

**PHENOL REMOVAL BY SEQUENTIAL BATCH REACTOR  
AND ADSORPTION**

**A DISSERTATION**

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

*of*

**MASTER OF TECHNOLOGY**

*in*

**CHEMICAL ENGINEERING**

**(With Specialization in Industrial Pollution Abatement)**

*By*

**PRATEEK**



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## DECLARATION

I hereby declare that the work being presented in the seminar report entitled “**Phenol removal by sequential batch reactor and adsorption**” in partial fulfilment of the requirements for the award of the degree of M. Tech. (with Specialization in Industrial Pollution Abatement) and submitted in the department of Chemical Engineering of the Indian Institute of Technology Roorkee. This is an authentic record of my own work carried out during the period from June, 2012 to June, 2013 under the supervision of **Dr. V. C. Srivastava**, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India. The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute.

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## CERTIFICATE

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

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## ABSTRACT

The present study involves the treatment of 4-nitrophenol (NP) bearing wastewater by biological treatment in a sequential batch reactor (SBR) without any adsorbent (called as blank-SBR) and an SBR loaded with granular activated carbon (GAC-SBR) and to compare the performance of two types of SBR's.

First, separate adsorption study with GAC alone was done and the parameters like pH, dose, time and temperature were optimized. The optimum pH was found to be at the natural pH i.e. pH 6.4. Optimum dose was found to be 4 g/l. Optimum time of contact of the experiments was 3 h and the kinetics study showed that 2<sup>nd</sup> order kinetics best-represented the kinetic data. The intramolecular diffusion model showed that the presence of boundary layer is the rate limiting step in the adsorption model as shown by Weber-Morris plot. The isotherm study showed that the adsorption was endothermic in nature. The thermodynamic study shows that negative value of  $\Delta G$  shows the spontaneity of the reaction. The positive value of  $\Delta S$  shows the feasibility of the reaction.

During SBR study, sludge was first acclimatized to consume NP. SBR study was done for varying HRT and the optimum HRT was found to be 1.67 d. The experiments were further done at increased adsorbent dose in GAC-SBR for 100 mg/l. The optimum dose was found to be 2.5 g/l. The effect of increasing concentration was studied and the percentage removal was found to decrease from 92 to 55% when the concentration increased from 100 to 300 mg/l. The study was also done for the binary mixture of NP and 4-chlorophenol. Removal of each was found to be influenced by the presence of the other compound.

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## NOMENCLATURE

NP	4-Nitrophenol
CP	4-Chlorophenol
BOD	Biological Oxygen Demand, mg/l
COD	Chemical Oxygen Demand, mg/l
GAC	Granulated Activated Carbon
HRT	Hydraulic Retention Time, d
$K_s$	Saturation Constant
$K_i$	Inhibition constant
DO	Dissolved Oxygen, mg/l
OUR	Oxygen Uptake Rate, mg O <sub>2</sub> /g VSS/h
SRT	Sludge Retention Time, d
MLSS	Mixed Liquor Suspended Solids, mg/l
MLVSS	Mixed Liquor Volatile Suspended Solids, mg/l
VER	Volume Exchange Ratio
SVI	Sludge Volume Index, ml/g
TDS	Total Dissolved Solids, mg/l
TSS	Total Suspended Solids, mg/l
$q_e$	Extent of adsorption, mg/g
$C_o$	Initial concentration, mg/l
$C_f$	Final concentration, mg/l

## **1 INTRODUCTION**

Phenols and its derivatives are abundantly produced in the environment by various chemical industries and because of high solubility in water it is affecting natural flora and fauna greatly [Aktaş and Ceçen, 2010] as these may be carcinogenic, teratogenic and mutagenic to them [Chi et al., 2013]. 4-Nitrophenol (NP) is widely found in effluent of various industries like pesticides, pharmaceuticals, petrochemicals and other industries [Chang et al., 2009]. These are also considered as toxic compounds [Half maximal effective concentration ( $EC_{50}$ ) = 64 mg/l] [Tomei and Annesini, 2005] and are listed as priority pollutants by U. S. environmental protection agency (USEPA) [Busca et al., 2008]. The concentration of NP in drinking and natural water as per USEPA is below 10 mg/l [Podeh et al., 1995; USEPA, 2005] whereas monthly average industrial effluent concentrations should not exceed 162 g/l [USEPA, 1988; Sahoo et al., 2011]. Therefore, proper disposal of these compounds becomes very necessary [Kulkarni, 2012]. Various methods of treatment of various kinds of phenols have been developed like adsorption, electro-coagulation, photo-oxidation, etc. which are related to high capital and operational cost [Meytal and Sheintuch, 1998; Subramanyam and Mishra, 2008].

### **1.1 Phenols**

Phenols, or phenolics, are compounds having hydroxyl group (-OH) attached to aromatic ring. It is also known as benzenol or carboic acid ( $C_6H_5OH$ ). Its products are emitted from various industries like coking plant, petrochemical industries, petroleum plants, dye manufacturing plants fertilizers as well as paint striping operations [Khan et al., 1981] and fibreboard manufacturing [Eroglu et al., 1994]. Even at low level concentration in the environment, it causes carboic odour in water and is well toxic to human beings also. It is a priority pollutant as identified by USEPA [Keith and Telliard, 1979] and the Ministry of Environment and Forests, Government of India. The permissible limit of phenols and its derivatives as per Bureau of Indian Standards (BIS) for disposal in surface waters is 1.0 mg/l [IS 2490, 1974] and 5.0 mg/l [IS 3306, 1974] in public sewers. Low concentration of phenol in the parts per billion ranges gives water a bad taste and odour [Mallinckrodt et al., 1998]. High phenol concentration up to 1000 mg/l was found in industrial wastewater [Yoong et al., 2001].

**1.1.1 Properties of phenols and alcohols:** Due to specific nature of bonding in phenols having oxygen directly attached to aromatic ring and relatively loose bond in between hydrogen and oxygen atom responsible to higher acidities in these compounds ( $pK_a$  is usually between 10 and 12). It forms stronger hydrogen bonds. Its solubility is high in water (with about 8.3 g dissolving in 100 ml (0.88 M)) and has higher boiling points. Its occurrence is either as colourless liquids or white solids at room temperature. It is highly toxic in nature [<http://en.wikipedia.org/wiki/Phenol>].

**1.1.2 Subcategories of phenolic compounds:** Phenols has the following 19 subcategories as follows: 1) Natural phenols, 2) Benzenediols, 3) Benzenetriols, 4) Bisphenols, 5) Cresols, 6) Hydroxybenzaldehydes, 7) Monohydroxybenzoic acids, 8) Naphthols, 9) Natural phenol glycosides, 10) Phenol antioxidants, 11) Phenol dyes, 12) Phenol ethers , 13) Picrates, 14) Quinolinols, 15) Salicylamides, 16) Salicylates, 17) Salicylic acids, 18) Trihydroxyanthraquinones, 19) Vanilloids [<http://en.wikipedia.org/wiki/Category:Phenols>].

**1.1.3 Derivatives of phenols and common sources of emission:** Phenolic compounds are exposed to the environment from various sources [Wolff et al., 2007]. Bisphenol A is emitted from dental treatment areas like polycarbonate containers as well as sealants. Pesticide industry mainly is the sources of chlorinated aromatic compounds. 4-tert-Octylphenol is produced detergent and surfactant. 5-chloro-2-(2, 4- dichlorophenoxy) phenol is originated from care products.

**1.1.4 Phenol emission from various industries and their ranges:** Phenolic wastewater are emitted in the environment by various industries such as coal plants, refineries, petrochemical industries, pharmaceuticals, fibre glass units, manufacturing of explosive, phenol-based polymerization process, plastic, producing units involving paints and varnish, textile units making use of organic dyes, antiseptics, antirust products, biocides, photographic chemicals, etc. The phenol concentration in steel, petroleum and LT coal industry ranges from 500-1000, 1500-2000 and 10240 mg/l, respectively [Behera, 2008].

**1.1.5 Recovery methods of phenols in waste water at different concentrations:** Phenols may be treated by chemical oxidation, bio-oxidation, or adsorption. Chemical oxidation has high operating cost but low capital cost whereas bio-oxidation has low operating cost and high capital cost. Adsorption has a both high operating cost and high capital cost. Hence all

the factors are responsible for the selection of the particular process. These variables along with concentration of phenol will determine the selection of the process. If phenol concentration ranges from 500-2000 or more, then either adsorption or extraction method is well suited. When the concentration is intermediate, then adsorption or biological treatment is suitable. However, when the concentration is less then chemical oxidation is used [SWTC, 2009].

**1.1.6 The phenol levels from effluent as per national standards:** Phenol is listed in environmental protection agency's (EPA) Priority Pollutants. Under Section 313 of the Emergency Planning and Community Right to Know Act of 1986 (EPCRA), it was found that more than one pound of phenol emitted into the air, water and land and thus enter into the Toxic Release Inventory (TRI). This may be due to 1) phenol has a high BOD and can deplete oxygen in the water in which it is present and is detrimental to the organisms that consume this oxygen for their growth, it is persistently present in the environment when produced in vast amount or continuously produced in large quantities. The national recommended water quality criteria was developed by EPA developed to provide guidance to States and Tribes for adopting water quality standards under section 304(a) of the Clean Water Act (CWA). The maximum national recommended water quality criterion for human health as well as consumption of water and organism level for phenol is 21 mg/l. Moreover, it is an organoleptic i.e. the criteria for odor and taste are 0.30 mg/l [EPA, 1999].

## **1.2 Wastewater Treatment Technology**

The wastewater technologies involve various stepwise treatments to have clean water at the end of the process. The wastewater initially contains a large number of toxic chemicals along with large numbers of suspended particles that have high BOD. So it is necessary to remove first from the wastewater. The screening is done initially in the primary treatment to remove the suspended particles that accounts for approximately 30-50% influent BOD. The screening is done followed by comminuting and grit removal to remove the solids from the solution. The water then undergoes secondary treatment either by physic-chemical process or biological methods. However, the biological methods are of low cost and low operational cost as compared to physic-chemical process. Also, processes such as adsorption requires careful disposal of adsorbent and this type of problem is not happens in case of biological processes. Moreover, the biological microorganisms are used and can be used again and again and can be grown as per the requirement. So, biological methods are nowadays used in



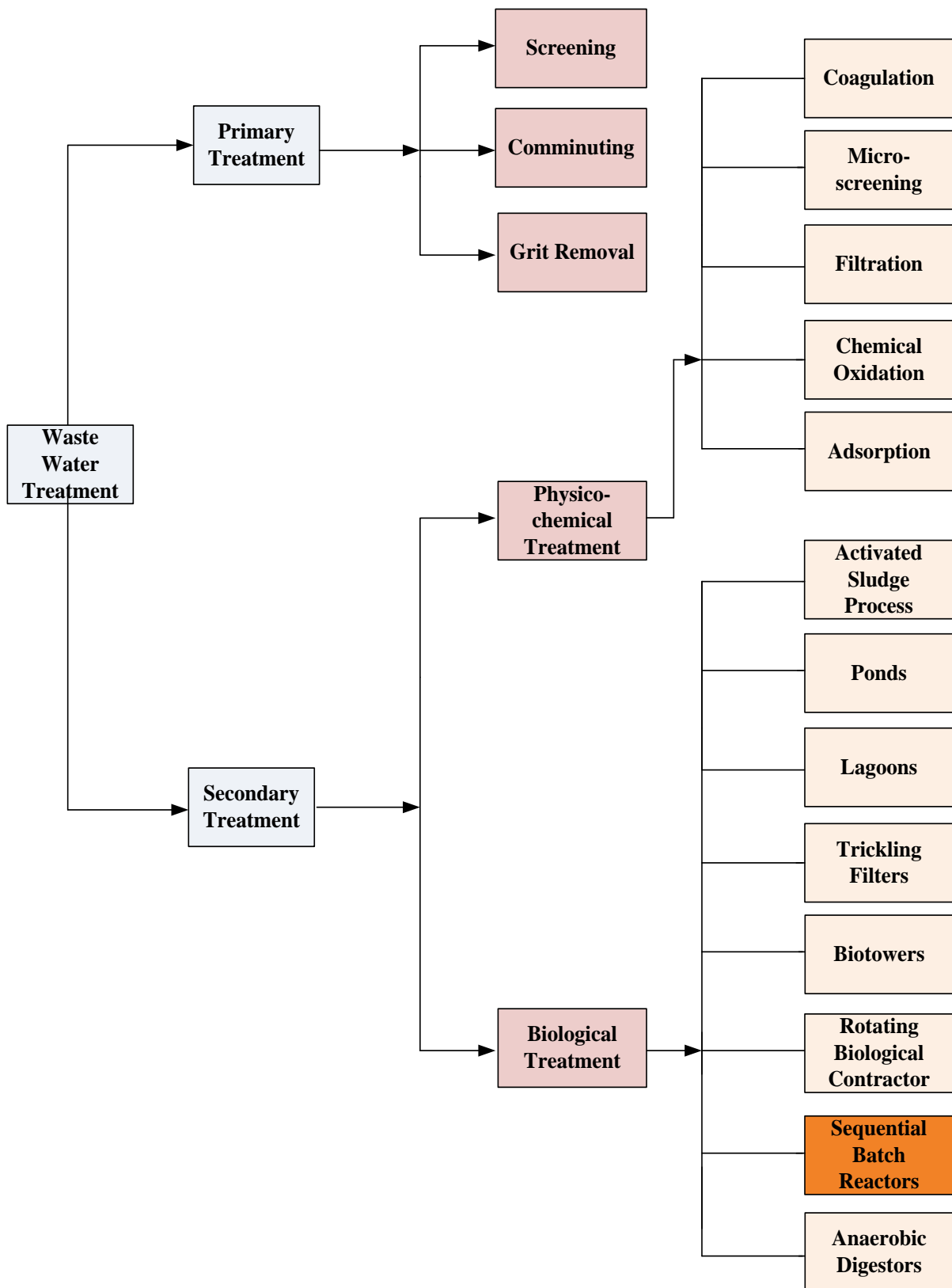


Figure 1.1 Wastewater treatment technologies [Peavy et al., 1985]

the industries and are more environment friendly as compared to other methods. The methods are as shown in figure 1.1.

### **1.3 Sequential Batch Reactor**

Sequential batch reactors (SBRs) now-a-days has become the most important instrument for wastewater treatment. These are widely used in areas of low or varying flow patterns and are used for municipal as well as industrial wastewaters and are quite popular in Europe, China as well as the United States. It is basically based on FILL-DRAW basis. A batch of wastewater is fed in the reactor and undesirable components are removed and then discharged. Mahvi [2008] proposed that equalization process; aeration process followed by clarification process all can be accomplished in one reactor. SBR came into picture since 1970s [Irvine and Davis, 1971]. Due to nature, and advances in process technology, there will be continued renewed interest in SBR for treatment of wastewater. The effluent from the SBR can be monitored and further treated if necessary The batch discharge of treated effluent allows close monitoring of the wastewater and further treatment, if necessary, to meet discharge licence to meet the discharge parameters. It is more economical as all the process is achieved in single basin [Ketchum et al., 1979]. These are nowadays widely used for number of reasons [[http://www.neiwpcc.org/neiwpcc\\_docs/sbr\\_manual.pdf](http://www.neiwpcc.org/neiwpcc_docs/sbr_manual.pdf)]:1) It requires a relatively small space as all the process is achieved in one basin instead of using more than one basin. The use of separate clarifier is also omitted as decanters are used more efficiently and resulting in low TSS around less than 10 mg/l. 2) Instead of biological removal, denitrification, nitrification and removal of phosphorus can also be achieved by adjusting the aerobic, anaerobic and anoxic conditions.3) The basins that are previously used can also be used for SBR as it needs only one basin 4) It is a cost effective method for treating wastewater as compared to other methods. It is also more flexible in process as different conditions can be adjusted which are necessary for the growth of microbes. i.e. [Andres et al., 2006]: 1) COD removal requires aerobic conditions, 2) COD/nitrogen removal requires aerobic/anoxic conditions and 3) COD/nitrogen/phosphorus removal requires aerobic/anoxic/anaerobic.

SBRs are proved to be a cost-effective method for removal of phenols and its derivatives [Sahinkaya and Dilek, 2007]. It consists of mainly five phases namely FILL, REACT, SETTLE, DECANT and IDLE phase [Uygur and Kargi, 2004]. The removal of phenols is more favourable in case of discontinuous reactors such as SBRs as compared to Continuous Stirred Tank Reactors (CSTRs) as it provides dynamic conditions necessary for

the growth of microorganisms. Moreover, it works on large number of operating conditions and flexibility of the operations [Ellis et al., 1996; Tomei et al., 2004]. The mixed culture of microorganisms has the ability to degrade the phenols derivatives after acclimatization [Buitron et al., 2005]. The biodegradable organic compounds have been classified as primary substrates (growth stimulating substrate) and co-metabolized species (non-growth substrates). The microorganisms are acclimatized in such a way as to utilize the non-growth substrates [Monsalvo et al., 2009]. Various mechanisms were suggested previously for biodegradation of NP by specific microorganisms. Spain and Gibson [1991] developed a mechanism in which the NP converted to  $\beta$ -ketoadebate via p-Benzoquinone, Hydroquinone,  $\gamma$ -Hydroxymuconic semialdehyde, Maleylacetate. Moreover, Jain et al. [1994] also proposed the degradation pathway via formation of 4-Nitrocatechol, 1, 2, 4-Benzenetriol followed by Maleylacetate and  $\beta$ -ketoadebate. The removal of NP by mixed culture was studied. Tomei et al. [2003] studied the kinetics of the biodegradation by mixed culture. It was found that Haldane equation well suited for the inhibition of microbes followed by high rate of removal, small acclimatization time and better settling properties of produced sludge thereby confirming the feasibility of the process. Tomei et al. [2004] found that long feed phase and high biomass concentration leads to effective removal of substrate and hence process efficiency improved. Ganesh et al. [2006] has performed the biodegradation of tannery wastewater by SBR involved simultaneous nitrification-denitrification during FILL phase. The simultaneous biodegradation of nitrogen-containing aromatic compounds (nitrobenzene (NB), NP, aniline (AN), and 2, 4- dinitrophenol (2, 4-DNP)) was done in SBR by Yu et al. [2007]. Moreover, they suggested the mechanisms of degradation of the compounds like AN and NB were degraded via catechol 2, 3-dioxygenase formation; NP was degraded via 1, 2, 4-benzentriol 1, 2-dioxygenase; and pathway for 2, 4-DNP was unknown. Kulkarni [2012] investigated the effect the effect of shock and mixed loading (NP, 2, 4-DNP and 2, 4, 6-trinitrophenol (2, 4, 6-TNP)). It was found that loading of 300 mg/l d result into 90% removal while at 600 mg/l d, the removal goes down to 50%. However, the improved removal efficiency was obtained with addition of suitable adsorbents for various adsorbates. Sirianuntapiboon and Ungkaprasatcha [2007] worked on the  $Pb^{2+}$  and  $Ni^{2+}$  removal by bio-sludge by blank SBR and granulated activated carbon (GAC) SBR or GAC-SBR. It was found that at the same hydraulic retention time (HRT), blank SBR showed better removal efficiency than GAC-SBR. Sharma et al. [2010] studied the biodegradation of resorcinol by SBR in which various parameters like mixed liquor suspended solid concentration (MLSS),

resorcinol initial concentration and fraction of aerated fill phase was optimized. Sirianuntapiboon and Sansak [2008] worked on the synthetic and raw textile wastewater containing dyes (direct blue 201 and direct red 23) using GAC and SBR. With increasing dyestuff concentration or decreasing bio-sludge concentration, the GAC-SBR efficiency decreased. Lim et al. [2010] treated landfill leachate using rice husk ash (RHA) as adsorbent using SBR.

#### **1.4 Objective of Work**

The aim of this research was to study the treatment of 4-nitrophenol bearing wastewater by biological treatment in a sequential batch reactor (SBR) without any adsorbent (called as blank-SBR) and an SBR loaded with granular activated carbon (GAC-SBR) and to compare the performance of two types of SBR's.

In the adsorption study the main objective was to investigate the viability of GAC for the removal of nitrophenol. The experiments were carried out to study the following:

- Effect of type of adsorbent, contact time, dose, pH and initial concentration of pollutant on the removal of nitrophenol from aqueous solution by batch process
- Kinetics of adsorptive removal of nitrophenol in batch adsorption study
- To perform the equilibrium isotherm study for removal of nitrophenol using GAC.

The operating conditions, for the biodegradation of nitrophenol in SBR were optimized and the following operating parameters were studied:

- Effect of cycle time, volume exchange ratio (VER) and hydraulic retention time (HRT)
- Effect of initial organic loading
- Effect of dose of GAC in GAC-SBR
- Contact time study of removal of nitrophenol in two types of SBR's.

Further, the study was extended to compare the results of GAC-SBR of binary mixtures i.e. NP and 4-chlorophenol.

## 2 LITERATURE REVIEW

The treatment of phenolic wastewater has been done previously by various means like adsorption, chemical oxidation, and other methods. The sequential batch reactor (SBR) proved to be the most effective in treating municipal and industrial wastewater. Various research papers have been published previously, which is mentioned below:

**2.1 Removal of 4-Nitrophenol (NP) from SBR:** The NP is emitted from various industries like distillery, petrochemical industries, insecticides, drugs, explosive industries. Its half maximal effective concentration ( $EC_{50}$ ) is 64 mg/l. The SBR offers the most cost effective method in removing NP as the sludge can be grown as per the requirement. Following papers discussed the NP removal by SBR.

Bhatti et al. [2002] used biomass retainer in the form of nonwovens which are of low cost and also durable for biological NP. The important parameter was acclimatized sludge degrading NP before its embedding on nonwovens. Results showed that nonwovens resulted in high removal of biological NP. A hydraulic retention time (HRT) of 11 h was sufficient to remove 500 mg/l of NP. Specific loading rates and volumetric loading rates were found to be 165 mg/g-MLSS/d and 1.6 g/l/d, respectively. The NP breakdown resulted in formation of nitrite that was completely converted to nitrate. Moreover, the sludge characteristics were also found in the paper.

Tomei et al. [2003] investigated the NP biodegradation in SBR. Biomass was grown on NP and biological substrate as the growth medium. Haldane equation was used to describe kinetics of NP removal. It was estimated that kinetics was similar in both cases: removal rate goes on increasing with NP/COD ratio. A relationship was developed between total biomass fraction and initial concentration of NP. Good settling, small acclimatization and removal rates were high which showed the suitability of the sludge for removal.

Tomei et al. [2004] studies involved with NP as the sole carbon source in SBR. It was found the instead of inhibition of microbes activity, complete NP removal was observed. Also, when the substrate concentration was very small at the end of filling time, the increased removal was observed. Increased efficiency was observed for long feed time and increased biomass concentration. Also, inhibition kinetics was correlated with Haldane equation with saturation constant ( $K_s$ ) (17.6 mg/l) and inhibition constant ( $K_i$ ) (30.7 mg/l) as saturation

constant and inhibition constant, respectively and removal rate was in between 3.3–8.4 (mg/VSS/d).

