

# USE OF SEQUENTIAL BATCH REACTOR FOR TREATMENT OF PHENOLIC WASTEWATER

## A DISSERTATION

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

*of*

## INTEGRATED DUAL DEGREE

(Bachelor of Technology & Master of Technology)

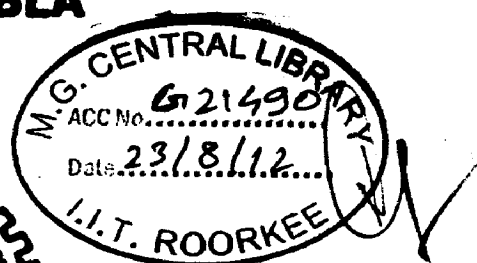
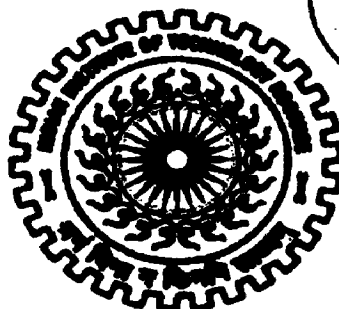
in

## CHEMICAL ENGINEERING

(With Specialization in Hydrocarbon Engineering)

By

**ADITYA DEMBLA**



**DEPARTMENT OF CHEMICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE  
ROORKEE -247 667 (INDIA)  
JUNE, 2012**

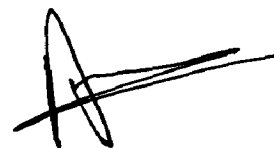
## CANDIDATE'S DECLARATION

---

I hereby assure that the work presented in this project report entitled "USE OF SEQUENTIAL BATCH REACTOR FOR TREATMENT OF PHENOLIC WASTEWATER" is submitted towards the partial fulfillment of the requirements for the award of the Integrated Dual Degree with specialization in Hydrocarbon Engineering and submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, is an authentic record of my original work carried out under the guidance of **Dr. V.C. SRIVASTAVA, Assistant Professor**, Department of Chemical Engineering, Indian Institute of Technology Roorkee. I have not submitted the matter embodied in this project report for the award of any other degree.

Place: Roorkee

Date: 07/06/2012



**ADITYA DEMBLA**

Enrol. No: 071101

## CERTIFICATE

---

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



**Dr. V.C. SRIVASTAVA**

Assistant Professor,

Department of Chemical Engineering,  
Indian Institute of Technology Roorkee.

## ACKNOWLEDGEMENT

---

It is a pleasure to thank the many people who made this thesis possible.

I am feeling great in expressing my profound sense of gratitude first and foremost to the almighty God because all the matter on the earth, undergo upto end by taking power from him and the power of taking powers also comes in the empire of him.

Now I welcome this opportunity to express my sincere gratitude to my guide **Dr. V.C. Srivastava**, Assistant Professor, Department of Chemical Engineering, and **Dr. I.D. Mall**, Professor, Department of Chemical Engineering, Indian institute of Technology Roorkee, whose strengthening presence was a source of great inspiration for the successful completion of this seminar report. His constant guidance, useful criticism and constant help in the hours of need had been immensely useful.

I would like to thank **Dr. V.K. Agarwal**, Professor and Head of the Department, Department of Chemical Engineering, IIT Roorkee, for being supportive throughout the journey.

I would like to gratefully acknowledge the support offered by **Mr. Rajendra Bhatnagar**, who has been abundantly helpful and has assisted me in numerous ways. I specially thank him for his patience.

I am greatly thankful to **Mr. Chandrakant Thakur**, Research Scholars, Department of Chemical Engineering and **Mr. Naved**, JRF, Department of Chemical Engineering, for their constant guidance and suggestions during the entire course of this work. Their co-operation and in-depth knowledge have made my work possible.

My final words go to my parents. I want to thank my family, whose love and guidance is with me in whatever I pursue.

On a different note, many people have been a part of my education and I am highly grateful to all of them.

