maintained daily by adding distilled water to the mark.

### 4.5.3 Studies on phytoremediation of Cr(VI) and phenol using water hyacinth in artificial photosynthesis chamber:

In the present study experiments were also carried out for the simultaneous uptake of Cr(VI) and phenol by aquatic macrophyte water hyacinth in the artificial photosynthesis chamber. Single and binary synthetic simulated wastewater is used for the experimentation for the uptake by water hyacinth. The run Nos for the uptake of Cr(VI) and phenol using single and binary substrate solution is given in table 4.34. The experimental data is given in annexure A.42 and A.43 for single and binary substrate solution.

**Table 4.34: Run Nos. of experiments conducted for the phytoremediation study for the removal of Cr(VI) and phenol**

| Photosynthesis chamber | Table No. (s) | Run No. (s) |
|---|---|---|
| Single substrate solution | A.42 | 1877-1939 |
| Binary solution | A.43 | 1940-2003 |

**4.6: Concluding remarks:** This chapter deals with the methodology used for the experimentation for the simultaneous removal of Cr(VI) and phenol in single and binary synthetic simulated waste water using various methods such as adsorption, bio removal, simultaneous adsorption and bioaccumulation of Cr(VI), simultaneous adsorption and biodegradation of phenol, continuous removal of Cr(VI) and phenol in tea waste biomass packed bed column, simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol in continuous bio column and phytoremediation.

# *Chapter – VI*

## SUMMARY OF THE WORK, CONCLUSION AND SCOPE FOR THE FUTURE

### 6.1 Summary of the present work

On the basis of present investigation and thus results generated for the removal of Cr(VI) and phenol from single and binary waste water using various treatment methods such as, adsorption, biological treatment, simultaneous adsorption and bioaccumulation of Cr(VI), simultaneous adsorption and biodegradation of phenol in continuous reactor followed by phyto-remediation have been summarized as follows:

### 6.1.1 Batch adsorption study for the formulation of the design

The removal of Cr(VI) and phenol from single and binary simulated synthetic waste water was carried out in a batch reactor using various adsorbents such as GAC (Granular activated carbon), Tea waste (TW), Rice husk (RH), Bagasse (BG), Bagasse fly ash (BFA), Distillery sludge (DS), Neem leaves (NL), Fe treated tea waste (Fe TW) and Fe treated rice husk (Fe RH). These have been summarized below:

- The preferential order for removal of Cr(VI) from single component solution by pretreated adsorbents were found as GAC> Fe TW> TW> Fe RH> BG > BFA > RH> NL > DS.
- The preferential order for removal of phenol from single component solution by pretreated adsorbents were found as GAC> Fe RH> RH> Fe TW> TW > BFA > NL> BG> DS.
- Based on the single component adsorption study GAC, TW and RH were selected for the co-adsorption of Cr(VI) and phenol from binary solution.
- Amongst the pretreated adsorbents, GAC, Fe TW and TW shows the maximum co adsorption of Cr(VI) and phenol from binary solution.
- simultaneous removal of Cr(VI) and phenol for various adsorbents were 10.50 g/L with 99.99 % removal of Cr(VI) and phenol for GAC, 15 g/L with 99.19 % removal of Cr(VI) and 95.07 % removal of phenol for TW, 20 g/L with 95.34 % removal of Cr(VI) and 99.12 % removal of phenol for RH, 15 g/L with 99.99 % removal of Cr(VI) and phenol for Fe TW and 10 g/L with 99.52 % of Cr(VI) and phenol for Fe RH was obtained at optimum process parameters.

- The thermodynamic study show, feasible and spontaneous nature of the sorption of Cr(VI) and phenol species onto the surface of adsorbents. The negative value of ΔG° (kJ/mol) and positive value of ΔH° (kJ/mol) obtained from the experimental results confirmed the endothermic reaction with increased randomness at solid-liquid interface during Cr(VI) and phenol ions adsorption onto the surface of pretreated adsorbents.
- Various single and multicomponent adsorption isotherms and kinetic models were applied to the experimental data. It is observed that for adsorption of Cr(VI) from single component solution Freundlich and Temkin isotherm models were fitted well to the experimental data while Langmuir isotherm was also fitted well to the experimental data except GAC, NL and Fe RH. In case of adsorption of phenol onto the surface of various adsorbents GAC, TW and RH follows Freundlich while BG, Fe TW and Fe RH obeys Langmuir adsorption isotherm and for BFA and DS Temkin adsorption isotherm fitted well confirmed by higher $R^2$ value. For the simultaneous adsorption of Cr(VI) and phenol in binary solution extended Langmuir and extended Freundlich were fitted well for Cr(VI) and phenol respectively onto the surface of GAC. For TW, RH and Fe TW extended Freundlich model were fitted well for both Cr(VI) and phenol. For Fe RH extended Langmuir for phenol and modified Redlich Peterson model well depicts the experimental data confirmed by the lower MPSD values.
- Statistical optimization of process parameters for the simultaneous removal of Cr(VI) and phenol using Fe TW was also carried out to find the effect of various parameters onto the percentage removal of one component Cr(VI) to the another component phenol. It was found that the percentage removal of Cr(VI) was increased in the presence of phenol. It can be due to the formation of complex or increase in the carbon content.
- The kinetic modelling was carried out which shows that GAC, TW, DS, NL, Fe RH and Fe TW for the adsorption of Cr(VI) from single component solution follows both pseudo first order and pseudo-second order model best with higher linear regression coefficients ($R^2$) while RH and BG follows the pseudo second order model. For the adsorption of phenol from single component solution TW, BG and RH fitted well with both pseudo first order, pseudo second order, BG, BFA, DS and NL follows pseudo first order and Fe TW, and Fe RH follow the pseudo second order model. In case of binary solution for the simultaneous removal of Cr(VI) and phenol both Cr(VI) and phenol follows the pseudo second order which is confirmed by high $R^2$ values and lower MPSD values.

### 6.1.2 Biological removal by suspended culture

- The optimum condition for the growth of *Escherichia coli* NCIM No. 5041 and *Bacillus* sp. MTCC No. 3166 was found to be at pH 7 and temperature 37 ºC.
- The bacterium *Escherichia coli* was found to be capable of bio accumulating of Cr(VI) while *Bacillus* sp. can bio accumulate and degrade both Cr(VI) and phenol, respectively.
- The pure culture of *Escherichia coli* was acclimatized to the various concentrations of Cr(VI) in single substrate solution while *Bacillus* sp. was acclimatized to the various concentrations of Cr(VI) and phenol for both single and binary substrate solution.
- The bacterium *Escherichia coli* was acclimatized to the toxic concentrations of Cr(VI) up to 25 mg/L while *Bacillus* sp. was acclimatized to the toxic concentrations of both Cr(VI) and phenol up to 50 mg/L and 100 mg/L, respectively for both single and binary substrate solution.
- The consortium culture of *Escherichia coli* and *Bacillus* sp. was also used for the simultaneous bioaccumulation of Cr(VI) and biodegradation of phenol from binary substrate solution.
- The bioaccumulation of Cr(VI) and biodegradation of phenol was found to be maximum for consortium culture of *Escherichia coli* and *Bacillus* sp. than pure culture of *Bacillus* sp. The possible reason behind this fact was that the metabolites formed during the biodegradation of phenol was utilized by *Escherichia coli* for the reduction of Cr(VI).
- Various kinetic models such as Monod, Haldane and sum of kinetic models were applied for the simultaneous bioaccumulation of Cr(VI) and biodegradation of phenol and the interaction parameters were calculated as $I_{12}$ is 7.8125 for Cr(VI) and $I_{21}$ is 2.03422 for phenol.
- Interaction parameters for binary substrate solution was more for Cr(VI) therefore Cr(VI) inhibits the biodegradation of phenol while phenol helps in the bioaccumulation of Cr(VI). Endogenous decay coefficient and yield coefficient were estimated for single and binary substrate solution. Yield coefficient of phenol was more than Cr(VI) for single and binary substrate solution while the endogenous decay coefficient was more for Cr(VI). The yield coefficient of Cr(VI) for binary substrate solution was more but endogenous decay coefficient was less in comparison to single substrate solution which shows that phenol improves the bioaccumulation of Cr(VI) using *Bacillus* sp.

### 6.1.3 Batch SAB (Simultaneous adsorption and bioremediation) study

The simultaneous adsorption and bioaccumulation (SAB) process proved to be better Cr(VI) and phenol removal process. Following are the major conclusions:

- In case of single component solution of Cr(VI) and phenol alone, bacterium immobilized on pretreated GAC and tea waste (TW) biomass removed maximum 99.99 % Cr(VI) and phenol in the SAB process as compared to other adsorbents.
- Therefore TW biomass was selected for the simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol immobilized with consortium culture of *Escherichia coli* and *Bacillus* sp.
- Co removal of Cr(VI) and phenol using consortium culture of *Escherichia coli* and *Bacillus* sp. immobilized onto the surface of tea waste biomass was found to be 99.99 % at optimum conditions of temperature 37 ºC, pH 7, initial concentration of Cr(VI) 100 mg/L, initial concentration of phenol 50 mg/L and contact time of 24 h for Cr(VI) and 45 h for phenol.
- Various equilibrium adsorption isotherm and kinetic models were applied to the experimental data and their suitability for several biosorbents was studied. The experimental results investigated that for simultaneous adsorption and bioaccumulation of Cr(VI) from single component solution of Cr(VI) both temkin and freundlich isotherm was agreed well with experimental data but the freundlich isotherm described better the experimental data which is confirmed by the higher $R^2$ value. Similarly, for the simultaneous adsorption and biodegradation of phenol Freundlich isotherm was suited well which indicated chemisorption is the mechanism of adsorption. When simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol was performed onto the surface of various adsorbents using consortium culture of Escherichia coli and Bacillus sp. extended Langmuir fitted well to the experimental data which is confirmed by lower MPSD value.
- In the present investigation, for the single component solution of Cr(VI) all the biosorbents immobilized with *Escherichia coli* and *Bacillus* sp. except *Escherichia coli* supported GAC follow pseudo second order kinetics. For the simultaneous adsorption and biodegradation of phenol *Bacillus* sp. supported onto GAC follows pseudo second order while Bacillus sp. supported onto the TW and RH follows the pseudo first order

model. The pseudo second order model was fitted well to the simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol.

- FTIR, SEM and EDX were carried out for the characterization of biosorbent to confirm simultaneous adsorption and bioaccumulation of Cr(VI) and simultaneous adsorption and biodegradation of phenol.

### 6.1.4 Continuous packed bed column study

- In this study simultaneous co-adsorption of Cr(VI) and phenol was carried out in tea waste biomass packed bed column reactor.
- The simultaneous 99.50 % removal of Cr(VI) and 97.54 % removal of phenol was obtained. The maximum adsorption capacity (mg/g) was also calculated for both Cr(VI) and phenol as 57.33 mg/g and 27.96 mg/g, respectively.
- The effect of process parameters such as flow rate (mL/min) and bed depth (cm) was investigated onto the simultaneous percentage removal of Cr(VI) and phenol. It was found that the percentage removal was increased on decreasing the flow rate (mL/min) and increasing the bed depth (cm).
- Various Kinetic models were applied to the experimental breakthrough data for both Cr(VI) and phenol. Yoon Nelson and Thomas model appeared to be the best model to predict the co-adsorption of Cr(VI) and phenol in tea waste biomass packed bed column which shows that the rate of adsorption is proportional to tea waste biomass residual capacity and the initial concentration of Cr(VI) and phenol. The desorption of Cr(VI) and phenol was also carried out for the regeneration of adsorbent bed in packed bed column using NaOH as desorbent.

### 6.1.5 Continuous removal of Cr(VI) and phenol in packed bed column immobilized with consortium culture of *Escherichia coli* and *Bacillus* sp.

- Simultaneous removal of Cr(VI) and phenol was also achieved in continuous bio column reactor packed with consortium culture of *Escherichia coli* and Bacillus sp. immobilized onto the surface of tea waste biomass.
- For simultaneous removal of Cr(VI) and phenol from binary synthetic waste water an EBCT of 4 h was found to be sufficient to bring down the effluent concentration below the prescribed regulatory level of Cr(VI) and phenol.

- Effect of bed height onto the simultaneous removal of Cr(VI) and phenol was investigated which shows that percentage removal of both Cr(VI) and phenol was increased with the increase in bed height. But after 4 days of operation percentage removal was become constant at all bed height.
- DO (Dissolved Oxygen) was found to be decreased with time, while pH was decreased initially and then became constant.
- A mass transfer study was carried out to find the first order degradation rate constant for phenol and bioaccumulation rate constant for Cr(VI) which in good agreement with experimental data.

### 6.1.6 Phytoremediation study

- Simultaneous phytoremediation of Cr(VI) and phenol was carried out in artificial photosynthesis chamber using aquatic macrophyte water hyacinth. The nutrient Hoagland solution was used for the growth of plant. The plant was exposed to the toxic concentrations of Cr(VI) and phenol in (2:1) ratio based upon the industrial waste water composition. The characteristics of plant biomass were studied using FTIR, SEM, EDX, chlorophyll, sugar and protein level of plant in presence and absence of Cr(VI) and phenol species. Following is the summary of work:
- In this study water hyacinth was used for the removal of Cr(VI) and phenol from single and binary solution of these, which proved to be a potential macrophyte for the removal of Cr(VI) and phenol. It was observed that uptake of Cr(VI) was more in the presence of phenol. This is due to the formation of complex by the combination of Cr(VI) and phenol which can be easily consumed by the plant. Phenol can also be utilized as carbon or carbohydrate energy source by the plant which improved the kinetics of Cr(VI) uptake.
- The maximum uptake capacity of Cr(VI) for a single component solution was found to be 2.36 (mg/g) which was less than a binary solution of Cr(VI) and phenol 2.46 (mg/g). The percentage removal of Cr(VI) and phenol increases with time and decreases with the increase in the initial concentration of Cr(VI) and phenol for both individual and combined solutions of Cr(VI) and phenol. It could be due to the toxic effect on the plant due to which dissolved oxygen, sugar and chlorophyll content of the plant were reduced. At the highest concentration of Cr (VI) and phenol the plants were at more stressed condition and the energy level of the plant was also reduced.

## 6.2 Conclusion

Major conclusion of the present study is as follows:

- In this study tea waste biomass is proved to be a potential biosorbent for the simultaneous removal of Cr(VI) and phenol from synthetic simulated and real industrial waste water.
- Surface modifaction of tea waste biomass with ferrous sulphate hepta hydrate ($FeSO_4.7H_2O$) enhance the percentage removal of both Cr(VI) and phenol as negatively charged chromate, dichromate and phenolate ions are attract of towards the positively charged adsorbent surface.
- Two bacterial strain namely *Escherichia coli* and *Bacillus* sp. are capable of bioaccumulating Cr(VI) and both bioaccumulation of Cr(VI) and biodegradation of phenol, respectively.
- The tea waste biomass immobilized with Escherichia coli and Bacillus sp. was used for the simultaneous adsorption and bioaccumulation of Cr(VI) and simultaneous adsorption and bioaccumulation Cr(VI) with biodegradation of phenol, respectively. Therefore the consortium culture of Escherichia coli and Bacillus sp immobilized on tea waste biomass was also used for the simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol.
- The continuous packed bed reactor is used for the simultaneous removal of Cr(VI) and phenol from simulated synthetic and real industrial waste water upto the 2000 mg/L of Cr(VI) and 1000 mg/L of phenol.
- In this study water hyacinth is proved to be an optional potential macrophyte for the removal of Cr(VI) and phenol to meet the limit of regulatory agencies from the discharge of industrial waste water.

## 6.3 Scope for the future work:

From the present investigation it is our believe that Cr(VI) and phenol can be removed efficiently using SBB reactor. On the basis of present investigations, the following recommendations have been made for the scope of future studies.

1. Investigation should be carried out with varieties of real industrial wastewater.

2. More surface modifications of biosorbents for the simultaneous removal of Cr(VI) and phenol can be carried out.
3. Some another type of reactors such as fluidized bed reactor and trickling bed reactor can be used for the simultaneous removal of Cr(VI) and phenol..
4. Phyto-remediation of Cr(VI) and phenol should be explored with different varieties of plants.
5. More types of treatment techniques such as electrocoagulation, capacitive deionization, membrane separation and Nano filtration can be applied for the simultaneous removal of Cr(VI) and phenol.

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1. Ankur Gupta, Chandrajit Balomajumder, Simultaneous removal of Cr(VI) and phenol from synthetic binary solution using consortium culture of Bacillus sp. and E. coli immobilized on tea waste biomass in packed bed reactor, Korean journal of chemical engineering, 33(2) (2016) 559-566 [Springer]

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## Manuscript: Under review

1. Michelis menton Kinetics for the simultaneous phytoremediation of Cr(VI) and phenol by determining the chlorophyll content using water hyacinth, Journal of water process engineering, 2016.
2. Statistical optimization of process parameters for the simultaneous adsorption of Cr(VI) and phenol onto Fe treated tea waste biomass, Journal of applied water science, 2016.
3. Ankur Gupta, Chandrajit Balomajumder, Simultaneous phytoremediation of Cr(VI) and phenol using aquatic macrophyte water hyacinth: Effect of pH and concentrations of Cr(VI) and phenol, Indian journal of plant physiology, 2016.
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1. Ankur Gupta, Chandrajit Balomajuder, Studies on treatment of Cr(VI) and phenol using various process using tea waste biomass: Comparison between Biotreatment, Adsorption, and simultaneous adsorption and Biotreatment.
2. Ankur Gupta, Chandrajit Balomajumder, Mono and binary adsorption of Cr(VI) and phenol from single and binary simulated solution using various adsorbents.
3. Ankur Gupta, Chandrajit Balomajumder, Treatment of Cr(VI) from real electroplating industrial waste water (Bharat heavy electroplating industry).

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## International and National conferences Attended:

1. International Conference on Advances in Chemical Engineering (ACE - 2013): Feb. 22 - 24, 2013
2. Short term course at Institutes of Engineers, Indian Institute of technology Roorkee on green revolution technologies 2011.

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Table A.1 Input and output parameters for the adsorption of Cr(VI) onto the surface of GAC using synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 1 | 1 | **2** | 30 | 4 | 100 | 24 | 99.99 |
| 1 | 2 | **3** | 30 | 4 | 100 | 24 | 97.98 |
| 1 | 3 | **4** | 30 | 4 | 100 | 24 | 87.06 |
| 1 | 4 | **5** | 30 | 4 | 100 | 24 | 79.92 |
| 1 | 5 | **6** | 30 | 4 | 100 | 24 | 68.54 |
| 1 | 6 | **7** | 30 | 4 | 100 | 24 | 56.08 |
| 1 | 7 | **8** | 30 | 4 | 100 | 24 | 49.78 |
| 1 | 8 | **9** | 30 | 4 | 100 | 24 | 35.34 |
| 1 | 9 | **10** | 30 | 4 | 100 | 24 | 23.67 |
| 1 | 10 | 2 | **10** | 4 | 100 | 24 | 91.25 |
| 1 | 11 | 2 | **20** | 4 | 100 | 24 | 93.54 |
| 1 | 12 | 2 | **30** | 4 | 100 | 24 | 96.11 |
| 1 | 13 | 2 | **40** | 4 | 100 | 24 | 99.04 |
| 1 | 14 | 2 | **50** | 4 | 100 | 24 | 99.65 |
| 1 | 15 | 2 | 30 | **2** | 100 | 24 | 80.23 |
| 1 | 16 | 2 | 30 | **2.4** | 100 | 24 | 85.89 |
| 1 | 17 | 2 | 30 | **2.8** | 100 | 24 | 90.56 |
| 1 | 18 | 2 | 30 | **3.2** | 100 | 24 | 93.10 |
| 1 | 19 | 2 | 30 | **3.6** | 100 | 24 | 94.95 |
| 1 | 20 | 2 | 30 | **4.0** | 100 | 24 | 98.99 |
| 1 | 21 | 2 | 30 | **4.4** | 100 | 24 | 99.99 |
| 1 | 22 | 2 | 30 | **4.8** | 100 | 24 | 99.99 |
| 1 | 23 | 2 | 30 | **5.2** | 100 | 24 | 99.99 |
| 1 | 24 | 2 | 30 | 4 | **100** | 24 | 99.99 |
| 1 | 25 | 2 | 30 | 4 | **150** | 24 | 98.80 |
| 1 | 26 | 2 | 30 | 4 | **200** | 24 | 97.84 |
| 1 | 27 | 2 | 30 | 4 | **250** | 24 | 95.30 |
| 1 | 28 | 2 | 30 | 4 | **300** | 24 | 91.72 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 29 | 2 | 30 | 4 | **350** | 24 | 87.91 |
| 1 | 30 | 2 | 30 | 4 | **400** | 24 | 85.78 |
| 1 | 31 | 2 | 30 | 4 | 100 | **0.25** | 98.37 |
| 1 | 32 | 2 | 30 | 4 | 100 | **0.5** | 98.61 |
| 1 | 33 | 2 | 30 | 4 | 100 | **0.75** | 98.82 |
| 1 | 34 | 2 | 30 | 4 | 100 | **1.0** | 99.38 |
| 1 | 35 | 2 | 30 | 4 | 100 | **1.25** | 99.56 |
| 1 | 36 | 2 | 30 | 4 | 100 | **1.5** | 99.98 |
| 1 | 37 | 2 | 30 | 4 | 100 | **1.75** | 99.99 |
| 1 | 38 | 2 | 30 | 4 | 100 | **2.0** | 99.99 |
| 1 | 39 | 2 | 30 | 4 | 100 | **2.25** | 99.99 |
| 1 | 40 | 2 | 30 | 4 | 100 | **2.50** | 99.99 |
| 1 | 41 | 2 | 30 | 4 | 100 | **2.75** | 99.99 |
| 1 | 42 | 2 | 30 | 4 | 100 | **3.0** | 99.99 |
| Run Nos. 10-14, 24-32 and 33-44 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | |

Table A.2 Input and output parameters for the adsorption of Cr(VI) onto the surface of Tea waste (TW) using synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 2 | 43 | **2** | 30 | 8 | 100 | 24 | 99.95 |
| 2 | 44 | **3** | 30 | 8 | 100 | 24 | 95.00 |
| 2 | 45 | **4** | 30 | 8 | 100 | 24 | 90.06 |
| 2 | 46 | **5** | 30 | 8 | 100 | 24 | 75.00 |
| 2 | 47 | **6** | 30 | 8 | 100 | 24 | 70.00 |
| 2 | 48 | **7** | 30 | 8 | 100 | 24 | 60.00 |
| 2 | 49 | **8** | 30 | 8 | 100 | 24 | 35.78 |
| 2 | 50 | **9** | 30 | 8 | 100 | 24 | 25.34 |
| 2 | 51 | **10** | 30 | 8 | 100 | 24 | 23.67 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 2 | 52 | 2 | **10** | 8 | 100 | 24 | 91.65 |
| 2 | 53 | 2 | **20** | 8 | 100 | 24 | 99.14 |
| 2 | 54 | 2 | **30** | 8 | 100 | 24 | 99.44 |
| 2 | 55 | 2 | **40** | 8 | 100 | 24 | 99.64 |
| 2 | 56 | 2 | **50** | 8 | 100 | 24 | 99.65 |
| 2 | 57 | 2 | 30 | **2** | 100 | 24 | 85.40 |
| 2 | 58 | 2 | 30 | **4** | 100 | 24 | 94.76 |
| 2 | 59 | 2 | 30 | **6** | 100 | 24 | 98.67 |
| 2 | 60 | 2 | 30 | **8** | 100 | 24 | 99.90 |
| 2 | 61 | 2 | 30 | **10** | 100 | 24 | 99.95 |
| 2 | 62 | 2 | 30 | **12** | 100 | 24 | 98.99 |
| 2 | 63 | 2 | 30 | **14** | 100 | 24 | 99.99 |
| 2 | 64 | 2 | 30 | **16** | 100 | 24 | 99.99 |
| 2 | 65 | 2 | 30 | 8 | **100** | 24 | 99.97 |
| 2 | 66 | 2 | 30 | 8 | **150** | 24 | 98.83 |
| 2 | 67 | 2 | 30 | 8 | **200** | 24 | 97.87 |
| 2 | 68 | 2 | 30 | 8 | **250** | 24 | 96.19 |
| 2 | 69 | 2 | 30 | 8 | **300** | 24 | 94.48 |
| 2 | 70 | 2 | 30 | 8 | **350** | 24 | 93.67 |
| 2 | 71 | 2 | 30 | 8 | **400** | 24 | 92.65 |
| 2 | 72 | 2 | 30 | 8 | 100 | **0.25** | 76.47 |
| 2 | 73 | 2 | 30 | 8 | 100 | **0.5** | 84.93 |
| 2 | 74 | 2 | 30 | 8 | 100 | **0.75** | 91.76 |
| 2 | 75 | 2 | 30 | 8 | 100 | **1.0** | 95.66 |
| 2 | 76 | 2 | 30 | 8 | 100 | **1.25** | 98.56 |
| 2 | 77 | 2 | 30 | 8 | 100 | **1.5** | 99.98 |
| 2 | 78 | 2 | 30 | 8 | 100 | **1.75** | 99.99 |
| 2 | 79 | 2 | 30 | 8 | 100 | **2.0** | 99.99 |
| Run Nos. 52-56, 65-71 and 72-79 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |  |  |

Table A.3 Input and output parameters for the adsorption of Cr(VI) onto the surface of Rice husk (RH) using synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 3 | 80 | **2** | 30 | 40 | 100 | 24 | 94.00 |
| 3 | 81 | **3** | 30 | 40 | 100 | 24 | 90.06 |
| 3 | 82 | **4** | 30 | 40 | 100 | 24 | 60.00 |
| 3 | 83 | **5** | 30 | 40 | 100 | 24 | 50.24 |
| 3 | 84 | **6** | 30 | 40 | 100 | 24 | 31.00 |
| 3 | 85 | **7** | 30 | 40 | 100 | 24 | 23.23 |
| 3 | 86 | **8** | 30 | 40 | 100 | 24 | 19.34 |
| 3 | 87 | **9** | 30 | 40 | 100 | 24 | 14.67 |
| 3 | 88 | **10** | 30 | 40 | 100 | 24 | 10.98 |
| 3 | 89 | 2 | **10** | 40 | 100 | 24 | 81.55 |
| 3 | 90 | 2 | **20** | 40 | 100 | 24 | 85.14 |
| 3 | 91 | 2 | **30** | 40 | 100 | 24 | 95.11 |
| 3 | 92 | 2 | **40** | 40 | 100 | 24 | 97.64 |
| 3 | 93 | 2 | **50** | 40 | 100 | 24 | 99.75 |
| 3 | 94 | 2 | 30 | **5** | 100 | 24 | 33.42 |
| 3 | 95 | 2 | 30 | **10** | 100 | 24 | 45.20 |
| 3 | 96 | 2 | 30 | **15** | 100 | 24 | 54.74 |
| 3 | 97 | 2 | 30 | **20** | 100 | 24 | 61.20 |
| 3 | 98 | 2 | 30 | **25** | 100 | 24 | 73.04 |
| 3 | 99 | 2 | 30 | **30** | 100 | 24 | 87.26 |
| 3 | 100 | 2 | 30 | **35** | 100 | 24 | 91.99 |
| 3 | 101 | 2 | 30 | **40** | 100 | 24 | 94.69 |
| 3 | 102 | 2 | 30 | **45** | 100 | 24 | 94.99 |
| 3 | 103 | 2 | 30 | **50** | 100 | 24 | 94.99 |
| 3 | 104 | 2 | 30 | 40 | **100** | 24 | 94.17 |
| 3 | 105 | 2 | 30 | 40 | **150** | 24 | 82.90 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 3 | 106 | 2 | 30 | 40 | **200** | 24 | 68.41 |
| 3 | 107 | 2 | 30 | 40 | **250** | 24 | 57.42 |
| 3 | 108 | 2 | 30 | 40 | **300** | 24 | 48.87 |
| 3 | 109 | 2 | 30 | 40 | **350** | 24 | 42.67 |
| 3 | 110 | 2 | 30 | 40 | **400** | 24 | 38.65 |
| 3 | 111 | 2 | 30 | 40 | 100 | **1** | 35.71 |
| 3 | 112 | 2 | 30 | 40 | 100 | **2** | 43.57 |
| 3 | 113 | 2 | 30 | 40 | 100 | **3** | 51.74 |
| 3 | 114 | 2 | 30 | 40 | 100 | **4** | 59.02 |
| 3 | 115 | 2 | 30 | 40 | 100 | **5** | 67.80 |
| 3 | 116 | 2 | 30 | 40 | 100 | **6** | 73.79 |
| 3 | 117 | 2 | 30 | 40 | 100 | **7** | 79.80 |
| 3 | 118 | 2 | 30 | 40 | 100 | **8** | 87.87 |
| 3 | 119 | 2 | 30 | 40 | 100 | **9** | 90.56 |
| 3 | 120 | 2 | 30 | 40 | 100 | **10** | 94.94 |
| 3 | 121 | 2 | 30 | 40 | 100 | **11** | 94.96 |
| 3 | 122 | 2 | 30 | 40 | 100 | **12** | 94.97 |
| Run Nos. 89-93, 94-103 and 111-122 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |  |  |