Tomei and Annesini [2005] studies involved NP removal with an integration of aerobic and anoxic cycles. The denitrification and oxidation kinetics of NP was further studied. The removal was found to be very high when NP as the only carbon source used in SBR. With initial concentration ( $C_0$ ) of 200-320 mg/l, NP and inorganic nitrogen content in effluent was found to be  $< 1$  mg/l. Denitrification resulted due to lower level of dissolved oxygen (DO)  $\leq 2$  mg/l. For COD/N less than or equal to 3, limiting effect of carbon was not observed, whereas at 2, decrease in denitrification was observed. Denitrification model was also proposed taking both nitrogen and carbonaceous limiting agents and correlated with experimental values.

**2.2 Removal of COD from Tannery Wastewater by SBR:** The effluents from tannery waste contain large number of chemicals along with metal ions, acids and dyes, etc. which are harmful to skin as well as environment too. However, as per the conventional methods which are costly and not flexible in operation, the SBR system provides the best method as compared to the others. The following paper investigated the removal of COD from tannery wastewater.

Ganesh and Ramanujam [2006] investigated the COD removal from tannery wastewater (TWW) by respirometry and SBR process. The time optimized for TWW was 12 h by measuring oxygen uptake ratio (OUR) and chemical oxygen demand (COD) uptake values. COD removal was related to  $O_2$  consumption. The biological activity was well determined by use of OUR plot. Its value was high at FEED phase, whereas became low at ht end of the process. At loading rate of  $1.9\text{--}2.1 \text{ kg/m}^3/\text{d}^{-1}$  and cycle of 12 h, removal of COD, TKN and  $NH_3\text{-N}$  were found to be 80–82%, 78–80% and 83–99%. It was found from the study that high efficiency was achieved as compared to normal suspended-aerobic systems. Also, influent which is readily consumed was 66–70%, which degrade slowly was 10–14%, and which are non-biodegradable was 17–21%. Respirometry method gives Respirometric constant ( $K_{La}$ ) of  $19 \pm 1.7/\text{h}$  except organic load was very high, the capacity of oxygen transfer was more as compared to OUR, and the process was aerobic throughout the process and nitrification–denitrification process was also observed during FEED Phase.

**2.3 Removal of Mixture of NP and its Derivatives by SBR:** The SBR method can also be used for the removal of mixtures of compounds of NP which was limited to the single compounds. The sludge can be grown for mixture and has enhanced capacity as previously.

Yu et al. [2007] studies involved with aromatic nitrogen compounds such as NB, 4-NP, AN and 2, 4-DNP. The experiments involved 50-180 mg/l of all the compounds. More than 99 % removal was obtained for loading rates of 0.36 kg/(m<sup>3</sup>/d), 0.3 kg/(m<sup>3</sup>/d), 0.25 kg/(m<sup>3</sup>/d), and 0.1 kg/(m<sup>3</sup>/d) for NB, NP, AN and DNP, respectively. Various Bacteria such as *Bacterioidetes*, *Proteobacteria* and *Candidata division TM7* were found in excess. Feeding and aeration parameters were varied for different cycles and it was generated the fact that they are able to adjust in the changing environment. The mechanisms developed for different types of compounds such as catechol 2, 3-dioxygenase formation takes place in AN and NB degradation and 1, 2, 4- benzotriol 1, 2-dioxygenase was developed during NP degradation, whereas the pathway for 2,4-DNP was not found.

Kulkarni [2012] studied shock effect of NPs on three SBRs using synthetic feed. *Thiosphaera pantotropha* congaing sludge was used to transform biologically NPs by Simultaneous SND. Three reactors used for the experiments with NP, 2, 4-DNP and 2, 4, 6-TNP having initial concentration of 200 mg/l whereas one reactor used for background. Having HRT of constant value of 48 h, shock loads of 400 mg/l, 600 mg/l and 800 mg/l was used. Duration of 4 days was given to shocks and the reactor then allowed for the normal loading which was 200 mg/l d. After every step, the reactor was allowed to recover its original performance. It was resulted from the study that for NP & 2, 4-DNP, 600 mg/l d of shock load was completely removed, whereas for 2, 4, 6-TNP, half degradation took place. Normally 8 to 10 days was required for recovering the original position. The experiment was done for the mixed loads of NP: 2, 4-DNP: 2, 4, 6-TNP in the ratio of 1:1:1 on the reactor third. It was depicted that for 300 mg/l d, about 90% removals took place whereas half of the removal took place for 600 mg/l d.

Chi et al. [2013] inoculated three strains such as *WBC-3*, *JMP134* and *NyZ215* that utilizes NP, 3NP and 2NP, respectively. In about 2-16 d, completer removal was took place for acclimatized sludge whereas for unacclimatized sludge, the removal was less. It was also depicted that these three strains were survived during the incubation. The contamination created by NPs had very little effect on the growth of bacteria which was determined by polymerized chain reaction (PCR) technique. Although dynamic changes occurred this was shown by gel electrophoresis.

Uygur and Kargi [2004] did experiments to know the viability of the sludge for removing phenols of different concentrations and to check the inhibition of the sludge. Different phases used were of anaerobic (1 h), oxic (3 h) and anoxic (1 h) and settling of 0.75 h. A sludge retention time (SRT) of 10 d was fixed for all the experiments. The concentrations were varied from 0-600 mg/l. COD, ammonium nitrogen and phosphate-phosphorus and nutrient level in effluent was investigated. Up to 400 mg/l, the complete degradation of Phenol took place and having no effect on the nutrient. However with  $C_o > 400$  mg/l, the adverse effect on nutrient removal was observed. COD (95%),  $NH_4-N$  (90%) and  $PO_4-P$  (65%) removal took place for  $C_o < 400$  mg/l. Also, settling volume index (SVI), which is important parameter for settling of sludge, for  $C_o < 400$  mg/l, its value 45 ml/g, and for  $C_o > 400$  mg/l, its value was 90 ml/g.

**2.4 Removal of 4-Chlorophenol (CP) by SBR:** Chlorophenols are also xenobiotic compounds as NPs. It can produce from various industries like agriculture (resins, herbicides, preservatives, etc.) The CP present in the water resulted in decrease in COD, nitrogen ( $N_2$ ) and phosphorous (P) uptake. So its removal is necessary both from surface and water too. The following paper establishes the relation of CP removal at different conditions.

Monsalvo et al. [2009] studied for removal of both CP and phenol at different temperatures. For a HRT of 10.5 d and Phenol at 525 mg/l, the CP concentration varied from 105 to 2100 mg/l. For CP concentrations up to the limit 1470 mg/l, complete removal of both compounds takes place. The removal of both compounds was depending on CP concentration and temperature. With mixed liquor suspended solids (MLSS) of 2100 mg/l and at higher temperature ( $35^\circ C$ ), maximum removal was observed with less toxicity in the effluent. The intermediate found during the degradation was 4-chlorocatechol (4-CC).

**2.5 Removal of NP by Adsorption:** Phenolic compounds are known as priority pollutant as it is detrimental to human as well as animals. It should be less than 1 mg/l in the wastewater. Although various methods are present the adsorption by modified clays has attracted attention towards itself. As it are organic compounds and can be modified to increase its capacity. The following paper derived the clays to modify its properties. Various parameters were discussed in the adsorption study.

Alkaram et al. [2009] used surfactants (HDTMA and KC) to modify modified natural bentonite and kaolinite to have following clays, i.e., BHM, KHM and KPM. These minerals were further examined by x-ray diffraction (XRD) and fourier transform infrared



spectroscopy (FTIR). Adsorption method of methylene blue was used to determine the surface area. Copper method using ethylenrdiamine complex was used for cation-exchange capacity and the total carbon (TC) analysis used for loading. The batch technique was used for adsorption and effect of time, temperature and pH was examined. The results depicts that modified clays was better as compared to unmodified clays. Further, adsorption process was found to increase with temperature which showed the phenomenon is endothermic. Effect of pH showed the removal increased with increasing pH and Freundlich and Langmuir isotherms best fitted the experimental values. Pseudo 2<sup>nd</sup> order kinetics was fitted for data.

**2.6 Biological Degradation Mechanism of NP:** The NP degradation has achieved a high success in the treatment of NP. However its degradation mechanism is not discussed often. The following paper discusses the degradation mechanisms.

Jain et al. [1994] derived the mechanism for the removal of NP biologically. The strains of *Pseudomonas* and *Moraxella spp.* were used for the purpose. The degradation was carried out by removal of nitro group. The hydroquinone thus formed undergone fission of ring by an enzyme dioxygenase. Further, they developed *Arthrobacter sp.*, JS443, which was capable of degrading NP. From radiotracer and gas chromatography-mass spectroscopy, (GC-MS), it was shown that 1, 2, 4- benzenetriol was formed during inoculation which was transformed to maleylacetic acid via I-ketoadipate pathway. There was formation of 4-nitrocatechol or 4-nitro-resorcinol by *JS443* and the monooxygenase system was responsible for the conversion.

Spain and Gibson [1994] derived *Moraxella* strain for the removal of NP via release of nitrite. Also, during acclimatization of sludge, a portion of hydroquinone (HQ) was also formed in 2, 2'-dipyridyl medium and the enzyme catalyzed reaction requires nicotinamide adenine dinucleotide phosphate-oxidase (NADPH) and O<sub>2</sub>. The high performance liquid chromatography (HPLC) was used for the determination of intermediate species. The HQ was converted to  $\gamma$ -hydroxymuconic semialdehyde, which was further converted to I-ketoadipic acid in the presence of NAD<sup>+</sup>. Now, this compound is converted to maleylacetic acid when pyruvate and lactic dehydrogenase also present in the medium. For potassium ferricyanide, the results were found to be similar. Later, the *spp.* grown also convert maleylacetic acid via oxidation of 1, 2, 4-benzenetriol and detected by DEAE-cellulose chromatography.

**2.7 Removal of Metal Ions by SBR:** SBR also proved to be the best method for the removal of metal ions from the wastewater along-with the organic compounds. The following paper discusses the removal of metal ions by SBR.

Sirianuntapiboon and Ungkaprasatcha [2007] used sludge for metal ( $Pb^{2+}$ ,  $Ni^{2+}$ ) removal and it was discovered that the capacity was reduced to 10–30%. When synthetic industrial estate wastewater was used as acclimatized medium, the capacity of adsorption was  $840\pm 20$  and  $720\pm 10$  mg/g for  $Pb^{2+}$  and  $Ni^{2+}$ , respectively. About 70–77% elution took place with  $HNO_3$  solution having concentration 0.1 mol/l. It was estimated that the removal increased with increase in HRT and the removal was more for unacclimatized sludge as compared to acclimatized sludge. The SVI < 80 ml/g was found.

**2.8 Effects of Inoculation of Known Microorganism in a SBR:** Normally mixed culture is used as the medium for the removal. However, single microorganism also provides the better medium for removal as it grown for the special purpose of removing the microorganisms.

Soda et al. [1998] developed microorganisms which was genetically modified (GEM) and named *Pseudomonas putida BH (pSI0-45)*, which has modified capacity for the removal of phenol as compared to the simple sludge. Normally, it is well known that higher concentration of phenol is detrimental to the microbes and hence adversely affect the process of removal thereby reducing the efficiency of the process. Moreover, the influent fluctuations have little effect on the removal of phenols. *Pseudomonas putida BH* was used for cloning the organisms for phenols degradation and also catalyzes the reaction. The results proved that complete removal of the phenol took place from SBR treatment with zero concentration of phenol in the effluent. When the feed was semi-continuous, the sludge settling get adversely affected and the SVI value also increased resulted in poor settling.

Ehlers and Rose [2005] cultivated white-rot fungal cultures, which was immobilised and used for the removal of phenol and 2, 4, 6-trichlorophenol (2, 4, 6-TCP) and the medium used for the process was pinewood chip and bead-packed consisting of foam glass. Moreover, ligninolytic *basidiomycetous fungi* were used previously for the removal of phenolic compounds containing chlorines. For *Phanerochaete chrysosporium fungi*, extra care had been taken for nutrition and their survival so pH, temperature, time and other parameters were also taken in consideration. It was found that the capacity can be increased by immobilizing the organism. The benefit of having SBR is of uniform distribution of sludge and more consistent with variation in influent concentration.

Moussavi et al. [2010] has done the experiments on the removal of phenols from saline wastewater by biological means. The organisms used during the process were *Halobacterhalobium*, which is a halophilic microbe and is useful in the removal of phenol. Experiments were performed for the treatment of saline WW containing 15% salt in the presence of halophilic microbe. 100% removal was observed for a solution of NaCl having concentration of 14%. The one of the advantage of using SBR that it is possible to have granules so the problem of sludge settleability improved along with reactor performance. So, GSBR system was used for different conditions like cycle time, filling time,  $C_o$  of phenol and shock loads. Moreover it was found that the GSBR technique gives better results as compared to normal process.

**2.9 Effects of Change in Temperature:** The various studies involve various different parameters. However the effect of temperature is not much discussed earlier.

Monsalvo et al. [2009] removed the CP from phenol consuming microbes and the temperature effects were also studied. The nutritional compounds were classified as growth and non-growth substrate. The non-growth substrate has some effect on the growth substrate. Moreover, the effect of temperature was also not focused previously for the removal as well as for intermediate formation. In the present work, the temperature was varied from 10-24°C and the results showed the 24°C was the optimum temperature in the treatment process.

**2.10 Removal of CP and its Derivatives by SBR:** A lot of study regarding the removal of CP by SBR. However the mixtures of CPs derivatives are not much studied previously. The following papers studied the mixtures of CPs.

Sahinkaya and Dilek [2006] studies involved for the removal of mixture of CP (200 mg/l) and 2, 4-DCP (110 mg/l) using SBR. Mixed culture was used for the accomplishment of the treatment as it utilises various chemicals present in the wastewater. It was found that in the presence of biogenic substrate, the removal of CP was decreased, while for 2, 4-DCP, the rate of removal was increased. It was clear that in the case of SBR, the problem of self and competitive inhibition was diminished and it provides better means for the removal of mixture of compounds. Moreover *Pseudomonas* sp. and *Pseudomonas stutzeri* were found to be in large quantity in the mixed culture.

Nalbur and Alkan [2007] used two compounds 2-CP and 2, 4-DCP to study the kinetics in removing these compounds from SBR. As it is known that various microbes are able to degrade the chlorinate compounds, so it is feasible method as compared to other

methods like oxidation, adsorption, etc. CSTRs also showed inhibitory effects on the removal with varying concentrations. So the study involved three steps mainly. The first step was determination of  $EC_{50}$  values followed by inhibitory effects on the sludge and inhibition kinetics from unacclimatized sludge.

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**2.11 Effects of Change in Concentration:** The papers regarding this section deals with the removal of phenols derivatives and the change in concentration is discussed along with other parameters also.

Kargi et al. [2005] used different sludge age and  $C_o$  of phenols for CP removal from SBR. The COD, phosphate ( $PO_4$ ), nitrogen ( $N_2$ ) removal was also observed. The initial concentration was varied from 0-400 mg/l. The results showed that with increasing sludge age, the removal goes on increasing whereas with increasing concentration, the removal was further decreased.

Papadimitriou et al. [2009] examined two reactor performances i.e., continuous stirred tank reactor (CSTR) and SBR for phenol and cyanide removal from the wastewater and toxicity was also assessed. The mixture of both compounds was previously not studied for the removal. The studies too involved with pure culture systems and the sludge treatment was not done previously. It was found that the SBR system proved to be the better model as compared to the CSTRs.

Leong et al. [2011] studies involved with varying concentration of phenols and the characteristics of the sludge was also examined in the experiment. In the ASP, the performance of the reactor depend on the characteristics of the sludge, also more than 70% removal was obtained for the initial concentration of 600 mg/l. A result showed that filamentous growth took place for lower phenol concentration of 400 mg/l and for 800 mg/l or more, dispersed growth took place. The result depicts that filamentous growth is limited when the influent concentration is high at the end of the FILL Phase but bacteria which form

floc undergo normal growth. For  $C_o > 400$  mg/l, the SVI increased drastically which may be due to breaking and inactivation of microbes.

**2.12 Effects of Addition of Adsorbents:** The following papers studied the removal of phenols derivatives with much more efficiency by addition of the adsorbents. The addition of adsorbents has improved efficiency as compared to the blank SBR. The adsorbent thus chosen as per the different variables taken into considerations like surface area and compatibility with the solution.

Mohan et al. [2005] studied for the complex effluent from industry under aerobic conditions using SBR. The one of the main difference in the SBR is that its volume changes with time as compared to the conventional process. The present work involved the study of different loading and the performance in treating wastewater.

Rao et al. [2005] studied the modified form of SBR known as SBGR, in which granular form is used as compared to suspended growth process in treating composite wastewater. The characteristics of the wastewater are as follows: BOD/COD ratio was low and it was around 0.3 and sulfate content was quite high i.e., 1.75 g/l and TDS concentration was also high (11 g/l). Substrate and sulphate removal study was performed for both suspended and granular SBR process. It was found that the biofilms attached on the adsorbent gives higher removal as compared to suspended growth. Moreover, the settling of the sludge also improved resulting in improved efficiency. The experiments were performed for different OLRs. The GAC was used as the adsorbent in the present study.

Wang et al. [2007] developed granules in SBR process for the removal of 2, 4-DCP. Previously, large work has been already done in the field of ASP, and suspended culture in SBR. However, a little work is done in the field of granular formation. This proves to be an innovative method for the removal in past few years. It eliminates the need of settling equipments. It also spares the advantage of prevention of microbes from toxicity and predation. The results showed that with increasing 2, 4-DCP concentration the sludge yield as well as hydrophobicity changed dramatically.

Lim et al. [2010] used rice husk as adsorbent in SBR to powdered activated carbon. The experiments were done for domestic and landfill leachate for COD as well as nitrogen removal. The leachate is generally known for its high COD and nitrogen in the form of ammonia as well as many xenobiotic chemicals and heavy chemicals. As SBR is more flexible in varying concentration, it provides better means for the removal as compared to other methods. However, leachate having high toxicity so it may inhibit the process so use of

activated carbon inhibit the effect. However, as compared to the cost of activated carbon as compared to rice husk, it is well established that the total cost of the process get reduced.

**2.13 Respirometry Method:** Respirometry method in SBR provides a better means for removing the phenolic wastewater from the solution. Various research papers have shown the above facts which are as discussed below.

Yoong et al. [1999] demonstrated that the inhibitory effect of particular substrate can be minimized by introducing the respirometry phenomenon. The phenol of having concentration up to 1300 mg/l used for the experiment and the optimum cycle time was studied. OUR was developed for the present work and it was found to have close relationship with the phenol. It was found that initially i.e. during FEED Phase, OUR was quite high and when the substrate removal took place i.e. at the end of the REACT Phase, the value of OUR got reduced. The main effect of the toxic compounds is that it may inhibit the process and resulting in the washout of the organisms. An HRT of having low value was found to be the suitable for this removal process. Also, for a short HRT, the REACT Phase also gets shorter; it resulted in enlarged capacity to small capital cost of the system. Moreover, at different HRTs, the removal efficiency of carbon was also examined.

Ganesh et al. [2006] joined together the SBR process and respirometry method in removing COD from tannery wastewater. As effluents from leather tannery is the origin of various chemicals. Simple processes such as adsorption or oxidation proved to be a highly costly method for removal. However, in case of SBR, it provides more flexibility as compared to other processes. Moreover, if comparing with CSTR, it is not as flexible as compared to SBR. At the same time it gives higher removal efficiencies of nitrogen as well as organics. Respirometric method is linked effectively with OUR. The characteristics of wastewater such as BOD, toxicity and other parameters can be determined by this method. One of the important parameter known as ORP can be used to determine anaerobic/aerobic/anoxic phases in the SBR. In this study the metabolic activity can be directly assessed by Respirometric measurements. Moreover, the removal of  $N_2$  and carbon was determined at two HRTs.

**2.14 Biodegradation of NP and Resorcinol:** The removal of mixtures of compounds which are structurally similar is not much studied. The following paper discussed the mixture of NP and resorcinol.

Sharma et al. [2010] studies involved different parameters like MLSS,  $C_o$ , and the fraction of aeration phase to fill phase in removing resorcinol from the synthetic wastewater.

It is listed in priority pollutant as it has high BOD, toxicity and biodegradability is considerably low. The MLSS was constantly maintained in the reactor by proper sludge wasting and it was found to be 3170 mg/l. various phases used in the SBR process have optimum timing. 1.75 h and 0.75 h were found for REACT and SETTLE Phase with a cycle time of 5 h. Further, the removal efficiency was found to be 85.81 % for  $C_o = 50$  mg/l. Moreover, to make the overall process economic, the sludge can be filtered and dried and can be used in incinerators or the ash that formed by burning can be blend with manure/ building block.

## 2.15 Literature Review Table

The following table 2.1 describes the comparative study of removal of phenolic waste from effluents of various industries.