**ADITYA DEMBLA**

## ABSTRACT

---

The aim of this research is to study the treatment of 4-chlorophenol bearing wastewater by biological treatment in an SBR without any adsorbent (blank SBR) and an SBR loaded with Granular activated carbon (GAC-SBR). The performance of two types of SBR's has been compared in terms of treatment of 4-chlorophenol (4-CP) bearing synthetic wastewater. Adsorbent dose used for GAC-SBR was 16 g/L. The test results revealed that GAC addition could improve the activity of the activated sludge. The GAC-SBR could treat 4-CP bearing wastewater with initial concentration of up to 1250 mg/L while blank SBR could treat 4-CP bearing wastewater with initial concentration of only up to 200 mg/L. Also by addition of adsorbent to SBR, the removal efficiency of SBR was increased from 75% (approx.) to more than 95%. It was observed that addition of GAC could enhance the ability of activated sludge in resisting the shock load of organics. Compared to the blank activated sludge, GAC added activated sludge could treat wastewater of significantly higher 4-CP concentration in a shorter cycle time. Characterization of the sludge was done using SEM/ EDX analysis. Settling and filterability characteristics of the sludge were also studied. In addition to this, experiments were carried out to study the adsorptive removal of 4-chlorophenol using GAC as adsorbent.

## TABLE OF CONTENTS

Chapter no.	Topic	Page no.
<b>1.</b>	<b>Introduction</b>	<b>1-11</b>
	1.1 General	1
	1.2 Chlorophenol	3
	1.2.1 Properties of 4-chlorophenol	4
	1.2.2 Discharge concentration of chlorophenol from various industries	5
	1.2.3 Health and related hazards of 4-chlorophenol	5
	1.2.3.1 Effect of short-term (acute) exposure	5
	1.2.3.2 Effect of long-term (acute) exposure	6
	1.2.4 Treatment of 4-chlorophenol	6
	1.3 Sequential batch reactor	7
	1.4 Adsorption	9
	1.5 Objective of work	10
<b>2.</b>	<b>Literature Review</b>	<b>12-27</b>
	2.1 General	12
	2.2 Coagulation/co-precipitation	12
	2.3 Electro-coagulation	13
	2.4 Electrochemical oxidation	14
	2.5 Adsorption	14
	2.6 Biological treatment	15
<b>3.</b>	<b>SBR and adsorption</b>	<b>28-41</b>
	3.1 Sequential Batch Reactor (SBR)	28
	3.1.1 SBR process description	28
	3.1.2 Continuous flow systems	30
	3.2 Design criteria of SBR	30
	3.2.1 Design parameters of SBR	31
	3.2.2 Determination of SBR operating cycle time	31
	3.2.3 Decanting system	32
	3.2.4 Blower requirement	32
	3.2.5 Bottom slope	33
	3.3 Adsorption	33
	3.3.1 General	33
	3.3.2 Adsorption in wastewater treatment	34
	3.3.3 Adsorption as a physical process	35

	3.3.4 Activated carbon as an Adsorbent	35
	3.3.5 Adsorption equilibrium	36
	3.4 Adsorption isotherms	36
	3.4.1 Langmuir Isotherm	37
	3.4.2 Freundlich Isotherm	37
	3.4.3 Redlich-Peterson (R-P) isotherm	39
	3.5 Adsorption Practices	39
	3.5.1 Batch Adsorption	39
	3.5.2 Multistage Crosscurrent Adsorption	39
	3.5.3 Multistage countercurrent adsorption	40
	3.6 Factors Affecting Adsorption	40
<b>4.</b>	<b>Experimental studies on SBR and adsorption</b>	<b>42-53</b>
	4.1 General	42
	4.2 Experimental setup for SBR	42
	4.2.1 Influent characteristics for SBR	44
	4.2.2 Sludge characteristics	45
	4.2.3 Adsorbent in SBR	46
	4.3 Experimental procedure	47
	4.3.1 Analytical methods	47
	4.3.2 Cycle time for SBR	49
	4.3.3 Effect of volume exchange ratio (VER) and hydraulic retention time (HRT)	49
	4.3.4 Effect of adsorbent dosage in GAC-SBR	50
	4.4 Influent characteristics for adsorption	50
	4.4.1 Batch experiments	50
	4.4.2 Effect of type of adsorbent	51
	4.4.3 Effect of adsorbent dosage	51
	4.4.4 Effect of pH	51
	4.4.5 Batch kinetics and isotherm study	51
	4.5 Studies on GAC and wasted sludge	52
	4.5.1 Settling and filterability of sludge	52
	4.5.2 BET surface area for GAC	53
	4.5.3 Physicochemical characterization	53
	4.5.4 EDAX	53
<b>5.</b>	<b>Results and discussions</b>	<b>54-77</b>
	5.1 Introduction	54
	5.2 Treatment of 4-chlorophenol bearing wastewater using blank SBR	54
	5.2.1 Cycle time optimization	54
	5.2.2 Effect of VER and HRT	55