Table A.4 Input and output parameters for the adsorption of Cr(VI) onto the surface of Bagasse (BG) using synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters |  |  |  |  | Output parameters |
|---|---|---|---|---|---|---|---|
|  |  | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 4 | 123 | **2** | 30 | 40 | 100 | 24 | 99.40 |
| 4 | 124 | **3** | 30 | 40 | 100 | 24 | 98.01 |
| 4 | 125 | **4** | 30 | 40 | 100 | 24 | 97.06 |
| 4 | 126 | **5** | 30 | 40 | 100 | 24 | 88.00 |
| 4 | 127 | **6** | 30 | 40 | 100 | 24 | 72.24 |
| 4 | 128 | **7** | 30 | 40 | 100 | 24 | 60.00 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 4 | 129 | **8** | 30 | 40 | 100 | 24 | 53.23 |
| 4 | 130 | **9** | 30 | 40 | 100 | 24 | 32.34 |
| 4 | 131 | **10** | 30 | 40 | 100 | 24 | 28.67 |
| 4 | 132 | 2 | **10** | 40 | 100 | 24 | 87.35 |
| 4 | 133 | 2 | **20** | 40 | 100 | 24 | 91.24 |
| 4 | 134 | 2 | **30** | 40 | 100 | 24 | 95.11 |
| 4 | 135 | 2 | **40** | 40 | 100 | 24 | 99.14 |
| 4 | 136 | 2 | **50** | 40 | 100 | 24 | 99.75 |
| 4 | 137 | 2 | 30 | **5** | 100 | 24 | 36.42 |
| 4 | 138 | 2 | 30 | **10** | 100 | 24 | 44.20 |
| 4 | 139 | 2 | 30 | **15** | 100 | 24 | 60.74 |
| 4 | 140 | 2 | 30 | **20** | 100 | 24 | 77.20 |
| 4 | 141 | 2 | 30 | **25** | 100 | 24 | 84.04 |
| 4 | 142 | 2 | 30 | **30** | 100 | 24 | 90.26 |
| 4 | 143 | 2 | 30 | **35** | 100 | 24 | 96.99 |
| 4 | 144 | 2 | 30 | **40** | 100 | 24 | 99.69 |
| 4 | 145 | 2 | 30 | **45** | 100 | 24 | 99.99 |
| 4 | 146 | 2 | 30 | **50** | 100 | 24 | 99.99 |
| 4 | 147 | 2 | 30 | 40 | **100** | 24 | 99.92 |
| 4 | 148 | 2 | 30 | 40 | **150** | 24 | 87.35 |
| 4 | 149 | 2 | 30 | 40 | **200** | 24 | 78.77 |
| 4 | 150 | 2 | 30 | 40 | **250** | 24 | 72.42 |
| 4 | 151 | 2 | 30 | 40 | **300** | 24 | 64.87 |
| 4 | 152 | 2 | 30 | 40 | **350** | 24 | 52.67 |
| 4 | 153 | 2 | 30 | 40 | **400** | 24 | 48.65 |
| 4 | 154 | 2 | 30 | 40 | 100 | **0.5** | 14.01 |
| 4 | 155 | 2 | 30 | 40 | 100 | **1** | 25.57 |
| 4 | 156 | 2 | 30 | 40 | 100 | **1.5** | 36.74 |
| 4 | 157 | 2 | 30 | 40 | 100 | **2** | 43.02 |
| 4 | 158 | 2 | 30 | 40 | 100 | **2.5** | 50.80 |
| 4 | 159 | 2 | 30 | 40 | 100 | **3** | 58.79 |
| 4 | 160 | 2 | 30 | 40 | 100 | **3.5** | 63.78 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 4 | 161 | 2 | 30 | 40 | 100 | **4** | 72.45 |
| 4 | 162 | 2 | 30 | 40 | 100 | **4.5** | 80.67 |
| 4 | 163 | 2 | 30 | 40 | 100 | **5** | 87.89 |
| 4 | 164 | 2 | 30 | 40 | 100 | **5.5** | 94.96 |
| 4 | 165 | 2 | 30 | 40 | 100 | **6.0** | 99.97 |
| 4 | 166 | 2 | 30 | 40 | 100 | **6.5** | 99.99 |
| Run Nos. 132-136, 147-153 and 154-166 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | |

Table A.5 Input and output parameters for the adsorption of Cr(VI) onto the surface of Bagasse fly ash (BFA) using synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 5 | 167 | **2** | 30 | 45 | 100 | 24 | 91.34 |
| 5 | 168 | **3** | 30 | 45 | 100 | 24 | 85.45 |
| 5 | 169 | **4** | 30 | 45 | 100 | 24 | 76.49 |
| 5 | 170 | **5** | 30 | 45 | 100 | 24 | 60.02 |
| 5 | 171 | **6** | 30 | 45 | 100 | 24 | 51.24 |
| 5 | 172 | **7** | 30 | 45 | 100 | 24 | 40.05 |
| 5 | 173 | **8** | 30 | 45 | 100 | 24 | 33.23 |
| 5 | 174 | **9** | 30 | 45 | 100 | 24 | 23.74 |
| 5 | 175 | **10** | 30 | 45 | 100 | 24 | 18.67 |
| 5 | 176 | 2 | **10** | 45 | 100 | 24 | 79.05 |
| 5 | 177 | 2 | **20** | 45 | 100 | 24 | 83.54 |
| 5 | 178 | 2 | **30** | 45 | 100 | 24 | 87.11 |
| 5 | 179 | 2 | **40** | 45 | 100 | 24 | 89.14 |
| 5 | 180 | 2 | **50** | 45 | 100 | 24 | 90.65 |
| 5 | 181 | 2 | 30 | **5** | 100 | 24 | 10.12 |
| 5 | 182 | 2 | 30 | **10** | 100 | 24 | 23.64 |
| 5 | 183 | 2 | 30 | **15** | 100 | 24 | 35.14 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 5 | 184 | 2 | 30 | **20** | 100 | 24 | 43.04 |
| 5 | 185 | 2 | 30 | **25** | 100 | 24 | 52.89 |
| 5 | 186 | 2 | 30 | **30** | 100 | 24 | 65.12 |
| 5 | 187 | 2 | 30 | **35** | 100 | 24 | 86.08 |
| 5 | 188 | 2 | 30 | **40** | 100 | 24 | 88.12 |
| 5 | 189 | 2 | 30 | **45** | 100 | 24 | 91.79 |
| 5 | 190 | 2 | 30 | **50** | 100 | 24 | 91.99 |
| 5 | 191 | 2 | 30 | 45 | **100** | 24 | 91.82 |
| 5 | 192 | 2 | 30 | 45 | **150** | 24 | 77.35 |
| 5 | 193 | 2 | 30 | 45 | **200** | 24 | 65.70 |
| 5 | 194 | 2 | 30 | 45 | **250** | 24 | 60.80 |
| 5 | 195 | 2 | 30 | 45 | **300** | 24 | 55.87 |
| 5 | 196 | 2 | 30 | 45 | **350** | 24 | 48.67 |
| 5 | 197 | 2 | 30 | 45 | **400** | 24 | 42.65 |
| 5 | 198 | 2 | 30 | 45 | 100 | **2** | 19.01 |
| 5 | 199 | 2 | 30 | 45 | 100 | **4** | 24.57 |
| 5 | 200 | 2 | 30 | 45 | 100 | **6** | 33.74 |
| 5 | 201 | 2 | 30 | 45 | 100 | **8** | 43.02 |
| 5 | 202 | 2 | 30 | 45 | 100 | **10** | 53.80 |
| 5 | 203 | 2 | 30 | 45 | 100 | **12** | 62.59 |
| 5 | 204 | 2 | 30 | 45 | 100 | **14** | 70.58 |
| 5 | 205 | 2 | 30 | 45 | 100 | **16** | 82.05 |
| 5 | 206 | 2 | 30 | 45 | 100 | **18** | 87.67 |
| 5 | 207 | 2 | 30 | 45 | 100 | **20** | 91.89 |
| 5 | 208 | 2 | 30 | 45 | 100 | **22** | 91.96 |
| Run Nos. 176-180, 191-197 and 198-208 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | |

Table A.6 Input and output parameters for the adsorption of Cr(VI) onto the surface of Distillery sludge (DS) using synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 6 | 209 | **2** | 30 | 26 | 100 | 24 | 81.75 |
| 6 | 210 | **3** | 30 | 26 | 100 | 24 | 75.16 |
| 6 | 211 | **4** | 30 | 26 | 100 | 24 | 69.25 |
| 6 | 212 | **5** | 30 | 26 | 100 | 24 | 53.23 |
| 6 | 213 | **6** | 30 | 26 | 100 | 24 | 47.34 |
| 6 | 214 | **7** | 30 | 26 | 100 | 24 | 40.89 |
| 6 | 215 | **8** | 30 | 26 | 100 | 24 | 33.45 |
| 6 | 216 | **9** | 30 | 26 | 100 | 24 | 27.65 |
| 6 | 217 | **10** | 30 | 26 | 100 | 24 | 23.67 |
| 6 | 218 | 2 | **10** | 26 | 100 | 24 | 54.35 |
| 6 | 219 | 2 | **20** | 26 | 100 | 24 | 59.84 |
| 6 | 220 | 2 | **30** | 26 | 100 | 24 | 73.12 |
| 6 | 221 | 2 | **40** | 26 | 100 | 24 | 76.34 |
| 6 | 222 | 2 | **50** | 26 | 100 | 24 | 79.95 |
| 6 | 223 | 2 | 30 | **10** | 100 | 24 | 11.06 |
| 6 | 224 | 2 | 30 | **12** | 100 | 24 | 20.18 |
| 6 | 225 | 2 | 30 | **14** | 100 | 24 | 34.12 |
| 6 | 226 | 2 | 30 | **16** | 100 | 24 | 47.09 |
| 6 | 227 | 2 | 30 | **18** | 100 | 24 | 52.89 |
| 6 | 228 | 2 | 30 | **20** | 100 | 24 | 60.08 |
| 6 | 229 | 2 | 30 | **22** | 100 | 24 | 65.12 |
| 6 | 230 | 2 | 30 | **24** | 100 | 24 | 78.02 |
| 6 | 231 | 2 | 30 | **26** | 100 | 24 | 81.79 |
| 6 | 232 | 2 | 30 | **28** | 100 | 24 | 81.92 |
| 6 | 233 | 2 | 30 | **30** | 100 | 24 | 81.92 |
| 6 | 234 | 2 | 30 | 26 | **100** | 24 | 81.95 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 6 | 235 | 2 | 30 | 26 | **150** | 24 | 74.26 |
| 6 | 236 | 2 | 30 | 26 | **200** | 24 | 67.50 |
| 6 | 237 | 2 | 30 | 26 | **250** | 24 | 64.00 |
| 6 | 238 | 2 | 30 | 26 | **300** | 24 | 58.87 |
| 6 | 239 | 2 | 30 | 26 | **350** | 24 | 46.77 |
| 6 | 240 | 2 | 30 | 26 | **400** | 24 | 40.45 |
| 6 | 241 | 2 | 30 | 26 | 100 | **1** | 40.35 |
| 6 | 242 | 2 | 30 | 26 | 100 | **2** | 47.33 |
| 6 | 243 | 2 | 30 | 26 | 100 | **3** | 59.01 |
| 6 | 244 | 2 | 30 | 26 | 100 | **4** | 61.11 |
| 6 | 245 | 2 | 30 | 26 | 100 | **5** | 69.46 |
| 6 | 246 | 2 | 30 | 26 | 100 | **6** | 73.58 |
| 6 | 247 | 2 | 30 | 26 | 100 | **7** | 75.12 |
| 6 | 248 | 2 | 30 | 26 | 100 | **8** | 78.02 |
| 6 | 249 | 2 | 30 | 26 | 100 | **9** | 80.67 |
| 6 | 250 | 2 | 30 | 26 | 100 | **10** | 81.89 |
| 6 | 251 | 2 | 30 | 26 | 100 | **11** | 81.96 |
| 6 | 252 | 2 | 30 | 26 | 100 | **12** | 81.99 |
| Run Nos. 218-222, 223-233 and 241-252 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | |

Table A.7 Input and output parameters for the adsorption of Cr(VI) onto the surface of Neem leaves (NL) using synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 7 | 253 | **2** | 30 | 20 | 100 | 24 | 99.96 |
| 7 | 254 | **3** | 30 | 20 | 100 | 24 | 90.56 |
| 7 | 255 | **4** | 30 | 20 | 100 | 24 | 69.96 |
| 7 | 256 | **5** | 30 | 20 | 100 | 24 | 55.95 |
| 7 | 257 | **6** | 30 | 20 | 100 | 24 | 49.50 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 7 | 258 | **7** | 30 | 20 | 100 | 24 | 38.75 |
| 7 | 259 | **8** | 30 | 20 | 100 | 24 | 31.55 |
| 7 | 260 | **9** | 30 | 20 | 100 | 24 | 25.57 |
| 7 | 261 | **10** | 30 | 20 | 100 | 24 | 23.12 |
| 7 | 262 | 2 | **10** | 20 | 100 | 24 | 93.35 |
| 7 | 263 | 2 | **20** | 20 | 100 | 24 | 97.24 |
| 7 | 264 | 2 | **30** | 20 | 100 | 24 | 99.32 |
| 7 | 265 | 2 | **40** | 20 | 100 | 24 | 99.64 |
| 7 | 266 | 2 | **50** | 20 | 100 | 24 | 99.95 |
| 7 | 267 | 2 | 30 | **5** | 100 | 24 | 89.55 |
| 7 | 268 | 2 | 30 | **10** | 100 | 24 | 96.75 |
| 7 | 269 | 2 | 30 | **15** | 100 | 24 | 97.50 |
| 7 | 270 | 2 | 30 | **20** | 100 | 24 | 99.39 |
| 7 | 271 | 2 | 30 | **25** | 100 | 24 | 99.89 |
| 7 | 272 | 2 | 30 | **30** | 100 | 24 | 99.98 |
| 7 | 273 | 2 | 30 | **35** | 100 | 24 | 99.99 |
| 7 | 274 | 2 | 30 | **40** | 100 | 24 | 99.99 |
| 7 | 275 | 2 | 30 | 26 | **100** | 24 | 99.96 |
| 7 | 276 | 2 | 30 | 26 | **150** | 24 | 92.38 |
| 7 | 277 | 2 | 30 | 26 | **200** | 24 | 87.86 |
| 7 | 278 | 2 | 30 | 26 | **250** | 24 | 79.00 |
| 7 | 279 | 2 | 30 | 26 | **300** | 24 | 71.87 |
| 7 | 280 | 2 | 30 | 26 | **350** | 24 | 66.77 |
| 7 | 281 | 2 | 30 | 26 | **400** | 24 | 60.45 |
| 7 | 282 | 2 | 30 | 26 | 100 | **2** | 34.95 |
| 7 | 283 | 2 | 30 | 26 | 100 | **4** | 41.33 |
| 7 | 284 | 2 | 30 | 26 | 100 | **6** | 48.31 |
| 7 | 285 | 2 | 30 | 26 | 100 | **8** | 57.11 |
| 7 | 286 | 2 | 30 | 26 | 100 | **10** | 62.96 |
| 7 | 287 | 2 | 30 | 26 | 100 | **12** | 69.58 |
| 7 | 288 | 2 | 30 | 26 | 100 | **14** | 77.12 |
| 7 | 289 | 2 | 30 | 26 | 100 | **16** | 84.02 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 7 | 290 | 2 | 30 | 26 | 100 | **18** | 91.67 |
| 7 | 291 | 2 | 30 | 26 | 100 | **20** | 95.89 |
| 7 | 292 | 2 | 30 | 26 | 100 | **22** | 99.96 |
| 7 | 293 | 2 | 30 | 26 | 100 | **24** | 99.99 |
| Run Nos. 262-266, 275-281 and 282-293 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | |

Table A.8 Input and output parameters for the adsorption of Cr(VI) onto the surface of Fe treated tea waste (Fe TW) using synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 8 | 294 | **2** | 30 | 6 | 100 | 24 | 99.99 |
| 8 | 295 | **3** | 30 | 6 | 100 | 24 | 98.96 |
| 8 | 296 | **4** | 30 | 6 | 100 | 24 | 97.96 |
| 8 | 297 | **5** | 30 | 6 | 100 | 24 | 95.95 |
| 8 | 298 | **6** | 30 | 6 | 100 | 24 | 90.80 |
| 8 | 299 | **7** | 30 | 6 | 100 | 24 | 80.55 |
| 8 | 300 | **8** | 30 | 6 | 100 | 24 | 74.55 |
| 8 | 301 | **9** | 30 | 6 | 100 | 24 | 70.97 |
| 8 | 302 | **10** | 30 | 6 | 100 | 24 | 65.72 |
| 8 | 303 | 2 | **10** | 6 | 100 | 24 | 92.67 |
| 8 | 304 | 2 | **20** | 6 | 100 | 24 | 95.56 |
| 8 | 305 | 2 | **30** | 6 | 100 | 24 | 99.33 |
| 8 | 306 | 2 | **40** | 6 | 100 | 24 | 99.64 |
| 8 | 307 | 2 | **50** | 6 | 100 | 24 | 99.95 |
| 8 | 308 | 2 | 30 | **2** | 100 | 24 | 71.55 |
| 8 | 309 | 2 | 30 | **4** | 100 | 24 | 91.75 |
| 8 | 310 | 2 | 30 | **6** | 100 | 24 | 99.10 |
| 8 | 311 | 2 | 30 | **8** | 100 | 24 | 99.39 |
| 8 | 312 | 2 | 30 | **10** | 100 | 24 | 99.89 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 8 | 313 | 2 | 30 | **12** | 100 | 24 | 99.98 |
| 8 | 314 | 2 | 30 | **14** | 100 | 24 | 99.99 |
| 8 | 315 | 2 | 30 | **16** | 100 | 24 | 99.99 |
| 8 | 316 | 2 | 30 | 6 | **100** | 24 | 99.96 |
| 8 | 317 | 2 | 30 | 6 | **150** | 24 | 98.38 |
| 8 | 318 | 2 | 30 | 6 | **200** | 24 | 92.86 |
| 8 | 319 | 2 | 30 | 6 | **250** | 24 | 91.00 |
| 8 | 320 | 2 | 30 | 6 | **300** | 24 | 89.87 |
| 8 | 321 | 2 | 30 | 6 | **350** | 24 | 84.77 |
| 8 | 322 | 2 | 30 | 6 | **400** | 24 | 80.45 |
| 8 | 323 | 2 | 30 | 6 | 100 | **0.25** | 82.98 |
| 8 | 324 | 2 | 30 | 6 | 100 | **0.50** | 84.33 |
| 8 | 325 | 2 | 30 | 6 | 100 | **0.75** | 90.81 |
| 8 | 326 | 2 | 30 | 6 | 100 | **1.0** | 93.11 |
| 8 | 327 | 2 | 30 | 6 | 100 | **1.25** | 94.96 |
| 8 | 328 | 2 | 30 | 6 | 100 | **1.50** | 96.58 |
| 8 | 329 | 2 | 30 | 6 | 100 | **1.75** | 98.12 |
| 8 | 330 | 2 | 30 | 6 | 100 | **2.0** | 99.02 |
| 8 | 331 | 2 | 30 | 6 | 100 | **2.5** | 99.99 |
| 8 | 332 | 2 | 30 | 6 | 100 | **3.0** | 99.99 |
| Run Nos. 303-307, 316-322 and 323-332 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |  |  |

Table A.9 Input and output parameters for the adsorption of Cr(VI) onto the surface of Fe treated Rice husk (Fe RH) using synthetic simulated single component solution

| Exp. Set No. | Run No. | Input parameters |  |  |  |  | Output parameters |
|---|---|---|---|---|---|---|---|
|  |  | pH | Temp (°C) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 9 | 333 | **2** | 30 | 28 | 100 | 24 | 99.99 |
| 9 | 334 | **3** | 30 | 28 | 100 | 24 | 92.70 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 9 | 335 | **4** | 30 | 28 | 100 | 24 | 85.00 |
| 9 | 336 | **5** | 30 | 28 | 100 | 24 | 77.00 |
| 9 | 337 | **6** | 30 | 28 | 100 | 24 | 68.00 |
| 9 | 338 | **7** | 30 | 28 | 100 | 24 | 60.00 |
| 9 | 339 | **8** | 30 | 28 | 100 | 24 | 43.66 |
| 9 | 340 | **9** | 30 | 28 | 100 | 24 | 40.00 |
| 9 | 341 | **10** | 30 | 28 | 100 | 24 | 32.00 |
| 9 | 342 | 2 | **10** | 28 | 100 | 24 | 81.55 |
| 9 | 343 | 2 | **20** | 28 | 100 | 24 | 85.14 |
| 9 | 344 | 2 | **30** | 28 | 100 | 24 | 95.11 |
| 9 | 345 | 2 | **40** | 28 | 100 | 24 | 97.44 |
| 9 | 346 | 2 | **50** | 28 | 100 | 24 | 98.65 |
| 9 | 347 | 2 | 30 | **4** | 100 | 24 | 84.96 |
| 9 | 348 | 2 | 30 | **8** | 100 | 24 | 88.94 |
| 9 | 349 | 2 | 30 | **12** | 100 | 24 | 90.40 |
| 9 | 350 | 2 | 30 | **16** | 100 | 24 | 94.78 |
| 9 | 351 | 2 | 30 | **20** | 100 | 24 | 95.80 |
| 9 | 352 | 2 | 30 | **24** | 100 | 24 | 96.98 |
| 9 | 353 | 2 | 30 | **28** | 100 | 24 | 98.99 |
| 9 | 354 | 2 | 30 | **32** | 100 | 24 | 99.99 |
| 9 | 355 | 2 | 30 | 28 | **100** | 24 | 98.60 |
| 9 | 356 | 2 | 30 | 28 | **150** | 24 | 89.70 |
| 9 | 357 | 2 | 30 | 28 | **200** | 24 | 77.17 |
| 9 | 358 | 2 | 30 | 28 | **250** | 24 | 73.82 |
| 9 | 359 | 2 | 30 | 28 | **300** | 24 | 66.34 |
| 9 | 360 | 2 | 30 | 28 | **350** | 24 | 59.77 |
| 9 | 361 | 2 | 30 | 28 | **400** | 24 | 57.45 |
| 9 | 362 | 2 | 30 | 28 | 100 | **0.5** | 69.15 |
| 9 | 363 | 2 | 30 | 28 | 100 | **1.5** | 74.16 |
| 9 | 364 | 2 | 30 | 28 | 100 | **2.5** | 82.00 |
| 9 | 365 | 2 | 30 | 28 | 100 | **3.5** | 87.31 |
| 9 | 366 | 2 | 30 | 28 | 100 | **4.5** | 91.34 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 9 | 367 | 2 | 30 | 28 | 100 | **5.5** | 96.39 |
| 9 | 368 | 2 | 30 | 28 | 100 | **6.5** | 98.12 |
| 9 | 369 | 2 | 30 | 28 | 100 | **7.5** | 99.02 |
| 9 | 370 | 2 | 30 | 28 | 100 | **8.5** | 99.99 |
| Run Nos. 342-346, 355-361 and 362-370 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |  |  |

Table A.10 Input and output parameters for the adsorption of phenol onto the surface of Granular activated carbon (GAC) using synthetic simulated single component solution

| Exp. Set No. | Run No. | Input parameters |  |  |  |  | Output parameters |
|---|---|---|---|---|---|---|---|
|  |  | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of phenol (mg/L) | Contact time h | % Removal of phenol |
| 10 | 371 | **2** | 30 | 16 | 100 | 48 | 43.53 |
| 10 | 372 | **3** | 30 | 16 | 100 | 48 | 45.78 |
| 10 | 373 | **4** | 30 | 16 | 100 | 48 | 57.61 |
| 10 | 374 | **5** | 30 | 16 | 100 | 48 | 61.21 |
| 10 | 375 | **6** | 30 | 16 | 100 | 48 | 77.44 |
| 10 | 376 | **7** | 30 | 16 | 100 | 48 | 94.66 |
| 10 | 377 | **8** | 30 | 16 | 100 | 48 | 99.66 |
| 10 | 378 | **9** | 30 | 16 | 100 | 48 | 91.00 |
| 10 | 379 | **10** | 30 | 16 | 100 | 48 | 87.00 |
| 10 | 380 | 8 | **10** | 16 | 100 | 48 | 99.55 |
| 10 | 381 | 8 | **20** | 16 | 100 | 48 | 99.65 |
| 10 | 382 | 8 | **30** | 16 | 100 | 48 | 94.75 |
| 10 | 383 | 8 | **40** | 16 | 100 | 48 | 91.93 |
| 10 | 384 | 8 | **50** | 16 | 100 | 48 | 87.86 |
| 10 | 385 | 8 | 30 | **4** | 100 | 48 | 75.68 |
| 10 | 386 | 8 | 30 | **8** | 100 | 48 | 87.77 |
| 10 | 387 | 8 | 30 | **12** | 100 | 48 | 94.87 |
| 10 | 388 | 8 | 30 | **16** | 100 | 48 | 99.22 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 10 | 389 | 8 | 30 | **20** | 100 | 48 | 99.50 |
| 10 | 390 | 8 | 30 | **24** | 100 | 48 | 99.75 |
| 10 | 391 | 8 | 30 | **28** | 100 | 48 | 99.80 |
| 10 | 392 | 8 | 30 | **32** | 100 | 48 | 99.99 |
| 10 | 393 | 8 | 30 | 16 | **100** | 48 | 99.02 |
| 10 | 394 | 8 | 30 | 16 | **150** | 48 | 93.16 |
| 10 | 395 | 8 | 30 | 16 | **200** | 48 | 92.33 |
| 10 | 396 | 8 | 30 | 16 | **250** | 48 | 83.61 |
| 10 | 397 | 8 | 30 | 16 | **300** | 48 | 81.34 |
| 10 | 398 | 8 | 30 | 16 | **350** | 48 | 76.77 |
| 10 | 399 | 8 | 30 | 16 | **400** | 48 | 74.45 |
| 10 | 400 | 8 | 30 | 16 | 100 | **1** | 40.88 |
| 10 | 401 | 8 | 30 | 16 | 100 | **2** | 57.77 |
| 10 | 402 | 8 | 30 | 16 | 100 | **3** | 66.87 |
| 10 | 403 | 8 | 30 | 16 | 100 | **4** | 72.66 |
| 10 | 404 | 8 | 30 | 16 | 100 | **5** | 79.77 |
| 10 | 405 | 8 | 30 | 16 | 100 | **6** | 84.77 |
| 10 | 406 | 8 | 30 | 16 | 100 | **7** | 89.77 |
| 10 | 407 | 8 | 30 | 16 | 100 | **8** | 92.78 |
| 10 | 408 | 8 | 30 | 16 | 100 | **9** | 94.99 |
| 10 | 409 | 8 | 30 | 16 | 100 | **10** | 96.97 |
| 10 | 410 | 8 | 30 | 16 | 100 | **11** | 97.89 |
| 10 | 411 | 8 | 30 | 16 | 100 | **12** | 99.67 |
| 10 | 412 | 8 | 30 | 16 | 100 | **13** | 99.70 |
| 10 | 413 | 8 | 30 | 16 | 100 | **14** | 99.99 |
| 10 | 414 | 8 | 30 | 16 | 100 | **15** | 99.99 |

Run Nos. 380-384, 393-399 and 400-414 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively

Table A.11 Input and output parameters for the adsorption of phenol onto the surface of Tea waste (TW) using synthetic simulated single component solution

| Exp. Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of phenol (mg/L) | Contact time h | % Removal of phenol |
| 11 | 415 | **2** | 30 | 40 | 100 | 48 | 56.11 |
| 11 | 416 | **3** | 30 | 40 | 100 | 48 | 63.35 |
| 11 | 417 | **4** | 30 | 40 | 100 | 48 | 74.55 |
| 11 | 418 | **5** | 30 | 40 | 100 | 48 | 82.11 |
| 11 | 419 | **6** | 30 | 40 | 100 | 48 | 91.04 |
| 11 | 420 | **7** | 30 | 40 | 100 | 48 | 98.75 |
| 11 | 421 | **8** | 30 | 40 | 100 | 48 | 99.53 |
| 11 | 422 | **9** | 30 | 40 | 100 | 48 | 96.55 |
| 11 | 423 | **10** | 30 | 40 | 100 | 48 | 89.57 |
| 11 | 424 | 8 | **10** | 40 | 100 | 48 | 97.75 |
| 11 | 425 | 8 | **20** | 40 | 100 | 48 | 96.65 |
| 11 | 426 | 8 | **30** | 40 | 100 | 48 | 95.55 |
| 11 | 427 | 8 | **40** | 40 | 100 | 48 | 93.93 |
| 11 | 428 | 8 | **50** | 40 | 100 | 48 | 91.05 |
| 11 | 429 | 8 | 30 | **5** | 100 | 48 | 33.90 |
| 11 | 430 | 8 | 30 | **10** | 100 | 48 | 40.88 |
| 11 | 431 | 8 | 30 | **15** | 100 | 48 | 52.35 |
| 11 | 432 | 8 | 30 | **20** | 100 | 48 | 60.22 |
| 11 | 433 | 8 | 30 | **25** | 100 | 48 | 71.35 |
| 11 | 434 | 8 | 30 | **30** | 100 | 48 | 77.48 |
| 11 | 435 | 8 | 30 | **35** | 100 | 48 | 84.55 |
| 11 | 436 | 8 | 30 | **40** | 100 | 48 | 84.99 |
| 11 | 437 | 8 | 30 | **45** | 100 | 48 | 84.99 |
| 11 | 438 | 8 | 30 | **50** | 100 | 48 | 84.99 |
| 11 | 439 | 8 | 30 | 40 | **100** | 48 | 84.79 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 11 | 440 | 8 | 30 | 40 | **150** | 48 | 70.23 |
| 11 | 441 | 8 | 30 | 40 | **200** | 48 | 56.55 |
| 11 | 442 | 8 | 30 | 40 | **250** | 48 | 51.38 |
| 11 | 443 | 8 | 30 | 40 | **300** | 48 | 45.49 |
| 11 | 444 | 8 | 30 | 40 | **350** | 48 | 40.38 |
| 11 | 445 | 8 | 30 | 40 | **400** | 48 | 35.45 |
| 11 | 446 | 8 | 30 | 40 | 100 | **2** | 19.25 |
| 11 | 447 | 8 | 30 | 40 | 100 | **4** | 26.92 |
| 11 | 448 | 8 | 30 | 40 | 100 | **6** | 33.87 |
| 11 | 449 | 8 | 30 | 40 | 100 | **8** | 46.77 |
| 11 | 450 | 8 | 30 | 40 | 100 | **10** | 53.05 |
| 11 | 451 | 8 | 30 | 40 | 100 | **12** | 62.61 |
| 11 | 452 | 8 | 30 | 40 | 100 | **14** | 69.01 |
| 11 | 453 | 8 | 30 | 40 | 100 | **16** | 76.78 |
| 11 | 454 | 8 | 30 | 40 | 100 | **18** | 82.49 |
| 11 | 455 | 8 | 30 | 40 | 100 | **20** | 84.97 |
| 11 | 456 | 8 | 30 | 40 | 100 | **22** | 84.99 |
| 11 | 457 | 8 | 30 | 40 | 100 | **24** | 84.99 |
| Run Nos. 424-428, 439-445 and 446-457 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | |

Table A.12 Input and output parameters for the adsorption of phenol onto the surface of Rice husk (RH) using synthetic simulated single component solution

| Exp. Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of phenol (mg/L) | Contact time h | % Removal of phenol |
| 12 | 458 | **2** | 30 | 35 | 100 | 48 | 45 |
| 12 | 459 | **3** | 30 | 35 | 100 | 48 | 48 |
| 12 | 460 | **4** | 30 | 35 | 100 | 48 | 65 |
| 12 | 461 | **5** | 30 | 35 | 100 | 48 | 75 |
| 12 | 462 | **6** | 30 | 35 | 100 | 48 | 96.90 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 12 | 463 | **7** | 30 | 35 | 100 | 48 | 99.90 |
| 12 | 464 | **8** | 30 | 35 | 100 | 48 | 71 |
| 12 | 465 | **9** | 30 | 35 | 100 | 48 | 60 |
| 12 | 466 | **10** | 30 | 35 | 100 | 48 | 50 |
| 12 | 467 | 7 | **10** | 35 | 100 | 48 | 98.75 |
| 12 | 468 | 7 | **20** | 35 | 100 | 48 | 97.65 |
| 12 | 469 | 7 | **30** | 35 | 100 | 48 | 95.55 |
| 12 | 470 | 7 | **40** | 35 | 100 | 48 | 89.93 |
| 12 | 471 | 7 | **50** | 35 | 100 | 48 | 81.05 |
| 12 | 472 | 7 | 30 | **5** | 100 | 48 | 56.75 |
| 12 | 473 | 7 | 30 | **10** | 100 | 48 | 63.88 |
| 12 | 474 | 7 | 30 | **15** | 100 | 48 | 74.11 |
| 12 | 475 | 7 | 30 | **20** | 100 | 48 | 82.08 |
| 12 | 476 | 7 | 30 | **25** | 100 | 48 | 91.88 |
| 12 | 477 | 7 | 30 | **30** | 100 | 48 | 97.77 |
| 12 | 478 | 7 | 30 | **35** | 100 | 48 | 99.75 |
| 12 | 479 | 7 | 30 | **40** | 100 | 48 | 99.79 |
| 12 | 480 | 7 | 30 | **45** | 100 | 48 | 99.99 |
| 12 | 481 | 7 | 30 | **50** | 100 | 48 | 99.99 |
| 12 | 482 | 7 | 30 | 35 | **100** | 48 | 99.99 |
| 12 | 483 | 7 | 30 | 35 | **150** | 48 | 92.93 |
| 12 | 484 | 7 | 30 | 35 | **200** | 48 | 67.05 |
| 12 | 485 | 7 | 30 | 35 | **250** | 48 | 59.45 |
| 12 | 486 | 7 | 30 | 35 | **300** | 48 | 54.22 |
| 12 | 487 | 7 | 30 | 35 | **350** | 48 | 49.38 |
| 12 | 488 | 7 | 30 | 35 | **400** | 48 | 45.45 |
| 12 | 489 | 7 | 30 | 35 | 100 | **2** | 10.77 |
| 12 | 490 | 7 | 30 | 35 | 100 | **4** | 19.78 |
| 12 | 491 | 7 | 30 | 35 | 100 | **6** | 29.88 |
| 12 | 492 | 7 | 30 | 35 | 100 | **8** | 36.33 |
| 12 | 493 | 7 | 30 | 35 | 100 | **10** | 45.56 |
| 12 | 494 | 7 | 30 | 35 | 100 | **12** | 53.08 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 12 | 495 | 7 | 30 | 35 | 100 | **14** | 59.66 |
| 12 | 496 | 7 | 30 | 35 | 100 | **16** | 68.62 |
| 12 | 497 | 7 | 30 | 35 | 100 | **18** | 74.76 |
| 12 | 498 | 7 | 30 | 35 | 100 | **20** | 84.61 |
| 12 | 499 | 7 | 30 | 35 | 100 | **22** | 94.65 |
| 12 | 500 | 7 | 30 | 35 | 100 | **24** | 96.99 |
| 12 | 501 | 7 | 30 | 35 | 100 | **26** | 99.99 |
| 12 | 502 | 7 | 30 | 35 | 100 | **28** | 99.99 |
| Run Nos. 467-471, 472-481 and 489-502 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |  |  |

Table A.13 Input and output parameters for the adsorption of phenol onto the surface of Bagasse (BG) using synthetic simulated single component solution

| Exp. Set No. | Run No. | Input parameters |  |  |  |  | Output parameters |
|---|---|---|---|---|---|---|---|
|  |  | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of phenol (mg/L) | Contact time h | % Removal of phenol |
| 13 | 503 | **2** | 30 | 45 | 100 | 48 | 37 |
| 13 | 504 | **3** | 30 | 45 | 100 | 48 | 44 |
| 13 | 505 | **4** | 30 | 45 | 100 | 48 | 58 |
| 13 | 506 | **5** | 30 | 45 | 100 | 48 | 67 |
| 13 | 507 | **6** | 30 | 45 | 100 | 48 | 76.90 |
| 13 | 508 | **7** | 30 | 45 | 100 | 48 | 81.90 |
| 13 | 509 | **8** | 30 | 45 | 100 | 48 | 71 |
| 13 | 510 | **9** | 30 | 45 | 100 | 48 | 60 |
| 13 | 511 | **10** | 30 | 45 | 100 | 48 | 50 |
| 13 | 512 | 7 | **10** | 45 | 100 | 48 | 91.55 |
| 13 | 513 | 7 | **20** | 45 | 100 | 48 | 89.65 |
| 13 | 514 | 7 | **30** | 45 | 100 | 48 | 86.75 |
| 13 | 515 | 7 | **40** | 45 | 100 | 48 | 89.93 |
| 13 | 516 | 7 | **50** | 45 | 100 | 48 | 81.93 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 13 | 517 | 7 | 30 | **5** | 100 | 48 | 23.16 |
| 13 | 518 | 7 | 30 | **10** | 100 | 48 | 29.08 |
| 13 | 519 | 7 | 30 | **15** | 100 | 48 | 34.11 |
| 13 | 520 | 7 | 30 | **20** | 100 | 48 | 40.08 |
| 13 | 521 | 7 | 30 | **25** | 100 | 48 | 48.18 |
| 13 | 522 | 7 | 30 | **30** | 100 | 48 | 56.27 |
| 13 | 523 | 7 | 30 | **35** | 100 | 48 | 66.95 |
| 13 | 524 | 7 | 30 | **40** | 100 | 48 | 74.19 |
| 13 | 525 | 7 | 30 | **45** | 100 | 48 | 80.26 |
| 13 | 526 | 7 | 30 | **50** | 100 | 48 | 80.99 |
| 13 | 527 | 7 | 30 | **55** | 100 | 48 | 80.99 |
| 13 | 528 | 7 | 30 | **60** | 100 | 48 | 80.99 |
| 13 | 529 | 7 | 30 | 45 | **100** | 48 | 80.25 |
| 13 | 530 | 7 | 30 | 45 | **150** | 48 | 62.93 |
| 13 | 531 | 7 | 30 | 45 | **200** | 48 | 67.05 |
| 13 | 532 | 7 | 30 | 45 | **250** | 48 | 55.45 |
| 13 | 533 | 7 | 30 | 45 | **300** | 48 | 48.22 |
| 13 | 534 | 7 | 30 | 45 | **350** | 48 | 45.38 |
| 13 | 535 | 7 | 30 | 45 | **400** | 48 | 41.05 |
| 13 | 536 | 7 | 30 | 45 | 100 | **2** | 12.44 |
| 13 | 537 | 7 | 30 | 45 | 100 | **4** | 18.66 |
| 13 | 538 | 7 | 30 | 45 | 100 | **6** | 26.35 |
| 13 | 539 | 7 | 30 | 45 | 100 | **8** | 31.95 |
| 13 | 540 | 7 | 30 | 45 | 100 | **10** | 36.44 |
| 13 | 541 | 7 | 30 | 45 | 100 | **12** | 49.44 |
| 13 | 542 | 7 | 30 | 45 | 100 | **14** | 58.77 |
| 13 | 543 | 7 | 30 | 45 | 100 | **16** | 66.77 |
| 13 | 544 | 7 | 30 | 45 | 100 | **18** | 75.35 |
| 13 | 545 | 7 | 30 | 45 | 100 | **20** | 80.61 |
| 13 | 546 | 7 | 30 | 45 | 100 | **22** | 80.65 |
| 13 | 547 | 7 | 30 | 45 | 100 | **24** | 80.99 |
| Run Nos. 512-516, 529-535 and 536-547 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | |

Table A.14 Input and output parameters for the adsorption of phenol onto the surface of Bagasse fly ash (BFA) using synthetic simulated single component solution

| Exp. Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of phenol (mg/L) | Contact time h | % Removal of phenol |
| 14 | 548 | **2** | 30 | 40 | 100 | 48 | 25.66 |
| 14 | 549 | **3** | 30 | 40 | 100 | 48 | 33.62 |
| 14 | 550 | **4** | 30 | 40 | 100 | 48 | 47.61 |
| 14 | 551 | **5** | 30 | 40 | 100 | 48 | 51.21 |
| 14 | 552 | **6** | 30 | 40 | 100 | 48 | 67.44 |
| 14 | 553 | **7** | 30 | 40 | 100 | 48 | 74.66 |
| 14 | 554 | **8** | 30 | 40 | 100 | 48 | 84.88 |
| 14 | 555 | **9** | 30 | 40 | 100 | 48 | 79.77 |
| 14 | 556 | **10** | 30 | 40 | 100 | 48 | 69.66 |
| 14 | 557 | 7 | **10** | 40 | 100 | 48 | 89.55 |
| 14 | 558 | 7 | **20** | 40 | 100 | 48 | 87.65 |
| 14 | 559 | 7 | **30** | 40 | 100 | 48 | 84.75 |
| 14 | 560 | 7 | **40** | 40 | 100 | 48 | 79.93 |
| 14 | 561 | 7 | **50** | 40 | 100 | 48 | 74.86 |
| 14 | 562 | 7 | 30 | **5** | 100 | 48 | 27.66 |
| 14 | 563 | 7 | 30 | **10** | 100 | 48 | 36.55 |
| 14 | 564 | 7 | 30 | **15** | 100 | 48 | 43.51 |
| 14 | 565 | 7 | 30 | **20** | 100 | 48 | 59.98 |
| 14 | 566 | 7 | 30 | **25** | 100 | 48 | 68.07 |
| 14 | 567 | 7 | 30 | **30** | 100 | 48 | 79.95 |
| 14 | 568 | 7 | 30 | **35** | 100 | 48 | 82.95 |
| 14 | 569 | 7 | 30 | **40** | 100 | 48 | 86.19 |
| 14 | 570 | 7 | 30 | **45** | 100 | 48 | 86.26 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 14 | 571 | 7 | 30 | **50** | 100 | 48 | 86.99 |
| 14 | 572 | 7 | 30 | 40 | **100** | 48 | 86.44 |
| 14 | 573 | 7 | 30 | 40 | **150** | 48 | 66.22 |
| 14 | 574 | 7 | 30 | 40 | **200** | 48 | 55.63 |
| 14 | 575 | 7 | 30 | 40 | **250** | 48 | 53.63 |
| 14 | 576 | 7 | 30 | 40 | **300** | 48 | 48.22 |
| 14 | 577 | 7 | 30 | 40 | **350** | 48 | 39.38 |
| 14 | 578 | 7 | 30 | 40 | **400** | 48 | 36.05 |
| 14 | 579 | 7 | 30 | 40 | 100 | **2** | 7.44 |
| 14 | 580 | 7 | 30 | 40 | 100 | **4** | 14.66 |
| 14 | 581 | 7 | 30 | 40 | 100 | **6** | 23.35 |
| 14 | 582 | 7 | 30 | 40 | 100 | **8** | 29.95 |
| 14 | 583 | 7 | 30 | 40 | 100 | **10** | 36.44 |
| 14 | 584 | 7 | 30 | 40 | 100 | **12** | 41.44 |
| 14 | 585 | 7 | 30 | 40 | 100 | **14** | 52.33 |
| 14 | 586 | 7 | 30 | 40 | 100 | **16** | 59.46 |
| 14 | 587 | 7 | 30 | 40 | 100 | **18** | 67.26 |
| 14 | 588 | 7 | 30 | 40 | 100 | **20** | 74.32 |
| 14 | 589 | 7 | 30 | 40 | 100 | **22** | 81.06 |
| 14 | 590 | 7 | 30 | 40 | 100 | **24** | 86.29 |
| 14 | 591 | 7 | 30 | 40 | 100 | **26** | 86.78 |
| 14 | 592 | 7 | 30 | 40 | 100 | **28** | 86.89 |
| 14 | 593 | 7 | 30 | 40 | 100 | **30** | 86.99 |
| Run Nos. 557-561, 572-578 and 579-593 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | |

Table A.15 Input and output parameters for the adsorption of phenol onto the surface of Distillery sludge (DS) using synthetic simulated single component solution

| Exp. Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of phenol (mg/L) | Contact time h | % Removal of phenol |
| 15 | 594 | **2** | 30 | 45 | 100 | 48 | 10.91 |
| 15 | 595 | **3** | 30 | 45 | 100 | 48 | 23.11 |
| 15 | 596 | **4** | 30 | 45 | 100 | 48 | 39.92 |
| 15 | 597 | **5** | 30 | 45 | 100 | 48 | 43.44 |
| 15 | 598 | **6** | 30 | 45 | 100 | 48 | 59.95 |
| 15 | 599 | **7** | 30 | 45 | 100 | 48 | 73.55 |
| 15 | 600 | **8** | 30 | 45 | 100 | 48 | 69.25 |
| 15 | 601 | **9** | 30 | 45 | 100 | 48 | 63.54 |
| 15 | 602 | **10** | 30 | 45 | 100 | 48 | 58.37 |
| 15 | 603 | 7 | **10** | 45 | 100 | 48 | 74.55 |
| 15 | 604 | 7 | **20** | 45 | 100 | 48 | 73.65 |
| 15 | 605 | 7 | **30** | 45 | 100 | 48 | 71.75 |
| 15 | 606 | 7 | **40** | 45 | 100 | 48 | 69.93 |
| 15 | 607 | 7 | **50** | 45 | 100 | 48 | 64.86 |
| 15 | 608 | 7 | 30 | **5** | 100 | 48 | 19.81 |
| 15 | 609 | 7 | 30 | **10** | 100 | 48 | 24.11 |
| 15 | 610 | 7 | 30 | **15** | 100 | 48 | 29.92 |
| 15 | 611 | 7 | 30 | **20** | 100 | 48 | 39.95 |
| 15 | 612 | 7 | 30 | **25** | 100 | 48 | 47.55 |
| 15 | 613 | 7 | 30 | **30** | 100 | 48 | 53.25 |
| 15 | 614 | 7 | 30 | **35** | 100 | 48 | 67.54 |
| 15 | 615 | 7 | 30 | **40** | 100 | 48 | 70.19 |
| 15 | 616 | 7 | 30 | **45** | 100 | 48 | 71.26 |
| 15 | 617 | 7 | 30 | **50** | 100 | 48 | 71.59 |
| 15 | 618 | 7 | 30 | **55** | 100 | 48 | 71.89 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 15 | 619 | 7 | 30 | **60** | 100 | 48 | 71.99 |
| 15 | 620 | 7 | 30 | 45 | **100** | 48 | 71.44 |
| 15 | 621 | 7 | 30 | 45 | **150** | 48 | 55.72 |
| 15 | 622 | 7 | 30 | 45 | **200** | 48 | 43.03 |
| 15 | 623 | 7 | 30 | 45 | **250** | 48 | 35.16 |
| 15 | 624 | 7 | 30 | 45 | **300** | 48 | 29.29 |
| 15 | 625 | 7 | 30 | 45 | **350** | 48 | 26.38 |
| 15 | 626 | 7 | 30 | 45 | **400** | 48 | 21.05 |
| 15 | 627 | 7 | 30 | 45 | 100 | **2** | 13.44 |
| 15 | 628 | 7 | 30 | 45 | 100 | **4** | 15.66 |
| 15 | 629 | 7 | 30 | 45 | 100 | **6** | 17.35 |
| 15 | 630 | 7 | 30 | 45 | 100 | **8** | 20.95 |
| 15 | 631 | 7 | 30 | 45 | 100 | **10** | 25.77 |
| 15 | 632 | 7 | 30 | 45 | 100 | **12** | 31.09 |
| 15 | 633 | 7 | 30 | 45 | 100 | **14** | 36.35 |
| 15 | 634 | 7 | 30 | 45 | 100 | **16** | 40.16 |
| 15 | 635 | 7 | 30 | 45 | 100 | **18** | 48.77 |
| 15 | 636 | 7 | 30 | 45 | 100 | **20** | 53.26 |
| 15 | 637 | 7 | 30 | 45 | 100 | **22** | 65.33 |
| 15 | 638 | 7 | 30 | 45 | 100 | **24** | 69.88 |
| 15 | 639 | 7 | 30 | 45 | 100 | **26** | 70.78 |
| 15 | 640 | 7 | 30 | 45 | 100 | **28** | 71.89 |
| 15 | 641 | 7 | 30 | 45 | 100 | **30** | 71.99 |
| 15 | 642 | 7 | 30 | 45 | 100 | **32** | 71.99 |

Run Nos. 603-607, 620-626 and 627-642 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively

Table A.16 Input and output parameters for the adsorption of phenol onto the surface of Neem leaves (NL) using synthetic simulated single component solution

| Exp. Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of phenol (mg/L) | Contact time h | % Removal of phenol |
| 16 | 643 | **2** | 30 | 40 | 100 | 48 | 24.00 |
| 16 | 644 | **3** | 30 | 40 | 100 | 48 | 29.00 |
| 16 | 645 | **4** | 30 | 40 | 100 | 48 | 34.00 |
| 16 | 646 | **5** | 30 | 40 | 100 | 48 | 40.00 |
| 16 | 647 | **6** | 30 | 40 | 100 | 48 | 58.00 |
| 16 | 648 | **7** | 30 | 40 | 100 | 48 | 76.00 |
| 16 | 649 | **8** | 30 | 40 | 100 | 48 | 84.00 |
| 16 | 650 | **9** | 30 | 40 | 100 | 48 | 80.00 |
| 16 | 651 | **10** | 30 | 40 | 100 | 48 | 71.00 |
| 16 | 652 | 8 | **10** | 40 | 100 | 48 | 87.86 |
| 16 | 653 | 8 | **20** | 40 | 100 | 48 | 86.93 |
| 16 | 654 | 8 | **30** | 40 | 100 | 48 | 84.75 |
| 16 | 655 | 8 | **40** | 40 | 100 | 48 | 79.65 |
| 16 | 656 | 8 | **50** | 40 | 100 | 48 | 74.55 |
| 16 | 657 | 8 | 30 | **5** | 100 | 48 | 37.65 |
| 16 | 658 | 8 | 30 | **10** | 100 | 48 | 40.11 |
| 16 | 659 | 8 | 30 | **15** | 100 | 48 | 44.12 |
| 16 | 660 | 8 | 30 | **20** | 100 | 48 | 49.46 |
| 16 | 661 | 8 | 30 | **25** | 100 | 48 | 57.66 |
| 16 | 662 | 8 | 30 | **30** | 100 | 48 | 69.33 |
| 16 | 663 | 8 | 30 | **35** | 100 | 48 | 79.06 |
| 16 | 664 | 8 | 30 | **40** | 100 | 48 | 84.19 |
| 16 | 665 | 8 | 30 | **45** | 100 | 48 | 84.26 |
| 16 | 666 | 8 | 30 | **50** | 100 | 48 | 84.59 |
| 16 | 667 | 8 | 30 | 40 | **100** | 48 | 84.20 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 16 | 668 | 8 | 30 | 40 | **150** | 48 | 86.44 |
| 16 | 669 | 8 | 30 | 40 | **200** | 48 | 67.06 |
| 16 | 670 | 8 | 30 | 40 | **250** | 48 | 59.16 |
| 16 | 671 | 8 | 30 | 40 | **300** | 48 | 53.29 |
| 16 | 672 | 8 | 30 | 40 | **350** | 48 | 46.38 |
| 16 | 673 | 8 | 30 | 40 | **400** | 48 | 44.05 |
| 16 | 674 | 8 | 30 | 40 | 100 | **2** | 11.02 |
| 16 | 675 | 8 | 30 | 40 | 100 | **4** | 15.22 |
| 16 | 676 | 8 | 30 | 40 | 100 | **6** | 19.95 |
| 16 | 677 | 8 | 30 | 40 | 100 | **8** | 25.99 |
| 16 | 678 | 8 | 30 | 40 | 100 | **10** | 31.57 |
| 16 | 679 | 8 | 30 | 40 | 100 | **12** | 36.56 |
| 16 | 680 | 8 | 30 | 40 | 100 | **14** | 41.07 |
| 16 | 681 | 8 | 30 | 40 | 100 | **16** | 46.32 |
| 16 | 682 | 8 | 30 | 40 | 100 | **18** | 59.02 |
| 16 | 683 | 8 | 30 | 40 | 100 | **20** | 66.91 |
| 16 | 684 | 8 | 30 | 40 | 100 | **22** | 71.44 |
| 16 | 685 | 8 | 30 | 40 | 100 | **24** | 75.24 |
| 16 | 686 | 8 | 30 | 40 | 100 | **26** | 80.43 |
| 16 | 687 | 8 | 30 | 40 | 100 | **28** | 84.89 |
| 16 | 688 | 8 | 30 | 40 | 100 | **30** | 84.99 |
| 16 | 689 | 8 | 30 | 40 | 100 | **32** | 84.99 |
| Run Nos. 652-656, 667-673 and 674-689 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |  |  |

Table A.17 Input and output parameters for the adsorption of phenol onto the surface of Fe treated tea waste (Fe TW) using synthetic simulated single component solution

| Exp. Set No. | Run No. | Input parameters | | | | | Output parameters |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of phenol (mg/L) | Contact time h | % Removal of phenol |
| 17 | 690 | **2** | 30 | 25 | 100 | 48 | 26.00 |
| 17 | 691 | **3** | 30 | 25 | 100 | 48 | 32.00 |
| 17 | 692 | **4** | 30 | 25 | 100 | 48 | 41.00 |
| 17 | 693 | **5** | 30 | 25 | 100 | 48 | 52.00 |
| 17 | 694 | **6** | 30 | 25 | 100 | 48 | 61.00 |
| 17 | 695 | **7** | 30 | 25 | 100 | 48 | 86.00 |
| 17 | 696 | **8** | 30 | 25 | 100 | 48 | 99.99 |
| 17 | 697 | **9** | 30 | 25 | 100 | 48 | 89.00 |
| 17 | 698 | **10** | 30 | 25 | 100 | 48 | 76.00 |
| 17 | 699 | 8 | **10** | 25 | 100 | 48 | 97.85 |
| 17 | 700 | 8 | **20** | 25 | 100 | 48 | 96.55 |
| 17 | 701 | 8 | **30** | 25 | 100 | 48 | 95.55 |
| 17 | 702 | 8 | **40** | 25 | 100 | 48 | 92.83 |
| 17 | 703 | 8 | **50** | 25 | 100 | 48 | 90.06 |
| 17 | 704 | 8 | 30 | **5** | 100 | 48 | 53.22 |
| 17 | 705 | 8 | 30 | **10** | 100 | 48 | 62.33 |
| 17 | 706 | 8 | 30 | **15** | 100 | 48 | 79.11 |
| 17 | 707 | 8 | 30 | **20** | 100 | 48 | 89.88 |
| 17 | 708 | 8 | 30 | **25** | 100 | 48 | 98.66 |
| 17 | 709 | 8 | 30 | **30** | 100 | 48 | 99.33 |
| 17 | 710 | 8 | 30 | **35** | 100 | 48 | 99.96 |
| 17 | 711 | 8 | 30 | **40** | 100 | 48 | 99.99 |
| 17 | 712 | 8 | 30 | 25 | **100** | 48 | 99.50 |
| 17 | 713 | 8 | 30 | 25 | **150** | 48 | 86.44 |
| 17 | 714 | 8 | 30 | 25 | **200** | 48 | 89.55 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 17 | 715 | 8 | 30 | 25 | **250** | 48 | 75.16 |
| 17 | 716 | 8 | 30 | 25 | **300** | 48 | 68.49 |
| 17 | 717 | 8 | 30 | 25 | **350** | 48 | 63.38 |
| 17 | 718 | 8 | 30 | 25 | **400** | 48 | 58.05 |
| 17 | 719 | 8 | 30 | 25 | 100 | **2** | 39.55 |
| 17 | 720 | 8 | 30 | 25 | 100 | **4** | 45.22 |
| 17 | 721 | 8 | 30 | 25 | 100 | **6** | 50.71 |
| 17 | 722 | 8 | 30 | 25 | 100 | **8** | 58.51 |
| 17 | 723 | 8 | 30 | 25 | 100 | **10** | 64.96 |
| 17 | 724 | 8 | 30 | 25 | 100 | **12** | 77.00 |
| 17 | 725 | 8 | 30 | 25 | 100 | **14** | 88.38 |
| 17 | 726 | 8 | 30 | 25 | 100 | **16** | 93.85 |
| 17 | 727 | 8 | 30 | 25 | 100 | **18** | 99.62 |
| 17 | 728 | 8 | 30 | 25 | 100 | **20** | 99.91 |
| 17 | 729 | 8 | 30 | 25 | 100 | **22** | 99.99 |
| Run Nos. 699-703, 712-718 and 719-729 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |  |  |