**Table 2.1 Literature review**

Type of industrial waste water	Micro-organisms	pH	T(°C)	COD (mg/l)	Scale and reactor conditions	Total cycle time (h)	HR T (d)	(%) Removal COD	Nutrient Removal (%) or production rate and others (%)	Influent Phenol concentration (mg/l) /others	Reference
Synthetic waste water	<i>P. putida</i> BH (pS 10-45) – (GEM)	7.2	25		Laboratory scale, shake flask	Shock loading- 14 Semicontinuous loading- 20			-GEM inoculated & control SBR- Phenol : 100 DOC : 80-95 Microorganism-		[Soda et al., 1998]
synthetic wastewater		7.08 ± 0.28		4800 ± 350		12	2	80- 82	-TKN = 78-80 -NH <sub>3</sub> – N = 83-99	-TKN = 255 ± 18 -NH <sub>3</sub> – N = 128 ± 20	[Ganesh et al., 2006]
Municipal Wastewater			25	920		39		95		2,4-DCP -50 to 100 mg/l	[Wang et al., 2007]
Municipal wastewater					CSTR and SBR	12	1.25	63 - 92	-Effluent toxicity reduction = 30 – 40	400 – 1200	[Papadimitriou et al., 2009]



synthetic wastewaters			20 - 35		lab-scale -working volume = 2.1 l	12	10.5		-Phenol removal = 100	Phenol = 525, CP = 105–2100	[Monsalvo et al., 2009]
synthetic wastewater		7.0	25±5	6780	laboratory-scale -working volume = 2.4 l	24	1.6	100 at C <sub>o</sub> = 3000 mg/l	-Phenol removal = 99	50 – 3325	[Moussavi et al., 2009]
Domestic wastewater and landfill leachate		8.4 – 8.7		750 – 850	Two SBRs which are identical and made of plexi glass -30 cm (L)×25 cm (W)×20 cm (H) -working volume = 10 l	24			-100 % removal of AN up to 215 mg/l	Bacto-peptone (100), glucose (280), CH <sub>3</sub> COONa (600), (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (250), KH <sub>2</sub> PO <sub>4</sub> (100), K <sub>2</sub> HPO <sub>4</sub> (100), MgSO <sub>4</sub> ·7H <sub>2</sub> O (100), CaCl <sub>2</sub> ·2H <sub>2</sub> O (30) and FeCl <sub>3</sub> ·6H <sub>2</sub> O (10), AN (50)	[Lim et al., 2010]
saline wastewater				227 – 4550	cylindrical bench scale reactor -15 cm (D) × 40 cm (H) -working volume = 4 l	14 – 24		99	-Phenol removal = 99	100–2000	[Moussavi et al., 2010]

Synthetic wastewater			28 ± 2		two identical well-mixed SBR -diameter = 13 cm -working volume = 2 l	5			-resorcinol removal: 85.81% at C <sub>0</sub> = 50 mg/l.	Resorcinol = 10-200	[Sharma et al., 2010]
Synthetic wastewater		7.0 ± 0.8			laboratory scale -6.5 cm (D) × 110 cm(H) - Working volume = 2.5l	46	4		-100 % degradation of FP. - 2-FP degrading strain retained.	2-FP = 2.38 mM (phases II, III and VII) and 4.76 mM	[Duque et al., 2011]
Real coal gasification wastewater			37 ± 2	2500	Two UASB reactors: -8 cm (D) × 100 cm (H) -working volume = 5l	35	2	-Aerobic digestion = 55-60 -Anaerobic digestion = 20	Phenol removal: 58-63	143-540	[Wang et al., 2011]
synthetic wastewater				5220	single tank reactor -dimension = 30 cm (H) × 15 cm (W) × 35 cm (L) -Working volume = 18l	12		Phenol concentration: -below 400 mg/l = 100 mg/l -above 400mg/l = 250mg/l	On increasing phenol concentration : -sludge morphology : normal floc to zoogloea floc, decrease in sludge settleability	100-400	[Leong et al., 2011]

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### 3 SEQUENTIAL BATCH REACTOR AND ADSORPTION

#### 3.1 Sequential Batch Reactor Process

**3.1.1 Basic treatment process:** The Sequencing Batch Reactor (SBR) is more commonly an activated sludge process (ASP) in which both bio reactions as well as separation among solid-liquid takes place in one reactor basin. It is the method of relatively low cost and small footprint at the same time and is nowadays more common method as compared to other methods. It utilizes a group of mixed culture i.e., different microorganisms that can adjust themselves to the varying conditions necessary for the growth of microbes so the process is quite handy and more flexible. It can be used for different purposes at the same time such as for the removal of chemical oxygen demand (COD) only which requires aerobic conditions, for COD as well as nitrogen removal which requires aerobic or anoxic conditions or for COD, nitrogen ( $N_2$ ) as well as phosphorous (P) removal which requires aerobic or anoxic or anaerobic conditions. Due to the presence of various parameters and different conditions, sometimes it becomes very difficult to optimize the parameters in the SBR. However, optimization can be achieved by running two or more reactors at the same time and determine the effluent quality as per the standards. Nowadays, for the treatment of domestic wastewater, it proves to be a best option for the treatment as it has simple configuration and at the same time all the phases work in the same basin. The flexibility of different conditions like aerobic or anaerobic or anoxic can be used to achieve desired degree of removal. It works on simply fill and draw basis in which various phases involved to have removal. It is well suited for the low or intermittent flow variations, which is not reliable in case of continuous stirred tank reactors (CSTRs). It is similar to the normal SBR, but the only difference lying in the continuity of the flow. Moreover, a baffle can be introduced to adjust the flow. The following steps are involved in the SBR process namely a) FILL, b) REACT, c) SETTLE, d) DECANT, and e) IDLE Phase. The variations in these phases along with variations in the oxygen availability, the desired degree of removal can be achieved. Bubble diffusers, which may be coarse or fine, or floating aerators or jet type can be used. The primary treatment involves screening, grit removal or comminution followed by secondary treatment which is basically biological method specially SBR process. Various parameters like hydraulic retention time (HRT), sludge retention time (SRT), dissolved oxygen (DO), organic loading rate as well as influent characteristics such as biological oxygen demand (BOD), chemical oxygen demand (COD), pH, etc, determine the performance of the SBR process. An SBR may be used as single basin or a number of basins used in parallel to achieve desired degree of removal.

**3.1.2 Steps in SBR process:** It involves following steps which can be varied as per the conditions.

**3.1.2.1 FILL phase:** The addition of the wastewater is done in the FILL Phase. This provides food for the microorganisms so that biochemical reaction may occur. The aeration and mixing can vary the conditions of the sludge for proper removal of the contaminant. It is of following three phases:

**Static Fill:** In this phase, no mixing and aeration takes place. It is used when no nitrification or denitrification takes place. It is also used when low flow rates are used. Also, this is a power saving phase as no mixers or aerators are used.

**Mixed Fill:** Only mixing take place and no aeration take place. The mixing results in uniform mixing of wastewater and sludge. As aerators remain off, anoxic conditions prevail in the system resulting into denitrification. However, when anaerobic conditions reached in the reactor, the phosphorous release take place which will again absorbed by them as aerobic conditions prevail.

**Aerated Fill:** In this, both mixing and aerators remain on. So, there is no scarcity of oxygen in the reactor. Moreover at the same time the anoxic/ anaerobic conditions get converted to aerobic one. No denitrification takes place in the presence of oxygen. DO should be maintained above 2 mg/l for maintaining aerobic environment in the reactor.

**3.1.2.2 REACT phase:** In this phase, no further addition of wastewater takes place while mixing and aeration is kept on and also removal of substrate takes place in this phase. The removal of BOD takes place in the phase. The nitrification takes place in this phase as aerobic condition prevails in this phase while the phosphorous which was released during the anaerobic phase gets again absorbed by the microbes.

**3.1.2.3 SETTLE phase:** In this phase the aerators and mixers remain off and the quiescent environment is maintained throughout the phase. The sludge undergoes settling thereby producing a constant mass of sludge. The mixture thus converted to a constant mass of sludge and clear supernatant above the sludge. The sludge produced by settling process is called sludge blanket. It is very important part of the process as there is some probability of withdrawing of the sludge during the DECANT Phase thereby degrading the quality of the effluent.

**3.1.2.4 DECANT phase:** In this, the clear supernatant is withdrawn from the reactor after the SETTLE Phase. After the completion of the settle phase, the operator sends signal to the decanter to open the valve. The decanters are of two types. The floating arm decanter provides flexibility of the operation to maintain the liquid level in the reactor. The fixed arm decanter is of low cost and can be adjusted as per the requirement. One thing should be noticed that the solids present in the reactor should not be washed out along with the foams or scum. Moreover to maintain the optimum conditions in the reactor during operation it is worth noting that the amount decanted should be same as that of influent volume in the reactor. Also to have increased efficiency of the decant phase, there should be maximum distance between the liquid level and the bottom of the reactor.

**3.1.3 Continuous SBR systems:** An ideal SBR is basically a batch system which allows definite volume of the influent volume to enter in the reactor and same for decanting. However this system can be modified to have continuous flow of liquid although the flow rate should be small so as not to affect the sludge settling characteristics. The batch system can be used as continuous only in emergency situations. The plants that operate the reactor as continuous has adverse effects in the performances such as effluent quality gets worsened, washout of the sludge may take place and the efficiency of the system gets reduced.

**3.1.4 Biodegradation phenomenon:** It is the phenomenon of degradation of contaminants present in the wastewater biologically i.e., in the presence of microorganisms. It has many benefits as compared to other treatment methods such as:

**3.1.4.1 Advantages:** The advantages of the biodegradation are as follows:

- The microorganisms do not produce harmful by-products at the end of the reaction.
- Its installation does not pose any problem and it is easy process as compared to other methods.
- It has high potential to remove the toxic contaminants to certain lower limits as given by Central Pollution Control Board.
- It is cost effective method as the microbes once acclimatized can be used without replacement for several times.
- The process is auto regulating and does not require any external source for the reaction.

**3.1.4.2 Disadvantages:** The disadvantages of the biodegradation are following:

- The mixed culture is normally used as the wastewater generally consists of various chemicals in varying amounts. So it is difficult to know the microbes which are responsible for the process and at the same time the mechanisms that involved in the reaction is also sometimes not known.
- The biological reaction once starts are difficult to adjust as various parameters needed for the reaction to take place.
- The response time is also slow and it takes time to adjust in the new environment and any change in the DO results in several minutes to cope up with the changes conditions.

**3.1.4.3 Features of the biological reactions:** The biological reactions differ from the physical processes. The features of the biological reaction are as follows:

- Simple attached or suspended growth of microorganisms takes place and it provides the means for the treatment of the wastewater i.e. removal of biological oxygen demand or chemical oxygen demand or removal of hydrocarbons.
- The removal rate is depend on the transfer of oxygen from the environment and to the surface of the biofilms so more transfer means more removal rate as compared to the lower oxygen transfer rates.

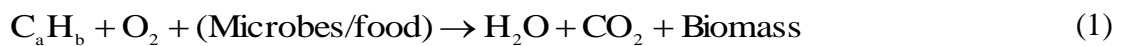
**3.1.4.4 Benefits of biological reactions:** The benefits of biological reactions are as discussed below:

- The rate of biological reaction depends on the amount of microorganisms or sludge volume. The greater the sludge volume the faster will be the reaction and vice versa. So increasing the amount of sludge resulting in increase in rate of reaction and hence increasing the efficiency of the reactor.
- It provides flexibility of operation based on influent conditions such as it can work with varying flow rate and adjust itself with the different organic loading.
- The maintenance required to these systems is also very less as compared to other methods.

*Pseudomonas Putida* is the most suitable microorganism for the wastewater treatment as it can adjust easily to the new environment of phenols. Moreover, it can utilise it for growth as well as maintenance of itself via metapathway. In this pathway the dehydroxylation of the compound takes place followed by formation of catechol derivative the ring thus

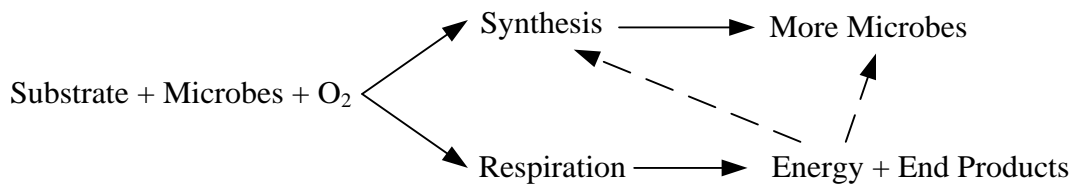
opened by oxidation of Meta position. The complex compound thus converted to simple molecule and this enter into TCA cycle to provide energy to the microbes.

**3.1.5 Degradation of the hydrocarbons under aerobic conditions:** The biological reaction is different under aerobic and anaerobic conditions bot. The yield of the reaction in aerobic conditions is better as compared to the anaerobic conditions. The microbe that consumes hydrocarbons in the presence of oxygen is called aerobes. It uses the influent waste as food and in the presence of oxygen it converts the substrate into small molecules. This process has several advantages such as the plant required is of small area, higher degree of removal can be achieved by this procedure and it requires small retention time of solids at the same time. The reaction involved in the procedure is written as (eqn 1):



So by the aerobic degradation of the carbon sources, the complex compound gets converted to simple water and carbon dioxide leaving a portion of the biomass as the end product.

**3.1.6 Pathway for digestion of substrate:** The digestion process of the substrate by aerobic microbes involve the oxidation of the substrate and in finally converted to smaller molecules such as carbon dioxide, nitrates, phosphates and water followed by production of biomass as the end product. Both nitrification as well as denitrification can take place simultaneously. The mechanism pathway can be described as follows (Figure 3.1):



**Figure 3.1 Degradation mechanism**

The enzymes mainly responsible for the oxidation includes oxygenases enzyme. The mono enzyme used in oxidation of both aromatic as well as aliphatic enzymes whereas di enzymes used for aromatics only. Nowadays peroxidises enzyme is normally used to degrade lignin. The substrate used act as electron donor and the rate of reaction as well as extent depend on the amount of oxygen present in the reactor.

### 3.1.7 Design and configuration of SBR

The configuration of a SBR consists of a large amount of variations. The major parts include inlet, outlet, reactor, aerators, settling devices and controllers. Two types of SBRs are common. The first one is race tank channels or configurations (figure 3.2). In this type, the height of the channel is determined by the aerators used in the tank. The ease of construction determines the width of the channel. Rotors which are horizontal and mounted on float are used for mixing as well as aerations. The foam also formed during the process and there is possibility of removal of scum from the system so scum protector is used to protect the scum from the reactor. However the disadvantages associated with this system is that it requires large area for installation. The second type of SBRs used is of rectangular type (figure 3.3). The design of the SBR include the minimum length to diameter ratio should be maintained above 3:1 so as to prevent the sludge from disintegration, to stop short circuiting and to avoid the wastage of sludge from the reactor basin during DECANT Phase in the SBR. This system is more important for the case where the FILL is continuous and the DECANT is not continuous. However, when both phases are intermittent then the length to width ratio is not of much importance. For having a large output or for large treatment is needed, two or more reaction tanks are used in parallel to meet the required specifications. It is used for municipal or industrial wastewater systems and used where the FILL Phase and DRAW Phase is not coinciding at the same time. This is commonly known as Multi-tank SBRs (figure 3.4). The influent wastewater undergoes primary treatment. This involves removal of suspended solids that accounts for the 50 % of the influent solids and responsible for 30% influent BOD. The removal is followed by secondary treatment and it is specifically a biological reaction which takes place in SBR as others may be the case.

**3.1.7.1 Decanters used in SBR:** The decanters used in the SBR process plays a crucial role in the treatment of wastewater. In the SBR, it is very important to not allow the sludge to remove from the reactor as it affects the process adversely.

The volume that can be decanted is given by (eqn 2):

$$v_d = VER v_{max} \quad (2)$$

where  $v_d$  is the volume to be decanted, VER is the volume exchange ratio and  $v_{max}$  is the maximum volume of the SBR.



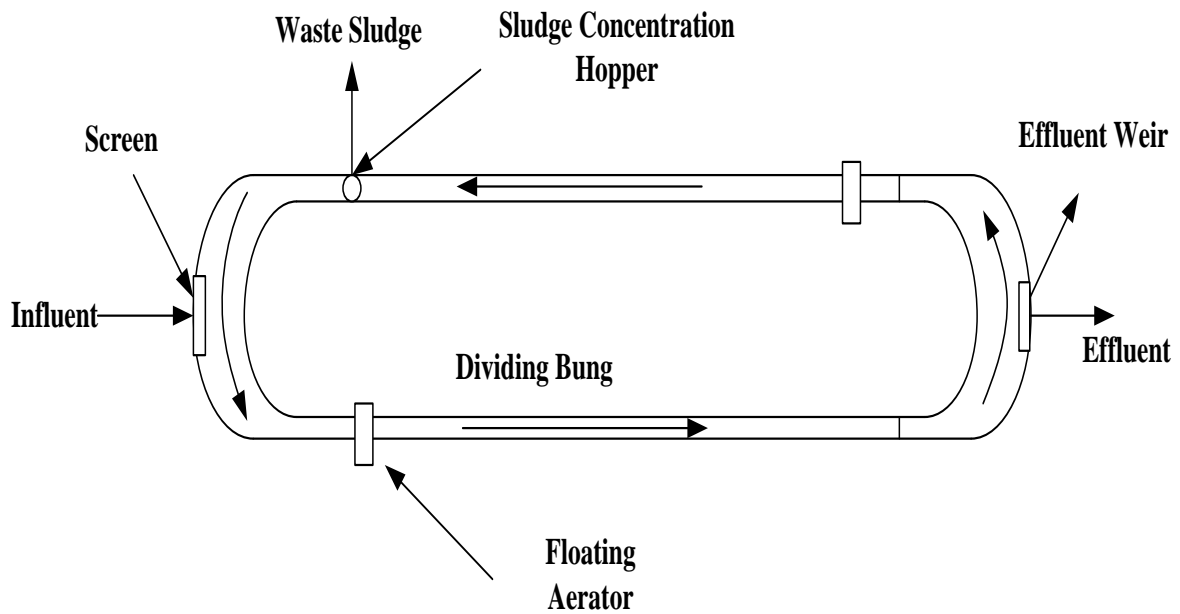


Figure 3.2 Race tank channels [Wilderer, 2001]

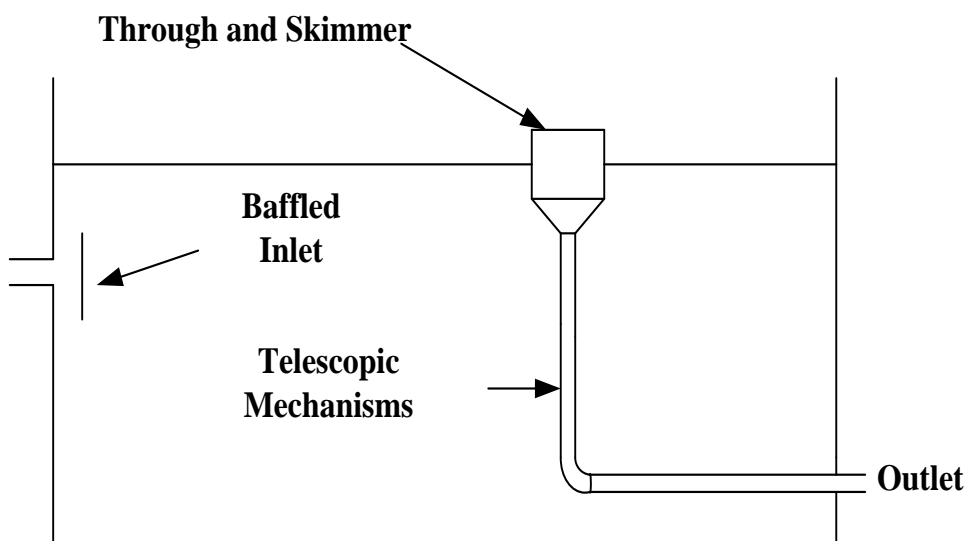
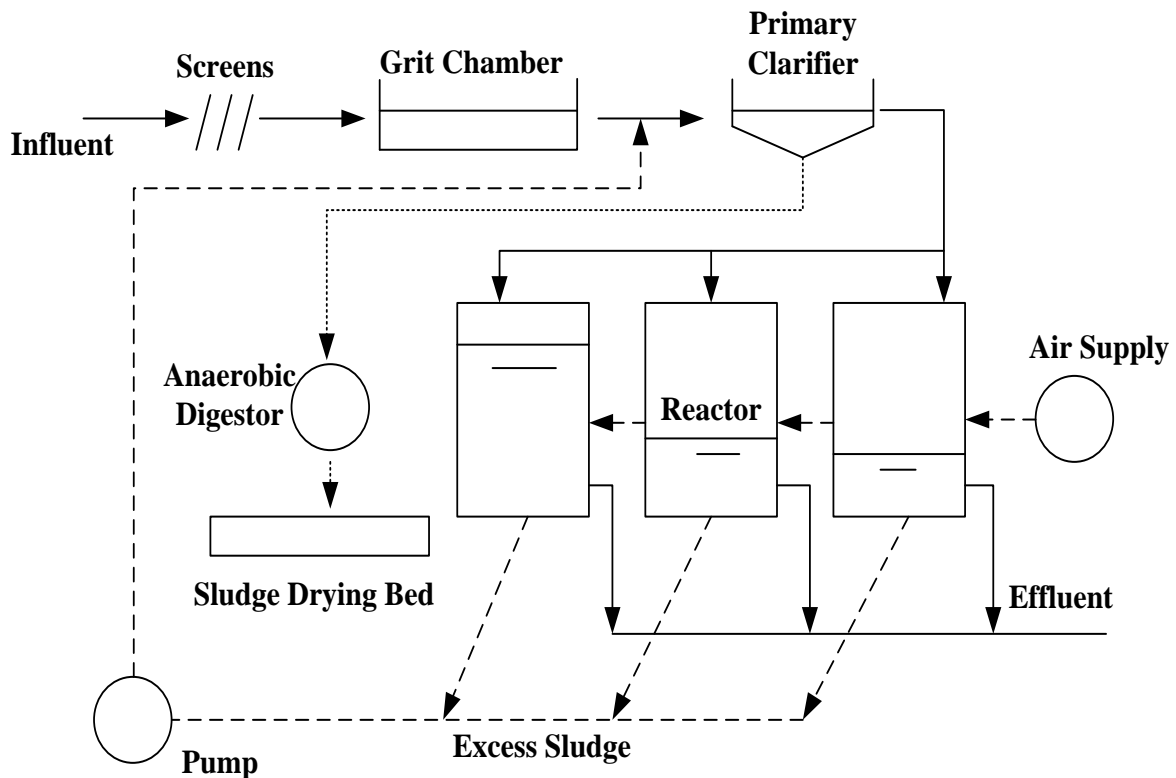


Figure 3.3 Rectangular type SBR [Wilderer, 2001]



**Figure 3.4 Multi-stage SBR system [Wilderer, 2001]**

**3.1.7.2 Considerations in design of a decanter:** In the reactor, it is necessary to not allow the fluid to enter into the decanting system. As in SBR, there are many phases like fill phase, react phase so the care should be taken not to enter the sludge or liquid into the system. The care should be taken at the point after the react phase i.e. when settling take place. The decanting process should be start at the time when there is definite volume of the sludge settles in the reactor. It is commonly 25 cm below the depth of the decanter or the baffle whatever is present in the reactor.

- The decant phase is important part of the SBR. The points which decide the successful decant phase is as follows:
  - ✓ The foam or scum that develops during the react phase must not come with the decanting process as it reduces the MLSS in the reactor.
  - ✓ The sludge that is well settled during the settle phase should not be disturbed during the decant phase nor it should be taken away with the decanter.
  - ✓ To maximize the efficiency of the equipment it should be time saving so the decant phase should be as small as possible to maintain the proper performance of the system.

✓ The Hydraulic Detention Time or Volume Exchange Ratio variation should be possible to have setting with the changed environment and the efficiency can be maximized. Although the variation in the VER is as small as 20%.

The baffle plays an important role in the decant process as it does not allow the scum to come outside the tank and help in maintaining the proper MLSS in the reactor.

**3.1.7.3 Types of decanters used in SBR:** There are normally two types of decanters used in the SBR process. The first one is motor driven and the second one is floating type. The basic types are as follows: a) simple floating b) moving arm with one part above the liquid during react phase c) floating with plate (motor driven) for scum prevention. Based on the mechanism it is of two types: floating and hydraulically operated (figure 3.5 and 3.6).

#### ***Motor driven decanters***

It is often used in Japan, Australia, USA and Europe. The inlet part is kept above the solution during fill and react phase whereas when decant process comes into picture it moves slowly down to supernatant and the removal of clear liquid takes place. However, care should be taken that no sludge should come out of the mixture.