	5.2.3 Effect of contact-time and initial concentration of 4-chlorophenol	56
	5.3 Treatment of 4-chlorophenol using adsorption	58
	5.3.1 Selection of Adsorbent	58
	5.3.2 Effect of adsorbent dosage	59
	5.3.3 Effect of pH	59
	5.3.4 Effect of contact-time and initial concentration of 4-chlorophenol	60
	5.3.5 Study of adsorption isotherms	62
	5.4 Treatment of 4-chlorophenol bearing wastewater using GAC-SBR (SBR with adsorbent)	63
	5.4.1 Effect of adsorbent dose in SBR	63
	5.4.2 Cycle time optimization	63
	5.4.3 Effect of VER and HRT	65
	5.4.4 Effect of contact-time and initial concentration of 4-chlorophenol	66
	5.5 Study on sludge	67
	5.5.1 Calculation of sludge retention time (SRT) and sludge wasting rate (SWR)	67
	5.5.2 Settling and sludge volume index (SVI)	68
	5.5.3 Filterability	70
	5.5.4 SEM and EDX analysis	71
	5.6 Study on adsorbent	75
	5.6.1 BET surface area analysis	75
	5.6.2 SEM and EDX analysis	75
6.	<b>Conclusions and recommendations</b>	<b>78-80</b>
	6.1 Conclusions	78
	6.1.1 Conclusions on adsorption of 4-chlorophenol	78
	6.1.2 Comparison of two SBR's	78
	6.1.3 Sludge	79
	6.2 Recommendations	80
	<b>References</b>	<b>81-87</b>
	<b>Publications</b>	<b>88</b>

## LIST OF FIGURES

Figure No.	Title	Page no.
1.1	Degradation pathway for chlorocatechol via ortho-ring fission	7
4.1	SBR used for the present study	43
4.2	Different views and stages of SBR	43
4.3	Schematic illustration of the SBR	44
4.4	Kankhal sewage treatment plant	45
4.5	UV-spectrophotometer Calibration for 4-chlorophenol	48
4.6	Absorbance of 4-chlorophenol at different wavelengths	48
4.7	Absorbance of sludge at different wavelengths	49
5.1	Percentage removal of 4-chlorophenol with time in blank SBR	55
5.2	Percentage removal of 4-chlorophenol in blank SBR at different HRT	56
5.3	Percentage removal of 4-chlorophenol at different initial concentrations of 4-chlorophenol in blank SBR	57
5.4	Contact-time data for removal of 4-chlorophenol for different initial concentrations of 4-chlorophenol in blank SBR	57
5.5	Removal of 4-chlorophenol by different adsorbents	58
5.6	Removal of 4-chlorophenol at different adsorbents dosages	59
5.7	Removal of 4-chlorophenol by adsorption at different pH	60
5.8	Percentage removal of 4-chlorophenol at different initial concentrations of 4-chlorophenol by adsorption	61
5.9	Contact-time data for the adsorptive removal of 4-chlorophenol at different initial concentrations of 4-chlorophenol	61
5.10	$q_e$ v/s $C_e$ plot for adsorption of 4-chlorophenol	62
5.11	Percentage removal of 4-chlorophenol at different doses of GAC in GAC-SBR	64
5.12	Percentage removal of 4-chlorophenol with time in GAC-SBR	64
5.13	Percentage removal of 4-chlorophenol at different values of HRT in GAC-SBR	65
5.14	Percentage removal of 4-chlorophenol at different initial concentrations of 4-chlorophenol in GAC-SBR	66
5.15	Contact-time data for removal of 4-chlorophenol for different initial concentrations of 4-chlorophenol in GAC-SBR	67
5.16	Settling curve of sludge before acclimatization	69
5.17	Settling curve of sludge after acclimatization	69
5.18	Filterability of sludge	70