Table A.18 Input and output parameters for the adsorption of phenol onto the surface of Fe treated Rice husk (Fe RH) using synthetic simulated single component solution

| Exp. Set No. | Run No. | Input parameters |  |  |  |  | Output parameters |
|---|---|---|---|---|---|---|---|
|  |  | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of phenol (mg/L) | Contact time h | % Removal of phenol |
| 18 | 730 | **2** | 30 | 24 | 100 | 48 | 20.00 |
| 18 | 731 | **3** | 30 | 24 | 100 | 48 | 28.98 |
| 18 | 732 | **4** | 30 | 24 | 100 | 48 | 32.34 |
| 18 | 733 | **5** | 30 | 24 | 100 | 48 | 40.89 |
| 18 | 734 | **6** | 30 | 24 | 100 | 48 | 60.98 |
| 18 | 735 | **7** | 30 | 24 | 100 | 48 | 89.89 |
| 18 | 736 | **8** | 30 | 24 | 100 | 48 | 99.99 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 18 | 737 | **9** | 30 | 24 | 100 | 48 | 87.90 |
| 18 | 738 | **10** | 30 | 24 | 100 | 48 | 80.09 |
| 18 | 739 | 8 | **10** | 24 | 100 | 48 | 98.65 |
| 18 | 740 | 8 | **20** | 24 | 100 | 48 | 97.25 |
| 18 | 741 | 8 | **30** | 24 | 100 | 48 | 95.85 |
| 18 | 742 | 8 | **40** | 24 | 100 | 48 | 89.83 |
| 18 | 743 | 8 | **50** | 24 | 100 | 48 | 79.06 |
| 18 | 744 | 8 | 30 | **4** | 100 | 48 | 64.33 |
| 18 | 745 | 8 | 30 | **8** | 100 | 48 | 70.55 |
| 18 | 746 | 8 | 30 | **12** | 100 | 48 | 79.95 |
| 18 | 747 | 8 | 30 | **16** | 100 | 48 | 87.57 |
| 18 | 748 | 8 | 30 | **20** | 100 | 48 | 96.45 |
| 18 | 749 | 8 | 30 | **24** | 100 | 48 | 99.59 |
| 18 | 750 | 8 | 30 | **28** | 100 | 48 | 99.96 |
| 18 | 751 | 8 | 30 | **32** | 100 | 48 | 99.99 |
| 18 | 752 | 8 | 30 | 24 | **100** | 48 | 99.29 |
| 18 | 753 | 8 | 30 | 24 | **150** | 48 | 93.17 |
| 18 | 754 | 8 | 30 | 24 | **200** | 48 | 89.92 |
| 18 | 755 | 8 | 30 | 24 | **250** | 48 | 87.84 |
| 18 | 756 | 8 | 30 | 24 | **300** | 48 | 86.72 |
| 18 | 757 | 8 | 30 | 24 | **350** | 48 | 83.38 |
| 18 | 758 | 8 | 30 | 24 | **400** | 48 | 82.05 |
| 18 | 759 | 8 | 30 | 24 | 100 | **2** | 14.88 |
| 18 | 760 | 8 | 30 | 24 | 100 | **4** | 25.88 |
| 18 | 761 | 8 | 30 | 24 | 100 | **6** | 34.88 |
| 18 | 762 | 8 | 30 | 24 | 100 | **8** | 46.13 |
| 18 | 763 | 8 | 30 | 24 | 100 | **10** | 52.43 |
| 18 | 764 | 8 | 30 | 24 | 100 | **12** | 60.54 |
| 18 | 765 | 8 | 30 | 24 | 100 | **14** | 69.06 |
| 18 | 766 | 8 | 30 | 24 | 100 | **16** | 77.46 |
| 18 | 767 | 8 | 30 | 24 | 100 | **18** | 89.57 |
| 18 | 768 | 8 | 30 | 24 | 100 | **20** | 94.55 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 18 | 769 | 8 | 30 | 24 | 100 | **22** | 99.59 |
| 18 | 770 | 8 | 30 | 24 | 100 | **24** | 99.99 |
| Run Nos. 739-742, 752-758 and 759-770 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |  |  |

Table A.19 Input and output parameters for the simultaneous adsorption of Cr(VI) and phenol onto the surface of Granular activated carbon (GAC) using synthetic simulated binary solution

| Exp. Set No. | Run No. | Input parameters |  |  |  |  |  |  | Output parameters |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time (h) Cr(VI) | Contact time (h) phenol | % Removal of Cr(VI) | % Removal of phenol |
| 19 | 771 | **2** | 30 | 24 | 100 | 50 | 48 | 48 | 76.22 | 38.10 |
| 19 | 772 | **3** | 30 | 24 | 100 | 50 | 48 | 48 | 87.95 | 55.00 |
| 19 | 773 | **4** | 30 | 24 | 100 | 50 | 48 | 48 | 95.57 | 70.22 |
| 19 | 774 | **5** | 30 | 24 | 100 | 50 | 48 | 48 | 99.25 | 96.44 |
| 19 | 775 | **6** | 30 | 24 | 100 | 50 | 48 | 48 | 90.33 | 91.70 |
| 19 | 776 | **7** | 30 | 24 | 100 | 50 | 48 | 48 | 81.25 | 78.45 |
| 19 | 777 | **8** | 30 | 24 | 100 | 50 | 48 | 48 | 64.10 | 64.44 |
| 19 | 778 | **9** | 30 | 24 | 100 | 50 | 48 | 48 | 56.11 | 48.22 |
| 19 | 779 | 5 | **10** | 24 | 100 | 50 | 48 | 48 | 95.55 | 98.65 |
| 19 | 780 | 5 | **20** | 24 | 100 | 50 | 48 | 48 | 96.65 | 97.25 |
| 19 | 781 | 5 | **30** | 24 | 100 | 50 | 48 | 48 | 97.75 | 95.85 |
| 19 | 782 | 5 | **40** | 24 | 100 | 50 | 48 | 48 | 98.93 | 89.83 |
| 19 | 783 | 5 | **50** | 24 | 100 | 50 | 48 | 48 | 87.86 | 79.06 |
| 19 | 784 | 5 | 30 | **1.5** | 100 | 50 | 48 | 48 | 79.33 | 66.00 |
| 19 | 785 | 5 | 30 | **3** | 100 | 50 | 48 | 48 | 83.83 | 76.95 |
| 19 | 786 | 5 | 30 | **4.5** | 100 | 50 | 48 | 48 | 87.81 | 82.44 |
| 19 | 787 | 5 | 30 | **6** | 100 | 50 | 48 | 48 | 90.74 | 86.44 |
| 19 | 788 | 5 | 30 | **7.5** | 100 | 50 | 48 | 48 | 94.77 | 91.54 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 19 | 789 | 5 | 30 | **9.0** | 100 | 50 | 48 | 48 | 98.44 | 97.07 |
| 19 | 790 | 5 | 30 | **10.50** | 100 | 50 | 48 | 48 | 99.86 | 99.59 |
| 19 | 791 | 5 | 30 | **12** | 100 | 50 | 48 | 48 | 99.86 | 99.96 |
| 19 | 792 | 5 | 30 | 24 | **100** | **50** | 48 | 48 | 99.96 | 98.96 |
| 19 | 793 | 5 | 30 | 24 | **150** | **75** | 48 | 48 | 98.51 | 91.94 |
| 19 | 794 | 5 | 30 | 24 | **200** | **100** | 48 | 48 | 95.67 | 80.67 |
| 19 | 795 | 5 | 30 | 24 | **250** | **125** | 48 | 48 | 92.63 | 79.63 |
| 19 | 796 | 5 | 30 | 24 | **300** | **150** | 48 | 48 | 88.18 | 72.18 |
| 19 | 797 | 5 | 30 | 24 | **350** | **175** | 48 | 48 | 86.92 | 72.12 |
| 19 | 798 | 5 | 30 | 24 | **400** | **200** | 48 | 48 | 86.05 | 72.05 |
| 19 | 799 | 5 | 30 | 24 | 100 | 50 | **0.5** | **0.5** | 79.70 | 26.84 |
| 19 | 800 | 5 | 30 | 24 | 100 | 50 | **1** | **1** | 84.00 | 40.70 |
| 19 | 801 | 5 | 30 | 24 | 100 | 50 | **1.5** | **1.5** | 91.23 | 56.22 |
| 19 | 802 | 5 | 30 | 24 | 100 | 50 | **2.0** | **2.0** | 94.68 | 75.00 |
| 19 | 803 | 5 | 30 | 24 | 100 | 50 | **2.5** | **2.5** | 97.98 | 89.36 |
| 19 | 804 | 5 | 30 | 24 | 100 | 50 | **3.0** | **3.0** | 98.67 | 93.14 |
| 19 | 805 | 5 | 30 | 24 | 100 | 50 | **3.5** | **3.5** | 99.99 | 99.00 |
| 19 | 806 | 5 | 30 | 24 | 100 | 50 | **4.0** | **4.0** | 99.99 | 99.39 |
| 19 | 807 | 5 | 30 | 24 | 100 | 50 | **4.5** | **4.5** | 99.99 | 99.58 |
| Run Nos. 779-783, 792-798 and 799-807 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | | | | |

Table A.20 Input and output parameters for the simultaneous adsorptionof Cr(VI) and phenol onto the surface of Tea waste (TW) using synthetic simulated binary solution

| Exp. Set No. | Run No. | Input parameters | | | | | | | Output parameters | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time (h) Cr(VI) | Contact time (h) phenol | % Removal of Cr(VI) | % Removal of phenol |
| 20 | 808 | **2** | 30 | 15 | 100 | 50 | 48 | 48 | 99.25 | 38.00 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 20 | 809 | **3** | 30 | 15 | 100 | 50 | 48 | 48 | 99.25 | 46.00 |
| 20 | 810 | **4** | 30 | 15 | 100 | 50 | 48 | 48 | 99.25 | 66.00 |
| 20 | 811 | **5** | 30 | 15 | 100 | 50 | 48 | 48 | 99.25 | 73.00 |
| 20 | 812 | **6** | 30 | 15 | 100 | 50 | 48 | 48 | 99.25 | 82.00 |
| 20 | 813 | **7** | 30 | 15 | 100 | 50 | 48 | 48 | 95.13 | 95.00 |
| 20 | 814 | **8** | 30 | 15 | 100 | 50 | 48 | 48 | 46.00 | 86.00 |
| 20 | 815 | **9** | 30 | 15 | 100 | 50 | 48 | 48 | 37.00 | 80.00 |
| 20 | 816 | 7 | **10** | 15 | 100 | 50 | 48 | 48 | 86.33 | 92.62 |
| 20 | 817 | 7 | **20** | 15 | 100 | 50 | 48 | 48 | 89.44 | 93.30 |
| 20 | 818 | 7 | **30** | 15 | 100 | 50 | 48 | 48 | 96.13 | 91.10 |
| 20 | 819 | 7 | **40** | 15 | 100 | 50 | 48 | 48 | 98.44 | 87.86 |
| 20 | 820 | 7 | **50** | 15 | 100 | 50 | 48 | 48 | 95.55 | 82.12 |
| 20 | 821 | 7 | 30 | **2.5** | 100 | 50 | 48 | 48 | 78.67 | 48.00 |
| 20 | 822 | 7 | 30 | **5.0** | 100 | 50 | 48 | 48 | 84.55 | 59.95 |
| 20 | 823 | 7 | 30 | **7.5** | 100 | 50 | 48 | 48 | 91.41 | 70.44 |
| 20 | 824 | 7 | 30 | **10** | 100 | 50 | 48 | 48 | 95.83 | 87.44 |
| 20 | 825 | 7 | 30 | **12.5** | 100 | 50 | 48 | 48 | 98.51 | 91.54 |
| 20 | 826 | 7 | 30 | **15.0** | 100 | 50 | 48 | 48 | 99.99 | 95.07 |
| 20 | 827 | 7 | 30 | **17.5** | 100 | 50 | 48 | 48 | 99.99 | 95.44 |
| 20 | 828 | 7 | 30 | **20** | 100 | 50 | 48 | 48 | 99.99 | 95.44 |
| 20 | 829 | 7 | 30 | 15 | **100** | **50** | 48 | 48 | 98.13 | 97.03 |
| 20 | 830 | 7 | 30 | 15 | **150** | **75** | 48 | 48 | 89.85 | 94.55 |
| 20 | 831 | 7 | 30 | 15 | **200** | **100** | 48 | 48 | 79.76 | 89.86 |
| 20 | 832 | 7 | 30 | 15 | **250** | **125** | 48 | 48 | 71.82 | 82.83 |
| 20 | 833 | 7 | 30 | 15 | **300** | **150** | 48 | 48 | 63.19 | 79.72 |
| 20 | 834 | 7 | 30 | 15 | **350** | **175** | 48 | 48 | 58.38 | 79.63 |
| 20 | 835 | 7 | 30 | 15 | **400** | **200** | 48 | 48 | 56.14 | 70.68 |
| 20 | 836 | 7 | 30 | 15 | 100 | 50 | **2** | **2** | 70.00 | 28.00 |
| 20 | 837 | 7 | 30 | 15 | 100 | 50 | **4** | **4** | 76.00 | 36.00 |
| 20 | 838 | 7 | 30 | 15 | 100 | 50 | **6** | **6** | 83.00 | 48.00 |
| 20 | 839 | 7 | 30 | 15 | 100 | 50 | **8** | **8** | 88.00 | 57.00 |
| 20 | 840 | 7 | 30 | 15 | 100 | 50 | **10** | **10** | 94.00 | 64.00 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 20 | 841 | 7 | 30 | 15 | 100 | 50 | **12** | **12** | 98.75 | 70.00 |
| 20 | 842 | 7 | 30 | 15 | 100 | 50 | **14** | **14** | 99.99 | 75.00 |
| 20 | 843 | 7 | 30 | 15 | 100 | 50 | **16** | **16** | 99.99 | 80.00 |
| 20 | 844 | 7 | 30 | 15 | 100 | 50 | **18** | **18** | 99.99 | 86.58 |
| 20 | 845 | 7 | 30 | 15 | 100 | 50 | **20** | **20** | 99.99 | 91.00 |
| 20 | 846 | 7 | 30 | 15 | 100 | 50 | **22** | **22** | 99.99 | 95.00 |
| 20 | 847 | 7 | 30 | 15 | 100 | 50 | **24** | **24** | 99.99 | 95.75 |
| 20 | 848 | 7 | 30 | 15 | 100 | 50 | **26** | **26** | 99.99 | 95.75 |
| Run Nos. 816-820, 829-835 and 836-848 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | | | | |

Table A.21 Input and output parameters for the simultaneous adsorptionof Cr(VI) and phenol onto the surface of Rice husk (RH) using synthetic simulated binary solution

| Exp. Set No. | Run No. | Input parameters | | | | | | | Output parameters | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time (h) Cr(VI) | Contact time (h) phenol | % Removal of Cr(VI) | % Removal of phenol |
| 21 | 849 | **2** | 30 | 20 | 100 | 50 | 48 | 48 | 94.05 | 50.05 |
| 21 | 850 | **3** | 30 | 20 | 100 | 50 | 48 | 48 | 95.85 | 76.85 |
| 21 | 851 | **4** | 30 | 20 | 100 | 50 | 48 | 48 | 96.11 | 86.11 |
| 21 | 852 | **5** | 30 | 20 | 100 | 50 | 48 | 48 | 98.22 | 99.33 |
| 21 | 853 | **6** | 30 | 20 | 100 | 50 | 48 | 48 | 93.02 | 93.02 |
| 21 | 854 | **7** | 30 | 20 | 100 | 50 | 48 | 48 | 79.01 | 91.01 |
| 21 | 855 | **8** | 30 | 20 | 100 | 50 | 48 | 48 | 63.12 | 89.12 |
| 21 | 856 | **9** | 30 | 20 | 100 | 50 | 48 | 48 | 58.11 | 86.11 |
| 21 | 857 | 5 | **10** | 20 | 100 | 50 | 48 | 48 | 90.35 | 96.65 |
| 21 | 858 | 5 | **20** | 20 | 100 | 50 | 48 | 48 | 95.24 | 95.55 |
| 21 | 859 | 5 | **30** | 20 | 100 | 50 | 48 | 48 | 97.32 | 93.93 |
| 21 | 860 | 5 | **40** | 20 | 100 | 50 | 48 | 48 | 99.74 | 91.06 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 21 | 861 | 5 | **50** | 20 | 100 | 50 | 48 | 48 | 99.75 | 89.86 |
| 21 | 862 | 5 | 30 | **2** | 100 | 50 | 48 | 48 | 41.22 | 51.11 |
| 21 | 863 | 5 | 30 | **4** | 100 | 50 | 48 | 48 | 58.83 | 59.06 |
| 21 | 864 | 5 | 30 | **6** | 100 | 50 | 48 | 48 | 64.81 | 68.44 |
| 21 | 865 | 5 | 30 | **8** | 100 | 50 | 48 | 48 | 70.74 | 75.94 |
| 21 | 866 | 5 | 30 | **10** | 100 | 50 | 48 | 48 | 79.77 | 81.54 |
| 21 | 867 | 5 | 30 | **12** | 100 | 50 | 48 | 48 | 84.44 | 89.07 |
| 21 | 868 | 5 | 30 | **14** | 100 | 50 | 48 | 48 | 89.46 | 93.06 |
| 21 | 869 | 5 | 30 | **16** | 100 | 50 | 48 | 48 | 93.46 | 96.06 |
| 21 | 870 | 5 | 30 | **18** | 100 | 50 | 48 | 48 | 95.44 | 98.44 |
| 21 | 871 | 5 | 30 | **20** | 100 | 50 | 48 | 48 | 98.55 | 99.33 |
| 21 | 872 | 5 | 30 | **22** | 100 | 50 | 48 | 48 | 99.76 | 99.76 |
| 21 | 873 | 5 | 30 | **24** | 100 | 50 | 48 | 48 | 99.77 | 99.77 |
| 21 | 874 | 5 | 30 | 20 | **100** | **50** | 48 | 48 | 99.77 | 99.58 |
| 21 | 875 | 5 | 30 | 20 | **150** | **75** | 48 | 48 | 92.97 | 85.01 |
| 21 | 876 | 5 | 30 | 20 | **200** | **100** | 48 | 48 | 82.47 | 73.84 |
| 21 | 877 | 5 | 30 | 20 | **250** | **125** | 48 | 48 | 78.34 | 67.67 |
| 21 | 878 | 5 | 30 | 20 | **300** | **150** | 48 | 48 | 71.37 | 65.45 |
| 21 | 879 | 5 | 30 | 20 | **350** | **175** | 48 | 48 | 72.27 | 61.07 |
| 21 | 880 | 5 | 30 | 20 | **400** | **200** | 48 | 48 | 67.46 | 55.09 |
| 21 | 881 | 5 | 30 | 20 | 100 | 50 | **1** | **1** | 59.70 | 50.02 |
| 21 | 882 | 5 | 30 | 20 | 100 | 50 | **2** | **2** | 64.00 | 64.35 |
| 21 | 883 | 5 | 30 | 20 | 100 | 50 | **3** | **3** | 68.57 | 71.11 |
| 21 | 884 | 5 | 30 | 20 | 100 | 50 | **4** | **4** | 72.01 | 76.50 |
| 21 | 885 | 5 | 30 | 20 | 100 | 50 | **5** | **5** | 76.09 | 80.68 |
| 21 | 886 | 5 | 30 | 20 | 100 | 50 | **6** | **6** | 80.52 | 84.57 |
| 21 | 887 | 5 | 30 | 20 | 100 | 50 | **7** | **7** | 86.17 | 89.50 |
| 21 | 888 | 5 | 30 | 20 | 100 | 50 | **8** | **8** | 89.64 | 94.68 |
| 21 | 889 | 5 | 30 | 20 | 100 | 50 | **9** | **9** | 92.51 | 97.79 |
| 21 | 890 | 5 | 30 | 20 | 100 | 50 | **10** | **10** | 95.18 | 98.55 |
| 21 | 891 | 5 | 30 | 20 | 100 | 50 | **11** | **11** | 96.96 | 99.55 |
| 21 | 892 | 5 | 30 | 20 | 100 | 50 | **12** | **12** | 98.31 | 99.95 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 21 | 893 | 5 | 30 | 20 | 100 | 50 | **13** | **13** | 99.18 | 99.95 |
| 21 | 894 | 5 | 30 | 20 | 100 | 50 | **14** | **14** | 99.34 | 99.95 |
| 21 | 895 | 5 | 30 | 20 | 100 | 50 | **15** | **15** | 99.58 | 99.95 |
| 21 | 896 | 5 | 30 | 20 | 100 | 50 | **16** | **16** | 99.64 | 99.95 |
| 21 | 897 | 5 | 30 | 20 | 100 | 50 | **17** | **17** | 99.65 | 99.95 |
| Run Nos. 857-861, 874-880 and 881-897 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively | | | | | | | | | | |

Table A.22 Input and output parameters for the simultaneous adsorptionof Cr(VI) and phenol onto the surface of Fe treated tea waste (Fe TW) using synthetic simulated binary solution

| Exp. Set No. | Run No. | Input parameters | | | | | | | Output parameters | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time (h) Cr(VI) | Contact time (h) phenol | % Removal of Cr(VI) | % Removal of phenol |
| 22 | 898 | **2** | 30 | 15 | 100 | 50 | 48 | 48 | 99.25 | 98.10 |
| 22 | 899 | **3** | 30 | 15 | 100 | 50 | 48 | 48 | 98.95 | 97.00 |
| 22 | 900 | **4** | 30 | 15 | 100 | 50 | 48 | 48 | 87.57 | 84.22 |
| 22 | 901 | **5** | 30 | 15 | 100 | 50 | 48 | 48 | 81.25 | 78.44 |
| 22 | 902 | **6** | 30 | 15 | 100 | 50 | 48 | 48 | 75.33 | 71.70 |
| 22 | 903 | **7** | 30 | 15 | 100 | 50 | 48 | 48 | 55.25 | 54.04 |
| 22 | 904 | **8** | 30 | 15 | 100 | 50 | 48 | 48 | 49.10 | 46.44 |
| 22 | 905 | **9** | 30 | 15 | 100 | 50 | 48 | 48 | 36.11 | 36.22 |
| 22 | 906 | 2 | **10** | 15 | 100 | 50 | 48 | 48 | 61.35 | 92.55 |
| 22 | 907 | 2 | **20** | 15 | 100 | 50 | 48 | 48 | 78.24 | 93.62 |
| 22 | 908 | 2 | **30** | 15 | 100 | 50 | 48 | 48 | 89.32 | 96.75 |
| 22 | 909 | 2 | **40** | 15 | 100 | 50 | 48 | 48 | 99.94 | 98.83 |
| 22 | 910 | 2 | **50** | 15 | 100 | 50 | 48 | 48 | 99.34 | 84.86 |
| 22 | 911 | 2 | 30 | **2.5** | 100 | 50 | 48 | 48 | 72.00 | 52.00 |
| 22 | 912 | 2 | 30 | **5** | 100 | 50 | 48 | 48 | 79.83 | 54.25 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 22 | 913 | 2 | 30 | **7.5** | 100 | 50 | 48 | 48 | 89.81 | 78.44 |
| 22 | 914 | 2 | 30 | **10** | 100 | 50 | 48 | 48 | 95.74 | 89.94 |
| 22 | 915 | 2 | 30 | **12.5** | 100 | 50 | 48 | 48 | 98.77 | 94.54 |
| 22 | 916 | 2 | 30 | **15** | 100 | 50 | 48 | 48 | 99.44 | 99.07 |
| 22 | 917 | 2 | 30 | **17.5** | 100 | 50 | 48 | 48 | 99.46 | 99.10 |
| 22 | 918 | 2 | 30 | **20** | 100 | 50 | 48 | 48 | 99.46 | 99.10 |
| 22 | 919 | 2 | 30 | 13 | **100** | **50** | 48 | 48 | 99.50 | 99.60 |
| 22 | 920 | 2 | 30 | 13 | **150** | **75** | 48 | 48 | 98.44 | 89.84 |
| 22 | 921 | 2 | 30 | 13 | **200** | **100** | 48 | 48 | 93.59 | 75.22 |
| 22 | 922 | 2 | 30 | 15 | **250** | **125** | 48 | 48 | 92.66 | 68.41 |
| 22 | 923 | 2 | 30 | 15 | **300** | **150** | 48 | 48 | 91.19 | 63.43 |
| 22 | 924 | 2 | 30 | 15 | **350** | **175** | 48 | 48 | 89.53 | 58.64 |
| 22 | 925 | 2 | 30 | 15 | **400** | **200** | 48 | 48 | 88.43 | 55.09 |
| 22 | 926 | 2 | 30 | 15 | 100 | 50 | **1** | **1** | 73.03 | 20.04 |
| 22 | 927 | 2 | 30 | 15 | 100 | 50 | **2** | **2** | 77.34 | 28.70 |
| 22 | 928 | 2 | 30 | 15 | 100 | 50 | **3** | **3** | 81.90 | 38.22 |
| 22 | 929 | 2 | 30 | 15 | 100 | 50 | **4** | **4** | 85.35 | 47.00 |
| 22 | 930 | 2 | 30 | 15 | 100 | 50 | **5** | **5** | 88.08 | 57.36 |
| 22 | 931 | 2 | 30 | 15 | 100 | 50 | **6** | **6** | 91.85 | 63.14 |
| 22 | 932 | 2 | 30 | 15 | 100 | 50 | **7** | **7** | 93.42 | 69.00 |
| 22 | 933 | 2 | 30 | 15 | 100 | 50 | **8** | **8** | 96.30 | 75.36 |
| 22 | 934 | 2 | 30 | 15 | 100 | 50 | **9** | **9** | 97.84 | 81.58 |
| 22 | 935 | 2 | 30 | 15 | 100 | 50 | **10** | **10** | 99.18 | 87.00 |
| 22 | 936 | 2 | 30 | 15 | 100 | 50 | **11** | **11** | 99.46 | 91.00 |
| 22 | 937 | 2 | 30 | 15 | 100 | 50 | **12** | **12** | 99.61 | 95.79 |
| 22 | 938 | 2 | 30 | 15 | 100 | 50 | **13** | **13** | 99.64 | 96.22 |
| 22 | 939 | 2 | 30 | 15 | 100 | 50 | **14** | **14** | 99.64 | 99.04 |
| 22 | 940 | 2 | 30 | 15 | 100 | 50 | **15** | **15** | 99.64 | 99.90 |
| 22 | 941 | 2 | 30 | 15 | 100 | 50 | **16** | **16** | 99.64 | 99.95 |
| 22 | 942 | 2 | 30 | 15 | 100 | 50 | **17** | **17** | 99.65 | 99.95 |

Run Nos. 906-910, 919-925 and 926-942 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively

Table A.23 Input and output parameters for the simultaneous adsorptionof Cr(VI) and phenol onto the surface of Fe treated Rice husk (Fe RH) using synthetic simulated binary solution

| Exp. Set No. | Run No. | Input parameters | | | | | | | Output parameters | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time (h) Cr(VI) | Contact time (h) phenol | % Removal of Cr(VI) | % Removal of phenol |
| 23 | 943 | **2** | 30 | 9 | 100 | 50 | 48 | 48 | 65.00 | 98.00 |
| 23 | 944 | **3** | 30 | 9 | 100 | 50 | 48 | 48 | 89.00 | 78.00 |
| 23 | 945 | **4** | 30 | 9 | 100 | 50 | 48 | 48 | 95.00 | 90.00 |
| 23 | 946 | **5** | 30 | 9 | 100 | 50 | 48 | 48 | 99.25 | 99.44 |
| 23 | 947 | **6** | 30 | 9 | 100 | 50 | 48 | 48 | 98.77 | 97.57 |
| 23 | 948 | **7** | 30 | 9 | 100 | 50 | 48 | 48 | 96.44 | 91.32 |
| 23 | 949 | **8** | 30 | 9 | 100 | 50 | 48 | 48 | 96.44 | 91.32 |
| 23 | 950 | **9** | 30 | 9 | 100 | 50 | 48 | 48 | 96.44 | 91.30 |
| 23 | 951 | 5 | **10** | 9 | 100 | 50 | 48 | 48 | 84.35 | 94.55 |
| 23 | 952 | 5 | **20** | 9 | 100 | 50 | 48 | 48 | 90.24 | 95.65 |
| 23 | 953 | 5 | **30** | 9 | 100 | 50 | 48 | 48 | 98.32 | 96.75 |
| 23 | 954 | 5 | **40** | 9 | 100 | 50 | 48 | 48 | 99.14 | 98.73 |
| 23 | 955 | 5 | **50** | 9 | 100 | 50 | 48 | 48 | 99.05 | 87.86 |
| 23 | 956 | 5 | 30 | **2** | 100 | 50 | 48 | 48 | 64.96 | 38.66 |
| 23 | 957 | 5 | 30 | **4** | 100 | 50 | 48 | 48 | 84.40 | 59.90 |
| 23 | 958 | 5 | 30 | **6** | 100 | 50 | 48 | 48 | 93.80 | 72.90 |
| 23 | 959 | 5 | 30 | **8** | 100 | 50 | 48 | 48 | 97.20 | 85.12 |
| 23 | 960 | 5 | 30 | **10** | 100 | 50 | 48 | 48 | 98.40 | 97.94 |
| 23 | 961 | 5 | 30 | **12** | 100 | 50 | 48 | 48 | 99.58 | 99.52 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 23 | 962 | 5 | 30 | **14** | 100 | 50 | 48 | 48 | 99.76 | 99.99 |
| 23 | 963 | 5 | 30 | **16** | 100 | 50 | 48 | 48 | 99.76 | 99.99 |
| 23 | 964 | 5 | 30 | 9 | **100** | **50** | 48 | 48 | 98.75 | 98.92 |
| 23 | 965 | 5 | 30 | 9 | **150** | **75** | 48 | 48 | 91.70 | 89.15 |
| 23 | 966 | 5 | 30 | 9 | **200** | **100** | 48 | 48 | 79.66 | 85.92 |
| 23 | 967 | 5 | 30 | 9 | **250** | **125** | 48 | 48 | 76.22 | 84.61 |
| 23 | 968 | 5 | 30 | 9 | **300** | **150** | 48 | 48 | 69.34 | 82.70 |
| 23 | 969 | 5 | 30 | 9 | **350** | **175** | 48 | 48 | 68.03 | 79.91 |
| 23 | 970 | 5 | 30 | 9 | **400** | **200** | 48 | 48 | 59.86 | 75.75 |
| 23 | 971 | 5 | 30 | 9 | 100 | 50 | **1** | **1** | 29.76 | 49.15 |
| 23 | 972 | 5 | 30 | 9 | 100 | 50 | **2** | **2** | 39.36 | 60.16 |
| 23 | 973 | 5 | 30 | 9 | 100 | 50 | **3** | **3** | 53.36 | 72.00 |
| 23 | 974 | 5 | 30 | 9 | 100 | 50 | **4** | **4** | 64.26 | 77.71 |
| 23 | 975 | 5 | 30 | 9 | 100 | 50 | **5** | **5** | 78.76 | 81.34 |
| 23 | 976 | 5 | 30 | 9 | 100 | 50 | **6** | **6** | 83.08 | 86.79 |
| 23 | 977 | 5 | 30 | 9 | 100 | 50 | **7** | **7** | 88.12 | 89.87 |
| 23 | 978 | 5 | 30 | 9 | 100 | 50 | **8** | **8** | 94.92 | 91.37 |
| 23 | 979 | 5 | 30 | 9 | 100 | 50 | **9** | **9** | 97.14 | 93.66 |
| 23 | 980 | 5 | 30 | 9 | 100 | 50 | **10** | **10** | 99.18 | 95.64 |
| 23 | 981 | 5 | 30 | 9 | 100 | 50 | **11** | **11** | 99.26 | 97.64 |
| 23 | 982 | 5 | 30 | 9 | 100 | 50 | **12** | **12** | 99.51 | 98.66 |
| 23 | 983 | 5 | 30 | 9 | 100 | 50 | **13** | **13** | 99.54 | 99.22 |
| 23 | 984 | 5 | 30 | 9 | 100 | 50 | **14** | **14** | 99.54 | 99.74 |

Run Nos. 951-955, 964-970 and 971-984 were used for thermodynamic, Equilibrium and Kinetic modeling, respectively

Table A.24 Growth studies of Bacillus sp. MTCC No. 3166 in single substrate solution

| Exp. Set No. | Run No. | Input parameters | | | | | Output parameters | | |
|---|---|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time (h) | *Bacillus* sp. biomass concentration (mg/L) | *Bacillus* sp. biomass concentration in the presence of Cr(VI) (mg/L) | *Bacillus* sp. biomass concentration in the presence of phenol (mg/L) |
| 24 | 985 | 7 | 37 | 10 | 20 | 3 | 0.1 | 0.07 | 0.09 |
| 24 | 986 | 7 | 37 | 10 | 20 | 6 | 0.24 | 0.09 | 0.1 |
| 24 | 987 | 7 | 37 | 10 | 20 | 9 | 1.394 | 0.15 | 0.14 |
| 24 | 988 | 7 | 37 | 10 | 20 | 12 | 1.557 | 0.23 | 0.18 |
| 24 | 989 | 7 | 37 | 10 | 20 | 15 | 1.806 | 0.67 | 1.02 |
| 24 | 990 | 7 | 37 | 10 | 20 | 18 | 1.931 | 1.123 | 1.234 |
| 24 | 991 | 7 | 37 | 10 | 20 | 21 | 2.012 | 1.345 | 1.443 |
| 24 | 992 | 7 | 37 | 10 | 20 | 24 | 2.037 | 1.523 | 1.646 |
| 24 | 993 | 7 | 37 | 10 | 20 | 27 | 2.047 | 1.533 | 1.678 |
| 24 | 994 | 7 | 37 | 10 | 20 | 30 | 2.057 | 1.534 | 1.68 |
| 24 | 995 | 7 | 37 | 10 | 20 | 33 | 2.023 | 1.535 | 1.682 |
| 24 | 996 | 7 | 37 | 10 | 20 | 36 | 1.989 | 1.421 | 1.666 |
| 24 | 997 | 7 | 37 | 10 | 20 | 39 | 1.971 | 1.401 | 1.534 |
| 24 | 998 | 7 | 37 | 10 | 20 | 42 | 1.928 | 1.372 | 1.523 |
| 24 | 999 | 7 | 37 | 10 | 20 | 45 | 1.915 | 1.342 | 1.512 |
| 24 | 1000 | 7 | 37 | 10 | 20 | 48 | 1.86 | 1.321 | 1.501 |
| 24 | 1001 | 7 | 37 | 10 | 20 | 51 | 1.832 | 1.301 | 1.487 |
| 24 | 1002 | 7 | 37 | 10 | 20 | 54 | 1.832 | 1.301 | 1.487 |
| 24 | 1003 | 7 | 37 | 10 | 20 | 57 | 1.832 | 1.301 | 1.487 |
| 24 | 1004 | 7 | 37 | 10 | 20 | 60 | 1.832 | 1.301 | 1.487 |
| 24 | 1002 | 7 | 37 | 10 | 20 | 63 | 1.736 | 1.293 | 1.477 |
| 24 | 1003 | 7 | 37 | 10 | 20 | 66 | 1.702 | 1.287 | 1.465 |

Table A.25 Growth studies of *Escherichia coli* MTCC No. 5041

| Exp. Set No. | Run No. | Input parameters | | | | Output parameters | |
|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Initial concentration of Cr(VI) (mg/L) | Contact time (h) | *Escherichia coli* biomass concentration (mg/L) | *Escherichia coli* biomass concentration in the presence of Cr(VI) (mg/L) |
| 25 | 1004 | 7 | 37 | 5 | 3 | 0.065 | 0.031 |
| 25 | 1005 | 7 | 37 | 5 | 6 | 0.145 | 0.032 |
| 25 | 1006 | 7 | 37 | 5 | 9 | 0.234 | 0.056 |
| 25 | 1007 | 7 | 37 | 5 | 12 | 0.356 | 0.221 |
| 25 | 1008 | 7 | 37 | 5 | 15 | 0.478 | 0.312 |
| 25 | 1009 | 7 | 37 | 5 | 18 | 0.658 | 0.532 |
| 25 | 1010 | 7 | 37 | 5 | 21 | 0.875 | 0.734 |
| 25 | 1011 | 7 | 37 | 5 | 24 | 1.129 | 0.982 |
| 25 | 1012 | 7 | 37 | 5 | 27 | 1.321 | 1.222 |
| 25 | 1013 | 7 | 37 | 5 | 30 | 1.322 | 1.223 |
| 25 | 1014 | 7 | 37 | 5 | 33 | 1.333 | 1.225 |
| 25 | 1015 | 7 | 37 | 5 | 36 | 1.235 | 1.126 |
| 25 | 1016 | 7 | 37 | 5 | 39 | 1.012 | 0.946 |
| 25 | 1017 | 7 | 37 | 5 | 42 | 0.901 | 0.806 |
| 25 | 1018 | 7 | 37 | 5 | 45 | 0.865 | 0.725 |
| 25 | 1019 | 7 | 37 | 5 | 48 | 0.743 | 0.656 |
| 25 | 1020 | 7 | 37 | 5 | 51 | 0.645 | 0.551 |
| 25 | 1021 | 7 | 37 | 5 | 54 | 0.546 | 0.444 |
| 25 | 1022 | 7 | 37 | 5 | 57 | 0.465 | 0.345 |
| 25 | 1023 | 7 | 37 | 5 | 60 | 0.345 | 0.221 |

Table A.26 Growth curve of pure culture of *Bacillus* sp. MTCC No. 3166 and consortium culture of *Bacillus* sp. MTCC No. 3166 and *Escherichia coli* MTCC No. 5041 for the simultaneous reduction and biodegradation of phenol in binary substrate solution

| Exp. Set No. | Run No. | Input parameters | | | | | Output parameters | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time (h) | pure culture of *Bacillus* sp. biomass concentration (mg/L) | pure culture of *Bacillus* sp. biomass concentration (mg/L) in the presence of Cr(VI) and phenol | Consortium culture of *Escherichia coli* and *Bacillus* sp. biomass concentration | Consortium culture of *Escherichia coli* and *Bacillus* sp. biomass concentration in the presence of Cr(VI) and phenol (mg/L) |
| 26 | 1024 | 7 | 37 | 10 | 20 | 3 | 0.1 | 0.13 | 0.55 | 0.33 |
| 26 | 1025 | 7 | 37 | 10 | 20 | 6 | 0.24 | 0.29 | 0.69 | 0.49 |
| 26 | 1026 | 7 | 37 | 10 | 20 | 9 | 1.394 | 0.45 | 1.844 | 0.65 |
| 26 | 1027 | 7 | 37 | 10 | 20 | 12 | 1.557 | 0.63 | 2.007 | 1.063 |
| 26 | 1028 | 7 | 37 | 10 | 20 | 15 | 1.806 | 1.167 | 2.256 | 1.267 |
| 26 | 1029 | 7 | 37 | 10 | 20 | 18 | 1.931 | 1.223 | 2.381 | 1.423 |
| 26 | 1030 | 7 | 37 | 10 | 20 | 21 | 2.012 | 1.445 | 2.462 | 1.745 |
| 26 | 1031 | 7 | 37 | 10 | 20 | 24 | 2.037 | 1.623 | 2.487 | 1.723 |
| 26 | 1032 | 7 | 37 | 10 | 20 | 27 | 2.047 | 1.633 | 2.497 | 1.733 |
| 26 | 1033 | 7 | 37 | 10 | 20 | 30 | 2.057 | 1.634 | 2.507 | 1.734 |
| 26 | 1034 | 7 | 37 | 10 | 20 | 33 | 2.023 | 1.635 | 2.473 | 1.735 |
| 26 | 1035 | 7 | 37 | 10 | 20 | 36 | 1.989 | 1.521 | 2.439 | 1.621 |
| 26 | 1036 | 7 | 37 | 10 | 20 | 39 | 1.971 | 1.501 | 2.421 | 1.601 |
| 26 | 1037 | 7 | 37 | 10 | 20 | 42 | 1.928 | 1.472 | 2.378 | 1.572 |
| 26 | 1038 | 7 | 37 | 10 | 20 | 45 | 1.915 | 1.242 | 2.365 | 1.442 |
| 26 | 1039 | 7 | 37 | 10 | 20 | 48 | 1.86 | 1.021 | 2.31 | 1.321 |
| 26 | 1040 | 7 | 37 | 10 | 20 | 51 | 1.832 | 0.985 | 2.282 | 1.285 |

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| 26 | 1041 | 7 | 37 | 10 | 20 | 54 | 1.736 | 0.834 | 2.186 | 1.034 |
| 26 | 1042 | 7 | 37 | 10 | 20 | 57 | 1.702 | 0.768 | 2.152 | 0.986 |
| 26 | 1043 | 7 | 37 | 10 | 20 | 60 | 1.702 | 0.768 | 2.152 | 0.986 |

Table A.27 Growth studies of Bacillus sp. MTCC No. 3166 for the acclimatization at different concentrations of Cr(VI) and phenol in single substrate solution

| Exp. Set No. | Run No. | Input parameters |  |  |  |  | Output parameters |  |
|---|---|---|---|---|---|---|---|---|
|  |  | pH | Temp (ºC) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time (h) | *Bacillus* sp. biomass concentration in the presence of Cr(VI) (mg/L) | *Bacillus* sp. biomass concentration in the presence of phenol (mg/L) |
| 27 | 1044 | 7 | 37 | **10** | **20** | 3 | 0.067 | 0.167 |
| 27 | 1045 | 7 | 37 | 10 | 20 | 6 | 0.069 | 0.169 |
| 27 | 1046 | 7 | 37 | 10 | 20 | 9 | 0.394 | 0.594 |
| 27 | 1047 | 7 | 37 | 10 | 20 | 12 | 0.557 | 0.707 |
| 27 | 1048 | 7 | 37 | 10 | 20 | 15 | 0.806 | 0.986 |
| 27 | 1049 | 7 | 37 | 10 | 20 | 18 | 0.931 | 1.299 |
| 27 | 1050 | 7 | 37 | 10 | 20 | 21 | 1.012 | 1.412 |
| 27 | 1051 | 7 | 37 | 10 | 20 | 24 | 1.037 | 1.437 |
| 27 | 1052 | 7 | 37 | 10 | 20 | 27 | 1.047 | 1.447 |
| 27 | 1053 | 7 | 37 | 10 | 20 | 30 | 1.057 | 1.457 |
| 27 | 1054 | 7 | 37 | 10 | 20 | 33 | 1.023 | 1.423 |
| 27 | 1055 | 7 | 37 | 10 | 20 | 36 | 0.989 | 1.389 |
| 27 | 1056 | 7 | 37 | 10 | 20 | 39 | 0.871 | 1.271 |
| 27 | 1057 | 7 | 37 | 10 | 20 | 42 | 0.728 | 1.028 |
| 27 | 1058 | 7 | 37 | 10 | 20 | 45 | 0.615 | 0.915 |
| 27 | 1059 | 7 | 37 | 10 | 20 | 48 | 0.586 | 0.786 |
| 27 | 1060 | 7 | 37 | 10 | 20 | 51 | 0.432 | 0.632 |
| 27 | 1061 | 7 | 37 | 10 | 20 | 63 | 0.336 | 0.536 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 27 | 1062 | 7 | 37 | 10 | 20 | 66 | 0.302 | 0.402 |
| 27 | 1063 | 7 | 37 | **20** | **40** | 3 | 0.017 | 0.121 |
| 27 | 1064 | 7 | 37 | 20 | 40 | 6 | 0.019 | 0.123 |
| 27 | 1065 | 7 | 37 | 20 | 40 | 9 | 0.035 | 0.132 |
| 27 | 1066 | 7 | 37 | 20 | 40 | 12 | 0.223 | 0.443 |
| 27 | 1067 | 7 | 37 | 20 | 40 | 15 | 0.467 | 0.667 |
| 27 | 1068 | 7 | 37 | 20 | 40 | 18 | 0.623 | 0.923 |
| 27 | 1069 | 7 | 37 | 20 | 40 | 21 | 0.945 | 1.245 |
| 27 | 1070 | 7 | 37 | 20 | 40 | 24 | 0.949 | 1.249 |
| 27 | 1071 | 7 | 37 | 20 | 40 | 27 | 0.953 | 1.253 |
| 27 | 1072 | 7 | 37 | 20 | 40 | 30 | 0.965 | 1.265 |
| 27 | 1073 | 7 | 37 | 20 | 40 | 33 | 0.834 | 1.234 |
| 27 | 1074 | 7 | 37 | 20 | 40 | 36 | 0.745 | 1.145 |
| 27 | 1075 | 7 | 37 | 20 | 40 | 39 | 0.656 | 1.056 |
| 27 | 1076 | 7 | 37 | 20 | 40 | 42 | 0.578 | 0.978 |
| 27 | 1077 | 7 | 37 | 20 | 40 | 45 | 0.476 | 0.876 |
| 27 | 1078 | 7 | 37 | 20 | 40 | 48 | 0.321 | 0.721 |
| 27 | 1079 | 7 | 37 | 20 | 40 | 51 | 0.289 | 0.689 |
| 27 | 1080 | 7 | 37 | 20 | 40 | 63 | 0.187 | 0.587 |
| 27 | 1081 | 7 | 37 | 20 | 40 | 66 | 0.126 | 0.426 |
| 27 | 1082 | 7 | 37 | **30** | **60** | 3 | 0.011 | 0.101 |
| 27 | 1083 | 7 | 37 | 30 | 60 | 6 | 0.012 | 0.112 |
| 27 | 1084 | 7 | 37 | 30 | 60 | 9 | 0.015 | 0.115 |
| 27 | 1085 | 7 | 37 | 30 | 60 | 12 | 0.023 | 0.123 |
| 27 | 1086 | 7 | 37 | 30 | 60 | 15 | 0.123 | 0.323 |
| 27 | 1087 | 7 | 37 | 30 | 60 | 18 | 0.321 | 0.621 |
| 27 | 1088 | 7 | 37 | 30 | 60 | 21 | 0.532 | 0.932 |
| 27 | 1089 | 7 | 37 | 30 | 60 | 24 | 0.744 | 1.144 |
| 27 | 1090 | 7 | 37 | 30 | 60 | 27 | 0.834 | 1.154 |
| 27 | 1091 | 7 | 37 | 30 | 60 | 30 | 0.838 | 1.158 |
| 27 | 1092 | 7 | 37 | 30 | 60 | 33 | 0.841 | 1.161 |
| 27 | 1093 | 7 | 37 | 30 | 60 | 36 | 0.815 | 1.015 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 27 | 1094 | 7 | 37 | 30 | 60 | 39 | 0.756 | 0.956 |
| 27 | 1095 | 7 | 37 | 30 | 60 | 42 | 0.664 | 0.864 |
| 27 | 1096 | 7 | 37 | 30 | 60 | 45 | 0.552 | 0.752 |
| 27 | 1097 | 7 | 37 | 30 | 60 | 48 | 0.413 | 0.613 |
| 27 | 1098 | 7 | 37 | 30 | 60 | 51 | 0.398 | 0.508 |
| 27 | 1099 | 7 | 37 | 30 | 60 | 63 | 0.301 | 0.401 |
| 27 | 1100 | 7 | 37 | 30 | 60 | 66 | 0.223 | 0.323 |
| 27 | 1101 | 7 | 37 | **40** | **80** | 3 | 0.005 | 0.086 |
| 27 | 1102 | 7 | 37 | 40 | 80 | 6 | 0.007 | 0.087 |
| 27 | 1103 | 7 | 37 | 40 | 80 | 9 | 0.009 | 0.088 |
| 27 | 1104 | 7 | 37 | 40 | 80 | 12 | 0.013 | 0.096 |
| 27 | 1105 | 7 | 37 | 40 | 80 | 15 | 0.022 | 0.123 |
| 27 | 1106 | 7 | 37 | 40 | 80 | 18 | 0.123 | 0.323 |
| 27 | 1107 | 7 | 37 | 40 | 80 | 21 | 0.222 | 0.622 |
| 27 | 1108 | 7 | 37 | 40 | 80 | 24 | 0.443 | 0.943 |
| 27 | 1109 | 7 | 37 | 40 | 80 | 27 | 0.678 | 1.078 |
| 27 | 1110 | 7 | 37 | 40 | 80 | 30 | 0.681 | 1.081 |
| 27 | 1111 | 7 | 37 | 40 | 80 | 33 | 0.689 | 1.083 |
| 27 | 1112 | 7 | 37 | 40 | 80 | 36 | 0.523 | 1.085 |
| 27 | 1113 | 7 | 37 | 40 | 80 | 39 | 0.423 | 0.973 |
| 27 | 1114 | 7 | 37 | 40 | 80 | 42 | 0.345 | 0.805 |
| 27 | 1115 | 7 | 37 | 40 | 80 | 45 | 0.226 | 0.626 |
| 27 | 1116 | 7 | 37 | 40 | 80 | 48 | 0.192 | 0.592 |
| 27 | 1117 | 7 | 37 | 40 | 80 | 51 | 0.123 | 0.423 |
| 27 | 1118 | 7 | 37 | 40 | 80 | 63 | 0.101 | 0.301 |
| 27 | 1119 | 7 | 37 | 40 | 80 | 66 | 0.098 | 0.208 |
| 27 | 1120 | 7 | 37 | **50** | **100** | 3 | 0.001 | 0.071 |
| 27 | 1121 | 7 | 37 | 50 | 100 | 6 | 0.003 | 0.073 |
| 27 | 1122 | 7 | 37 | 50 | 100 | 9 | 0.005 | 0.075 |
| 27 | 1123 | 7 | 37 | 50 | 100 | 12 | 0.007 | 0.077 |
| 27 | 1124 | 7 | 37 | 50 | 100 | 15 | 0.009 | 0.079 |
| 27 | 1125 | 7 | 37 | 50 | 100 | 18 | 0.057 | 0.087 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 27 | 1126 | 7 | 37 | 50 | 100 | 21 | 0.198 | 0.199 |
| 27 | 1127 | 7 | 37 | 50 | 100 | 24 | 0.245 | 0.255 |
| 27 | 1128 | 7 | 37 | 50 | 100 | 27 | 0.356 | 0.456 |
| 27 | 1129 | 7 | 37 | 50 | 100 | 30 | 0.432 | 0.532 |
| 27 | 1130 | 7 | 37 | 50 | 100 | 33 | 0.435 | 0.535 |
| 27 | 1131 | 7 | 37 | 50 | 100 | 36 | 0.444 | 0.544 |
| 27 | 1132 | 7 | 37 | 50 | 100 | 39 | 0.281 | 0.581 |
| 27 | 1133 | 7 | 37 | 50 | 100 | 42 | 0.212 | 0.312 |
| 27 | 1134 | 7 | 37 | 50 | 100 | 45 | 0.189 | 0.289 |
| 27 | 1135 | 7 | 37 | 50 | 100 | 48 | 0.152 | 0.152 |
| 27 | 1136 | 7 | 37 | 50 | 100 | 51 | 0.134 | 0.144 |
| 27 | 1137 | 7 | 37 | 50 | 100 | 63 | 0.101 | 0.121 |
| 27 | 1138 | 7 | 37 | 50 | 100 | 66 | 0.067 | 0.107 |

Table A.28 Acclimatization of *Escherichia coli* MTCC No. 5041 to the various concentrations of Cr(VI) in single substrate solution

| Exp. Set No. | Run No. | Input parameters | | | | Output parameters |
|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Initial concentration of Cr(VI) (mg/L) | Contact time (h) | *Escherichia coli* biomass concentration in the presence of Cr(VI) (mg/L) |
| 28 | 1139 | 7 | 37 | **5** | 3 | 0.036 |
| 28 | 1140 | 7 | 37 | 5 | 6 | 0.038 |
| 28 | 1141 | 7 | 37 | 5 | 9 | 0.363 |
| 28 | 1142 | 7 | 37 | 5 | 12 | 0.526 |
| 28 | 1143 | 7 | 37 | 5 | 15 | 0.775 |
| 28 | 1144 | 7 | 37 | 5 | 18 | 0.9 |
| 28 | 1145 | 7 | 37 | 5 | 21 | 0.981 |
| 28 | 1146 | 7 | 37 | 5 | 24 | 1.006 |
| 28 | 1147 | 7 | 37 | 5 | 27 | 1.016 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 28 | 1148 | 7 | 37 | 5 | 30 | 1.026 |
| 28 | 1149 | 7 | 37 | 5 | 33 | 0.992 |
| 28 | 1150 | 7 | 37 | 5 | 36 | 0.958 |
| 28 | 1151 | 7 | 37 | 5 | 39 | 0.84 |
| 28 | 1152 | 7 | 37 | 5 | 42 | 0.697 |
| 28 | 1153 | 7 | 37 | 5 | 45 | 0.584 |
| 28 | 1154 | 7 | 37 | 5 | 48 | 0.555 |
| 28 | 1155 | 7 | 37 | 5 | 51 | 0.401 |
| 28 | 1156 | 7 | 37 | 5 | 63 | 0.305 |
| 28 | 1157 | 7 | 37 | 5 | 66 | 0.271 |
| 28 | 1158 | 7 | 37 | **10** | 3 | 0.007 |
| 28 | 1159 | 7 | 37 | 10 | 6 | 0.009 |
| 28 | 1160 | 7 | 37 | 10 | 9 | 0.025 |
| 28 | 1161 | 7 | 37 | 10 | 12 | 0.213 |
| 28 | 1162 | 7 | 37 | 10 | 15 | 0.457 |
| 28 | 1163 | 7 | 37 | 10 | 18 | 0.613 |
| 28 | 1164 | 7 | 37 | 10 | 21 | 0.935 |
| 28 | 1165 | 7 | 37 | 10 | 24 | 0.939 |
| 28 | 1166 | 7 | 37 | 10 | 27 | 0.943 |
| 28 | 1167 | 7 | 37 | 10 | 30 | 0.955 |
| 28 | 1168 | 7 | 37 | 10 | 33 | 0.824 |
| 28 | 1169 | 7 | 37 | 10 | 36 | 0.735 |
| 28 | 1170 | 7 | 37 | 10 | 39 | 0.646 |
| 28 | 1171 | 7 | 37 | 10 | 42 | 0.568 |
| 28 | 1172 | 7 | 37 | 10 | 45 | 0.466 |
| 28 | 1173 | 7 | 37 | 10 | 48 | 0.311 |
| 28 | 1174 | 7 | 37 | 10 | 51 | 0.279 |
| 28 | 1175 | 7 | 37 | 10 | 63 | 0.177 |
| 28 | 1176 | 7 | 37 | 10 | 66 | 0.116 |
| 28 | 1177 | 7 | 37 | **15** | 3 | 0.002 |
| 28 | 1178 | 7 | 37 | 15 | 6 | 0.003 |
| 28 | 1179 | 7 | 37 | 15 | 9 | 0.006 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 28 | 1180 | 7 | 37 | 15 | 12 | 0.014 |
| 28 | 1181 | 7 | 37 | 15 | 15 | 0.114 |
| 28 | 1182 | 7 | 37 | 15 | 18 | 0.312 |
| 28 | 1183 | 7 | 37 | 15 | 21 | 0.523 |
| 28 | 1184 | 7 | 37 | 15 | 24 | 0.735 |
| 28 | 1185 | 7 | 37 | 15 | 27 | 0.825 |
| 28 | 1186 | 7 | 37 | 15 | 30 | 0.829 |
| 28 | 1187 | 7 | 37 | 15 | 33 | 0.832 |
| 28 | 1188 | 7 | 37 | 15 | 36 | 0.806 |
| 28 | 1189 | 7 | 37 | 15 | 39 | 0.747 |
| 28 | 1190 | 7 | 37 | 15 | 42 | 0.655 |
| 28 | 1191 | 7 | 37 | 15 | 45 | 0.543 |
| 28 | 1192 | 7 | 37 | 15 | 48 | 0.404 |
| 28 | 1193 | 7 | 37 | 15 | 51 | 0.389 |
| 28 | 1194 | 7 | 37 | 15 | 63 | 0.292 |
| 28 | 1195 | 7 | 37 | 15 | 66 | 0.214 |
| 28 | 1196 | 7 | 37 | **20** | 3 | 0.0009 |
| 28 | 1197 | 7 | 37 | 20 | 6 | 0.001 |
| 28 | 1198 | 7 | 37 | 20 | 9 | 0.005 |
| 28 | 1199 | 7 | 37 | 20 | 12 | 0.006 |
| 28 | 1200 | 7 | 37 | 20 | 15 | 0.007 |
| 28 | 1201 | 7 | 37 | 20 | 18 | 0.109 |
| 28 | 1202 | 7 | 37 | 20 | 21 | 0.231 |
| 28 | 1203 | 7 | 37 | 20 | 24 | 0.445 |
| 28 | 1204 | 7 | 37 | 20 | 27 | 0.756 |
| 28 | 1205 | 7 | 37 | 20 | 30 | 0.758 |
| 28 | 1206 | 7 | 37 | 20 | 33 | 0.761 |
| 28 | 1207 | 7 | 37 | 20 | 36 | 0.762 |
| 28 | 1208 | 7 | 37 | 20 | 39 | 0.701 |
| 28 | 1209 | 7 | 37 | 20 | 42 | 0.678 |
| 28 | 1210 | 7 | 37 | 20 | 45 | 0.589 |
| 28 | 1211 | 7 | 37 | 20 | 48 | 0.307 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 28 | 1212 | 7 | 37 | 20 | 51 | 0.227 |
| 28 | 1213 | 7 | 37 | 20 | 63 | 0.189 |
| 28 | 1214 | 7 | 37 | 20 | 66 | 0.101 |
| 28 | 1215 | 7 | 37 | **25** | 3 | 0.0003 |
| 28 | 1216 | 7 | 37 | 25 | 6 | 0.0004 |
| 28 | 1217 | 7 | 37 | 25 | 9 | 0.0007 |
| 28 | 1218 | 7 | 37 | 25 | 12 | 0.0009 |
| 28 | 1219 | 7 | 37 | 25 | 15 | 0.083 |
| 28 | 1220 | 7 | 37 | 25 | 18 | 0.108 |
| 28 | 1221 | 7 | 37 | 25 | 21 | 0.223 |
| 28 | 1222 | 7 | 37 | 25 | 24 | 0.345 |
| 28 | 1223 | 7 | 37 | 25 | 27 | 0.556 |
| 28 | 1224 | 7 | 37 | 25 | 30 | 0.557 |
| 28 | 1225 | 7 | 37 | 25 | 33 | 0.559 |
| 28 | 1226 | 7 | 37 | 25 | 36 | 0.561 |
| 28 | 1227 | 7 | 37 | 25 | 39 | 0.564 |
| 28 | 1228 | 7 | 37 | 25 | 42 | 0.456 |
| 28 | 1229 | 7 | 37 | 25 | 45 | 0.387 |
| 28 | 1230 | 7 | 37 | 25 | 48 | 0.234 |
| 28 | 1231 | 7 | 37 | 25 | 51 | 0.198 |
| 28 | 1232 | 7 | 37 | 25 | 63 | 0.121 |
| 28 | 1233 | 7 | 37 | 25 | 66 | 0.102 |