#### ***Floating type decanter***

The decanter is kept at certain height below the water level and help in maintain the constant hydrostatic pressure thereby maintain the constant flow. Moreover the device acts as baffle so as not to allow the scum on its way thereby improving the efficiency of the process.

The efficiency of the decanter depends on Effluent pipe diameter as well as the hydrostatic pressure at the orifice in the decanter. This should not be increased above the certain threshold value for having high efficiency.

#### ***Fixed level type decanter***

The orifice is made at one or more points in the reactor tank. Depending on the height of the liquid level in the tank the orifice is allowed to open. When the liquid is just near the orifice the orifice corresponding to that height gets closed and the liquid is allowed to settle. The benefit of this type of decanter is that the reactor length is large as compared to diameter so it requires small surface area. However, when the tank is shallow then it takes more time to settle the sludge and to fall below the orifice thereby time required becomes longer as compared to the normal operation. The other disadvantages include improving the efficiency of the process the orifice should produce high hydrostatic pressure so there is possibility of the sludge to come that is near the orifice so the care should be taken at this point. The effluent velocity can be determined from the given equation 3:

$$v = C_o a(2gH) \quad (3)$$

where,  $C_o$  is discharge coefficient,  $a$  is area of cross-section of the orifice,  $H$  is the head pressure between the top level and the point of discharge.

**3.1.8 Advantages and disadvantages of SBR:** The advantages and disadvantages of SBR is as follows.

**3.1.8.1 Advantages:** The advantages of the decanters are that just after the settling phase, the decant phase can be started. The height that determines the opening of the valve or pump port is should be more than 25 cm. Depending on the turbidity of the solution below the orifice which can be checked by the software in the plant, after the threshold value the decant process can be started.

**3.1.8.2 Disadvantages:** The design of the decanter depends on the reactor height as the decanter has to move up or down in the tank. Moreover, the decanter has both fixed and moving parts which increases the possibility of corrosion and turbulence in the reactor.

**3.1.9 The foam or scum removal:** Scum formation in the SBR is very adverse phenomenon in the process. It generally reduces the performance in the phenomenon. There is probability of loss of microorganisms from the vessel after the settle phase. It also causes problem in summer as it produces unwanted odour while in winter it may freeze thereby causes hindrance in functioning in the decanter and aerators too.

***Formation of scum in the reactor***

Various reasons can be drawn for its production:

- The microorganisms that grow might be of filamentous nature thus producing scum in the vessel.
- In various reactors that are working on the removal of nutrient of advanced type i.e. nitrification, denitrification or phosphate removal take place the result is formation of scum.
- In industries that are associated with presence of light polymers like oil or grease.
- The presence of certain compounds like surfactant, biological compounds like proteins, fats and salt.

- Sometimes, the foam develops when the microbes are not well coordinate with the new environment and is produced at the starting of the process.

**Table 3.1 Advantages and disadvantages of SBR**

<b>Advantages</b>	<b>Disadvantages</b>
Less volume required as all the steps can be achieved in single reactor.	Sophistication of higher level as compared to ASP required in case of larger size.
The requirement of space is also small as no different basins required as in ASP.	Maintenance is also a problem as more number of automated switches/ controls etc required.
Common wall construction for rectangular tanks.	There is some probability of removal of sludge in case not well settled during DRAW Phase.
Can be easily expanded in modules.	The aeration equipments may plug depending on the cycle.
It is more flexible in operation as well as in control.	The equalization is required for the effluent in SBR.
Different phases can be controlled as per the requirement.	The temperature of the system must not be changed during the process as it is directly related to life of microbes.
The pumping of return sludge may not need.	Settling is strongly depending on sludge characteristics.

Source: [EPA, 1999].

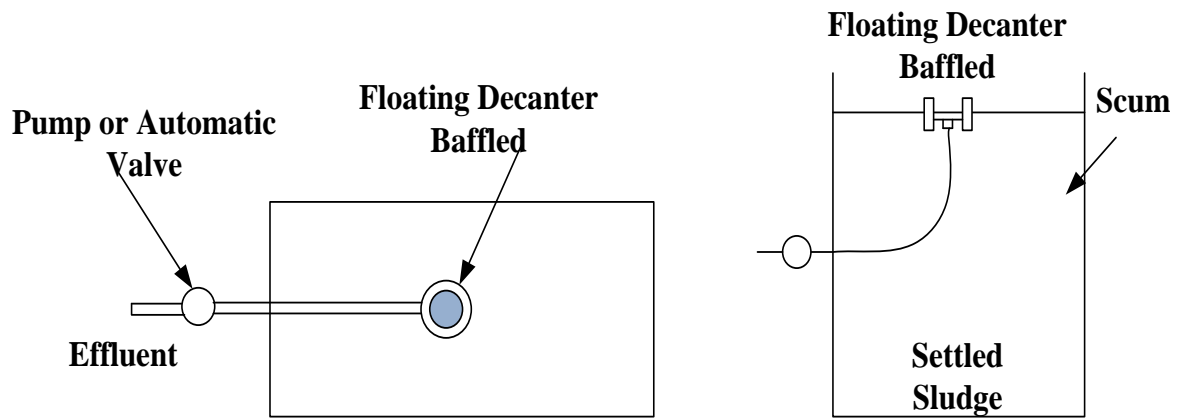


Figure 3.5 Schematic representation of a floating type decanter (a) Plan view (b) Section view [Wilderer, 2001]

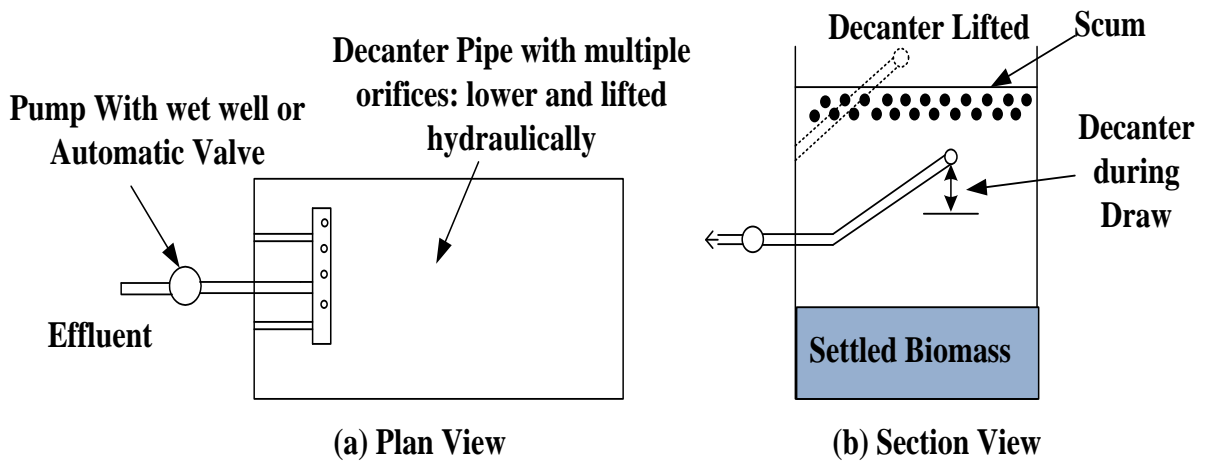


Figure 3.6 Schematic representation of Hydraulically operated decanter (a) Plan view (b) Section View [Wilderer, 2001]

### 3.1.10 Other parameters taken into consideration while performing experiments in SBR

**3.1.10.1 Air Blowers:** The air requirement is one of the key factors in the SBR process. It is made by positive displacement type or centrifugal type. The oxygen thus used in the respirometry of the microorganisms.

**3.1.10.2 Nutrients:** The biological reaction takes place in the presence of oxygen and degradation of nutrients takes place. Under lab scale the nitrogen, phosphorous, carbon, potassium, sodium and others are needed in definite quantity to have proper growth. However in municipal wastewater, it is already enriched in nutrients so addition of nutrients is not necessary.

**3.1.10.3 Waste sludge removal:** To maintain proper MLSS in the reactor, a definite amount of the sludge is to be removed from the system as growth will take place in the react phase.

**3.1.10.4 Sludge digester:** The sludge that is removed from the reactor basin is stored in the digester and the equalization is also takes place here.

**3.1.10.5 Control systems:** The SCADA system is used to control all the operations in the reactor which controls the DO level, temperature variation, etc.

**3.1.11 Certain definitions regarding activated sludge process:** Various parameters are necessary for designing the SBR.

**Hydraulic Retention Time (HRT):** It is the average length of time for which the sludge remains in the reactor based on the influent flow. It is less than SRT (eqn 4).

$$\Theta = \frac{V}{Q_o} \quad (4)$$

where  $Q_o$  is the influent flow rate and  $V$  is the volume of the reactor.

**Food to Microorganisms Ratio (F/M Ratio):** It is the ratio of BOD removal from the reactor during react phase and the total sludge in the bioreactor (eqn 5).

$$\frac{F}{M} = \frac{Q(S_o - S)}{VX} \quad (5)$$

Its unit is kg of BOD/kg of biomass.d.

**Sludge Retention Time (SRT):** It is the time for which the sludge remains in the reactor. It is expressed in days (eqn 6).

$$\frac{1}{\Theta_c} = \frac{Y(S_o - S)}{\Theta X} - k_d \quad (6)$$

where  $\Theta_c$  is sludge retention time,  $\Theta$  is the hydraulic retention time,  $k_d$  is decay rate constant,  $S_o$  is influent BOD,  $S$  is effluent BOD,  $Y$  is yield and  $X$  is MLSS of the sludge.

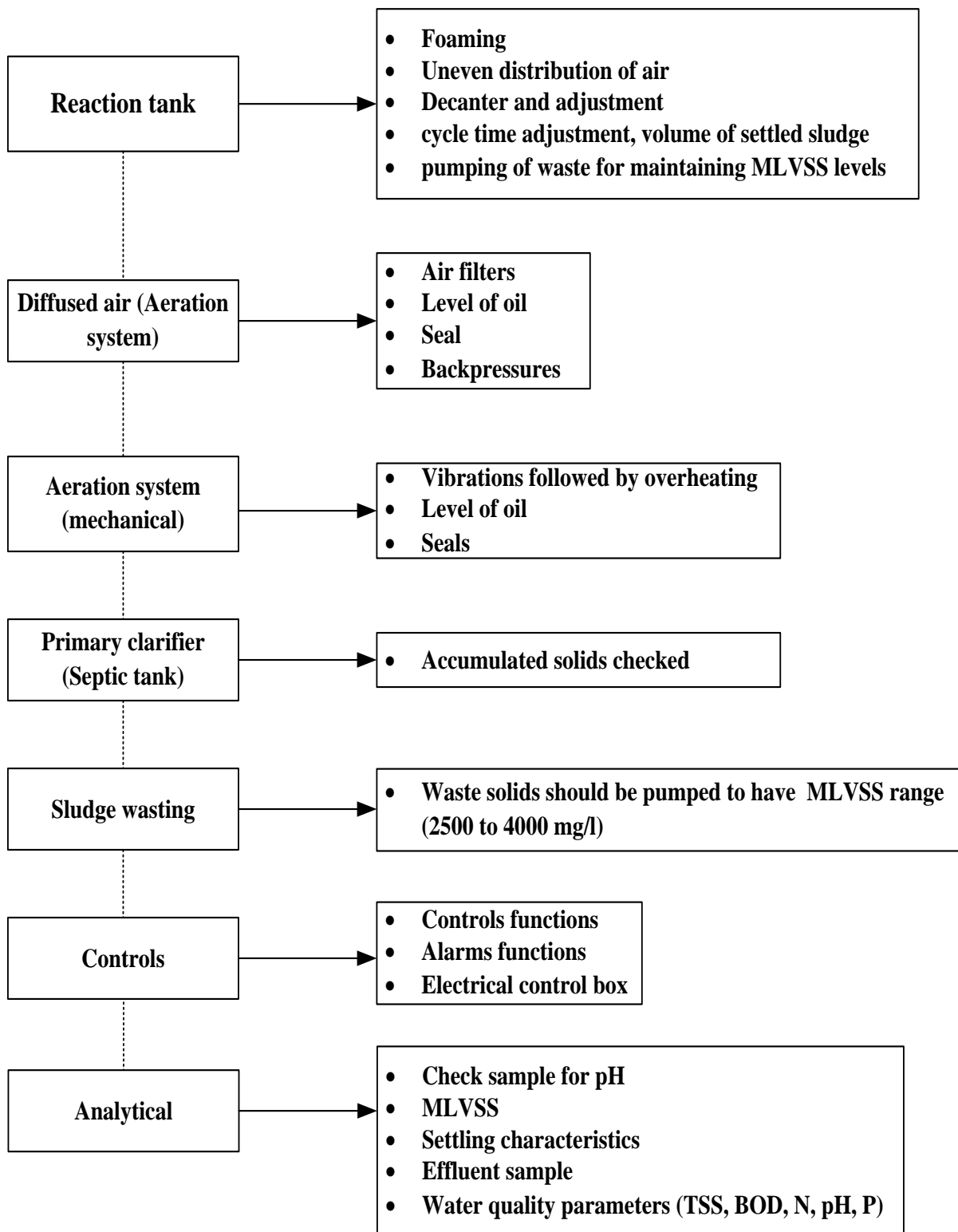
**3.1.12 Maintenance of SBRs under varying operations conditions:** The SBR under operation are necessary to undergo maintenance for its proper working. The following parts in SBR and their remedies are as given in the figure 3.7.

### 3.2 Adsorption Process

It is basically a surface phenomenon which involves the attachment of foreign compounds such as molecules or atoms onto another molecules surface. The movement medium may be either gas or liquid depending on the situation. The compound that adsorbs on the surface of foreign compounds are known as adsorbate and the compound on which the adsorption takes place is called adsorbent. The adsorption mechanism proceeds via the formation of a thin film on the adsorbent surface. Another similar phenomenon is called absorption which is a phenomenon in bulk. This is the process of dissolving of one compound into the other compounds. In this the whole system take part in the phenomenon while in adsorption only the surface involves, so it is a surface phenomenon. Another word that collects both adsorption and absorption is called sorption while the opposite of adsorption i.e. removal of adsorbate from the surface of adsorbent is called desorption.

The forces that are responsible for the adsorption process are mainly surface forces. In the adsorbent on which the adsorption takes place, a molecule is well surrounded by the other molecules and it experiences the same forces from all the molecules at the same time. However the molecule on the surface is not surrounded by similar atoms and experienced unbalanced forces as it is surrounded by different medium in the environment so this causes the forces of attraction on the outer molecule and this is responsible for the adsorption process so it is basically a surface phenomenon. There are normally two kind s of adsorption process which is physisorption and chemisorption.





**Figure 3.7 Maintenance of SBR under varying conditions**

**3.2.1 Types of adsorption:** The adsorption is of mainly two types:

**3.2.1.1 Physisorption:** It is the type of adsorption in which weak van der Waals forces are responsible for the adsorption. It is basically an exothermic process (enthalpy = 20-40 KJ/mol) and as per the Le-Chatelier's Principle, the reaction goes on increasing with decreasing temperature. When the pressure of the gas is increased in a gas solid adsorption, the increase in pressure increases the rate of adsorption. However at low pressure and at high temperature the desorption phenomenon favoured. As the forces that is responsible for the adsorption process is van der Waals forces and can be applied to any system so the adsorption process is not substrate specific i.e. it is applicable to all compounds. One of the main reasons for increased adsorption is the increase of surface area. The process of adsorption has direct relationship with area available in which the process takes place.

**3.2.1.2 Chemisorption:** It is the type of adsorption in which strong chemical forces are responsible for the adsorption. It is basically an exothermic process (enthalpy = 80-240 KJ/mol) and as per the Le-Chatelier's Principle, the reaction goes on increasing with decreasing temperature. One thing should be noticed that in spite of exothermic nature of the reaction, it requires some increased temperature to pass the kinetic barrier so after that threshold value, increasing temperature decreases the rate of adsorption. When the pressure of the gas is increased in a gas solid adsorption, the increase in pressure increases the rate of adsorption. The increased pressure is required for the chemisorptions to take place. As the forces that is responsible for the adsorption process is chemical forces in which chemical bonds are formed so it is highly specific in nature and cannot be applied to any adsorbate as compared to the physisorption and can be applied to any system so the adsorption process is not substrate specific i.e. it is applicable to all compounds. One of the main reasons for increased adsorption is the increase of surface area. The adsorption process is directly related to the surface area. The greater the surface area the greater will be the adsorption.

**3.2.2 Isotherms Models:** The isotherm model provides the details regarding the mechanism of adsorption and shows the relationship between the amounts of adsorbate adsorbed on to the adsorbent. The rate of adsorption depends on various factors like pH, temperature, time, adsorbent dose. Initially the adsorption rate will be high as the availability of large number of pores inside the adsorbent but later the adsorption goes on decreasing as the number of pores

goes on filling and at the same time the molecules have to travel longer distances in the adsorbent surface so diffusion comes into picture later. Various mathematical models have been developed to determine the extent of adsorption with equilibrium concentration such as Freundlich, Langmuir adsorption, etc. These are described below.

**3.2.2.1. Frenundlich Adsorption:** This is the first known adsorption isotherm model and relates the non-ideal as well as reversible adsorption. This mechanism does not restrict the formation of monolayer adsorption. The adsorbent surface occupied with a large number of pores depending on the compound so the binding sites having strong energy gets adsorbed first followed by other sites depending on the energy. Heterogeneous system is well defined by this model. The intensity of adsorption depends on mainly the slope which ranges between 0 to 1. As the value of slope goes on increasing the rate of adsorption also goes on increasing. The linalized equation is given as follows:

$$q_e = K_f C_e^{1/n} \quad (7)$$

where  $q_e$  is equilibrium adsorption of adsorbate on to the adsorbent (mg/g),  $K_f$  is constant (mg/g)(dm<sup>3</sup>/g)<sup>n</sup>,  $C_e$  is the equilibrium concentration (mg/l).

**3.2.2.2 Langmuir Adsorption:** It is also a two parameter model and is originally developed to show the relationship of adsorbed gas on to the solid surface which was activated carbon. It assumes mono layer adsorption in which only one layer of adsorbed molecule is formed. The adsorption is directly related to the number of active sites. Moreover there is no lateral hindrance among the sites and the adsorption is specific in nature. This model also shows that the adsorption is highly homogeneous in nature. Each molecule has fixed and same enthalpies and same energy so once the adsorption took place at one sit the adsorption will not take place further at that site.

The force of attraction goes on decreasing with increasing distances as per this model. The Langmuir model is as follows in eqn 8:

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \quad (8)$$

where  $Q_o$  is maximum adsorption (mg/g),  $b$  is isotherm constant (dm<sup>3</sup>/g)

## 4 MATERIALS AND METHODS

The materials include the sludge, adsorbent and the instruments which are required to measure the values during the experiment.

**4.1 Synthetic Wastewater:** Synthetic wastewater (SWW) of 4-Nitrophenol (NP) having initial concentration of 100 mg/l was used for present study. The NP extrapure AR was obtained from Sisco Research Laboratories Pvt. Ltd. (Batch No: T-8361567), Mumbai, India. A stock solution was prepared by adding 1g of NP in 1l of distilled water (DW). The solubility of NP is 1.6 g/100 ml at 25°C. As NP is sparingly soluble in cold water, so it is made soluble by heating the DW to 25°C. The test solutions were further diluted to desired concentration by adding distilled water in the stock solution [[http://www.chemicalbook.com/ChemicalProductProperty\\_EN\\_CB7852550.htm](http://www.chemicalbook.com/ChemicalProductProperty_EN_CB7852550.htm)].

**4.2 Adsorbent:** Granulated activated carbon (GAC), LR was obtained from G. S. Chemicals Testing Lab & Allied Industries, New Delhi, India and it was used as such for the adsorption study.

**4.3 Instrumentation:** The instruments include X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), chemical oxygen demand (COD) analysis. These are described as follows.

**4.3.1 Examination of the compounds by X-ray diffraction (XRD):** The instrument used for the analysis of the XRD was Phillips (Holland) diffraction unit (Model PW1140/90). The target element used was Cu and the filter medium used was nickel. 1°/min was the goniometric speed. Goniometric speed was maintained at. The sample is placed at a certain angle and the detector arm measures the angle at double the angle at which the sample is placed. The care should be taken that the sample should not fall from the sample holder. The sample rotated at an angle between 5-90°. The international center diffraction data (ICDD) is used to analyze the graph obtained from the experiment. The XRD analysis uses Bragg's law for constructive interference which is mentioned below in eqn 9:

$$n\lambda = 2d\sin\Theta \quad (9)$$

where,  $n$  is the constant and is an integer,  $\lambda$  is the wavelength of the X-ray used,  $d$  is the intramolecular distance and  $\Theta$  is the angle of incidence. The orientation of atoms in crystals, distance among the atoms, and texture of the crystals can be found out by X-ray analysis.

**4.3.2 UV-VIS spectrophotometer:** The initial NP and residual concentrations concentration was determined by UV spectrophotometer (UV-1800, SHIMADZU, A114548) with maximum wavelength ( $\lambda_{\max}$ ) of 316 nm for NP. As the curve is linear upto 30 mg/l, so the sample was diluted to measurable concentration.

It works on the Beer-Lambert law, which is given as follows (eqn 10):

$$A = \log_{10}(I_o/I) = eCL \quad (10)$$

where,  $A$  is the absorbance measured in Absorbance Unit (AU),  $I_o$  is the influent intensity,  $I$  is the intensity transmitted,  $e$  is molar absorptivity,  $C$  is the concentration of the solution and  $L$  is the length through which the rays are passed.

**4.3.3 pH meter:** pH adjustments was carried out by HI 2211 pH/ORP meter and purchased from HANNA Instruments.

**4.3.4 Orbital shaker:** Shaking was done in Orbital Shaking Incubator and purchased from Remi Instruments and kinetic study was done at 15°C, 30°C and 45°C while rest of the experiment was done at 30°C.

**4.1.3.5 Chemical oxygen demand:** Chemical Oxygen Demand (COD) was determined by spectrophotometer (HACH/ DR 5000). The digestion of the sample was done in CSB/COD reactor AL 38 SC, Aqualytic, (Serial No. 0908/ 2210) of 400 W. The digestion period was 2 h for 105°C.

**4.1.3.6 TOC Analyzer:** The Total Organic Carbon (TOC) was measured by TOC-VCPH, Total Organic Carbon Analyzer Shimadzu and ASI-V Shimadzu (Serial No. 521048).

**4.1.3.7 Fe-SEM Analyzer:** The Fe-SEM was carried out by Quanta 200 F (FEI Netherlands) with gold splutter coater of Baltech.

**4.1.3.8 DO meter:** Dissolved oxygen (DO) meter used was of HACH, HQ40d, multi. It consists of salt solution in which the oxygen is selectively permeable through it and the change in electrostatic potential is shown in the form of display. It also shows the temperature of the solution at the time of measurement.