5.19	SEM of sludge before acclimatization	72
5.20	SEM of sludge after acclimatization	73
5.21	EDX of non-acclimatized sludge	74
5.22	EDX of acclimatized sludge	74
5.23	SEM of GAC before treatment	76
5.24	SEM of GAC after treatment	76
5.25	EDX of non-treated GAC	77
5.26	EDX of treated GAC	77

## LIST OF TABLES

---

<b>Table No.</b>	<b>Title</b>	<b>Page no.</b>
1.1	Physical properties of 4-chlorophenol	4
2.1	Important remarks and results from various literatures	25
3.1	Comparison of Langmuir and Freundlich Adsorption	38
4.1	Operating conditions of the two reactors	44
4.2	Size pattern of the adsorbent particles used in SBR	46
5.1	Removal efficiencies of blank SBR at different VER and HRT	55
5.2	Kinetic parameters values for the removal of 4-chlorophenol by blank SBR	57
5.3	Kinetic parameters values for the adsorptive removal of 4-chlorophenol	61
5.4	Isotherm parameters values for the removal of 4-chlorophenol by GAC	63
5.5	Removal efficiencies of GAC-SBR at different VER and HRT	65
5.6	Kinetic parameters values for the adsorptive removal of 4-chlorophenol	66
5.7	Relative percentage of elements in non-acclimatized and acclimatized sludge	71
5.8	Relative percentage of elements in non-treated and treated GAC	75
6.1	Performance comparison of blank SBR and GAC-SBR	79

# CHAPTER I

## *INTRODUCTION*

---

### **1.1 General**

Many processes in the chemical, pharmaceutical, plastic, petrochemical industries, etc., generate wastewater which contains organic toxic compounds out of which a large fraction is in the environment is in the form of very dilute groundwater and surface water. The presence of these contaminants besides destroying the natural sources especially groundwater, also gives health problems to human beings such as allergy, skin diseases, respiratory system disorders, heart disease, carcinogenic and many others. Such wastewaters should be treated and reutilized in areas where water resources are scarce, hence the importance for the improvement of the wastewater treatment technologies. The ability of biological treatments for such wastewaters is based on the capacity of microorganisms, specifically bacteria, to degrade a great quantity of toxic substances. These pollutants present in wastes act as food by the bacteria and these, while feeding, increase the microorganism population along with the treatment of the waste water. Some microorganisms perform the treatment process in the presence of air (aerobic bacteria) and others in its absence (anaerobic bacteria) [Mohan and Sharma, 2001]. For the aerobic reactions the air is dissolved in the water by means of aerator systems. Bioreactor is basically a tank, within which the proper conditions for the bio-reaction to take place are guaranteed, on a large scale basis [Levin and Gealt, 1993].

The sequential batch reactor (SBR) has an increased flexibility and efficiency as compared to continuous reactors. For this very reason the term SBR is used as a synonym for wastewater treatment plant technology where the volume in the reactor tank is variable in time [Wilderer et al., 2006]. The processes occurring in an SBR are identical to those of a conventional continuous activated sludge system except an important difference between the both. In former, all the stages of the process are performed in the same reactor, with different phases separated in time, whereas in latter, the different stages are performed simultaneously, in different tanks or tank sections [Betancur et al., 2009].

Phenolic compounds are widely produced in the processing industries as well as in chemistry. Also they are abundantly present in the environment having been detected in wastewater, rivers and soils. In addition, the presence of substituted groups in phenols (i.e. in nitro and chloro-phenols) increases the toxic effects exerted by them on human health and the environmental life and their characteristics of persistence in the environment. Therefore, a high efficiency treatment of wastewater contaminated by these compounds is required prior to their discharge into the environment [Tomei et al., 2004].