Table A.29 Growth curve of pure culture of *Bacillus* sp. MTCC No. 3166 and consortium culture of *Bacillus* sp. MTCC No. 3166 and *Escherichia coli* MTCC No. 5041 for the simultaneous reduction and biodegradation of phenol in binary substrate solution

| Exp. Set No. | Run No. | Input parameters | | | | | Output parameters | |
|---|---|---|---|---|---|---|---|---|
| | | pH | Temp (ºC) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time (h) | Pure culture of *Bacillus* sp. biomass concentration in the presence of Cr(VI) and phenol (mg/L) | Consortium culture of *Escherichia coli* and *Bacillus* sp. biomass concentration in the presence of Cr(VI) and phenol (mg/L) |
| 29 | 1234 | 7 | 37 | **10** | **20** | 3 | 0.067 | 0.203 |
| 29 | 1235 | 7 | 37 | 10 | 20 | 6 | 0.069 | 0.205 |
| 29 | 1236 | 7 | 37 | 10 | 20 | 9 | 0.394 | 0.221 |
| 29 | 1237 | 7 | 37 | 10 | 20 | 12 | 0.557 | 0.409 |
| 29 | 1238 | 7 | 37 | 10 | 20 | 15 | 0.806 | 1.067 |
| 29 | 1239 | 7 | 37 | 10 | 20 | 18 | 0.931 | 1.11 |
| 29 | 1240 | 7 | 37 | 10 | 20 | 21 | 1.012 | 1.131 |
| 29 | 1241 | 7 | 37 | 10 | 20 | 24 | 1.037 | 1.135 |
| 29 | 1242 | 7 | 37 | 10 | 20 | 27 | 1.047 | 1.139 |
| 29 | 1243 | 7 | 37 | 10 | 20 | 30 | 1.057 | 1.151 |
| 29 | 1244 | 7 | 37 | 10 | 20 | 33 | 1.023 | 1.02 |
| 29 | 1245 | 7 | 37 | 10 | 20 | 36 | 0.989 | 0.931 |
| 29 | 1246 | 7 | 37 | 10 | 20 | 39 | 0.871 | 0.842 |
| 29 | 1247 | 7 | 37 | 10 | 20 | 42 | 0.728 | 0.764 |
| 29 | 1248 | 7 | 37 | 10 | 20 | 45 | 0.615 | 0.662 |
| 29 | 1249 | 7 | 37 | 10 | 20 | 48 | 0.586 | 0.507 |
| 29 | 1250 | 7 | 37 | 10 | 20 | 51 | 0.432 | 0.475 |
| 29 | 1251 | 7 | 37 | 10 | 20 | 63 | 0.336 | 0.373 |
| 29 | 1252 | 7 | 37 | 10 | 20 | 66 | 0.302 | 0.312 |
| 29 | 1253 | 7 | 37 | **20** | **40** | 3 | 0.017 | 0.107 |
| 29 | 1254 | 7 | 37 | 20 | 40 | 6 | 0.019 | 0.109 |
| 29 | 1255 | 7 | 37 | 20 | 40 | 9 | 0.035 | 0.125 |
| 29 | 1256 | 7 | 37 | 20 | 40 | 12 | 0.223 | 0.313 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 29 | 1257 | 7 | 37 | 20 | 40 | 15 | 0.467 | 0.923 |
| 29 | 1258 | 7 | 37 | 20 | 40 | 18 | 0.623 | 0.999 |
| 29 | 1259 | 7 | 37 | 20 | 40 | 21 | 0.945 | 1.035 |
| 29 | 1260 | 7 | 37 | 20 | 40 | 24 | 0.949 | 1.039 |
| 29 | 1261 | 7 | 37 | 20 | 40 | 27 | 0.953 | 1.043 |
| 29 | 1262 | 7 | 37 | 20 | 40 | 30 | 0.965 | 1.055 |
| 29 | 1263 | 7 | 37 | 20 | 40 | 33 | 0.834 | 0.924 |
| 29 | 1264 | 7 | 37 | 20 | 40 | 36 | 0.745 | 0.835 |
| 29 | 1265 | 7 | 37 | 20 | 40 | 39 | 0.656 | 0.746 |
| 29 | 1266 | 7 | 37 | 20 | 40 | 42 | 0.578 | 0.668 |
| 29 | 1267 | 7 | 37 | 20 | 40 | 45 | 0.476 | 0.566 |
| 29 | 1268 | 7 | 37 | 20 | 40 | 48 | 0.321 | 0.411 |
| 29 | 1269 | 7 | 37 | 20 | 40 | 51 | 0.289 | 0.379 |
| 29 | 1270 | 7 | 37 | 20 | 40 | 63 | 0.187 | 0.277 |
| 29 | 1271 | 7 | 37 | 20 | 40 | 66 | 0.126 | 0.216 |
| 29 | 1272 | 7 | 37 | **30** | **60** | 3 | 0.011 | 0.091 |
| 29 | 1273 | 7 | 37 | 30 | 60 | 6 | 0.012 | 0.092 |
| 29 | 1274 | 7 | 37 | 30 | 60 | 9 | 0.015 | 0.095 |
| 29 | 1275 | 7 | 37 | 30 | 60 | 12 | 0.023 | 0.103 |
| 29 | 1276 | 7 | 37 | 30 | 60 | 15 | 0.123 | 0.203 |
| 29 | 1277 | 7 | 37 | 30 | 60 | 18 | 0.321 | 0.789 |
| 29 | 1278 | 7 | 37 | 30 | 60 | 21 | 0.532 | 0.8 |
| 29 | 1279 | 7 | 37 | 30 | 60 | 24 | 0.744 | 0.824 |
| 29 | 1280 | 7 | 37 | 30 | 60 | 27 | 0.834 | 0.914 |
| 29 | 1281 | 7 | 37 | 30 | 60 | 30 | 0.838 | 0.918 |
| 29 | 1282 | 7 | 37 | 30 | 60 | 33 | 0.841 | 0.921 |
| 29 | 1283 | 7 | 37 | 30 | 60 | 36 | 0.815 | 0.895 |
| 29 | 1284 | 7 | 37 | 30 | 60 | 39 | 0.756 | 0.836 |
| 29 | 1285 | 7 | 37 | 30 | 60 | 42 | 0.664 | 0.744 |
| 29 | 1286 | 7 | 37 | 30 | 60 | 45 | 0.552 | 0.632 |
| 29 | 1287 | 7 | 37 | 30 | 60 | 48 | 0.413 | 0.493 |
| 29 | 1288 | 7 | 37 | 30 | 60 | 51 | 0.398 | 0.478 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 29 | 1289 | 7 | 37 | 30 | 60 | 63 | 0.301 | 0.381 |
| 29 | 1290 | 7 | 37 | 30 | 60 | 66 | 0.223 | 0.303 |
| 29 | 1291 | 7 | 37 | **40** | **80** | 3 | 0.005 | 0.074 |
| 29 | 1292 | 7 | 37 | 40 | 80 | 6 | 0.007 | 0.076 |
| 29 | 1293 | 7 | 37 | 40 | 80 | 9 | 0.009 | 0.078 |
| 29 | 1294 | 7 | 37 | 40 | 80 | 12 | 0.013 | 0.082 |
| 29 | 1295 | 7 | 37 | 40 | 80 | 15 | 0.022 | 0.091 |
| 29 | 1296 | 7 | 37 | 40 | 80 | 18 | 0.123 | 0.192 |
| 29 | 1297 | 7 | 37 | 40 | 80 | 21 | 0.222 | 0.591 |
| 29 | 1298 | 7 | 37 | 40 | 80 | 24 | 0.443 | 0.701 |
| 29 | 1299 | 7 | 37 | 40 | 80 | 27 | 0.678 | 0.747 |
| 29 | 1300 | 7 | 37 | 40 | 80 | 30 | 0.681 | 0.75 |
| 29 | 1301 | 7 | 37 | 40 | 80 | 33 | 0.689 | 0.758 |
| 29 | 1302 | 7 | 37 | 40 | 80 | 36 | 0.523 | 0.592 |
| 29 | 1303 | 7 | 37 | 40 | 80 | 39 | 0.423 | 0.492 |
| 29 | 1304 | 7 | 37 | 40 | 80 | 42 | 0.345 | 0.414 |
| 29 | 1305 | 7 | 37 | 40 | 80 | 45 | 0.226 | 0.295 |
| 29 | 1306 | 7 | 37 | 40 | 80 | 48 | 0.192 | 0.261 |
| 29 | 1307 | 7 | 37 | 40 | 80 | 51 | 0.123 | 0.192 |
| 29 | 1308 | 7 | 37 | 40 | 80 | 63 | 0.101 | 0.17 |
| 29 | 1309 | 7 | 37 | 40 | 80 | 66 | 0.098 | 0.167 |
| 29 | 1310 | 7 | 37 | **50** | **100** | 3 | 0.001 | 0.059 |
| 29 | 1311 | 7 | 37 | 50 | 100 | 6 | 0.003 | 0.061 |
| 29 | 1312 | 7 | 37 | 50 | 100 | 9 | 0.005 | 0.063 |
| 29 | 1313 | 7 | 37 | 50 | 100 | 12 | 0.007 | 0.065 |
| 29 | 1314 | 7 | 37 | 50 | 100 | 15 | 0.009 | 0.067 |
| 29 | 1315 | 7 | 37 | 50 | 100 | 18 | 0.057 | 0.115 |
| 29 | 1316 | 7 | 37 | 50 | 100 | 21 | 0.198 | 0.256 |
| 29 | 1317 | 7 | 37 | 50 | 100 | 24 | 0.245 | 0.303 |
| 29 | 1318 | 7 | 37 | 50 | 100 | 27 | 0.356 | 0.414 |
| 29 | 1319 | 7 | 37 | 50 | 100 | 30 | 0.432 | 0.49 |
| 29 | 1320 | 7 | 37 | 50 | 100 | 33 | 0.435 | 0.493 |

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| 29 | 1321 | 7 | 37 | 50 | 100 | 36 | 0.444 | 0.502 |
| 29 | 1322 | 7 | 37 | 50 | 100 | 39 | 0.281 | 0.339 |
| 29 | 1323 | 7 | 37 | 50 | 100 | 42 | 0.212 | 0.27 |
| 29 | 1324 | 7 | 37 | 50 | 100 | 45 | 0.189 | 0.247 |
| 29 | 1325 | 7 | 37 | 50 | 100 | 48 | 0.152 | 0.21 |
| 29 | 1326 | 7 | 37 | 50 | 100 | 51 | 0.134 | 0.192 |
| 29 | 1327 | 7 | 37 | 50 | 100 | 63 | 0.101 | 0.159 |
| 29 | 1328 | 7 | 37 | 50 | 100 | 66 | 0.067 | 0.125 |

Table A.30 Input and output parameters for the simultaneous adsorption and bioaccumulation of Cr(VI) using *Escherichia coli* immobilized GAC for synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters |  |  | Output parameters |
|---|---|---|---|---|---|
|  |  | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 30 | 1329 | **1.25** | 100 | 90 | 15 |
| 30 | 1330 | **2.5** | 100 | 90 | 20 |
| 30 | 1331 | **3.75** | 100 | 90 | 26 |
| 30 | 1332 | **5** | 100 | 90 | 30 |
| 30 | 1333 | **6.25** | 100 | 90 | 35 |
| 30 | 1334 | **7.5** | 100 | 90 | 48 |
| 30 | 1335 | **8.75** | 100 | 90 | 55 |
| 30 | 1336 | **10** | 100 | 90 | 64 |
| 30 | 1337 | **11.25** | 100 | 90 | 78 |
| 30 | 1338 | **12.5** | 100 | 90 | 98.98 |
| 30 | 1339 | **13.75** | 100 | 90 | 99.80 |
| 30 | 1340 | **15** | 100 | 90 | 99.84 |
| 30 | 1341 | **16.25** | 100 | 90 | 99.90 |
| 30 | 1342 | **17.5** | 100 | 90 | 99.99 |
| 30 | 1343 | 12.5 | **100** | 90 | 98.52 |
| 30 | 1344 | 12.5 | **150** | 90 | 79.85 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 30 | 1345 | 12.5 | **200** | 90 | 67.61 |
| 30 | 1346 | 12.5 | **250** | 90 | 57.29 |
| 30 | 1347 | 12.5 | **300** | 90 | 51.11 |
| 30 | 1348 | 12.5 | **350** | 90 | 45.49 |
| 30 | 1349 | 12.5 | **400** | 90 | 41.42 |
| 30 | 1350 | 12.5 | **450** | 90 | 36.22 |
| 30 | 1351 | 12.5 | **500** | 90 | 30.00 |
| 30 | 1352 | 12.5 | 100 | **6** | 14.07 |
| 30 | 1353 | 12.5 | 100 | **12** | 32.59 |
| 30 | 1354 | 12.5 | 100 | **18** | 39.19 |
| 30 | 1355 | 12.5 | 100 | **24** | 46.58 |
| 30 | 1356 | 12.5 | 100 | **30** | 53.79 |
| 30 | 1357 | 12.5 | 100 | **36** | 73.25 |
| 30 | 1358 | 12.5 | 100 | **42** | 80.44 |
| 30 | 1359 | 12.5 | 100 | **48** | 87.92 |
| 30 | 1360 | 12.5 | 100 | **54** | 95.92 |
| 30 | 1361 | 12.5 | 100 | **60** | 99.62 |
| 30 | 1362 | 12.5 | 100 | **66** | 99.99 |
| Run Nos. 1343-1351, 1352-1362 were used for Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |

Table A.31 Input and output parameters for the simultaneous adsorption and bioaccumulation of Cr(VI) using *Bacillus* sp. immobilized GAC for synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters |  |  | Output parameters |
|---|---|---|---|---|---|
|  |  | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 31 | 1363 | **1.25** | 100 | 90 | 7.88 |
| 31 | 1364 | **2.5** | 100 | 90 | 25.44 |
| 31 | 1365 | **3.75** | 100 | 90 | 35.68 |
| 31 | 1366 | **5** | 100 | 90 | 49.04 |
| 31 | 1367 | **6.25** | 100 | 90 | 58.79 |

| | | | | | |
|---|---|---|---|---|---|
| 31 | 1368 | **7.5** | 100 | 90 | 71.57 |
| 31 | 1369 | **8.75** | 100 | 90 | 82.66 |
| 31 | 1370 | **10** | 100 | 90 | 90.44 |
| 31 | 1371 | **11.25** | 100 | 90 | 98.84 |
| 31 | 1372 | **12.5** | 100 | 90 | 99.31 |
| 31 | 1373 | **13.75** | 100 | 90 | 99.60 |
| 31 | 1374 | **15** | 100 | 90 | 99.74 |
| 31 | 1375 | **16.25** | 100 | 90 | 99.80 |
| 31 | 1376 | 12.5 | **100** | 90 | 99.13 |
| 31 | 1377 | 12.5 | **150** | 90 | 84.97 |
| 31 | 1378 | 12.5 | **200** | 90 | 79.56 |
| 31 | 1379 | 12.5 | **250** | 90 | 73.61 |
| 31 | 1380 | 12.5 | **300** | 90 | 68.11 |
| 31 | 1381 | 12.5 | **350** | 90 | 64.22 |
| 31 | 1382 | 12.5 | **400** | 90 | 59.78 |
| 31 | 1383 | 12.5 | **450** | 90 | 55.56 |
| 31 | 1384 | 12.5 | **500** | 90 | 48.80 |
| 31 | 1385 | 12.5 | 100 | **6** | 7.40 |
| 31 | 1386 | 12.5 | 100 | **12** | 25.92 |
| 31 | 1387 | 12.5 | 100 | **18** | 32.53 |
| 31 | 1388 | 12.5 | 100 | **24** | 39.91 |
| 31 | 1389 | 12.5 | 100 | **30** | 47.12 |
| 31 | 1390 | 12.5 | 100 | **36** | 66.59 |
| 31 | 1391 | 12.5 | 100 | **42** | 73.77 |
| 31 | 1392 | 12.5 | 100 | **48** | 81.25 |
| 31 | 1393 | 12.5 | 100 | **54** | 89.25 |
| 31 | 1394 | 12.5 | 100 | **60** | 95.65 |
| 31 | 1395 | 12.5 | 100 | **66** | 99.99 |
| 31 | 1396 | 12.5 | 100 | **72** | 99.99 |
| 31 | 1397 | 12.5 | 100 | **78** | 99.99 |
| 31 | 1398 | 12.5 | 100 | **84** | 99.99 |

Run Nos. 1376-1384, 1385-1398 were used for Equilibrium and Kinetic modeling, respectively

Table A.32 Input and output parameters for the simultaneous adsorption and bioaccumulation of Cr(VI) using *Escherichia coli* immobilized TW for synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | Output parameters |
|---|---|---|---|---|---|
| | | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 32 | 1399 | **1.25** | 100 | 90 | 91.28 |
| 32 | 1400 | **2.5** | 100 | 90 | 95.44 |
| 32 | 1401 | **3.75** | 100 | 90 | 98.68 |
| 32 | 1402 | **5** | 100 | 90 | 99.04 |
| 32 | 1403 | **6.25** | 100 | 90 | 99.79 |
| 32 | 1404 | **7.5** | 100 | 90 | 99.87 |
| 32 | 1405 | **8.75** | 100 | 90 | 99.96 |
| 32 | 1406 | **10** | 100 | 90 | 99.99 |
| 32 | 1407 | 5 | **100** | 90 | 99.99 |
| 32 | 1408 | 5 | **150** | 90 | 99.99 |
| 32 | 1409 | 5 | **200** | 90 | 96.80 |
| 32 | 1410 | 5 | **250** | 90 | 96.23 |
| 32 | 1411 | 5 | **300** | 90 | 94.89 |
| 32 | 1412 | 5 | **350** | 90 | 92.32 |
| 32 | 1413 | 5 | **400** | 90 | 88.55 |
| 32 | 1414 | 5 | **450** | 90 | 87.37 |
| 32 | 1415 | 5 | **500** | 90 | 84.34 |
| 32 | 1416 | 5 | 100 | **3** | 75.41 |
| 32 | 1417 | 5 | 100 | **6** | 77.15 |
| 32 | 1418 | 5 | 100 | **9** | 79.53 |
| 32 | 1419 | 5 | 100 | **12** | 83.93 |
| 32 | 1420 | 5 | 100 | **15** | 89.93 |
| 32 | 1421 | 5 | 100 | **18** | 91.93 |
| 32 | 1422 | 5 | 100 | **21** | 95.27 |

| | | | | | |
|---|---|---|---|---|---|
| 32 | 1423 | 5 | 100 | **24** | 98.37 |
| 32 | 1424 | 5 | 100 | **27** | 99.56 |
| 32 | 1425 | 5 | 100 | **30** | 95.65 |
| 32 | 1426 | 5 | 100 | **33** | 99.99 |
| 32 | 1427 | 5 | 100 | **36** | 99.99 |
| Run Nos. 1407-1415, 1416-1427 were used for Equilibrium and Kinetic modeling, respectively | | | | | |

Table A.33 Input and output parameters for the simultaneous adsorption and bioaccumulation of Cr(VI) using *Bacillus* sp. immobilized TW for synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | Output parameters |
|---|---|---|---|---|---|
| | | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 33 | 1428 | **1** | 100 | 90 | 45.92 |
| 33 | 1429 | **2** | 100 | 90 | 53.51 |
| 33 | 1430 | **3** | 100 | 90 | 59.92 |
| 33 | 1431 | **4** | 100 | 90 | 69.73 |
| 33 | 1432 | **5** | 100 | 90 | 77.21 |
| 33 | 1433 | **6** | 100 | 90 | 89.81 |
| 33 | 1434 | **7** | 100 | 90 | 99.57 |
| 33 | 1435 | **8** | 100 | 90 | 99.69 |
| 33 | 1436 | **9** | 100 | 90 | 99.99 |
| 33 | 1437 | **10** | 100 | 90 | 99.99 |
| 33 | 1438 | 7 | **100** | 90 | 99.93 |
| 33 | 1439 | 7 | **150** | 90 | 99.70 |
| 33 | 1440 | 7 | **200** | 90 | 82.13 |
| 33 | 1441 | 7 | **250** | 90 | 74.24 |
| 33 | 1442 | 7 | **300** | 90 | 70.63 |
| 33 | 1443 | 7 | **350** | 90 | 65.69 |
| 33 | 1444 | 7 | **400** | 90 | 61.11 |
| 33 | 1445 | 7 | **450** | 90 | 58.68 |

| | | | | | |
|---|---|---|---|---|---|
| 33 | 1446 | 7 | **500** | 90 | 55.94 |
| 33 | 1447 | 7 | 100 | **6** | 14.06 |
| 33 | 1448 | 7 | 100 | **12** | 32.59 |
| 33 | 1449 | 7 | 100 | **18** | 46.58 |
| 33 | 1450 | 7 | 100 | **24** | 53.79 |
| 33 | 1451 | 7 | 100 | **30** | 73.25 |
| 33 | 1452 | 7 | 100 | **36** | 80.44 |
| 33 | 1453 | 7 | 100 | **42** | 87.92 |
| 33 | 1454 | 7 | 100 | **48** | 95.92 |
| 33 | 1455 | 7 | 100 | **54** | 99.36 |
| 33 | 1456 | 7 | 100 | **60** | 99.95 |
| 33 | 1457 | 7 | 100 | **66** | 99.99 |
| Run Nos. 1438-1446, 1447-1457 were used for Equilibrium and Kinetic modeling, respectively | | | | | |

Table A.34 Input and output parameters for the simultaneous adsorption and bioaccumulation of Cr(VI) using *Escherichia coli* immobilized RH for synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | Output parameters |
|---|---|---|---|---|---|
| | | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 34 | 1458 | **1.25** | 100 | 90 | 81.59 |
| 34 | 1459 | **2.5** | 100 | 90 | 83.51 |
| 34 | 1460 | **3.75** | 100 | 90 | 88.50 |
| 34 | 1461 | **5** | 100 | 90 | 89.73 |
| 34 | 1462 | **6.25** | 100 | 90 | 91.82 |
| 34 | 1463 | **7.5** | 100 | 90 | 92.81 |
| 34 | 1464 | **8.75** | 100 | 90 | 93.88 |
| 34 | 1465 | **10** | 100 | 90 | 95.69 |
| 34 | 1466 | **11.25** | 100 | 90 | 97.69 |
| 34 | 1467 | **12.5** | 100 | 90 | 99.99 |
| 34 | 1468 | **13.75** | 100 | 90 | 99.99 |

| | | | | | |
|---|---|---|---|---|---|
| 34 | 1469 | **15** | 100 | 90 | 99.99 |
| 34 | 1470 | 12.5 | **100** | 90 | 99.99 |
| 34 | 1471 | 12.5 | **150** | 90 | 96.47 |
| 34 | 1472 | 12.5 | **200** | 90 | 94.85 |
| 34 | 1473 | 12.5 | **250** | 90 | 91.98 |
| 34 | 1474 | 12.5 | **300** | 90 | 89.20 |
| 34 | 1475 | 12.5 | **350** | 90 | 87.55 |
| 34 | 1476 | 12.5 | **400** | 90 | 85.89 |
| 34 | 1477 | 12.5 | **450** | 90 | 81.68 |
| 34 | 1478 | 12.5 | **500** | 90 | 78.94 |
| 34 | 1479 | 12.5 | 100 | **6** | 31.88 |
| 34 | 1480 | 12.5 | 100 | **12** | 43.76 |
| 34 | 1481 | 12.5 | 100 | **18** | 56.66 |
| 34 | 1482 | 12.5 | 100 | **24** | 66.88 |
| 34 | 1483 | 12.5 | 100 | **30** | 75.24 |
| 34 | 1484 | 12.5 | 100 | **36** | 79.55 |
| 34 | 1485 | 12.5 | 100 | **42** | 83.92 |
| 34 | 1486 | 12.5 | 100 | **48** | 88.83 |
| 34 | 1487 | 12.5 | 100 | **54** | 94.91 |
| 34 | 1488 | 12.5 | 100 | **60** | 99.95 |
| 34 | 1489 | 12.5 | 100 | **66** | 99.99 |
| Run Nos. 1470-1478, 1479-1489 were used for Equilibrium and Kinetic modeling, respectively | | | | | |

Table A.35 Input and output parameters for the simultaneous adsorption and bioaccumulation of Cr(VI) using *Bacillus* sp.immobilized RH for synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | Output parameters |
|---|---|---|---|---|---|
| | | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 35 | 1490 | **1.25** | 100 | 90 | 34.88 |
| 35 | 1491 | **2.5** | 100 | 90 | 55.22 |

| | | | | | |
|---|---|---|---|---|---|
| 35 | 1492 | **3.75** | 100 | 90 | 65.22 |
| 35 | 1493 | **5** | 100 | 90 | 79.19 |
| 35 | 1494 | **6.25** | 100 | 90 | 85.13 |
| 35 | 1495 | **7.5** | 100 | 90 | 89.55 |
| 35 | 1496 | **8.75** | 100 | 90 | 94.33 |
| 35 | 1497 | **10** | 100 | 90 | 98.77 |
| 35 | 1498 | **11.25** | 100 | 90 | 99.69 |
| 35 | 1499 | **12.5** | 100 | 90 | 99.99 |
| 35 | 1500 | 10 | **100** | 90 | 99.99 |
| 35 | 1501 | 10 | **150** | 90 | 96.47 |
| 35 | 1502 | 10 | **200** | 90 | 94.85 |
| 35 | 1503 | 10 | **250** | 90 | 91.98 |
| 35 | 1504 | 10 | **300** | 90 | 89.20 |
| 35 | 1505 | 10 | **350** | 90 | 87.55 |
| 35 | 1506 | 10 | **400** | 90 | 85.89 |
| 35 | 1507 | 10 | **450** | 90 | 81.68 |
| 35 | 1508 | 10 | **500** | 90 | 78.94 |
| 35 | 1509 | 10 | 100 | **6** | 60.67 |
| 35 | 1510 | 10 | 100 | **12** | 70.55 |
| 35 | 1511 | 10 | 100 | **18** | 81.09 |
| 35 | 1512 | 10 | 100 | **24** | 85.30 |
| 35 | 1513 | 10 | 100 | **30** | 93.66 |
| 35 | 1514 | 10 | 100 | **36** | 95.21 |
| 35 | 1515 | 10 | 100 | **42** | 98.45 |
| 35 | 1516 | 10 | 100 | **48** | 99.89 |
| 35 | 1517 | 10 | 100 | **54** | 94.90 |
| 35 | 1518 | 10 | 100 | **60** | 99.93 |
| Run Nos. 1500-1508, 1509-1518 were used for Equilibrium and Kinetic modeling, respectively | | | | | |