#### 4.1.4 Batch adsorption study

The batch experiment was carried out in a 250 ml stopper conical flask by adding a known amount of the GAC (g/l) in 100 ml of NP solution and initial pH was adjusted by using H<sub>2</sub>SO<sub>4</sub> and NaOH solutions. The mixture was agitated in a temperature controlled orbital shaker with a constant speed of 150 rpm at a specific temperature (like 15°C, 30°C and 45°C).

The percentage removal of NP was calculated using the following relation 11:

$$\text{Percent removal} = \frac{(C_0 - C_e) 100}{C_0} \quad (11)$$

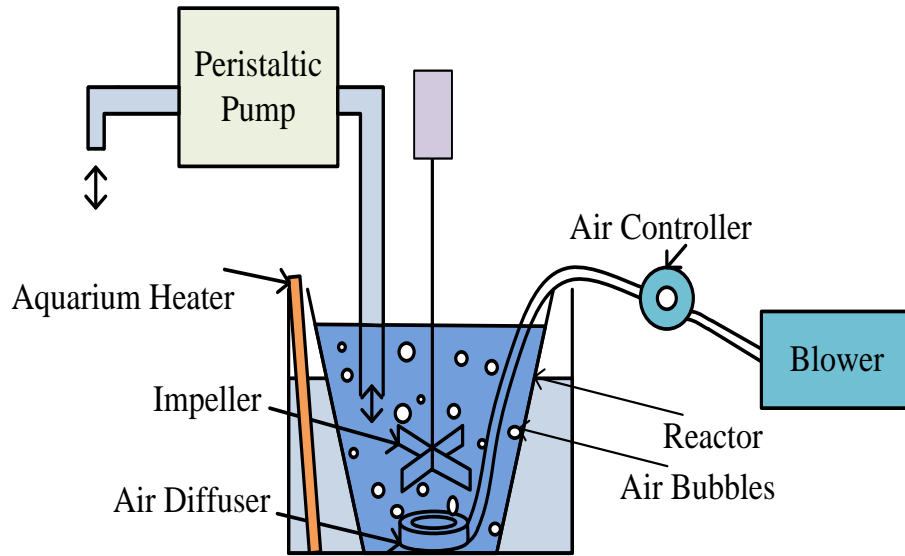
Similarly for the equilibrium adsorption uptake,  $q_e$  (mg/g) were calculated as (eqn 12):

$$q_e = \frac{(C_0 - C_e) V}{w} \quad (12)$$

where,  $C_e$  is the equilibrium adsorbate concentration,  $V$  is the volume of the adsorbate (l) and  $w$  is the mass of adsorbent (g).

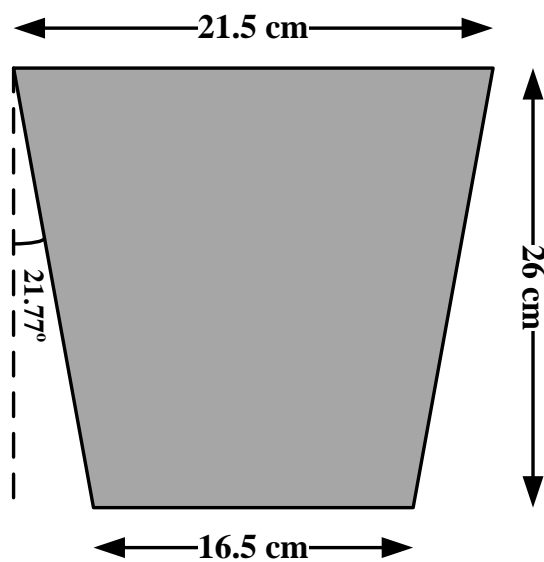
**4.2 Activated Sludge:** The Activated Sludge (AS) was collected from Sewage Treatment Plant (STP), Haridwar at the end of the REACT phase in Sequential Batch Process during wastewater treatment. The screening of the sludge was done to remove coarser particles including grit, solid particles, etc. to have uniform sludge for the process. The acclimatization of the sludge was done with SWW up to 50 mg/l. This process involved use of nutrient medium of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (0.1 g/l), CaCl<sub>2</sub> · 2H<sub>2</sub>O (0.062 g/l), FeCl<sub>3</sub>·6H<sub>2</sub>O (0.016 g/l), MgSO<sub>4</sub>·7H<sub>2</sub>O (0.205 g/l), K<sub>2</sub>HPO<sub>4</sub> (0.8 g/l) and KH<sub>2</sub>PO<sub>4</sub> (0.2 g/l) [Bhatti et al., 2002]. These nutrients were added with varying concentration for the acclimatization. During acclimatization process, the concentration of the nutrient medium was decreased to 0 mg/l whereas that of SWW was increased from 0 to 50 mg/l. The mixed liquor suspended solids (MLSS) was maintained above 3000 mg/l (3000-4000 mg/l) for every cycle.

**4.3 Experimental Programme:** The experimental setup included a reactor (figure 4.1) having diameter as shown in figure 4.2 and volume of 5l. The stirrer (Lab Stirrer, Remi) was used for uniform mixing of sludge with the nutrient medium and its rpm was maintained as such that it didn't create any vortex in the system so that uniform blending of DO was maintained all over the sludge volume. The air pump with diffuser was used for aeration purpose and the latter was sintered in the bottom of the reactor. An aquarium heater (Aquarium heater (20°C-34°C), 200 Watts) was used for maintaining the uniform temperature in the reactor between 28±2°C which is necessary for the activity of the microorganisms. A DO probe was used to measure the dissolved oxygen in the sludge. It was maintained between 2-4 mg/l. DO of less than 2 mg/l resulted in thickening of the sludge whereas greater than 4 mg/l resulted in bulking of sludge, thus posing difficulty in settling of sludge. A peristaltic pump (Miclins Peristaltic Pump, PP20) was used during FILL and DECANT phase in SBR. The cycle time ( $T_c$ ) of 6 h was selected in which the FILL, REACT, SETTLE, DECANT and IDLE phase in the ratio of 0:4:1:0.5:0.5. The FILL phase was instantaneous unless mentioned otherwise. For having a constant mixed liquor suspended solids (MLSS) in the reactor, sludge wasting was done after each cycle. The sludge retention time (SRT) of 30 d was used for the purpose. The filter paper used for filtering the sludge (MLSS determination) was of Glass Microfibre Filters–Whatman, 934-AHTM, Circles 47 mm, radius = 1.5  $\mu\text{m}$ .



**Figure 4.1** Experimental setup of sequential batch reactor

**Reactor vessel:** It was a tapered cylinder with specifications as shown in the figure 4.2:



**Figure 4.2** Batch reactor



## 5 CHARACTERIZATIONS, ADSORPTION AND SEQUENTIAL BATCH REACTOR

## 5.1 Characterization of Adsorbent and Sludge

The characterization of both sludge and adsorbent was done to estimate the characteristics of both adsorbent and sludge by proximate, ultimate, X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), etc. analysis was done.

**5.1.1 Characterization of adsorbent:** The granulated activated carbon (GAC) was used as adsorbent. The characterization was as follows:

**5.1.1.1 Proximate Analysis:** The proximate analysis of the blank sample was done to determine the moisture, volatile and ash content. The analysis showed that moisture content was 14.64%, volatile content was 6.39%, ash content was 11.93% and fixed carbon was found to be 67.04%.

**5.1.1.2 Ultimate Analysis of loaded GAC:** The ultimate analysis was done to determine carbon, hydrogen, nitrogen, sulphur content. The ultimate analysis of blank and loaded sample is as shown in table 5.1.

**Table 5.1 Ultimate analysis of blank and loaded GAC**

Elements %	Blank	Loaded
<b>C</b>	83.36	88.24
<b>H</b>	0.196	0.252
<b>N</b>	0.193	0.121
<b>S</b>	0.0	0.0
<b>O</b>	16.251	11.387
<b>Weight used (mg)</b>	3.172	3.2080

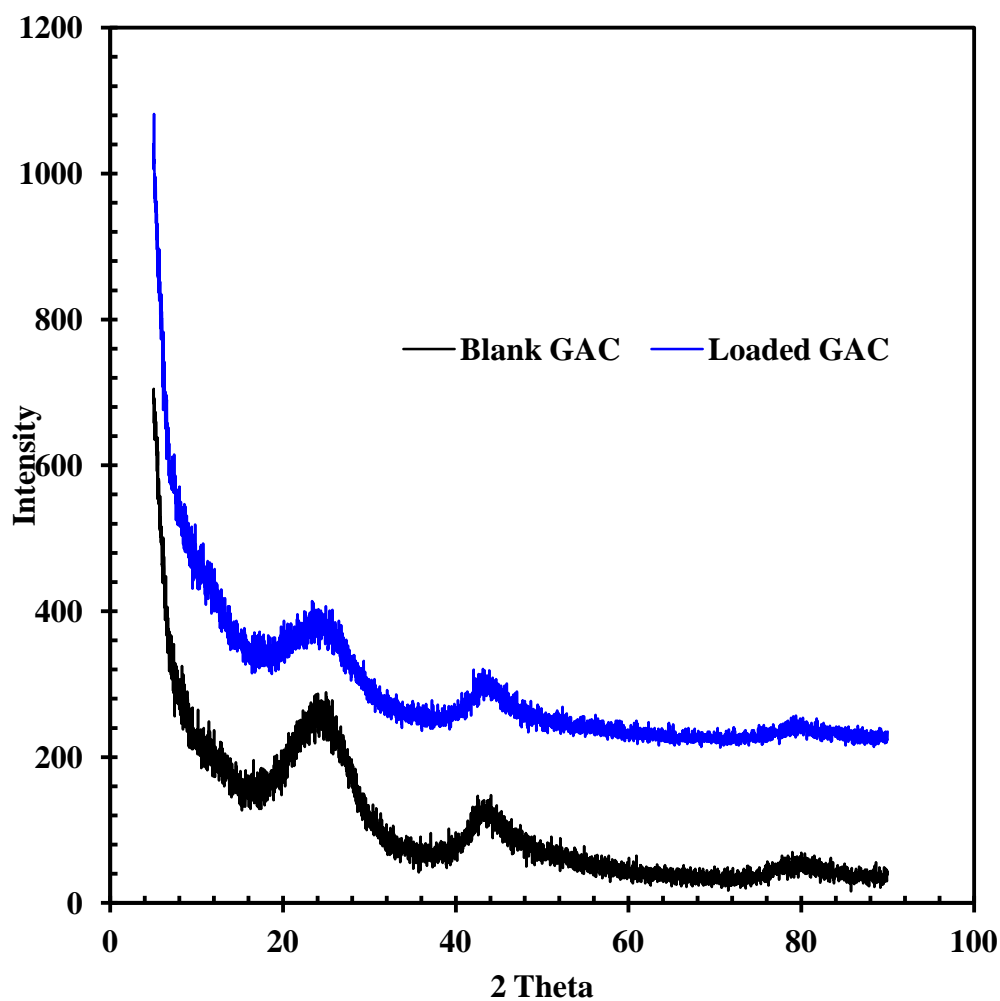
**5.1.1.3 Selection of adsorbents:** The three adsorbents GAC, bagasse fly ash (BFA) and rice husk ash (RHA) were initially selected for the use of adsorbents. The density and surface area were determined and following results were found. Since, density of GAC was higher as compared to the BFA and RHA, so it did not pose any problem in settling of the sludge. Hence, it was chosen as the adsorbent for the present study. Moreover, it would not dissolve in the solution as compared to BFA and RHA (table 5.2).

**Table 5.2 Properties of Adsorbents**

Adsorbent	BET surface area (m <sup>2</sup> /g)	Density (kg/m <sup>3</sup> )
GAC	590.00	0.61
BFA	316.83	0.08
RHA	41.08	0.18

**5.1.1.4 XRD of Blank and Loaded GAC:** The XRD result showed the absence of any crystalline group in the adsorbent whereas that of sludge, mainly calcite and silica was present (figure 5.1).

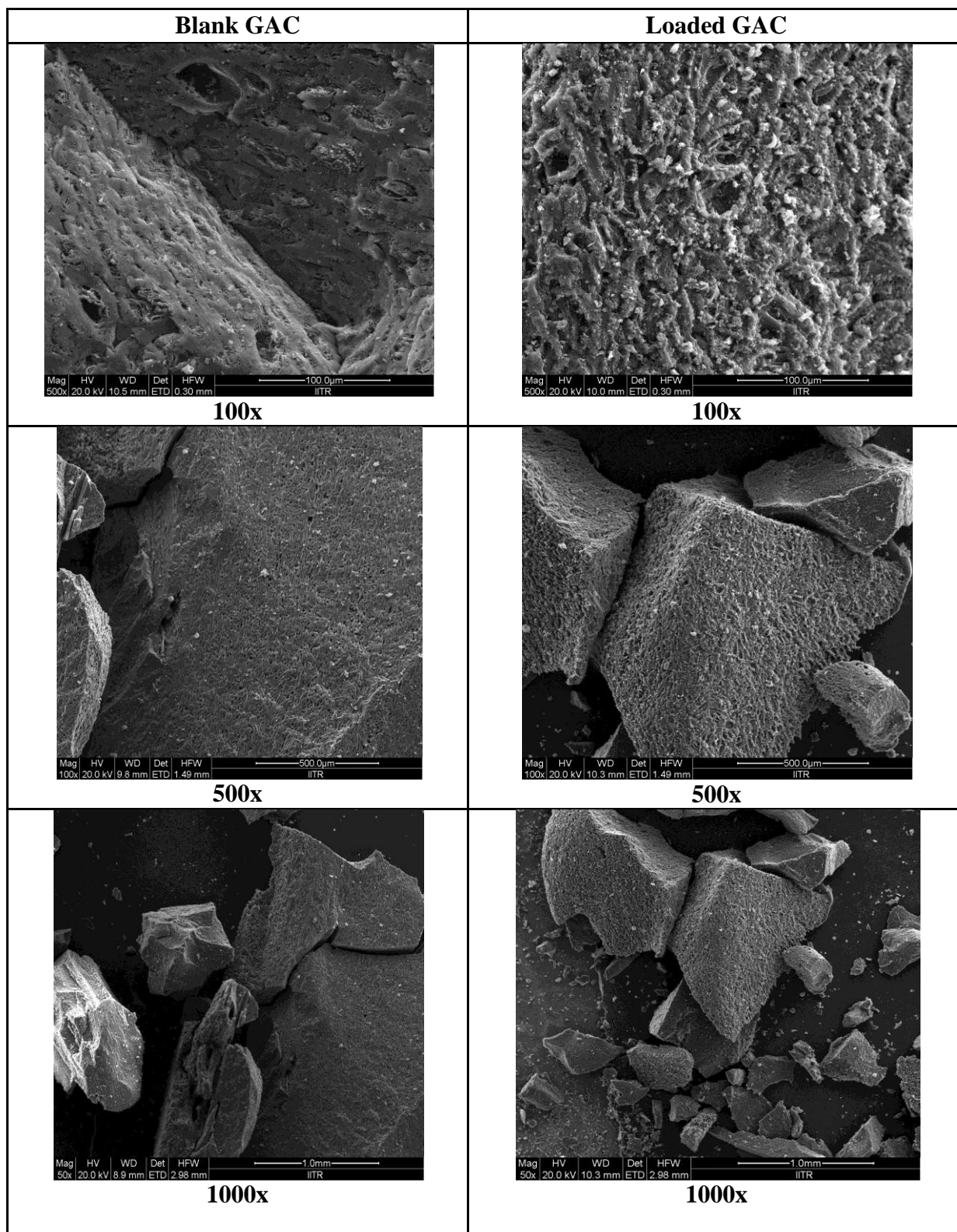
**5.1.1.5 Fe-SEM of adsorbent (GAC):** The Fe-SEM of GAC showed that initially large number of pores is available which was filled by the adsorbate after the adsorption (figure 5.2).



**Figure 5.1 XRD analysis of blank and loaded GAC**

**5.1.1.6 Thermal Oxidation and Disposal of the Spent GAC:** The GAC used in adsorption becomes waste after the adsorption. Moreover it contains toxic chemicals which are adsorbed on to the surface. So its proper is very crucial in regard to the environment. The spent GAC can be used for some other beneficial purposes. Thermogravimetry analysis (TGA) was done to know the degradation of the adsorbent with temperature. The TGA, differential thermal analysis (DTA), and first derivative curve (DTG) curves of the blank GAC and NP-loaded GAC at a heating rate of 10°C/min are shown in figure 5.3 and 5.4, respectively. The analysis of the TGA/DTA/DTG was done from 0 to 1000°C. The TGA analysis shows the moisture loss and loss of light molecules from the adsorbent surface up to 500°C. It was observed that the loss of moisture content was 50 to 100°C for virgin GAC and NP loaded GAC was 16.9% and 12.41%, respectively. When the temperature was increased further from 100°C to 500°C, the weight loss 17.32% and 12.75% for virgin GAC and NP loaded GAC was observed. The weight loss was observed between 500 to 600°C for virgin GAC and NP loaded GAC was 65.426% and 74.78%, respectively. The DTA curve shows that the peak is exothermic in nature. This shows the degradation of sample through oxidation. The peak lies in between 450-600°C. The DTG curve shows that the broad which shows the combustion of derivative species. It also shows the rate of loss of species with time. The spent GAC can be blended with fire bricks or with concrete. Also, it can be incinerated so as to remove NP and it can be used as such after treatment.

**5.1.1.7 The FTIR analysis of the GAC:** The FTIR study is used to know the bonds responsible for the reaction. The FTIR shows the change in bond as well as the bonds initially present in the sample. The electromagnetic radiation of frequency in the range of 4000-400  $\text{cm}^{-1}$  is applied to the sample and the bond of similar frequency gets excited when it falls on the surface of the sample. The bond may undergo translational, vibrational, rotational or electronic changes in respond to the electromagnetic waves radiation. The spectra thus formed can be interpreted. O-H stretch generally falls in the range of 3570-3200  $\text{cm}^{-1}$  so the first broad peak represents the O-H stretch (figure 5.6). Also, it may represent heterocyclic amine N-H stretch. The peak around 2925  $\text{cm}^{-1}$  is mainly due to methylene C-H stretch, which ranges from 2935-2915  $\text{cm}^{-1}$ . 2549  $\text{cm}^{-1}$  peak shows the thiol S-H group stretch. The range of 1637  $\text{cm}^{-1}$  shows the secondary amine stretch group. 1749  $\text{cm}^{-1}$  peak represents the alkyl carbonate group stretch. The peak of 1454  $\text{cm}^{-1}$  is due to alkene ring stretch. The 1235  $\text{cm}^{-1}$  represents the tertiary amine stretch. The peak of 1046  $\text{cm}^{-1}$  may be due to the presence



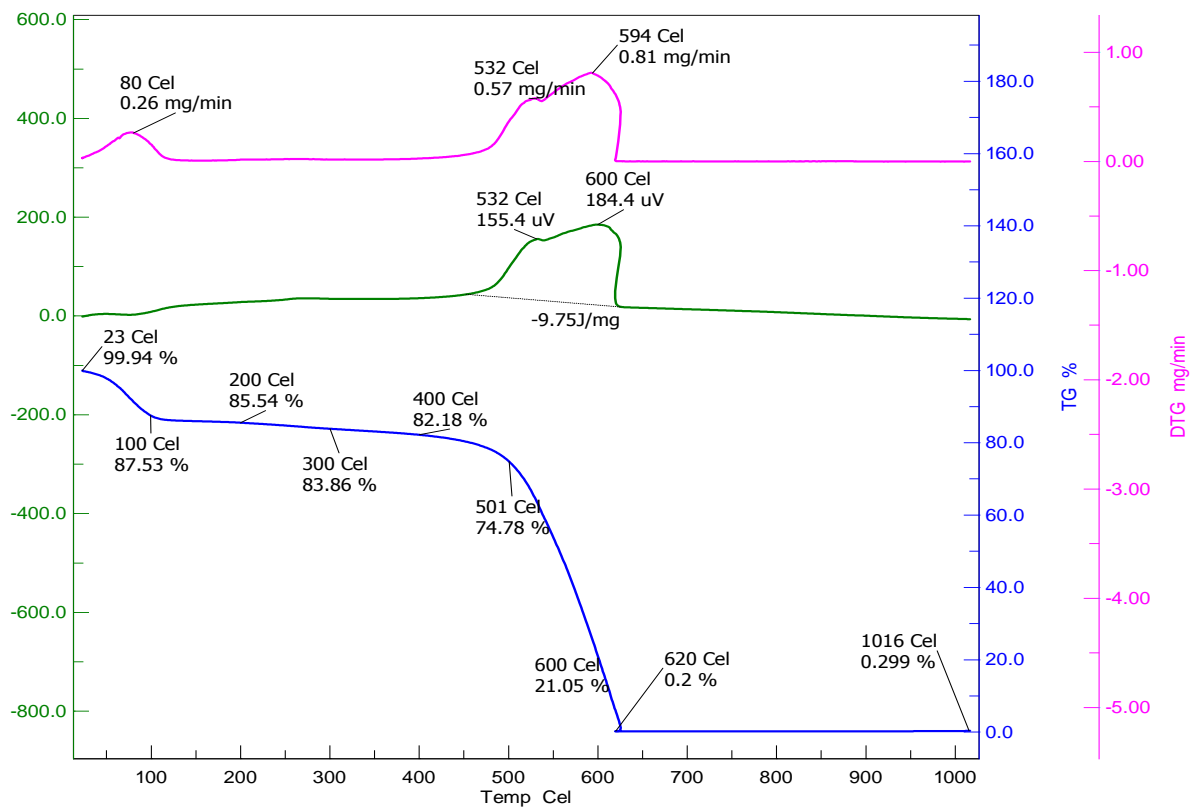
**Figure 5.2 FE-SEM of blank and loaded GAC**

of aliphatic C-F group. The small peak of  $605\text{ cm}^{-1}$  is due to alcoholic O-H stretch [Coates, 2000].

**5.1.2 Characterization of Sludge:** The sludge was used as adsorbent in the SBR. The characterization of the sludge was as follows:

**5.1.2.1 XRD of acclimatized and unacclimatized sludge:** The XRD result showed that the sludge mainly consists of calcite and silica (figure 5.5).

**5.1.2.2 FE-SEM of sludge:** The Fe-SEM results showed that the acclimatized sludge was filamentous as compared to unacclimatized sludge thus pose difficulty in settling (figure 5.7).



**Figure 5.3 TGA/DTG/TG curve for blank GAC**

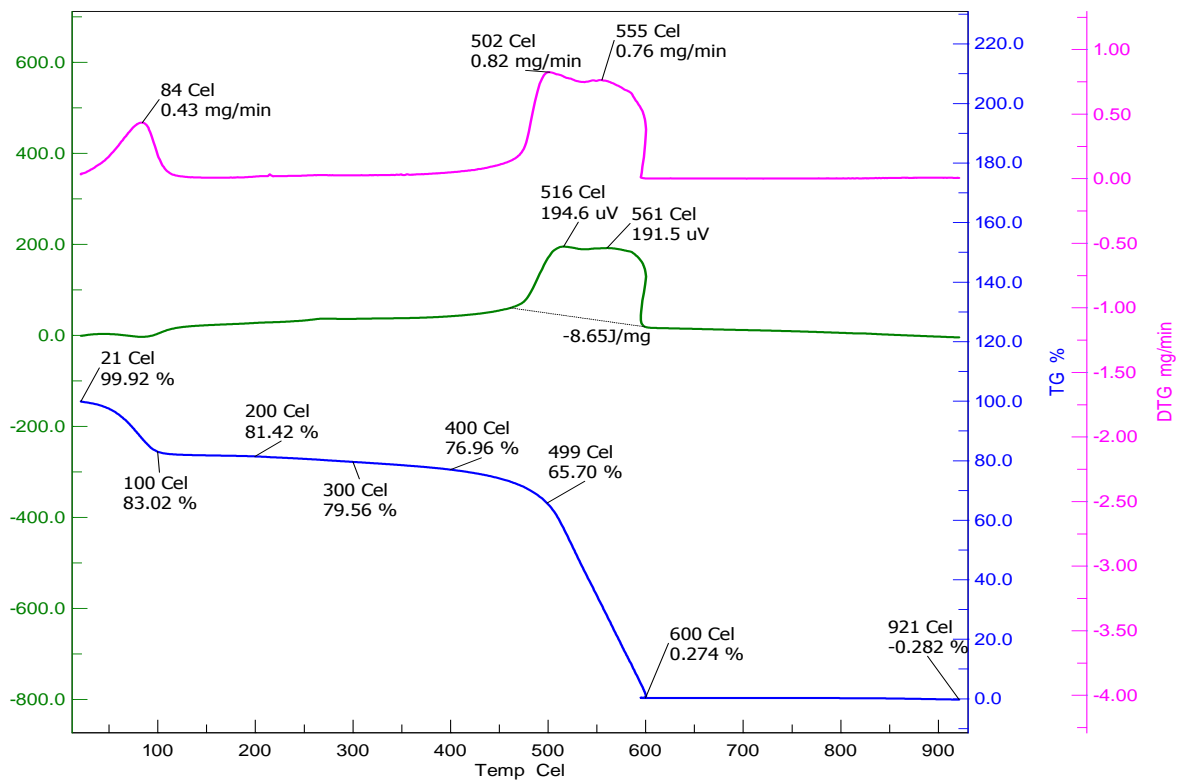


Figure 5.4 TGA/DTG/TG curve for loaded GAC

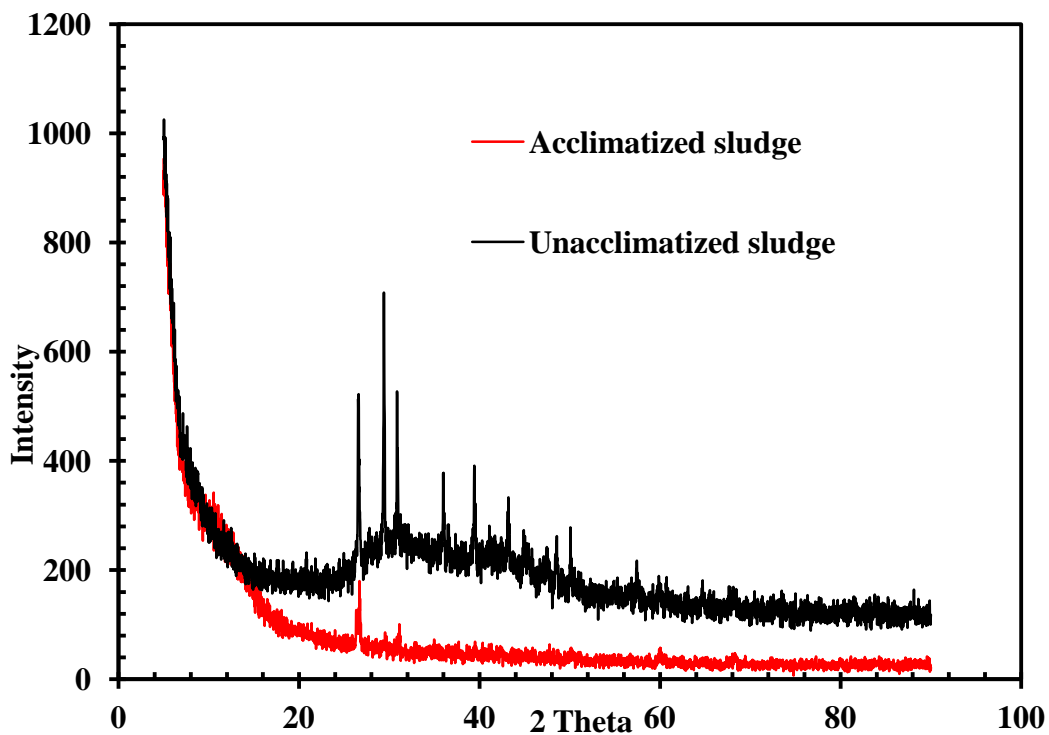


Figure 5.5 XRD analysis of acclimatized and unacclimatized sludge

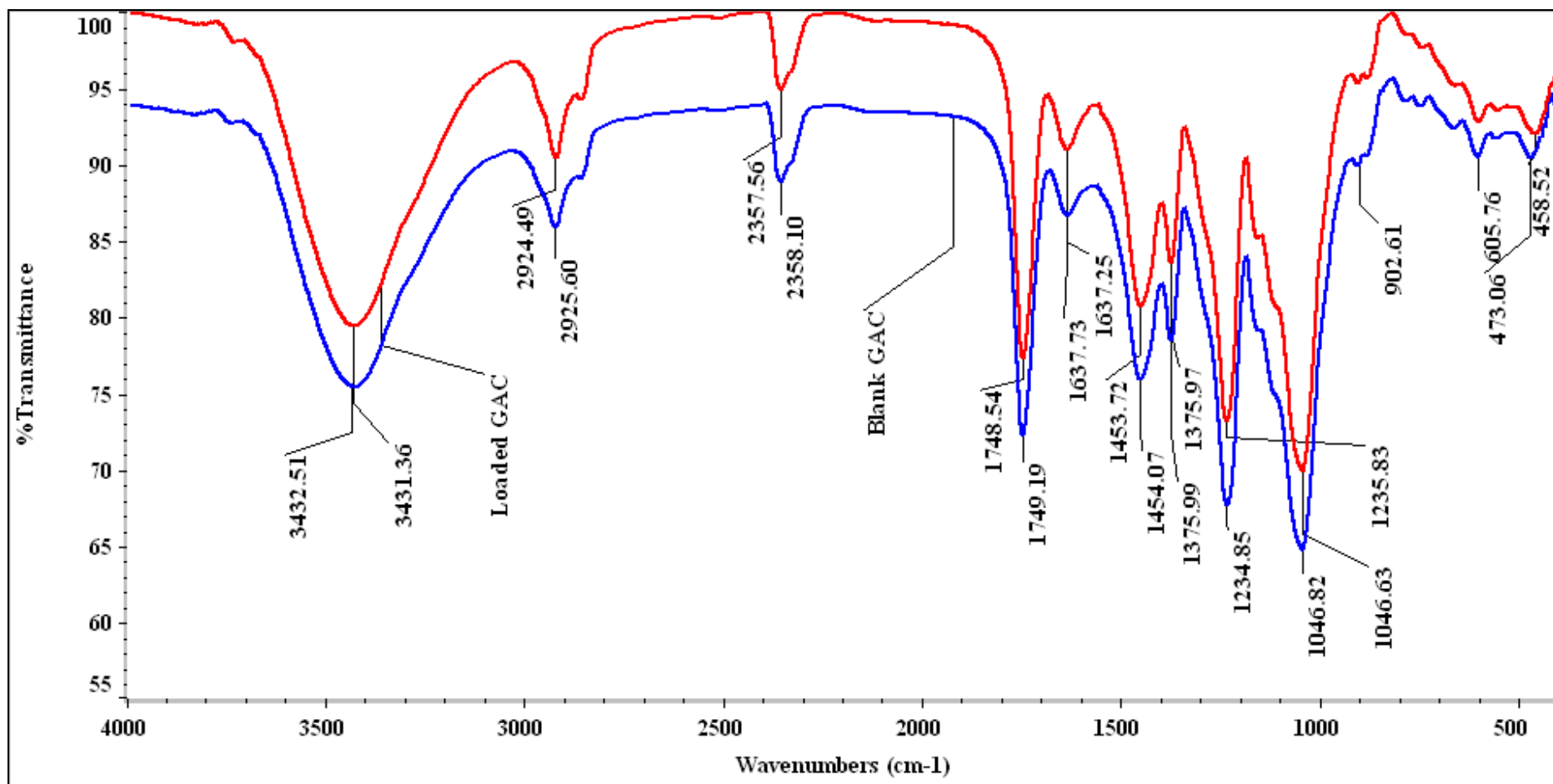
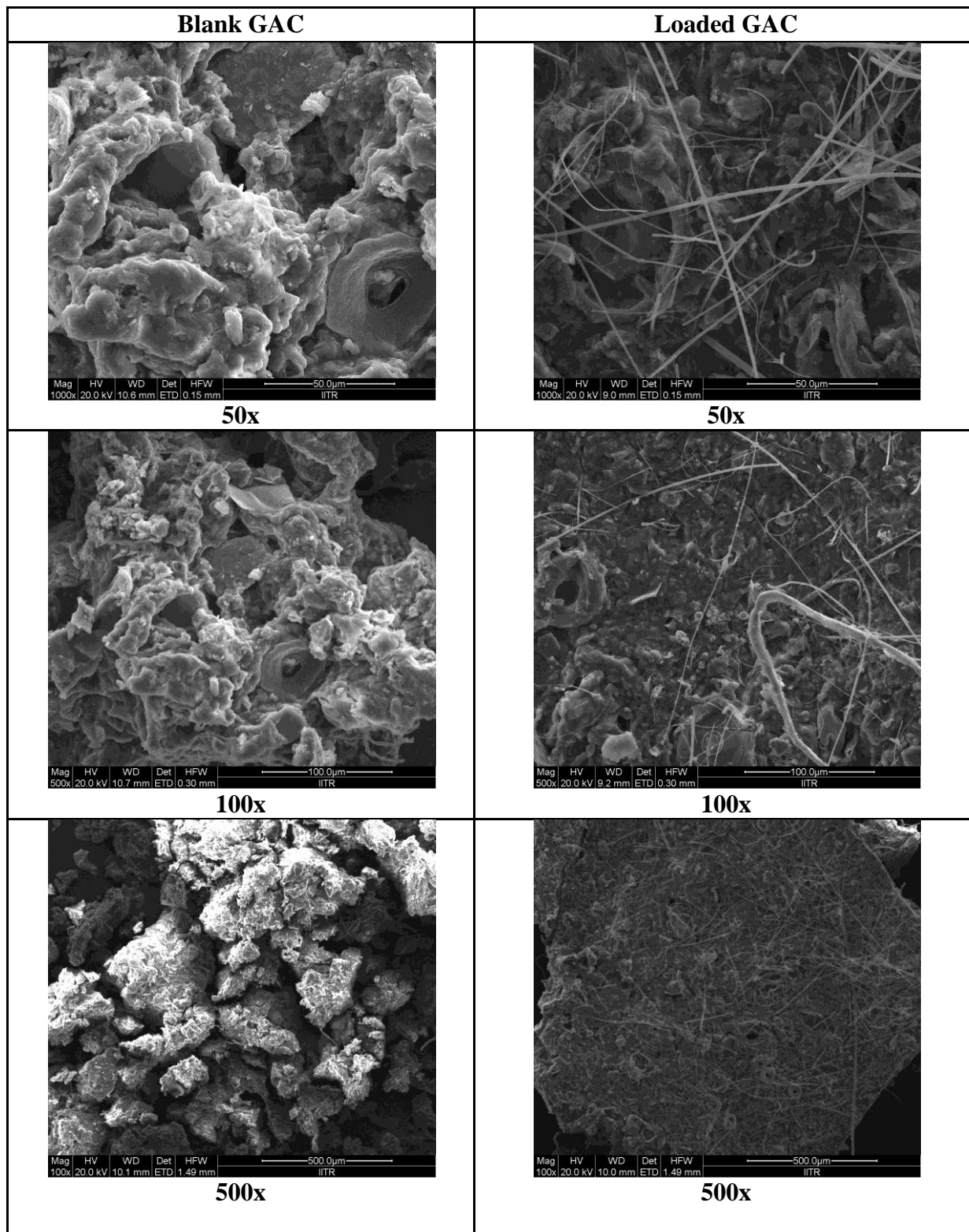


Figure 5.6 FTIR of Blank and Loaded GAC



**Figure 5.7 FE-SEM of unacclimatized and acclimatized sludge**



**5.1.2.3 Chemical Oxygen Demand (COD):** It is the most important parameter for the wastewater characterization. It is defined as the amount of oxygen required to oxidize the organic as well as inorganic matter present in the wastewater. Following reagents are used in making solution for COD estimation

**a) Standard potassium dichromate 0.25 N:** It was obtained by dissolving 12.26 g potassium dichromate ( $K_2Cr_2O_7$ ), which was dried for  $180^\circ C$  for 2 h in distilled water and diluted to 1 l.

**b) Sulphuric acid reagent:** 1 g of silver sulphate was dissolved in every 75 ml acid.

**c) Ferroin indicator solution:** 1.485 g 1-10 phenanthroline sulphate monohydrate was dissolved with 0.695 g ferrous sulphate ( $FeSO_4 \cdot 7H_2O$ ) in water and was further diluted to 100 ml.

**d) Standard ferrous ammonium sulphate solution:** 98 g ferrous ammonium sulphate ( $FeSO_4 (NH_4)_2 SO_4$ ) was dissolved in distilled water. 20 ml conc.  $H_2SO_4$  was added and allowed to cool and diluted to 1.0 l. It was further standardized against the  $K_2Cr_2O_7$  every day for every use.

**Open Reflux Method:** Took about 50 ml sample and diluted to 50 ml in a refluxing flask. The boiling chips were added and 1 g  $HgSO_4$  and 5.0 ml  $H_2SO_4$  was added slowly to dissolve  $HgSO_4$ . The mixture was cooled. 25.0 ml 0.25 N  $K_2Cr_2O_7$  solution was further added and mixed. The condenser was attached and cooling water was started. The remaining acid reagent (70 ml) was added through the open end of the condenser and the the reflux mixture was mixed. Heat applied and refluxing of the mixture was done for 2h followed by cooling. Diluted the mixture to about 300 ml and titrated against excess of dichromate with standard ferrous ammonium sulphate solution using ferroin indicator. The colour changed from yellow to green-blue and finally red. The ml of titrant used was noted. The above procedure was repeated for the blank sample (eqn 13).

$$COD (mg/l) = \frac{(A - B) \times C \times 1000}{ml \text{ sample}} \quad (13)$$

The COD of the sludge (unacclimatized sludge) was found to be 20 mg/l. The COD was less which may be explained as the sludge was collected from the STP at the end of the REACT phase so all the removal was already taken place.

**5.1.2.4 Colourimetry:** It is used for the determination of true and apparent colour. The unit of colour is Hazen or Pt/Co unit. The True colour was obtained without filtering and apparent

colour was obtained by filtering the sludge. The procedure involved the calibration with distilled water followed by injection of samples to be measured. The true colour and apparent colour of the sludge was 5000 and 1900 Hazen or Pt/Co unit. It means the suspended content of the solution is more as compared to the dissolved content.

**5.1.2.5 Settleability:** The well mixed sludge was filled in 1 l measuring cylinder and allowed to settle without disturbances. The layer separating the sludge and clear water was noted with time at the end of 30 min (figure 5.8). Different layers were formed during the settling phenomenon as clarified zone formed at the top of the cylinder followed by thickening zone the length of which decreases with time, the uniform settling zone vanishes after some time and the compression zone formed at the bottom of the cylinder whose length goes on increasing with time.

**5.1.2.6 Sludge Settled Volume (SSV):** It is the volume occupied by the activated settled sludge after a specified period of time (eqn 14). The most common SSV calculated for 30 min known as  $SSV_{30}$ .

$$SSV = \frac{\text{Settled sludge (ml)} \times 1000 \text{ ml/l}}{\text{Sample (ml)}} \quad (14)$$

Therefore, the SSV value was found to be 292 ml/l.

**5.1.2.7 Mixed Liquor Suspended Solids (MLSS):** It refers to the amount of suspended solids in the aeration tank during the process. Its unit is mg/l. The more is the MLSS, the more will be the consumption of nutrients, and hence more will be the removal take place. It includes unsettled sludge plus activated sludge in the tank (eqn 15).

$$MLSS = \frac{(A - B) \text{ (mg)}}{\text{Volume of Solution (l)}} \quad (15)$$

where,

A = Mass of crucible + filter paper + sludge dried at 105°C for 1 h

B = Mass of crucible + filter paper

The initial MLSS of the AS was 7884.6 mg/l.

**5.1.2.8 Mixed Liquor Volatile Suspended Solids (MLVSS):** It is the amount of living organisms present in the sludge per litre (eqn 16).

$$\text{MLVSS} = \frac{(A - B) \text{ (mg)}}{\text{Volume of Solution (l)}} \quad (16)$$

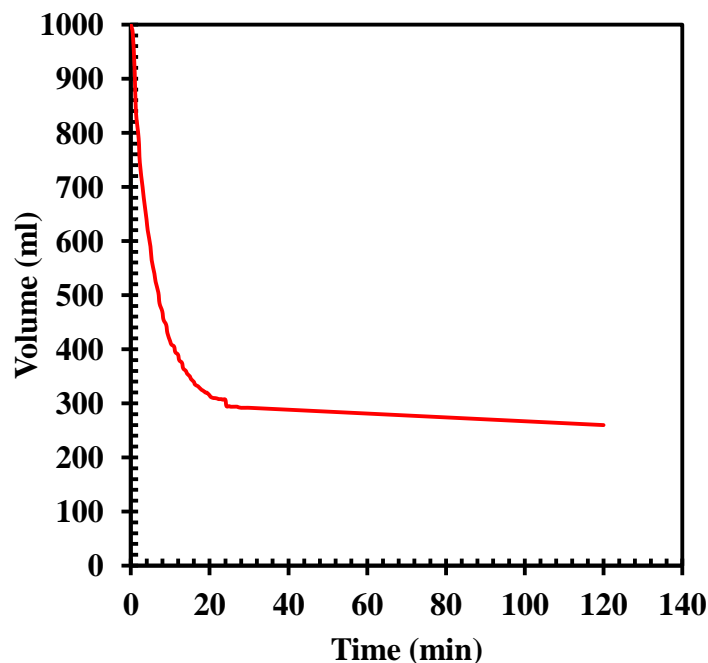
A = Mass of crucible + filter paper + sludge dried at 500°C for 1 h

B = Mass of crucible + filter paper

The initial MLVSS was 2646 mg/l.

**5.1.2.9 Sludge Volume Index (SVI):** It is the volume in ml occupied by 1g of the Activated Sludge (eqn 17). It worked as a quality indicator for the settling quality of the AS. If it is less than 100, it means that the sludge is old and has very good settling quality. If it's value between 100 and 200, the settling is good. If it is greater than 250, the sludge is bulking sludge and has poor settling. The SSV was found to be 370.03 ml/l.

$$\text{SVI} = \frac{\text{SSV(ml/l)} \times 1000 \text{ mg/g}}{\text{MLSS (mg/l)}} \quad (17)$$



**Figure 5.8 Settleability of the sludge with time**

As the SVI is less than 100, it shows the good settling characteristics of the sludge with time.

**5.1.2.10 Total Dissolved Solids (TDS):** It is the amount of dissolved solids present in the known amount of the sludge/ water. It was obtained as following in relation 18:

$$\text{TDS} = \frac{(A - B) \text{ (g)}}{\text{Volume of Solution (ml)}} \times \frac{1000 \text{ mg}}{1 \text{ g}} \times \frac{1000 \text{ ml}}{1 \text{ l}} \quad (18)$$

where,

A = Weight of beaker + sample after drying at 105°C (g)

B = Weight of beaker (g)

V = Volume of the solution (ml)

**Here, A = 56.85336 g, B = 56.84360 g, V = 25 ml**

$$\begin{aligned} \text{TDS} &= \frac{(56.85336 - 56.84360) \text{ (g)}}{50 \text{ ml}} \times \frac{1000 \text{ mg}}{1 \text{ g}} \times \frac{1000 \text{ ml}}{1 \text{ l}} \\ &= 1952 \text{ mg/l} \end{aligned}$$

Hence, the amount of TDS was 1952 mg/l.

**5.1.2.11 Determination of organic/inorganic content in the sludge (Total Organic Carbon (TOC)/ Inorganic Carbon (IC)/ Total Carbon (TC)):** The TOC, TC and IC of the sludge were found to be 395.6, 533.2 and 137.6 ppm as determined by the TOC analyzer. The results shows that the organic content of the solution is more as compared to the inorganic content the reason also valid as the sludge basically is a biological matter and hence have a higher content.

## 5.2 Adsorption study

The adsorption study was done first to examine the removal parameters and to determine the optimum dose for the adsorption and this provided the base for the SBR process. Following parameters were studied like pH, dose, kinetics and temperature during the study.

**5.2.1 Effect of pH:** The figure 5.9 shows the variation of % removal with pH. The pH study was done between 2 to 4. It is clear that at low pH 4, the presence of electron withdrawing nitro ( $\text{NO}_2$ ) group which undergoes substitution. The acidic strength of the compound increases as substitution results in more withdrawing of electrons from the oxygen atom. This increase in acidic strength results in more attraction of compound with negatively charged GAC adsorbent. At pH 6.4, acidic strength decreased so adsorption increased. However, as the pH increased, the NP converted into phenolate anions; this will cause reduction in adsorption due to more and more repulsion with the negatively charged adsorbent surface. Furthermore, phenolate anions have more affinity to the aqueous solution rather than adsorbent surface thereby contributing to low adsorption. So solubility of NP at different pH is also a major contributing factor for the variation in % removal. So, the optimum pH was found to be 6.4 i.e. natural pH and the removal was 90%.

**5.2.2 Effect of adsorbents dosage (m):** The effect of m value also studied for values ranging from 0-20 g/l, while  $C_o$  was 100 mg/l,  $T = 303 \text{ K}$ ,  $\text{pH}_o = 6.4$  and  $t = 6 \text{ h}$ . As the m value was increased, the intake of NP onto GAC first increased rapidly then became constant (figure 5.10). The intake of NP was found to be 94.8% at  $m = 4 \text{ g/l}$ , beyond which the removal increased only slightly and attained a steady removal of 98.6%. An increase in value of dose of GAC from 4-20 g/l increased NP intake by 3.8% only. Therefore, the optimum m ( $m_{\text{opt}}$ ) for GAC was found to be 4 g/l. After optimum condition, the removal becomes almost constant which may be due to the equilibrium attained in the solution. Hence, further increase in dose does not result in more percent removal.