Table A.36 Input and output parameters for the simultaneous adsorption and biodegradation of phenol using *Bacillus* sp.immobilized GAC for synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | Output parameters |
|---|---|---|---|---|---|
| | | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 36 | 1519 | **0.5** | 100 | 90 | 56.10 |
| 36 | 1520 | **1.0** | 100 | 90 | 61.55 |
| 36 | 1521 | **1.5** | 100 | 90 | 66.86 |
| 36 | 1522 | **2.0** | 100 | 90 | 71.78 |
| 36 | 1523 | **2.5** | 100 | 90 | 79.33 |
| 36 | 1524 | **3.0** | 100 | 90 | 85.23 |
| 36 | 1525 | **3.5** | 100 | 90 | 90.44 |
| 36 | 1526 | **4.0** | 100 | 90 | 96.48 |
| 36 | 1527 | **4.5** | 100 | 90 | 98.50 |
| 36 | 1528 | **5.0** | 100 | 90 | 99.99 |
| 36 | 1529 | 4.5 | **100** | 90 | 99.64 |
| 36 | 1530 | 4.5 | **150** | 90 | 96.27 |
| 36 | 1531 | 4.5 | **200** | 90 | 88.69 |
| 36 | 1532 | 4.5 | **250** | 90 | 83.65 |
| 36 | 1533 | 4.5 | **300** | 90 | 78.20 |
| 36 | 1534 | 4.5 | **350** | 90 | 67.55 |
| 36 | 1535 | 4.5 | **400** | 90 | 61.89 |
| 36 | 1536 | 4.5 | **450** | 90 | 51.68 |
| 36 | 1537 | 4.5 | **500** | 90 | 48.94 |
| 36 | 1538 | 4.5 | 100 | **2** | 49.67 |
| 36 | 1539 | 4.5 | 100 | **4** | 60.55 |
| 36 | 1540 | 4.5 | 100 | **6** | 81.09 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 36 | 1541 | 4.5 | 100 | **8** | 91.30 |
| 36 | 1542 | 4.5 | 100 | **10** | 96.66 |
| 36 | 1543 | 4.5 | 100 | **12** | 98.21 |
| 36 | 1544 | 4.5 | 100 | **14** | 98.45 |
| 36 | 1545 | 4.5 | 100 | **16** | 99.89 |
| Run Nos. 1529-1537, 1538-1545 were used for Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |

Table A.37 Input and output parameters for the simultaneous adsorption and biodegradation of phenol using *Bacillus* sp.immobilized TW for synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters |  |  | Output parameters |
|---|---|---|---|---|---|
|  |  | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 37 | 1546 | **1.25** | 100 | 90 | 43.10 |
| 37 | 1547 | **2.5** | 100 | 90 | 54.55 |
| 37 | 1548 | **3.75** | 100 | 90 | 63.88 |
| 37 | 1549 | **5** | 100 | 90 | 76.79 |
| 37 | 1550 | **6.25** | 100 | 90 | 79.33 |
| 37 | 1551 | **7.5** | 100 | 90 | 89.33 |
| 37 | 1552 | **8.75** | 100 | 90 | 99.44 |
| 37 | 1553 | **10** | 100 | 90 | 99.48 |
| 37 | 1554 | **11.25** | 100 | 90 | 99.50 |
| 37 | 1555 | 8.75 | **100** | 90 | 99.44 |
| 37 | 1556 | 8.75 | **150** | 90 | 92.90 |
| 37 | 1557 | 8.75 | **200** | 90 | 86.17 |
| 37 | 1558 | 8.75 | **250** | 90 | 84.07 |
| 37 | 1559 | 8.75 | **300** | 90 | 81.42 |
| 37 | 1560 | 8.75 | **350** | 90 | 74.44 |
| 37 | 1561 | 8.75 | **400** | 90 | 69.08 |
| 37 | 1562 | 8.75 | **450** | 90 | 59.92 |
| 37 | 1563 | 8.75 | **500** | 90 | 51.00 |

| | | | | | |
|---|---|---|---|---|---|
| 37 | 1564 | 8.75 | 100 | **3** | 19.66 |
| 37 | 1565 | 8.75 | 100 | **6** | 25.52 |
| 37 | 1566 | 8.75 | 100 | **9** | 29.66 |
| 37 | 1567 | 8.75 | 100 | **12** | 34.25 |
| 37 | 1568 | 8.75 | 100 | **15** | 39.55 |
| 37 | 1569 | 8.75 | 100 | **18** | 46.08 |
| 37 | 1570 | 8.75 | 100 | **21** | 54.55 |
| 37 | 1571 | 8.75 | 100 | **24** | 63.55 |
| 37 | 1572 | 8.75 | 100 | **27** | 72.21 |
| 37 | 1573 | 8.75 | 100 | **30** | 80.23 |
| 37 | 1574 | 8.75 | 100 | **33** | 94.27 |
| 37 | 1575 | 8.75 | 100 | **36** | 99.78 |
| 37 | 1576 | 8.75 | 100 | **39** | 99.88 |
| Run Nos. 1555-1563, 1564-1576 were used for Equilibrium and Kinetic modeling, respectively | | | | | |

Table A.38 Input and output parameters for the simultaneous adsorption and biodegradation of phenol using *Bacillus* sp.immobilized RH for synthetic simulated single component solution

| Exp Set No. | Run No. | Input parameters | | | Output parameters |
|---|---|---|---|---|---|
| | | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Contact time h | % Removal of Cr(VI) |
| 38 | 1577 | **1.25** | 100 | 90 | 51.11 |
| 38 | 1578 | **2.5** | 100 | 90 | 59.55 |
| 38 | 1579 | **3.75** | 100 | 90 | 67.86 |
| 38 | 1580 | **5** | 100 | 90 | 81.78 |
| 38 | 1581 | **6.25** | 100 | 90 | 91.33 |
| 38 | 1582 | **7.5** | 100 | 90 | 99.33 |
| 38 | 1583 | **8.75** | 100 | 90 | 99.64 |
| 38 | 1584 | **10** | 100 | 90 | 99.78 |
| 38 | 1585 | **11.25** | 100 | 90 | 99.80 |
| 38 | 1586 | 7.5 | **100** | 90 | 99.34 |

| | | | | | |
|---|---|---|---|---|---|
| 38 | 1587 | 7.5 | **150** | 90 | 92.89 |
| 38 | 1588 | 7.5 | **200** | 90 | 83.19 |
| 38 | 1589 | 7.5 | **250** | 90 | 75.09 |
| 38 | 1590 | 7.5 | **300** | 90 | 68.42 |
| 38 | 1591 | 7.5 | **350** | 90 | 64.44 |
| 38 | 1592 | 7.5 | **400** | 90 | 56.08 |
| 38 | 1593 | 7.5 | **450** | 90 | 53.26 |
| 38 | 1594 | 7.5 | **500** | 90 | 46.20 |
| 38 | 1595 | 7.5 | 100 | **3** | 29.66 |
| 38 | 1596 | 7.5 | 100 | **6** | 35.52 |
| 38 | 1597 | 7.5 | 100 | **9** | 49.66 |
| 38 | 1598 | 7.5 | 100 | **12** | 54.25 |
| 38 | 1599 | 7.5 | 100 | **15** | 61.55 |
| 38 | 1600 | 7.5 | 100 | **18** | 66.08 |
| 38 | 1601 | 7.5 | 100 | **21** | 72.55 |
| 38 | 1602 | 7.5 | 100 | **24** | 78.55 |
| 38 | 1603 | 7.5 | 100 | **27** | 83.21 |
| 38 | 1604 | 7.5 | 100 | **30** | 89.23 |
| 38 | 1605 | 7.5 | 100 | **33** | 94.27 |
| 38 | 1606 | 7.5 | 100 | **36** | 97.78 |
| 38 | 1607 | 7.5 | 100 | **39** | 98.88 |
| 38 | 1608 | 7.5 | 100 | **42** | 99.99 |
| Run Nos. 1586-1594, 1595-1608 were used for Equilibrium and Kinetic modeling, respectively | | | | | |

Table A.39 Input and output parameters for the simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol using consortium culture of *Escherichia coli* and *Bacillus* sp.immobilized TW in synthetic simulated binary solution

| Exp Set No. | Run No. | Input parameters | | | | | Output parameters | |
|---|---|---|---|---|---|---|---|---|
| | | Adsorbent dose (g/L) | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time h Cr(VI) | Contact time (h) phenol | % Removal of Cr(VI) | % Removal of phenol |
| 39 | 1609 | **1.25** | 100 | 50 | 90 | 90 | 56.66 | 36.10 |
| 39 | 1610 | **2.5** | 100 | 50 | 90 | 90 | 64.33 | 44.55 |
| 39 | 1611 | **3.75** | 100 | 50 | 90 | 90 | 69.26 | 53.88 |
| 39 | 1612 | **5** | 100 | 50 | 90 | 90 | 77.25 | 66.79 |
| 39 | 1613 | **6.25** | 100 | 50 | 90 | 90 | 94.77 | 74.33 |
| 39 | 1614 | **7.5** | 100 | 50 | 90 | 90 | 99.53 | 80.11 |
| 39 | 1615 | **8.75** | 100 | 50 | 90 | 90 | 99.74 | 80.91 |
| 39 | 1616 | **10** | 100 | 50 | 90 | 90 | 99.98 | 80.92 |
| 39 | 1617 | 7.5 | **100** | **50** | 90 | 90 | 99.94 | 99.08 |
| 39 | 1618 | 7.5 | **150** | **75** | 90 | 90 | 99.89 | 93.80 |
| 39 | 1619 | 7.5 | **200** | **100** | 90 | 90 | 82.13 | 89.33 |
| 39 | 1620 | 7.5 | **250** | **125** | 90 | 90 | 74.73 | 83.31 |
| 39 | 1621 | 7.5 | **300** | **150** | 90 | 90 | 70.63 | 75.57 |
| 39 | 1622 | 7.5 | **350** | **175** | 90 | 90 | 65.59 | 74.32 |
| 39 | 1623 | 7.5 | **400** | **200** | 90 | 90 | 61.11 | 72.98 |
| 39 | 1624 | 7.5 | **450** | **225** | 90 | 90 | 58.68 | 71.09 |
| 39 | 1625 | 7.5 | **500** | **250** | 90 | 90 | 55.76 | 66.89 |
| 39 | 1626 | 7.5 | 100 | 50 | **3** | **3** | 29.066 | 29.655 |
| 39 | 1627 | 7.5 | 100 | 50 | **6** | **6** | 37.343 | 34.524 |
| 39 | 1628 | 7.5 | 100 | 50 | **9** | **9** | 47.633 | 37.655 |
| 39 | 1629 | 7.5 | 100 | 50 | **12** | **12** | 52.766 | 40.246 |
| 39 | 1630 | 7.5 | 100 | 50 | **15** | **15** | 66.013 | 46.544 |
| 39 | 1631 | 7.5 | 100 | 50 | **18** | **18** | 63.266 | 51.077 |

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| 39 | 1632 | 7.5 | 100 | 50 | **21** | **21** | 74.655 | 54.544 |
| 39 | 1633 | 7.5 | 100 | 50 | **24** | **24** | 80.616 | 56.544 |
| 39 | 1634 | 7.5 | 100 | 50 | **27** | **27** | 80.618 | 62.311 |
| 39 | 1635 | 7.5 | 100 | 50 | **30** | **30** | 89.23 | 69.232 |
| 39 | 1636 | 7.5 | 100 | 50 | **33** | **33** | 94.27 | 74.266 |
| 39 | 1637 | 7.5 | 100 | 50 | **36** | **36** | 97.78 | 81.055 |
| 39 | 1638 | 7.5 | 100 | 50 | **39** | **39** | 98.88 | 87.655 |
| 39 | 1639 | 7.5 | 100 | 50 | **42** | **42** | 99.99 | 91.077 |
| 39 | 1640 | 7.5 | 100 | 50 | **45** | **45** | 99.99 | 98.748 |
| 39 | 1641 | 7.5 | 100 | 50 | **48** | **48** | 99.99 | 99.522 |
| 39 | 1642 | 7.5 | 100 | 50 | **51** | **51** | 99.99 | 99.523 |
| Run Nos. 1617-1625, 1626-1642 were used for Equilibrium and Kinetic modeling, respectively |  |  |  |  |  |  |  |  |

Table A.40 Input and output parameters for the simultaneous adsorption and bioaccumulation of Cr(VI) and phenol in continuous reactor

| Exp Set No. | Run No. | Input parameters |  |  |  |  |  | Output parameters |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | pH | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time minute | Flow rate mL/min | Bed height cm | $C/C_o$ Cr(VI) | $C/C_o$ phenol |
| 40 | 1643 | 7 | 100 | 50 | 5 | **5.46** | 93 | 0.005 | 0.0246 |
| 40 | 1644 | 7 | 100 | 50 | 10 | 5.46 | 93 | 0.015 | 0.0684 |
| 40 | 1645 | 7 | 100 | 50 | 15 | 5.46 | 93 | 0.035 | 0.1134 |
| 40 | 1646 | 7 | 100 | 50 | 20 | 5.46 | 93 | 0.082 | 0.1868 |
| 40 | 1647 | 7 | 100 | 50 | 25 | 5.46 | 93 | 0.105 | 0.2774 |
| 40 | 1648 | 7 | 100 | 50 | 30 | 5.46 | 93 | 0.143 | 0.3068 |
| 40 | 1649 | 7 | 100 | 50 | 35 | 5.46 | 93 | 0.1834 | 0.3932 |
| 40 | 1650 | 7 | 100 | 50 | 40 | 5.46 | 93 | 0.2243 | 0.473 |
| 40 | 1651 | 7 | 100 | 50 | 45 | 5.46 | 93 | 0.2834 | 0.5486 |
| 40 | 1652 | 7 | 100 | 50 | 50 | 5.46 | 93 | 0.3334 | 0.5978 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 1653 | 7 | 100 | 50 | 55 | 5.46 | 93 | 0.4067 | 0.6006 |
| 40 | 1654 | 7 | 100 | 50 | 60 | 5.46 | 93 | 0.4703 | 0.6246 |
| 40 | 1655 | 7 | 100 | 50 | 65 | 5.46 | 93 | 0.5145 | 0.6378 |
| 40 | 1656 | 7 | 100 | 50 | 70 | 5.46 | 93 | 0.5144 | 0.6374 |
| 40 | 1657 | 7 | 100 | 50 | 75 | 5.46 | 93 | 0.5143 | 0.6372 |
| 40 | 1658 | 7 | 100 | 50 | 80 | 5.46 | 93 | 0.5143 | 0.6372 |
| 40 | 1659 | 7 | 100 | 50 | 85 | 5.46 | 93 | 0.5143 | 0.6372 |
| 40 | 1660 | 7 | 100 | 50 | 5 | **8.19** | 93 | 0.0093 | 0.0446 |
| 40 | 1661 | 7 | 100 | 50 | 10 | 8.19 | 93 | 0.035 | 0.1084 |
| 40 | 1662 | 7 | 100 | 50 | 15 | 8.19 | 93 | 0.075 | 0.1738 |
| 40 | 1663 | 7 | 100 | 50 | 20 | 8.19 | 93 | 0.102 | 0.2468 |
| 40 | 1664 | 7 | 100 | 50 | 25 | 8.19 | 93 | 0.155 | 0.3374 |
| 40 | 1665 | 7 | 100 | 50 | 30 | 8.19 | 93 | 0.183 | 0.4068 |
| 40 | 1666 | 7 | 100 | 50 | 35 | 8.19 | 93 | 0.2634 | 0.4932 |
| 40 | 1667 | 7 | 100 | 50 | 40 | 8.19 | 93 | 0.2943 | 0.573 |
| 40 | 1668 | 7 | 100 | 50 | 45 | 8.19 | 93 | 0.3234 | 0.6486 |
| 40 | 1669 | 7 | 100 | 50 | 50 | 8.19 | 93 | 0.3634 | 0.7038 |
| 40 | 1670 | 7 | 100 | 50 | 55 | 8.19 | 93 | 0.4567 | 0.8006 |
| 40 | 1671 | 7 | 100 | 50 | 60 | 8.19 | 93 | 0.5003 | 0.9046 |
| 40 | 1672 | 7 | 100 | 50 | 65 | 8.19 | 93 | 0.5645 | 0.9046 |
| 40 | 1673 | 7 | 100 | 50 | 70 | 8.19 | 93 | 0.5645 | 0.9046 |
| 40 | 1674 | 7 | 100 | 50 | 75 | 8.19 | 93 | 0.5645 | 0.9046 |
| 40 | 1675 | 7 | 100 | 50 | 80 | 8.19 | 93 | 0.5645 | 0.9046 |
| 40 | 1676 | 7 | 100 | 50 | 85 | 8.19 | 93 | 0.5645 | 0.9046 |
| 40 | 1677 | 7 | 100 | 50 | 5 | **16.3** | 93 | 0.0125 | 0.1046 |
| 40 | 1678 | 7 | 100 | 50 | 10 | 16.3 | 93 | 0.045 | 0.1484 |
| 40 | 1679 | 7 | 100 | 50 | 15 | 16.3 | 93 | 0.095 | 0.2122 |
| 40 | 1680 | 7 | 100 | 50 | 20 | 16.3 | 93 | 0.132 | 0.2868 |
| 40 | 1681 | 7 | 100 | 50 | 25 | 16.3 | 93 | 0.165 | 0.3774 |
| 40 | 1682 | 7 | 100 | 50 | 30 | 16.3 | 93 | 0.193 | 0.4268 |
| 40 | 1683 | 7 | 100 | 50 | 35 | 16.3 | 93 | 0.2734 | 0.5132 |
| 40 | 1684 | 7 | 100 | 50 | 40 | 16.3 | 93 | 0.3043 | 0.693 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 1685 | 7 | 100 | 50 | 45 | 16.3 | 93 | 0.3434 | 0.7686 |
| 40 | 1686 | 7 | 100 | 50 | 50 | 16.3 | 93 | 0.3834 | 0.8238 |
| 40 | 1687 | 7 | 100 | 50 | 55 | 16.3 | 93 | 0.4767 | 0.9666 |
| 40 | 1688 | 7 | 100 | 50 | 60 | 16.3 | 93 | 0.5403 | 0.9666 |
| 40 | 1689 | 7 | 100 | 50 | 65 | 16.3 | 93 | 0.5845 | 0.9666 |
| 40 | 1690 | 7 | 100 | 50 | 70 | 16.3 | 93 | 0.5845 | 0.9666 |
| 40 | 1691 | 7 | 100 | 50 | 75 | 16.3 | 93 | 0.5845 | 0.9666 |
| 40 | 1692 | 7 | 100 | 50 | 80 | 16.3 | 93 | 0.5845 | 0.9666 |
| 40 | 1693 | 7 | 100 | 50 | 85 | 16.3 | 93 | 0.5845 | 0.9666 |
| 40 | 1694 | 7 | 100 | 50 | 5 | 5.46 | **36** | 0.2845 | 0.569 |
| 40 | 1695 | 7 | 100 | 50 | 10 | 5.46 | 36 | 0.3228 | 0.6456 |
| 40 | 1696 | 7 | 100 | 50 | 15 | 5.46 | 36 | 0.3589 | 0.7178 |
| 40 | 1697 | 7 | 100 | 50 | 20 | 5.46 | 36 | 0.4087 | 0.8174 |
| 40 | 1698 | 7 | 100 | 50 | 25 | 5.46 | 36 | 0.4465 | 0.893 |
| 40 | 1699 | 7 | 100 | 50 | 30 | 5.46 | 36 | 0.4876 | 0.9752 |
| 40 | 1700 | 7 | 100 | 50 | 35 | 5.46 | 36 | 0.5123 | 1.0246 |
| 40 | 1701 | 7 | 100 | 50 | 40 | 5.46 | 36 | 0.5587 | 1.1174 |
| 40 | 1702 | 7 | 100 | 50 | 45 | 5.46 | 36 | 0.5687 | 1.1374 |
| 40 | 1703 | 7 | 100 | 50 | 50 | 5.46 | 36 | 0.5798 | 1.1596 |
| 40 | 1704 | 7 | 100 | 50 | 55 | 5.46 | 36 | 0.5898 | 1.1796 |
| 40 | 1705 | 7 | 100 | 50 | 60 | 5.46 | 36 | 0.5898 | 1.1796 |
| 40 | 1706 | 7 | 100 | 50 | 65 | 5.46 | 36 | 0.5898 | 1.1796 |
| 40 | 1707 | 7 | 100 | 50 | 70 | 5.46 | 36 | 0.5898 | 1.1796 |
| 40 | 1708 | 7 | 100 | 50 | 75 | 5.46 | 36 | 0.5898 | 1.1796 |
| 40 | 1709 | 7 | 100 | 50 | 80 | 5.46 | 36 | 0.5898 | 1.1796 |
| 40 | 1710 | 7 | 100 | 50 | 85 | 5.46 | 36 | 0.5898 | 1.1796 |
| 40 | 1711 | 7 | 100 | 50 | 5 | 5.46 | **54** | 0.125 | 0.3444 |
| 40 | 1712 | 7 | 100 | 50 | 10 | 5.46 | 54 | 0.1615 | 0.4354 |
| 40 | 1713 | 7 | 100 | 50 | 15 | 5.46 | 54 | 0.2045 | 0.5338 |
| 40 | 1714 | 7 | 100 | 50 | 20 | 5.46 | 54 | 0.2422 | 0.6088 |
| 40 | 1715 | 7 | 100 | 50 | 25 | 5.46 | 54 | 0.2851 | 0.7376 |
| 40 | 1716 | 7 | 100 | 50 | 30 | 5.46 | 54 | 0.3213 | 0.8086 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 1717 | 7 | 100 | 50 | 35 | 5.46 | 54 | 0.3544 | 0.8896 |
| 40 | 1718 | 7 | 100 | 50 | 40 | 5.46 | 54 | 0.3963 | 0.9722 |
| 40 | 1719 | 7 | 100 | 50 | 45 | 5.46 | 54 | 0.4314 | 1.0302 |
| 40 | 1720 | 7 | 100 | 50 | 50 | 5.46 | 54 | 0.4734 | 1.0482 |
| 40 | 1721 | 7 | 100 | 50 | 55 | 5.46 | 54 | 0.505 | 1.0826 |
| 40 | 1722 | 7 | 100 | 50 | 60 | 5.46 | 54 | 0.5323 | 1.1246 |
| 40 | 1723 | 7 | 100 | 50 | 65 | 5.46 | 54 | 0.5555 | 1.1246 |
| 40 | 1724 | 7 | 100 | 50 | 70 | 5.46 | 54 | 0.5555 | 1.1246 |
| 40 | 1725 | 7 | 100 | 50 | 75 | 5.46 | 54 | 0.5555 | 1.1246 |
| 40 | 1726 | 7 | 100 | 50 | 80 | 5.46 | 54 | 0.5555 | 1.1246 |
| 40 | 1727 | 7 | 100 | 50 | 85 | 5.46 | 54 | 0.5555 | 1.1246 |
| 40 | 1728 | 7 | 100 | 50 | 5 | 5.46 | **72** | 0.065 | 0.1844 |
| 40 | 1729 | 7 | 100 | 50 | 10 | 5.46 | 72 | 0.105 | 0.2688 |
| 40 | 1730 | 7 | 100 | 50 | 15 | 5.46 | 72 | 0.145 | 0.3538 |
| 40 | 1731 | 7 | 100 | 50 | 20 | 5.46 | 72 | 0.172 | 0.4288 |
| 40 | 1732 | 7 | 100 | 50 | 25 | 5.46 | 72 | 0.205 | 0.5174 |
| 40 | 1733 | 7 | 100 | 50 | 30 | 5.46 | 72 | 0.243 | 0.5866 |
| 40 | 1734 | 7 | 100 | 50 | 35 | 5.46 | 72 | 0.2834 | 0.6536 |
| 40 | 1735 | 7 | 100 | 50 | 40 | 5.46 | 72 | 0.3143 | 0.7126 |
| 40 | 1736 | 7 | 100 | 50 | 45 | 5.46 | 72 | 0.3434 | 0.7688 |
| 40 | 1737 | 7 | 100 | 50 | 50 | 5.46 | 72 | 0.3834 | 0.8282 |
| 40 | 1738 | 7 | 100 | 50 | 55 | 5.46 | 72 | 0.4267 | 0.9026 |
| 40 | 1739 | 7 | 100 | 50 | 60 | 5.46 | 72 | 0.4803 | 1.0046 |
| 40 | 1740 | 7 | 100 | 50 | 65 | 5.46 | 72 | 0.5247 | 1.0978 |
| 40 | 1741 | 7 | 100 | 50 | 70 | 5.46 | 72 | 0.5247 | 1.0978 |
| 40 | 1742 | 7 | 100 | 50 | 75 | 5.46 | 72 | 0.5247 | 1.0978 |
| 40 | 1743 | 7 | 100 | 50 | 80 | 5.46 | 72 | 0.5247 | 1.0978 |
| 40 | 1744 | 7 | 100 | 50 | 85 | 5.46 | 72 | 0.5247 | 1.0978 |
| 40 | 1745 | 7 | 100 | 50 | 5 | 5.46 | **93** | 0.005 | 0.0246 |
| 40 | 1746 | 7 | 100 | 50 | 10 | 5.46 | 93 | 0.015 | 0.0684 |
| 40 | 1747 | 7 | 100 | 50 | 15 | 5.46 | 93 | 0.035 | 0.1134 |
| 40 | 1748 | 7 | 100 | 50 | 20 | 5.46 | 93 | 0.082 | 0.1868 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 1749 | 7 | 100 | 50 | 25 | 5.46 | 93 | 0.105 | 0.2774 |
| 40 | 1750 | 7 | 100 | 50 | 30 | 5.46 | 93 | 0.143 | 0.3068 |
| 40 | 1751 | 7 | 100 | 50 | 35 | 5.46 | 93 | 0.1834 | 0.3932 |
| 40 | 1752 | 7 | 100 | 50 | 40 | 5.46 | 93 | 0.2243 | 0.473 |
| 40 | 1753 | 7 | 100 | 50 | 45 | 5.46 | 93 | 0.2834 | 0.5486 |
| 40 | 1754 | 7 | 100 | 50 | 50 | 5.46 | 93 | 0.3334 | 0.5978 |
| 40 | 1755 | 7 | 100 | 50 | 55 | 5.46 | 93 | 0.4067 | 0.6006 |
| 40 | 1756 | 7 | 100 | 50 | 60 | 5.46 | 93 | 0.4703 | 0.6246 |
| 40 | 1757 | 7 | 100 | 50 | 65 | 5.46 | 93 | 0.5145 | 0.6378 |
| 40 | 1758 | 7 | 100 | 50 | 70 | 5.46 | 93 | 0.5144 | 0.6374 |
| 40 | 1759 | 7 | 100 | 50 | 75 | 5.46 | 93 | 0.5143 | 0.6372 |
| 40 | 1760 | 7 | 100 | 50 | 80 | 5.46 | 93 | 0.5143 | 0.6372 |
| 40 | 1761 | 7 | 100 | 50 | 85 | 5.46 | 93 | 0.5143 | 0.6372 |