**5.2.3 Effect of contact time:** Figure 5.11 shows the effect of contact time, (by data points) on adsorptive removal of NP by GAC. For this, solution of NP having  $C_o = 100 \text{ mg/l}$  and  $\text{pH}_o = 6.4$ , were kept in contact with the GAC ( $m_{\text{opt}} = 4 \text{ g/l}$ ) and  $T = 303 \text{ K}$ .

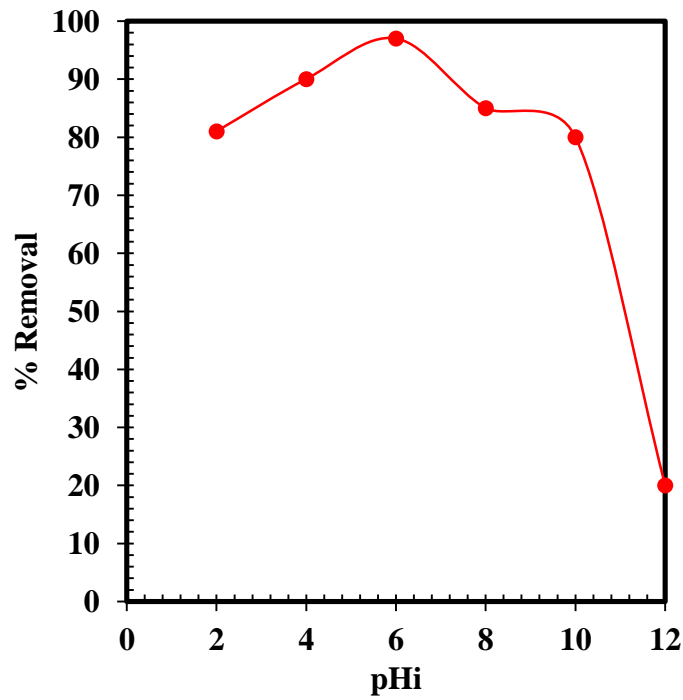


Figure 5.9 Effect of pH on adsorption of NP on GAC (m = 10 g/l, T = 303K)

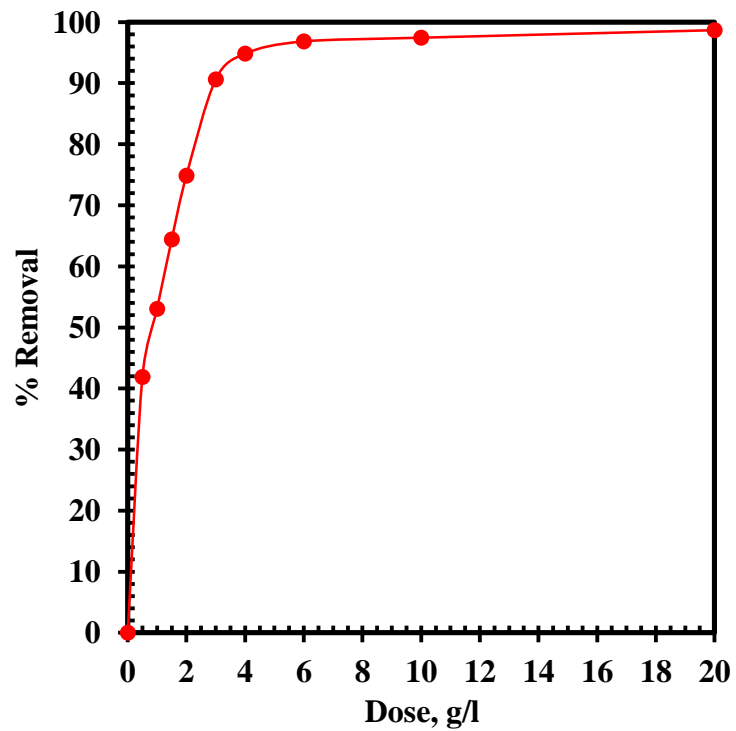


Figure 5.10 Effect of adsorbent dose on the adsorption of NP on GAC (pH 6.4, T = 303K)

The curve shows that initially the rate of intake is very fast which may be explained due to the presence of large number of vacant sites. From the curve it is clear that the uptake increases initially for 3 h.

The adsorption phenomenon is high due to adsorption at the surface only however later the adsorption process becomes slow due to the intraparticle diffusion as the particles have to travel longer distances in the molecule. However at the same time keeping all parameters constant the increase in concentration increases the rate of adsorption as the concentration increases the driving force necessary for adsorption.

The time data is fitted for pseudo 1<sup>st</sup> and 2<sup>nd</sup> order kinetics, which is given as follows:

Pseudo-1<sup>st</sup> -order model is given as in eqn 19:

$$q_t = q_e [1 - \exp(-k_f t)] \quad (19)$$

Where  $q_t$  is NP adsorbed (mg/g) at time (t) (min) and  $k_f$  is the pseudo first-order adsorption rate constant ( $\text{min}^{-1}$ ).

Pseudo-2<sup>nd</sup> -order model is in eqn 20:

$$q_t = \frac{tk_s q_e^2}{1 + tk_s q_e} \quad (20)$$

At time goes to zero, initial adsorption rate,  $h$  (mg/g min), is defined as (eqn 21);

$$h = k_s q_e^2 \quad (21)$$

Where,  $k_s$  is the pseudo second-order adsorption rate constant (g/mg min).

Table 5.2 shows the fitting of the experimental values to determine the kinetic parameters like  $k_f$ ,  $h$ ,  $q_e$  and  $k_s$  along with the correlation coefficients, SSE and RMSE values for both pseudo-first order and pseudo second order models. The  $R^2$  values show that the pseudo-second-order model best fits adsorption kinetic data. Figure 5.12 shows the best fitting of the experimental value in the pseudo 2<sup>nd</sup> order kinetics.

**5.2.4 Adsorption control mechanism:** The adsorption process is assumed to be controlled by intraparticle diffusion. This is the rate controlling step in the process. Weber and Morris proposed the intraparticle diffusion model as (eqn 22):

$$q_t = k_{id} t^{1/2} + I \quad (22)$$

where  $k_{id}$  is intraparticle diffusion rate constant ( $\text{mg/g} \cdot \text{min}^{1/2}$ ),  $I$  is intercept which represent the thickness of boundary layer. A larger intercept means is represented by greater thickness.

A plot between  $q_t$  vs  $t^{1/2}$  shows a multi-linear plot (table 5.3) which means more than one rate controlling steps are involved in the adsorption (figure 5.13).

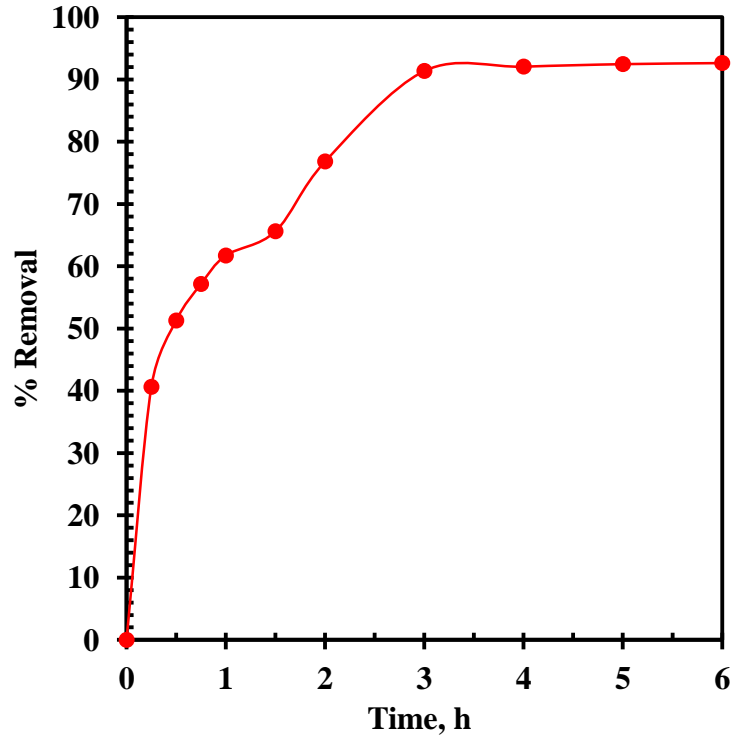


Figure 5.11 Effect of contact time on the adsorption of NP on GAC (pH 6.4, m = 4 g/l, T=303K)

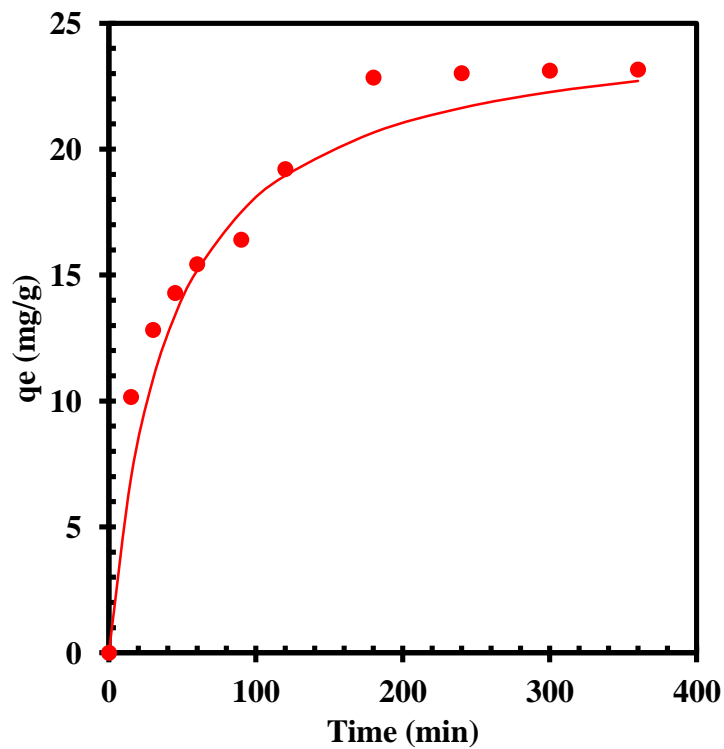
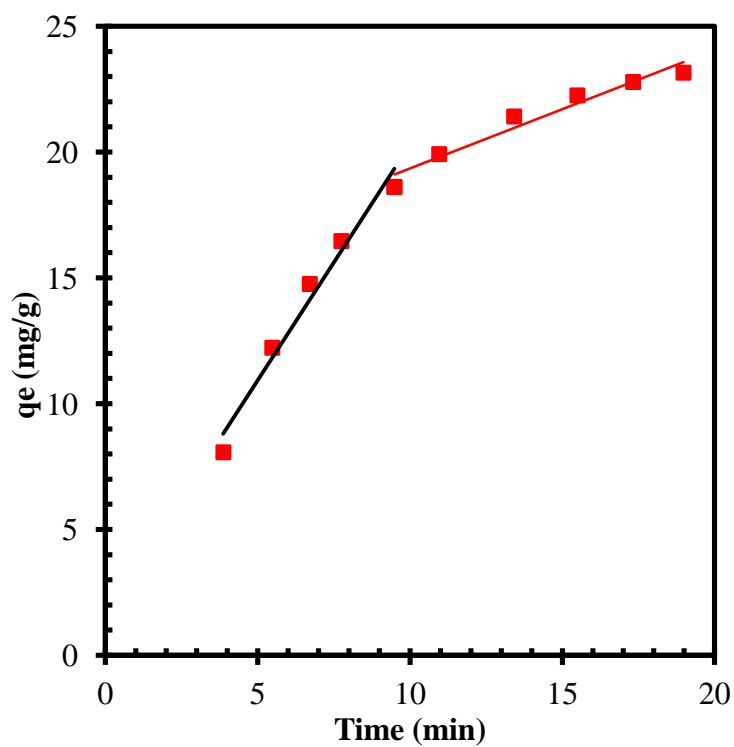


Figure 5.12 Effect of contact time on the adsorption of NP on GAC at pH 6.4, m = 4 g/l. Points and line represents experimental values and pseudo second order model



**Table 5.2 Kinetic parameters for the removal of NP by GAC (t = 3 h, C<sub>o</sub> = 100 mg/l, m = 4 g/l, T= 303 K)**

<b>Kinetics</b>	<b>NP-GAC</b>
<b>Pseudo 1<sup>st</sup> order</b>	
k <sub>f</sub> (min <sup>-1</sup> )	0.0229
q <sub>e</sub> (mg/g)	22.313
SSE	33.077
R <sup>2</sup> (non-linear)	<b>0.942</b>
RMSE	0.575
<b>Pseudo 2<sup>nd</sup> order</b>	
k <sub>s</sub> (g/mg min)	0.00125
q <sub>e</sub> (mg/g)	25.206
SSE	14.137
R <sup>2</sup> (non-linear)	<b>0.973</b>
RMSE	0.375



**Figure 5.13 Weber–Morris plot for the adsorption of NP by GAC (t = 6 h, C<sub>o</sub> = 100 mg/l, m<sub>opt</sub> = 4 g/l)**

**Table 5.3 Kinetic parameters for the removal of NP by GAC (t = 3 h, C<sub>0</sub> = 100 mg/l, m = 4 g/l, T= 303 K)**

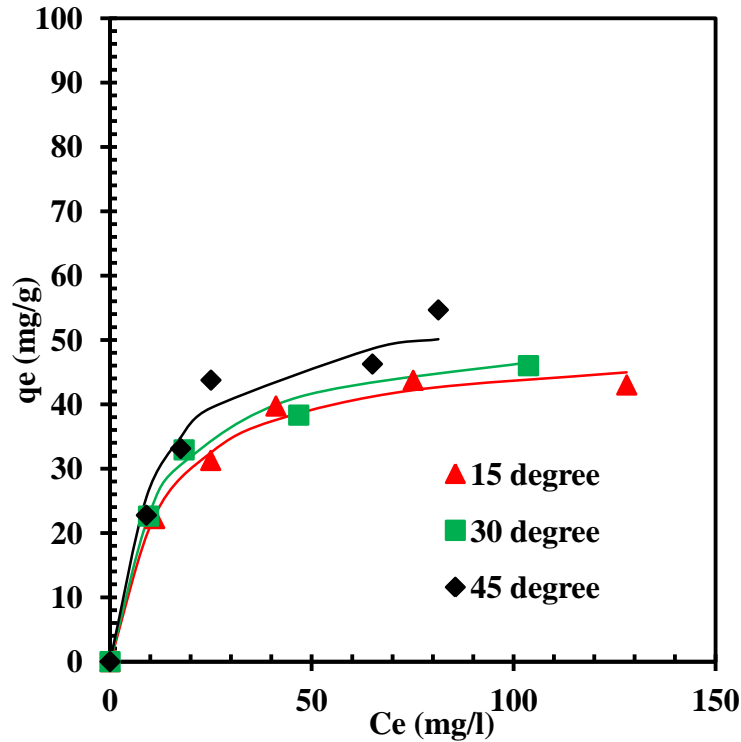
<b>Kinetics</b>	<b>NP-GAC</b>
<b>1<sup>st</sup> Intercept</b>	
k <sub>id1</sub> (mg/g. min <sup>1/2</sup> )	1.87
I <sub>1</sub>	1.54
SSE	1.78
R <sup>2</sup> (non-linear)	0.97
<b>2<sup>nd</sup> Intercept</b>	
k <sub>id2</sub> (mg/g. min <sup>1/2</sup> )	0.47
I <sub>2</sub>	14.65
SSE	0.74
R <sup>2</sup> (non-linear)	0.95

**5.2.5 Adsorption isotherm modelling:** The increase in temperature of the adsorption process was found to have direct relationship with the removal and increases as temperature increases from 15 to 45°C for C<sub>0</sub> =100–300 mg/l, m = 4 g/l, t = 3 h and pH<sub>0</sub>= 6.4 (Figure 5.14). Therefore, the adsorption process confirms to be endothermic. The increase in adsorption extent shows that the process involves both i.e. physical as well as chemical adsorption. One of the reasons for the improved adsorption is the formation of new sites and the activation of the surface of the adsorbent (figure 5.14).

In order to have most appropriate fitting of the experimental values, the fitting was done for different isotherms. The designing of the adsorption is done by establishing the equilibrium correlation of the experimental data with the equilibrium concentration. Various isotherm models have been developed for the fitting of experimental isotherms values. Non-linear fit was used for the experimental values fitting and models like Freundlich, Tempkin, etc. were used for the fitting as given in Srivastava et al. [2007]. It is clear that Langmuir isotherm best fits the experimental data (table 5.4).

**Table 5.4 Isotherm parameters for the removal of NP by GAC at different temperatures (288, 303 and 318K)**

Isotherms	Parameters	NP-GAC		
		Temperature (K)		
		288	303	318
<b>Langmuir</b> $q_e = \frac{Q_o b C_e}{1 + b C_e}$	Q <sub>o</sub>	49.60	52.12	56.96
	b	0.076	0.08	0.09
	R <sup>2</sup>	0.99	0.99	0.96
	SSE	12.45	17.39	141.81
<b>Freundlich</b> $q_e = K_F C_e^{1/n}$	K <sub>F</sub>	14.45	13.69	16.56
	1/n	0.24	0.26	0.25
	R <sup>2</sup>	0.98	0.99	0.95
	SSE	51.79	19.34	188.52
<b>Redlich-Peterson</b> $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	a <sub>R</sub>	0.023	0.24	0.006
	K <sub>R</sub>	2.65	6.78	3.00
	g	1.17	0.88	1.50
	R <sup>2</sup>	0.99	0.99	0.97
	SSE	5.821	13.44	118.24
<b>Hill</b> $q_e = \frac{Q_{sH} C_e^{nH}}{k_D + C_e^{nH}}$	Q <sub>sH</sub>	35.99	37.76	39.92
	k <sub>D</sub>	1	1	1
	n	100	100	100
	R <sup>2</sup>	0.76	0.727	0.69
	SSE	334.4	446.1	601.7
<b>Sips</b> $q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	K <sub>s</sub>	0.039	8.36	0.43
	a <sub>s</sub>	0.039	0.135	0.009
	β <sub>s</sub>	1.30	0.68	2.06
	R <sup>2</sup>	0.99	0.99	0.94
	SSE	9.26	14.74	110.4
<b>Koble–Corrigan</b> $q_e = \frac{A C_e^n}{1 + B C_e^n}$	A	0.039	8.36	0.43
	B	0.039	0.135	0.009
	n	1.30	0.68	2.07
	R <sup>2</sup>	0.99	0.99	0.94
	SSE	9.26	14.74	110.4
<b>Toth</b> $q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	K <sub>T</sub>	272.4	25.04	13040
	1/t	1.32	0.85	2.025
	a <sub>T</sub>	31.94	5.38	56.76
	R <sup>2</sup>	0.99	0.99	0.94
	SSE	4.93	13.12	123.7



**Figure 5.14 Equilibrium adsorption isotherms at different temperatures for NP loaded GAC system (t= 4 h, Co = 100 mg/l, m =4 g/l)**

**5.2.6. Determination of thermodynamic parameters:** The thermodynamic parameters were determined at different temperatures mainly 288, 303 and 318 K, respectively. The process involved:

- (i) A curve was drawn between  $q_e$  and  $C_e$  at different temperatures.
- (ii) The slope gives the value of  $K$  (l/kg).
- (iii) Now, a curve was again drawn between  $\ln K$  and  $1/T$  (Figure 5.15). The slope and intercept gives the value of enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and Gibbs free energy ( $\Delta G$ ) (eqn 24, 25) as per the equations given below (table 5.5):

**Change in the Gibbs free energy ( $\Delta G^\circ$ ):** It indicates degree of spontaneity and must be negative (eqn 23).

$$\Delta G^\circ = -RT \ln K \quad (23)$$

**The change in temperature and equilibrium constant** is related as follows:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (24)$$

Also, 
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (25)$$

After integration and rearrangements gives (van't Hoff equation) (eqn 26)

where, 
$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (26)$$

$\Delta G^\circ$  is the Gibbs free energy change (kJ/mol),  $\Delta H^\circ$  is the change in enthalpy (kJ/mol),  $\Delta S^\circ$  is the entropy change (J/mol K),  $T$  is the absolute temperature (K),  $K = q_e/C_e$  and is called as linear adsorption distribution coefficient.

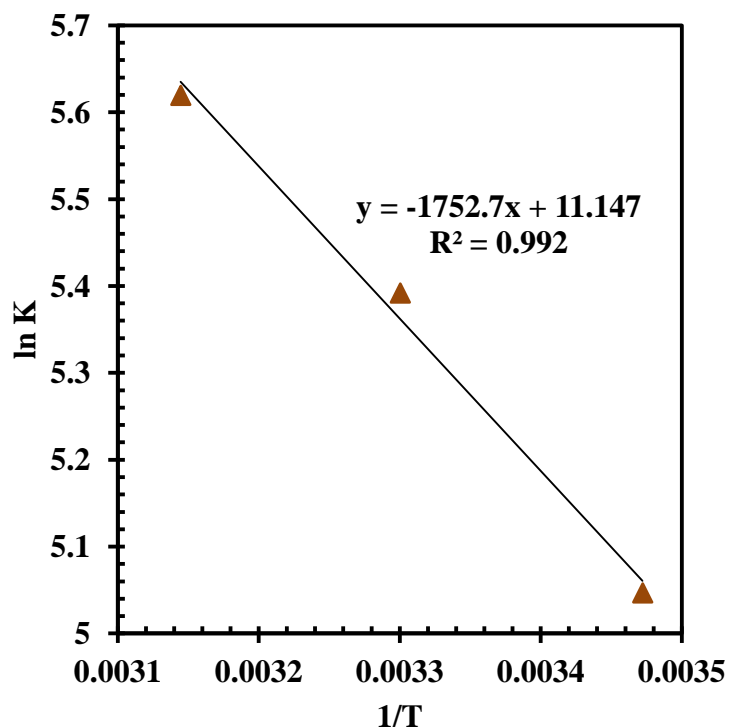


Figure 5.15  $\ln K$  vs  $1/T$  at different temperatures for NP loaded GAC system ( $t = 4$  h,  $C_0 = 100$  mg/l,  $m = 4$  g/l)

Table 5.5 Thermodynamic parameters for the removal of NP by GAC at optimum conditions ( $t = 3$  h,  $m = 4$  g/l)

Thermodynamic Parameters	Values
Enthalpy ( $\Delta H$ ), KJ/mol	14.57
Entropy ( $\Delta S$ ), J/mol/K	93.0
<b>Gibbs Free Energy (<math>\Delta G</math>), KJ/mol at different temperatures (K)</b>	
$\Delta G_{288}$	-12.12
$\Delta G_{303}$	-13.51
$\Delta G_{318}$	-14.90

### 5.3 SBR

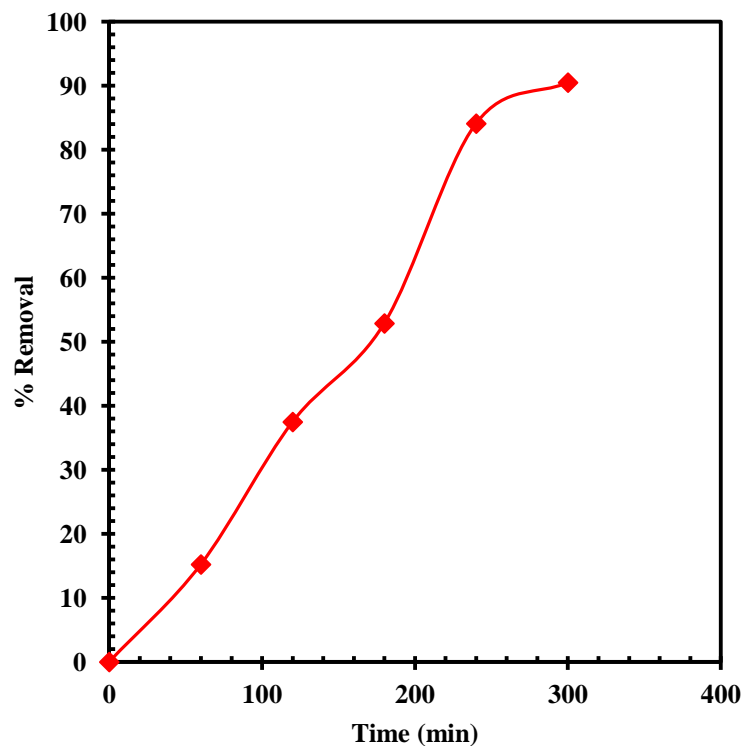
The adsorption result is followed by the SBR experiment to examine the removal efficiency of the sludge and to compare the results of the two.

**5.3.1 Treatment of synthetic waste water (SWW) containing NP with blank SBR:** The SBR cycle is optimized under blank conditions without addition of the adsorbent.

**5.3.1.1 Cycle time optimization:** The total cycle time ( $T_c$ ) for the treatment process involves addition of FILL ( $T_f$ ), REACT ( $T_r$ ), SETTLE ( $T_s$ ), DECANT ( $T_d$ ), IDLE ( $T_i$ ) time and given by the equation 27:

$$T_c = T_f + T_r + T_s + T_d + T_i \quad (27)$$

In the present study, the  $T_f$  was selected as instantaneous fill (unless otherwise mentioned) with mixing as well as aeration on so as to have presence of enough oxygen during the FILL phase and didn't allow denitrification. The  $T_r$  was taken as 4h as the % removal becomes comparatively constant after 4h. The  $T_s$ ,  $T_d$  and  $T_i$  were 1 h, 30 min and 30 min, respectively (Figure 5.16). Hence,  $T_c$  was calculated as 480 min (6h).



**Figure 5.16 Percent removal of NP with time in Blank SBR**

**5.3.1.2 Effect of volume exchange ratio (VER) and hydraulic retention time (HRT) on percentage removal:** It involved the variation in the fill volume in the reactor. The SWW of NP having concentration of 30 mg/l was used for the study. The fill volume was varied from 1 l to 2.5 l. The VER and HRT were varied from 0.2 to 0.5 and 1.67 to 0.67, respectively [Tomei et al., 2003]. From the table, it is clear that the maximum removal was obtained for VER = 0.2 or HRT = 1.67 d, which was 90.46%. Hence, the optimum HRT was 1.67 d (figure 5.17 and table 5.6 (a)).

**Table 5.6 % Removal with varying VER and HRT at  $C_o = 35$  mg/l, MLSS = 3000 mg/l for blank SBR and  $C_o = 100$  mg/l, MLSS = 3000 mg/l,  $m = 2.5$  g/l for GAC-SBR**

<b>(a) Blank SBR</b>					
$V_t$ (L)	$V_{Sludge}$ (L)	$V_f$ (L)	$VER = V_f/V_t$	$HRT = (1/VER)*(T_c/24)$ (d)	% Removal
5	4	1	0.2	1.67	90.46
5	3.5	1.5	0.3	1.11	77.25
5	3	2	0.4	0.83	68.64
5	2.5	2.5	0.5	0.67	66.73
<b>(b) GAC-SBR</b>					
5	4	1	0.2	1.67	92.72
5	3.5	1.5	0.3	1.11	90.17
5	3	2	0.4	0.83	85.24
5	2.5	2.5	0.5	0.67	81.92

**5.3.2 Effect of dose study with concentration:** The effect of percentage removal with increasing dose concentration and varying concentration was studied with MLSS = 3000 mg/l. It was found that with increasing dose, the percentage removal also increases which may be explained due to the fact that the number of pores goes on increasing with adsorbent concentration. The dose was increased from 1 to 2.5 g/l with increasing concentration and the relation is shown on figure 5.18. The optimum dose was coming out to be 2.5 g/L for  $C_o = 100$  mg/l.

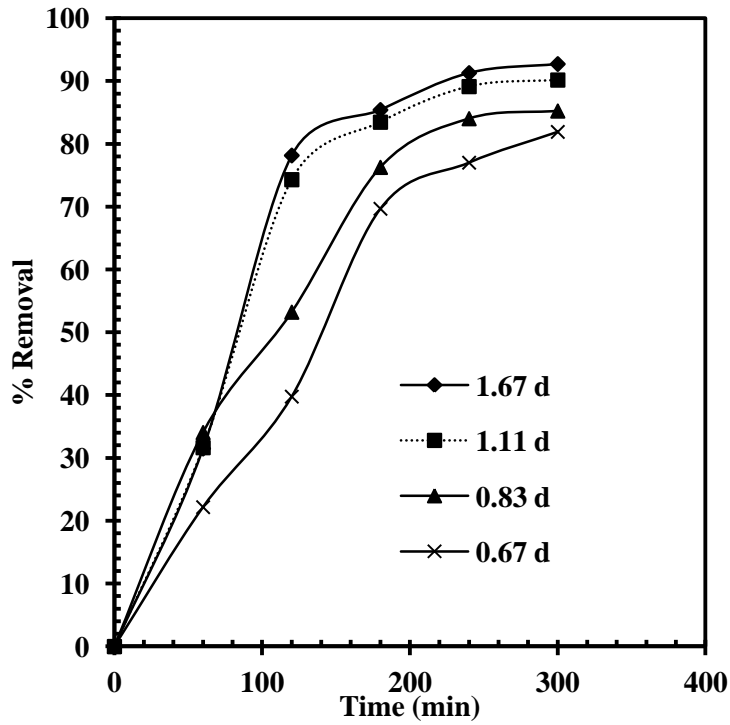


Figure 5.17 Variation of percent removal with time at different HRTs ( $C_o = 35 \text{ mg/l}$ ,  $T = 30^\circ\text{C}$ ,  $\text{rpm} = 150$ ,  $\text{MLSS} = 3000 \text{ mg/l}$ )

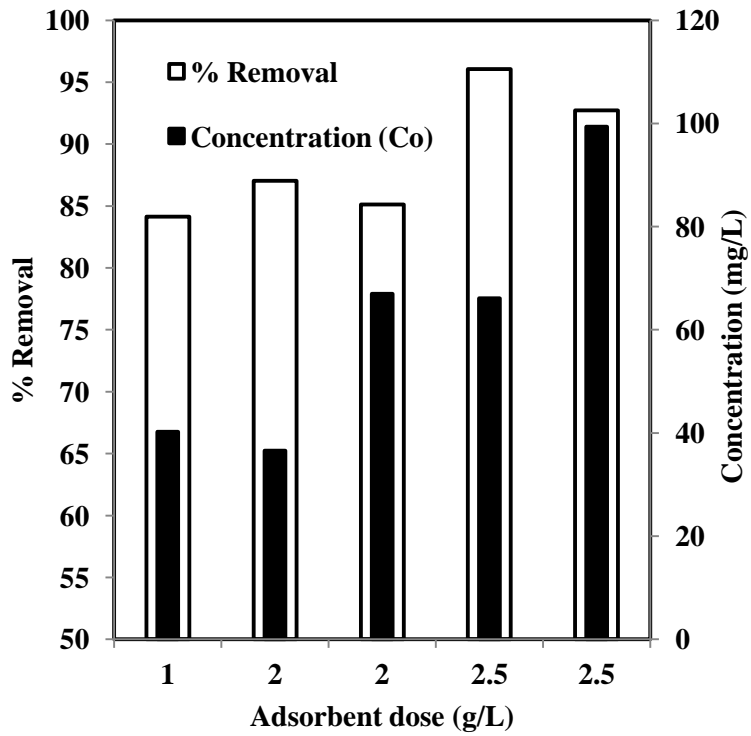
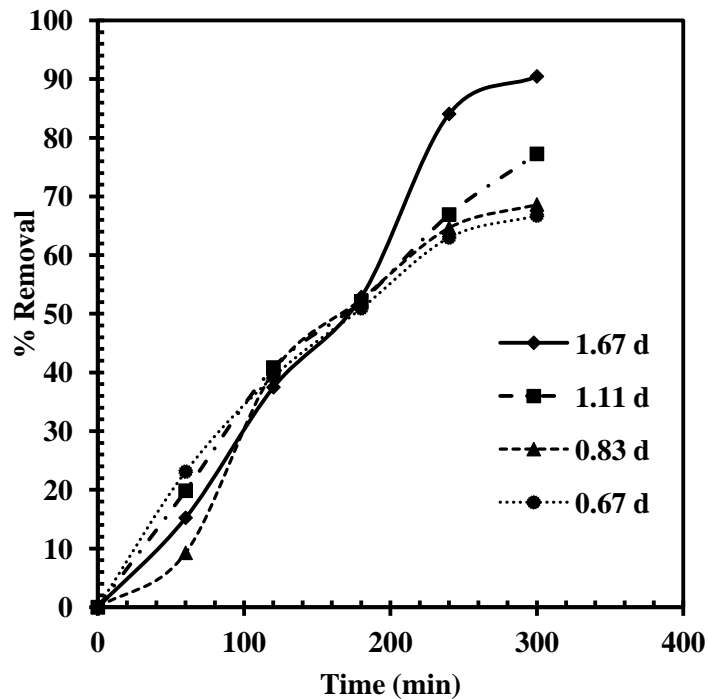


Figure 5.18 Variation of percent removal with concentration (mg/l) and dose (g/l) ( $C_o = 35\text{-}100 \text{ mg/l}$ ,  $T = 30^\circ\text{C}$ ,  $\text{rpm} = 150$ ,  $\text{MLSS} = 3000 \text{ mg/l}$ )

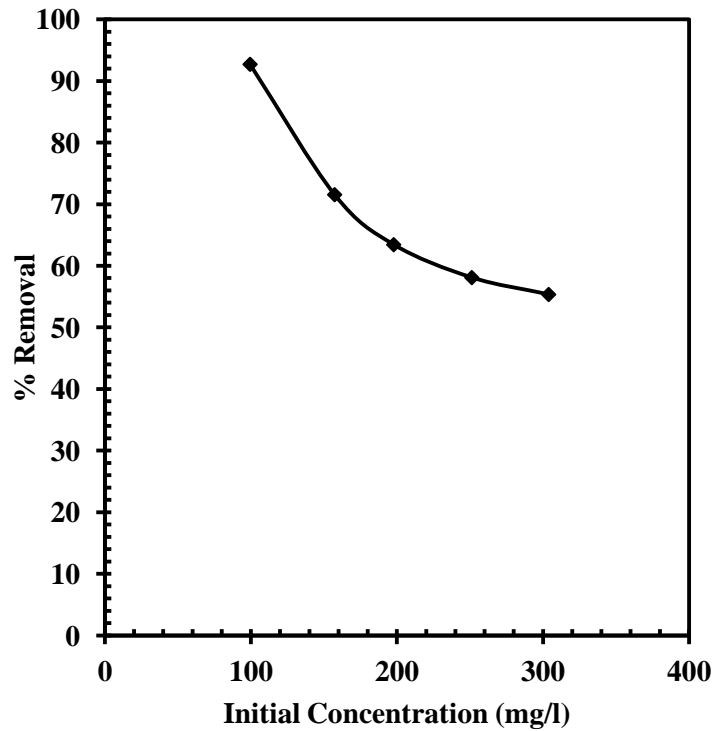




**Figure 5.19** Variation of percentage removal with time at different HRTs for GAC-SBR ( $C_o = 100$  mg/l,  $T = 30^\circ\text{C}$ , rpm = 150, MLSS = 3000 mg/l)

**5.3.3 Effect of VER and HRT on percentage removal in GAC-SBR:** The effect of VER and HRT was studied at  $C_o = 100$  mg/l, MLSS = 3000 mg/l,  $m = 2.5$  g/L and  $T_c = 8$  h (table 5.6 (b) and figure 5.19). The fill volume was varied from 1 l to 2.5 l. The VER and HRT were varied from 0.2 to 0.5 and 1.67 to 0.67, respectively. At VER = 0.2 or HRT = 1.67 d, maximum percent removal was obtained which was 92.72%. Hence, the optimum HRT was 1.67 d.

**5.3.4 Effect of increasing initial concentration on percentage removal in GAC-SBR:** The effect of percentage removal with increasing initial concentration of NP was observed. The concentration was increased from 100 to 300 mg/l. It was found from the curve that % removal decreased with increased concentration, which can be explained due to the fact that increased concentration of NP caused inhibitory effects on the microorganisms. The result showed that % removal decreased from 92 % to 55 % (figure 5.20).



**Figure 5.20** Variation of percentage removal with concentration (mg/l) in GAC-SBR ( $C_0 = 100\text{-}300$  mg/l,  $T = 30^\circ\text{C}$ , rpm = 150, MLSS = 3000 mg/l).

**5.3.5 Effect of mixture of NP and CP on the removal in GAC-SBR:** The removal of mixture of NP and CP was also studied in GAC-SBR. The CP was chosen for the study as its maximum wavelength was 225 nm [Neppolian et al., 2007] by UV-VIS spectrophotometer and it should not be similar to that of NP which is 316 nm to avoid overlapping of curves. The calibration curve was made for the mixture of NP and CP at different concentration using the relation as described in Haghseresht et al. [2003] as (eqn 28, 29):

$$C_{\text{CP}} = \frac{A_{\text{CP}}^{\lambda_1}}{S_{\text{CP}}^{\lambda_1}} \quad (28)$$

$$C_{\text{NP}} = \frac{A^{\lambda_2}}{S_{\text{NP}}^{\lambda_2}} - \frac{A_{\text{CP}}^{\lambda_1} S_{\text{CP}}^{\lambda_2}}{S_{\text{CP}}^{\lambda_1} S_{\text{NP}}^{\lambda_2}} \quad (29)$$

where, A is absorbance of CP and NP at wavelengths  $\lambda_1$  (225 nm) and  $\lambda_2$  (316 nm) and S is slope of calibration curves at of single components at both wavelengths.  $\lambda_1$  is the absorbance where only one compound absorbs the light. The concentration of binary mixture was varied from 25 mg/l to 100 mg/l (figure 5.21).

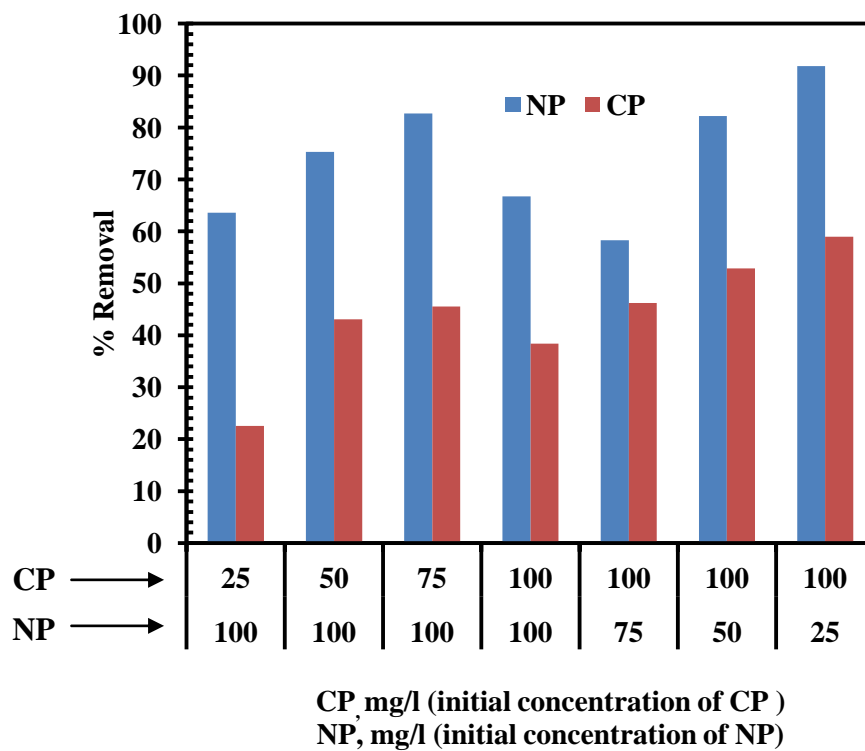
**5.3.5.1 Calibration curve for binary compounds (NP+CP):** The calibration curve was made by using MS Excel by minimizing the error as shown in table 5.6.  $\lambda_{\max}$  for NP and CP was found to be 316 and 225 nm. The concentration of binary mixture was found out by UV-VIS Spectrophotometer by measuring the absorbance of the two compounds and the concentration was measured from the table 5.7.

**Table 5.7 % Calibration curve for the binary mixture of NP and CP**

Act. Conc.	Act. Conc.	NP	CP	Meas. Conc.	Meas. Conc.	Error	Error
mg/l						NP	CP
NP	CP	316 nm	225 nm	NP	CP		
5	5	0.363	0.592	5.222	5.005	4.440	0.096
5	10	0.363	0.944	5.222	10.312	4.440	3.119
5	15	0.363	1.267	5.222	15.182	4.440	1.211
5	20	0.361	1.587	5.193	20.028	3.864	0.139
5	25	0.371	1.922	5.337	24.971	6.741	0.118
10	5	0.726	0.829	10.444	4.657	4.440	6.853
10	10	0.695	1.178	9.998	10.254	0.020	2.540
10	15	0.715	1.5	10.286	14.893	2.857	0.715
10	20	0.707	1.83	10.171	19.954	1.706	0.228
10	25	0.691	2.153	9.940	24.997	0.595	0.012
15	5	1.06	1.09	15.249	4.985	1.658	0.301
15	10	1.062	1.432	15.278	10.120	1.850	1.196
15	15	1.057	1.768	15.206	15.239	1.371	1.596
15	20	1.036	2.079	14.903	20.155	0.643	0.776
15	25	1.039	2.385	14.947	24.736	0.356	1.055
20	5	1.318	1.303	18.960	5.410	5.199	8.195
20	10	1.337	1.661	19.234	10.602	3.832	6.020
20	15	1.355	1.978	19.493	15.187	2.537	1.246
20	20	1.342	2.277	19.305	19.835	3.473	0.823
20	25	1.36	2.563	19.564	23.953	2.178	4.188
25	5	1.744	1.581	25.089	5.000	0.354	0.000
25	10	1.737	1.91	24.988	10.036	0.049	0.359
25	15	1.728	2.211	24.858	14.671	0.567	2.192
25	20	1.715	2.502	24.671	19.199	1.315	4.005
25	25	1.725	2.793	24.815	23.478	0.739	6.087

### 5.3.5.2 Discussion of percentage removal of NP+CP at different concentrations

The removal study for binary mixture of NP and CP were studied in this section. The result was as shown in figure 5.21. The experiment was conducted initially for NP having 100 mg/l and CP concentration goes on increasing from 25 to 100 mg/l and then the concentration of both was reversed i.e. CP concentration was fixed for 100 mg/l and the NP concentration was decreased from 100 to 25 mg/l. The resulting graph for study of mixture shows that initially with addition of CP in the NP solution resulting in the decrease in removal of NP. This may be due to the detrimental effect of CP on microorganisms that were previously grown for NP solution. However, with increasing CP concentration, the removal of both NP and CP goes on increasing. When the CP concentration was fixed to 100 mg/l and NP concentration goes on decreasing, the removal of NP was found to increase generally as shown in the figure below.



**Figure 5.21 Variation of percent removal with concentration (mg/l) in GAC-SBR for binary mixture (NP+CP) ( $C_0 = 25-100$  mg/l,  $T = 30^\circ\text{C}$ , rpm = 150, MLSS = 3000 mg/l)**

## 6 CONCLUSIONS AND RECOMMENDATIONS

In the present study, experiments were done for the treatment of 4-nitrophenol (NP) bearing wastewater by biological treatment in a sequential batch reactor (SBR) without any adsorbent (called as blank-SBR), and in a SBR loaded with granular activated carbon (GAC-SBR). Adsorption experiments were done with SBR alone.

### 6.1 Conclusions

The present study involves the removal of 4-nitrophenol (NP) from the synthetic wastewater from adsorption and sequential batch reactor (SBR) process. Following conclusions can be drawn from the experimental studies:

1. The comparison of adsorbents showed that the surface area of granulated activated carbon (GAC) was higher as compared to the bagasse fly ash (BFA) and rice husk ash (RHA).
2. The optimum pH was found to be at the natural pH i.e. pH 6.4.
3. Optimum dose was found to be 4 g/l.
4. Optimum time of contact of the experiments was 3 h and the kinetics study showed that 2<sup>nd</sup> order kinetics best-represented the kinetic data.
5. The Weber-Morris intra-molecular diffusion model showed that the presence of boundary layer is the rate limiting step during the adsorption process.
6. The isotherm study showed that the adsorption was endothermic.
7. The thermodynamic study revealed negative value of Gibbs free energy ( $\Delta G$ ) indicating spontaneity of the reaction. The positive value of entropy ( $\Delta S$ ) showed the feasibility of the reaction.
8. Treatment in SBR was done by varying hydraulic retention time (HRT). Optimum HRT was found to be 1.67 d for both blank-SBR and GAC-SBR.
9. The optimum dose was found to be 2.5 g/l. The effect of increasing concentration was studied and the percentage removal was found to decrease from 92 to 55% when the concentration was increased from 100 to 300 mg/l.
10. The mixture study was also done for the mixture of NP and 4-chlorophenol (CP). The removal of NP first decreased with addition of CP. However, when the concentration of CP was decreased with constant NP concentration, the percent removal of NP also increased.

## **6.2 Recommendations**

Based on the present experiments and results, following recommendations can be drawn as follows:

1. The experiment can be extended for more phenolic derivatives along with NP and CP to measure the removal efficiency.
2. The present study was done at room temperature i.e. 30°C, the experiment can be done at various temperatures to measure effect on micro-organisms.
3. The pure culture can be grown instead of mixed culture from the sludge to improve the specific removal of NP.

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