Table A.41 Input and output parameters for the simultaneous adsorption and bioaccumulation of Cr(VI) with biodegradation of phenol in continuous bio column reactor

| Exp Set No. | Run No. | Input parameters | | | | | | Output parameters | |
|---|---|---|---|---|---|---|---|---|---|
| | | pH | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time minute | EBCT h | Bed height cm | $C/C_o$ Cr(VI) | $C/C_o$ phenol |
| 41 | 1762 | 7 | 2000 | 1000 | 6 | **4** | 93 | 0.50023 | 0.72879 |
| 41 | 1763 | 7 | 2000 | 1000 | 12 | 4 | 93 | 0.60523 | 0.87085 |
| 41 | 1764 | 7 | 2000 | 1000 | 18 | 4 | 93 | 0.70077 | 0.91322 |
| 41 | 1765 | 7 | 2000 | 1000 | 24 | 4 | 93 | 0.8381 | 0.98956 |
| 41 | 1766 | 7 | 2000 | 1000 | 30 | 4 | 93 | 0.7503 | 0.91033 |
| 41 | 1767 | 7 | 2000 | 1000 | 36 | 4 | 93 | 0.71173 | 0.82311 |
| 41 | 1768 | 7 | 2000 | 1000 | 42 | 4 | 93 | 0.62623 | 0.75063 |
| 41 | 1769 | 7 | 2000 | 1000 | 48 | 4 | 93 | 0.56022 | 0.63881 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 1770 | 7 | 2000 | 1000 | 54 | 4 | 93 | 0.54539 | 0.57655 |
| 41 | 1771 | 7 | 2000 | 1000 | 60 | 4 | 93 | 0.451 | 0.49031 |
| 41 | 1772 | 7 | 2000 | 1000 | 66 | 4 | 93 | 0.43449 | 0.40562 |
| 41 | 1773 | 7 | 2000 | 1000 | 72 | 4 | 93 | 0.37112 | 0.3594 |
| 41 | 1774 | 7 | 2000 | 1000 | 78 | 4 | 93 | 0.31333 | 0.25115 |
| 41 | 1775 | 7 | 2000 | 1000 | 84 | 4 | 93 | 0.25011 | 0.20029 |
| 41 | 1776 | 7 | 2000 | 1000 | 90 | 4 | 93 | 0.2066 | 0.18515 |
| 41 | 1777 | 7 | 2000 | 1000 | 94 | 4 | 93 | 0.18061 | 0.17056 |
| 41 | 1778 | 7 | 2000 | 1000 | 99 | 4 | 93 | 0.1216 | 0.17045 |
| 41 | 1779 | 7 | 2000 | 1000 | 102 | 4 | 93 | 0.05912 | 0.1702 |
| 41 | 1780 | 7 | 2000 | 1000 | 108 | 4 | 93 | 0.04523 | 0.15719 |
| 41 | 1781 | 7 | 2000 | 1000 | 114 | 4 | 93 | 0.02517 | 0.17 |
| 41 | 1782 | 7 | 2000 | 1000 | 120 | 4 | 93 | 2.51E-02 | 0.17 |
| 41 | 1783 | 7 | 2000 | 1000 | 126 | 4 | 93 | 2.51E-02 | 0.17 |
| 41 | 1784 | 7 | 2000 | 1000 | 6 | **8** | 93 | 0.35023 | 0.52889 |
| 41 | 1785 | 7 | 2000 | 1000 | 12 | 8 | 93 | 0.50523 | 0.67083 |
| 41 | 1786 | 7 | 2000 | 1000 | 18 | 8 | 93 | 0.70077 | 0.71312 |
| 41 | 1787 | 7 | 2000 | 1000 | 24 | 8 | 93 | 0.7881 | 0.80023 |
| 41 | 1788 | 7 | 2000 | 1000 | 30 | 8 | 93 | 0.7003 | 0.88023 |
| 41 | 1789 | 7 | 2000 | 1000 | 36 | 8 | 93 | 0.61172 | 0.72312 |
| 41 | 1790 | 7 | 2000 | 1000 | 42 | 8 | 93 | 0.52623 | 0.65083 |
| 41 | 1791 | 7 | 2000 | 1000 | 48 | 8 | 93 | 0.41022 | 0.53889 |
| 41 | 1792 | 7 | 2000 | 1000 | 54 | 8 | 93 | 0.34539 | 0.47645 |
| 41 | 1793 | 7 | 2000 | 1000 | 60 | 8 | 93 | 0.251 | 0.40034 |
| 41 | 1794 | 7 | 2000 | 1000 | 66 | 8 | 93 | 0.18449 | 0.3356 |
| 41 | 1795 | 7 | 2000 | 1000 | 72 | 8 | 93 | 0.12112 | 0.3094 |
| 41 | 1796 | 7 | 2000 | 1000 | 78 | 8 | 93 | 0.06333 | 0.25145 |
| 41 | 1797 | 7 | 2000 | 1000 | 84 | 8 | 93 | 0.0501 | 0.20089 |
| 41 | 1798 | 7 | 2000 | 1000 | 90 | 8 | 93 | 0.0416 | 0.18345 |
| 41 | 1799 | 7 | 2000 | 1000 | 94 | 8 | 93 | 0.03061 | 0.17056 |
| 41 | 1800 | 7 | 2000 | 1000 | 99 | 8 | 93 | 0.0216 | 0.15045 |
| 41 | 1801 | 7 | 2000 | 1000 | 102 | 8 | 93 | 0.01412 | 0.1502 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 1802 | 7 | 2000 | 1000 | 108 | 8 | 93 | 0.00923 | 0.15019 |
| 41 | 1803 | 7 | 2000 | 1000 | 114 | 8 | 93 | 0.00517 | 0.15 |
| 41 | 1804 | 7 | 2000 | 1000 | 120 | 8 | 93 | 0.00507 | 0.15 |
| 41 | 1805 | 7 | 2000 | 1000 | 126 | 8 | 93 | 0.00507 | 0.15 |
| 41 | 1806 | 7 | 2000 | 1000 | 6 | **12** | 93 | 0.300175 | 0.42889 |
| 41 | 1807 | 7 | 2000 | 1000 | 12 | 12 | 93 | 0.405325 | 0.57083 |
| 41 | 1808 | 7 | 2000 | 1000 | 18 | 12 | 93 | 0.45077 | 0.61312 |
| 41 | 1809 | 7 | 2000 | 1000 | 24 | 12 | 93 | 0.5381 | 0.70023 |
| 41 | 1810 | 7 | 2000 | 1000 | 30 | 12 | 93 | 0.4528 | 0.61023 |
| 41 | 1811 | 7 | 2000 | 1000 | 36 | 12 | 93 | 0.411725 | 0.52312 |
| 41 | 1812 | 7 | 2000 | 1000 | 42 | 12 | 93 | 0.376425 | 0.45083 |
| 41 | 1813 | 7 | 2000 | 1000 | 48 | 12 | 93 | 0.310365 | 0.33889 |
| 41 | 1814 | 7 | 2000 | 1000 | 54 | 12 | 93 | 0.24539 | 0.27645 |
| 41 | 1815 | 7 | 2000 | 1000 | 60 | 12 | 93 | 0.175995 | 0.20034 |
| 41 | 1816 | 7 | 2000 | 1000 | 66 | 12 | 93 | 0.10949 | 0.1556 |
| 41 | 1817 | 7 | 2000 | 1000 | 72 | 12 | 93 | 0.071115 | 0.1354 |
| 41 | 1817 | 7 | 2000 | 1000 | 78 | 12 | 93 | 0.063325 | 0.11045 |
| 41 | 1818 | 7 | 2000 | 1000 | 84 | 12 | 93 | 0.045105 | 0.10089 |
| 41 | 1819 | 7 | 2000 | 1000 | 90 | 12 | 93 | 0.036595 | 0.09045 |
| 41 | 1820 | 7 | 2000 | 1000 | 94 | 12 | 93 | 0.025605 | 0.09056 |
| 41 | 1821 | 7 | 2000 | 1000 | 99 | 12 | 93 | 0.0166 | 0.09045 |
| 41 | 1822 | 7 | 2000 | 1000 | 102 | 12 | 93 | 0.009115 | 0.0902 |
| 41 | 1823 | 7 | 2000 | 1000 | 108 | 12 | 93 | 0.004225 | 0.09019 |
| 41 | 1824 | 7 | 2000 | 1000 | 114 | 12 | 93 | 0.00117 | 0.09019 |
| 41 | 1825 | 7 | 2000 | 1000 | 120 | 12 | 93 | 0.00057 | 0.09019 |
| 41 | 1826 | 7 | 2000 | 1000 | 126 | 12 | 93 | 0.00057 | 0.09019 |
| 41 | 1827 | 7 | 2000 | 1000 | 24 | 12 | **18** | 0.406725 | 0.52312 |
| 41 | 1828 | 7 | 2000 | 1000 | 48 | 12 | 18 | 0.29009 | 0.31034 |
| 41 | 1829 | 7 | 2000 | 1000 | 72 | 12 | 18 | 0.11449 | 0.2334 |
| 41 | 1830 | 7 | 2000 | 1000 | 96 | 12 | 18 | 0.091595 | 0.10459 |
| 41 | 1831 | 7 | 2000 | 1000 | 120 | 12 | 18 | 0.036595 | 0.08969 |
| 41 | 1832 | 7 | 2000 | 1000 | 144 | 12 | 18 | 0.009115 | 0.08969 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 1833 | 7 | 2000 | 1000 | 168 | 12 | 18 | 0.004725 | 0.08969 |
| 41 | 1834 | 7 | 2000 | 1000 | 192 | 12 | 18 | 0.00062 | 0.08969 |
| 41 | 1835 | 7 | 2000 | 1000 | 216 | 12 | 18 | 0.000535 | 0.08969 |
| 41 | 1836 | 7 | 2000 | 1000 | 240 | 12 | 18 | 0.000445 | 0.08969 |
| 41 | 1837 | 7 | 2000 | 1000 | 24 | 12 | **36** | 0.356725 | 0.32312 |
| 41 | 1838 | 7 | 2000 | 1000 | 48 | 12 | 36 | 0.25509 | 0.21234 |
| 41 | 1839 | 7 | 2000 | 1000 | 72 | 12 | 36 | 0.09359 | 0.1034 |
| 41 | 1840 | 7 | 2000 | 1000 | 96 | 12 | 36 | 0.060545 | 0.09067 |
| 41 | 1841 | 7 | 2000 | 1000 | 120 | 12 | 36 | 0.031595 | 0.08345 |
| 41 | 1842 | 7 | 2000 | 1000 | 144 | 12 | 36 | 0.009115 | 0.08345 |
| 41 | 1843 | 7 | 2000 | 1000 | 168 | 12 | 36 | 0.002725 | 0.08345 |
| 41 | 1844 | 7 | 2000 | 1000 | 192 | 12 | 36 | 0.00067 | 0.08345 |
| 41 | 1845 | 7 | 2000 | 1000 | 216 | 12 | 36 | 0.00057 | 0.08345 |
| 41 | 1846 | 7 | 2000 | 1000 | 240 | 12 | 36 | 0.00052 | 0.08345 |
| 41 | 1847 | 7 | 2000 | 1000 | 24 | 12 | **54** | 0.306725 | 0.22312 |
| 41 | 1848 | 7 | 2000 | 1000 | 48 | 12 | 54 | 0.20509 | 0.10234 |
| 41 | 1849 | 7 | 2000 | 1000 | 72 | 12 | 54 | 0.05359 | 0.0964 |
| 41 | 1850 | 7 | 2000 | 1000 | 96 | 12 | 54 | 0.040045 | 0.08267 |
| 41 | 1851 | 7 | 2000 | 1000 | 120 | 12 | 54 | 0.026595 | 0.08045 |
| 41 | 1852 | 7 | 2000 | 1000 | 144 | 12 | 54 | 0.005115 | 0.08045 |
| 41 | 1853 | 7 | 2000 | 1000 | 168 | 12 | 54 | 0.002225 | 0.08045 |
| 41 | 1854 | 7 | 2000 | 1000 | 192 | 12 | 54 | 0.00082 | 0.08045 |
| 41 | 1855 | 7 | 2000 | 1000 | 216 | 12 | 54 | 0.00072 | 0.08045 |
| 41 | 1856 | 7 | 2000 | 1000 | 240 | 12 | 54 | 0.00062 | 0.08045 |
| 41 | 1857 | 7 | 2000 | 1000 | 24 | 12 | **72** | 0.276525 | 0.19545 |
| 41 | 1858 | 7 | 2000 | 1000 | 48 | 12 | 72 | 0.17014 | 0.08934 |
| 41 | 1859 | 7 | 2000 | 1000 | 72 | 12 | 72 | 0.04509 | 0.0804 |
| 41 | 1860 | 7 | 2000 | 1000 | 96 | 12 | 72 | 0.035045 | 0.07867 |
| 41 | 1861 | 7 | 2000 | 1000 | 120 | 12 | 72 | 0.021595 | 0.07543 |
| 41 | 1862 | 7 | 2000 | 1000 | 144 | 12 | 72 | 0.004115 | 0.07543 |
| 41 | 1863 | 7 | 2000 | 1000 | 168 | 12 | 72 | 0.001725 | 0.07543 |
| 41 | 1865 | 7 | 2000 | 1000 | 192 | 12 | 72 | 0.00087 | 0.07543 |

|  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 1865 | 7 | 2000 | 1000 | 216 | 12 | 72 | 0.00077 | 0.07543 |
| 41 | 1866 | 7 | 2000 | 1000 | 240 | 12 | 72 | 0.00067 | 0.07543 |
| 41 | 1867 | 7 | 2000 | 1000 | 24 | 12 | **93** | 0.226525 | 0.11045 |
| 41 | 1868 | 7 | 2000 | 1000 | 48 | 12 | 93 | 0.12014 | 0.07934 |
| 41 | 1869 | 7 | 2000 | 1000 | 72 | 12 | 93 | 0.03509 | 0.0704 |
| 41 | 1870 | 7 | 2000 | 1000 | 96 | 12 | 93 | 0.030045 | 0.06867 |
| 41 | 1871 | 7 | 2000 | 1000 | 120 | 12 | 93 | 0.016595 | 0.06543 |
| 41 | 1872 | 7 | 2000 | 1000 | 144 | 12 | 93 | 0.002615 | 0.06543 |
| 41 | 1873 | 7 | 2000 | 1000 | 168 | 12 | 93 | 0.001225 | 0.06543 |
| 41 | 1874 | 7 | 2000 | 1000 | 192 | 12 | 93 | 0.00062 | 0.06543 |
| 41 | 1875 | 7 | 2000 | 1000 | 216 | 12 | 93 | 0.00062 | 0.06543 |
| 41 | 1876 | 7 | 2000 | 1000 | 240 | 12 | 93 | 0.00062 | 0.06543 |

Table A.42 Phytoremediation of Cr(VI) and phenol from single substrate solution

| Exp Set No. | Run No. | Output parameters |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  | pH | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time days | % Removal of Cr(VI) | % Removal of Phenol |
| 42 | 1877 | 7 | **5** | **10** | 1 | 14.8 | 18.6 |
| 42 | 1878 | 7 | 5 | 10 | 2 | 20.2 | 32.8 |
| 42 | 1879 | 7 | 5 | 10 | 3 | 29.4 | 54.6 |
| 42 | 1880 | 7 | 5 | 10 | 4 | 37.8 | 61.1 |
| 42 | 1881 | 7 | 5 | 10 | 5 | 43 | 69.9 |
| 42 | 1882 | 7 | 5 | 10 | 6 | 51.4 | 73.6 |
| 42 | 1883 | 7 | 5 | 10 | 7 | 59.8 | 78.8 |
| 42 | 1884 | 7 | 5 | 10 | 8 | 63.6 | 82.5 |
| 42 | 1885 | 7 | 5 | 10 | 9 | 69.6 | 89.7 |
| 42 | 1886 | 7 | 5 | 10 | 10 | 75.4 | 91.5 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 42 | 1887 | 7 | 5 | 10 | 11 | 79.8 | 95.5 |
| 42 | 1888 | 7 | 5 | 10 | 12 | 83.2 | 98.6 |
| 42 | 1889 | 7 | 5 | 10 | 13 | 94.8 | 99.8 |
| 42 | 1890 | 7 | 5 | 10 | 14 | 98.8 | 99.8 |
| 42 | 1891 | 7 | 5 | 10 | 15 | 99 | 99.8 |
| 42 | 1892 | 7 | 5 | 10 | 16 | 99 | 99.8 |
| 42 | 1893 | 7 | **10** | **20** | 1 | 16.2 | 8.25 |
| 42 | 1894 | 7 | 10 | 20 | 2 | 29.8 | 14.55 |
| 42 | 1895 | 7 | 10 | 20 | 3 | 38.6 | 19.4 |
| 42 | 1896 | 7 | 10 | 20 | 4 | 41.6 | 21.8 |
| 42 | 1897 | 7 | 10 | 20 | 5 | 45.7 | 29.4 |
| 42 | 1898 | 7 | 10 | 20 | 6 | 50.8 | 35.15 |
| 42 | 1899 | 7 | 10 | 20 | 7 | 57.2 | 44.75 |
| 42 | 1900 | 7 | 10 | 20 | 8 | 60.6 | 49.1 |
| 42 | 1901 | 7 | 10 | 20 | 9 | 67.2 | 55.25 |
| 42 | 1902 | 7 | 10 | 20 | 10 | 71.1 | 67.25 |
| 42 | 1903 | 7 | 10 | 20 | 11 | 75 | 74.85 |
| 42 | 1904 | 7 | 10 | 20 | 12 | 79.9 | 76.2 |
| 42 | 1905 | 7 | 10 | 20 | 13 | 81.4 | 79.75 |
| 42 | 1906 | 7 | 10 | 20 | 14 | 82.7 | 82.3 |
| 42 | 1907 | 7 | 10 | 20 | 15 | 82.9 | 83.85 |
| 42 | 1908 | 7 | 10 | 20 | 16 | 83 | 83.9 |
| 42 | 1909 | 7 | **15** | **30** | 1 | 1.733 | 6.166 |
| 42 | 1910 | 7 | 15 | 30 | 2 | 9.73 | 12.7 |
| 42 | 1911 | 7 | 15 | 30 | 3 | 14.06 | 17.6 |
| 42 | 1912 | 7 | 15 | 30 | 4 | 19.13 | 24.53 |
| 42 | 1913 | 7 | 15 | 30 | 5 | 22.2 | 30.26 |
| 42 | 1914 | 7 | 15 | 30 | 6 | 25.13 | 36.76 |
| 42 | 1915 | 7 | 15 | 30 | 7 | 29.46 | 45.83 |
| 42 | 1916 | 7 | 15 | 30 | 8 | 33.00 | 51.06 |
| 42 | 1917 | 7 | 15 | 30 | 9 | 37.00 | 56.83 |
| 42 | 1918 | 7 | 15 | 30 | 10 | 39.8 | 61.5 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 42 | 1919 | 7 | 15 | 30 | 11 | 43.46 | 64.56 |
| 42 | 1920 | 7 | 15 | 30 | 12 | 45.66 | 67.46 |
| 42 | 1921 | 7 | 15 | 30 | 13 | 50.86 | 73.16 |
| 42 | 1922 | 7 | 15 | 30 | 14 | 53.06 | 71.86 |
| 42 | 1923 | 7 | 15 | 30 | 15 | 53.20 | 72.23 |
| 42 | 1924 | 7 | 15 | 30 | 16 | 53.20 | 72.26 |
| 42 | 1925 | 7 | **20** | **40** | 1 | 4.625 | 4.625 |
| 42 | 1926 | 7 | 20 | 40 | 2 | 8.025 | 8.025 |
| 42 | 1927 | 7 | 20 | 40 | 3 | 13.70 | 13.70 |
| 42 | 1928 | 7 | 20 | 40 | 4 | 17.90 | 17.90 |
| 42 | 1929 | 7 | 20 | 40 | 5 | 22.95 | 22.95 |
| 42 | 1929 | 7 | 20 | 40 | 6 | 28.08 | 28.08 |
| 42 | 1930 | 7 | 20 | 40 | 7 | 34.63 | 34.63 |
| 42 | 1931 | 7 | 20 | 40 | 8 | 38.55 | 38.55 |
| 42 | 1932 | 7 | 20 | 40 | 9 | 43.88 | 43.89 |
| 42 | 1933 | 7 | 20 | 40 | 10 | 48.38 | 48.38 |
| 42 | 1934 | 7 | 20 | 40 | 11 | 54.68 | 54.68 |
| 42 | 1935 | 7 | 20 | 40 | 12 | 59.60 | 59.60 |
| 42 | 1936 | 7 | 20 | 40 | 13 | 64.89 | 64.88 |
| 42 | 1937 | 7 | 20 | 40 | 14 | 68.9 | 68.90 |
| 42 | 1938 | 7 | 20 | 40 | 15 | 69.18 | 69.18 |
| 42 | 1939 | 7 | 20 | 40 | 16 | 69.20 | 69.20 |

Table A.43 Simultaneous phytoremediation of Cr(VI) and phenol from binary substrate solution

| Exp Set No. | Run No. | Output parameters | | | | | |
|---|---|---|---|---|---|---|---|
| | | pH | Initial concentration of Cr(VI) (mg/L) | Initial concentration of phenol (mg/L) | Contact time days | % Removal of Cr(VI) | % Removal of Phenol |
| 43 | 1940 | 7 | **5** | **10** | 1 | 34.8 | 7.6 |
| 43 | 1941 | 7 | 5 | 10 | 2 | 40.2 | 13.8 |
| 43 | 1942 | 7 | 5 | 10 | 3 | 69.4 | 23.6 |
| 43 | 1943 | 7 | 5 | 10 | 4 | 77.8 | 30.1 |
| 43 | 1944 | 7 | 5 | 10 | 5 | 83 | 48.9 |
| 43 | 1945 | 7 | 5 | 10 | 6 | 91.4 | 54.6 |
| 43 | 1946 | 7 | 5 | 10 | 7 | 99 | 66.8 |
| 43 | 1947 | 7 | 5 | 10 | 8 | 99 | 70.5 |
| 43 | 1948 | 7 | 5 | 10 | 9 | 99 | 88.7 |
| 43 | 1949 | 7 | 5 | 10 | 10 | 99 | 91.5 |
| 43 | 1950 | 7 | 5 | 10 | 11 | 99 | 92.5 |
| 43 | 1951 | 7 | 5 | 10 | 12 | 99 | 92.6 |
| 43 | 1952 | 7 | 5 | 10 | 13 | 99 | 92.8 |
| 43 | 1953 | 7 | 5 | 10 | 14 | 99 | 92.8 |
| 43 | 1954 | 7 | 5 | 10 | 15 | 99 | 92.8 |
| 43 | 1955 | 7 | 5 | 10 | 16 | 99 | 92.8 |
| 43 | 1956 | 7 | **10** | **20** | 1 | 26.2 | 18.95 |
| 43 | 1957 | 7 | 10 | 20 | 2 | 39.8 | 17.29 |
| 43 | 1958 | 7 | 10 | 20 | 3 | 48.6 | 16.22 |
| 43 | 1959 | 7 | 10 | 20 | 4 | 51.6 | 15.74 |
| 43 | 1960 | 7 | 10 | 20 | 5 | 65.7 | 14.19 |
| 43 | 1961 | 7 | 10 | 20 | 6 | 70.8 | 13.77 |
| 43 | 1962 | 7 | 10 | 20 | 7 | 87.2 | 12.55 |
| 43 | 1963 | 7 | 10 | 20 | 8 | 90.4 | 11.28 |
| 43 | 1964 | 7 | 10 | 20 | 9 | 94.6 | 10.85 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 43 | 1965 | 7 | 10 | 20 | 10 | 98.9 | 9.65 |
| 43 | 1966 | 7 | 10 | 20 | 11 | 99.1 | 8.13 |
| 43 | 1967 | 7 | 10 | 20 | 12 | 99.1 | 7.66 |
| 43 | 1968 | 7 | 10 | 20 | 13 | 99.1 | 6.15 |
| 43 | 1969 | 7 | 10 | 20 | 14 | 99.1 | 5.44 |
| 43 | 1970 | 7 | 10 | 20 | 15 | 99.1 | 5.01 |
| 43 | 1971 | 7 | 10 | 20 | 16 | 99.1 | 4.98 |
| 43 | 1972 | 7 | **15** | **30** | 1 | 9.73 | 2.70 |
| 43 | 1973 | 7 | 15 | 30 | 2 | 19.07 | 9.43 |
| 43 | 1974 | 7 | 15 | 30 | 3 | 28.73 | 13.93 |
| 43 | 1975 | 7 | 15 | 30 | 4 | 41.13 | 17.80 |
| 43 | 1976 | 7 | 15 | 30 | 5 | 48.87 | 23.53 |
| 43 | 1977 | 7 | 15 | 30 | 6 | 59.13 | 30.43 |
| 43 | 1978 | 7 | 15 | 30 | 7 | 64.80 | 38.83 |
| 43 | 1979 | 7 | 15 | 30 | 8 | 73.00 | 40.73 |
| 43 | 1980 | 7 | 15 | 30 | 9 | 79.00 | 43.47 |
| 43 | 1981 | 7 | 15 | 30 | 10 | 86.47 | 47.83 |
| 43 | 1982 | 7 | 15 | 30 | 11 | 89.47 | 50.90 |
| 43 | 1983 | 7 | 15 | 30 | 12 | 89.47 | 54.30 |
| 43 | 1984 | 7 | 15 | 30 | 13 | 89.47 | 59.73 |
| 43 | 1985 | 7 | 15 | 30 | 14 | 89.47 | 61.87 |
| 43 | 1986 | 7 | 15 | 30 | 15 | 89.47 | 65 |
| 43 | 1987 | 7 | 15 | 30 | 16 | 89.47 | 65 |
| 43 | 1988 | 7 | **20** | **40** | 1 | 8.75 | 2.10 |
| 43 | 1989 | 7 | 20 | 40 | 2 | 16.55 | 5.78 |
| 43 | 1990 | 7 | 20 | 40 | 3 | 27.35 | 8.95 |
| 43 | 1991 | 7 | 20 | 40 | 4 | 36.30 | 13.40 |
| 43 | 1992 | 7 | 20 | 40 | 5 | 43.90 | 18.20 |
| 43 | 1993 | 7 | 20 | 40 | 6 | 46.65 | 20.83 |
| 43 | 1994 | 7 | 20 | 40 | 7 | 54.75 | 23.63 |
| 43 | 1995 | 7 | 20 | 40 | 8 | 56.10 | 28.80 |
| 43 | 1996 | 7 | 20 | 40 | 9 | 64.75 | 34.13 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 43 | 1997 | 7 | 20 | 40 | 10 | 66.75 | 36.38 |
| 43 | 1998 | 7 | 20 | 40 | 11 | 74.85 | 39.43 |
| 43 | 1999 | 7 | 20 | 40 | 12 | 79.20 | 41.60 |
| 43 | 2000 | 7 | 20 | 40 | 13 | 80.75 | 44.63 |
| 43 | 2001 | 7 | 20 | 40 | 14 | 83.80 | 46.65 |
| 43 | 2002 | 7 | 20 | 40 | 15 | 83.95 | 50.00 |
| 43 | 2003 | 7 | 20 | 40 | 16 | 84.00 | 50.20 |

**B1: Preparation of single and binary stock solution of chromium and Phenol:** Stock solution of chromium was prepared by dissolving 2.82 g of potassium dichromate ($K_2Cr_2O_7$) in 1 L of distilled water. The pH of stock solution was maintained using 1 N HCl and NaOH. The stock solution of phenol was prepared by dissolving 1 g of pure phenol crystal in 1 L of distilled water. To avoid the photo-oxidation of phenol it was stored in brown glass bottles. Binary simulated synthetic solution of Cr(VI) and phenol (2:1) (v/v) was prepared by mixing adequate volume of single component stock solution of Cr(VI) and phenol.

**B2: Spectrophotometric method for the determination of chromium:** The residual concentration of chromium was analysed using 1, 5 diphenyl carbazide spectrophotometric method. The reagent solution were prepared by dissolving 250 mg 1,5-diphenyl carbazide in 50 mL acetone and stored in a brown bottle. Solution was discarded when it became discolored. Sulphuric acid ($H_2SO_4$) was used to maintain the pH. The stock solution of potassium dichromate ($K_2Cr_2O_7$) was diluted to obtain the standard solution concentration ranges from 0.2 to 1.8 ppm by adding the required amount of reagent solution. Calibration curve plotted between the absorbance and known concentration of chromium. The absorbance was taken in UV spectrophotometer at 540 nm.

**B3: Spectrophotometric method for determination of phenol:** The residual concentration of phenol in UV spectrophotometer was determined using 4 amino antipyrene method at 510 nm. The residual concentration of chromium is directly proportional to the color intensity of solution.

Following reagents are used for the analysis of phenol:

1. Buffer solution: 16.9 g of ammonium chloride ($NH_4Cl$) was dissolved in 143 ml of conc. Ammonium hydroxide ($NH_4OH$) and the solution was diluted to 250 ml with distilled water.
2. Aminoantipyrene solution: 2 g of 4-amino antipyrene (4-AAP) was dissolved in distilled water and the solution was diluted to 100 ml.
3. Potassium ferricyanide solution: 8 g of potassium ferricyanide [$K_3Fe(CN)_6$] was dissolved in 100 ml distilled water.

   The standard solution of phenol was prepared for the concentration of phenol varied from 1-10 mg/L. After adding 2 ml all the reagents described above in standard solution of phenol at different concentration the reddish brown color was observed then its absorbance was taken at 510 nm after 15 min.