Hence, it is the need of the hour to find alternative methods to reduce the amount and environmental sensitivity of the liquid waste produced. The promising options for treatment are through biological, chemical and physical methods. However certain economical and energy constrains are associated with all these processes. An eco-friendly and economically viable technology is much desirable in the days. Biological oxidation method is basically to destruct the organic solvents into harmless materials such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Apart from biological treatment processes, adsorption has been found to be very promising for the removal of organic compounds from wastewaters. The most commonly used adsorbent for the treatment of various types of wastewaters is activated carbon. But activated carbon, besides being used at a large scale in industries, remains a costly adsorbent. However, many investigators have utilized several low-cost adsorbents like coal fly ash (CFA), rice husk ash (RHA), bagasse fly ash (BFA), etc. for the treatment of a wide variety of wastewaters [Kushwaha et al., 2010].

The activated sludge process has been traditionally applied to treat industrial wastewater, but the nature of such discharges is found to cause operational problems in continuous flow systems very often mainly in the case of wastewaters containing toxic compounds generated by several chemical facilities. In such waters, the mass of toxic contaminants could vary in time and space [Edwards,1995]; thus, to degrade these contaminants efficiently, the treatment plants must be designed with excess capacity. The main problem faced by continuous reactors is that they are designed to work under steady-state conditions but, in reality, industrial effluents present great variability, despite equalizer tanks, giving transitory conditions.

SBRs are used all over the world and have been around since the 1920s. Municipalities, resorts and a number of industries, including pulp and paper, tanneries and textiles, dairy have been using SBR's for practical wastewater treatment. With their growing

popularity in different countries, mainly U.S., Europe and China, they are being used successfully to treat both industrial and municipal wastewaters, particularly in areas characterized varying flow patterns. Improvements in technology and equipment, especially in computer control systems and aeration and agitation devices, have made SBR's a more viable choice over the conventional or less successful activated-sludge system.

SBR is nothing but the batch operation in sequence. In this system, wastewater is added to a single "batch" reactor which is treated to remove undesirable components or wastes and finally discharged. SBR's have several substantial benefits over alternative conventional flow systems for the biological treatment of both industrial and domestic wastewater [Sharma et al., 2010]. All the SBR's five steps in common, carried out in a fixed sequence as follows: (1) fill, (2) react phase, (3) settle phase, (4) decant phase, (5) idle phase. During the fill, the influent wastewater is fed to the reactor followed by the react phase in which the reactor is operated in a batch mode with aeration and agitation. A number of process modifications have been made in time to achieve specific treatment objectives.

Adsorption is a process in which a solid (adsorbent) is used for removing a soluble substance from the solvent (water, in present study). The soluble substance accumulated on surface of solid is called the adsorbate and the adsorbing substance is called adsorbent. Activated carbon, a very common adsorbent, is produced specifically so as to achieve a very huge surface area (between 500 - 1500 m<sup>2</sup>/g). This big internal surface makes activated carbon ideal for adsorption process. Activated carbon comes in two variations: Powder Activated Carbon (PAC) and Granular Activated Carbon (GAC). Both of them are widely used as adsorbents in waste water and gas treatments as well as in catalysis [Lisovskii et al., 1997]. In the present study GAC is used as the adsorbent.

## 1.2 Chlorophenol

The molecular formula for chlorophenols is C<sub>6</sub>H<sub>n</sub>Cl<sub>m</sub>O where m = 1 to 5, n = 1 to 4. Chlorophenols are widely used as anti-mildew agents, preservatives, disinfectants and fungicides [Rao 1978, Sittig 1981]. Chlorophenols are also formed during the chlorination of wastewaters, and are often the by-product of the breakdown of chloro-aromatics and pesticides [Pritchard et al., 1987]. Chlorophenols are carcinogenic and can condense to chlorodibenzodioxins, which are extremely toxic and hazardous to the environment [Rochkind et al., 1986]. (language change)

Chlorophenols are a group of chemicals in which chlorines (between one and five) have been added to phenol. Phenol, an aromatic compound derived from benzene, the simplest aromatic hydrocarbon, is obtained by adding a hydroxyl group to a carbon to replace hydrogen. There are five basic types of chlorophenols: mono-chlorophenols, di-chlorophenols, tri-chlorophenols, tetra-chlorophenols, and penta-chlorophenols. In all, there are nineteen different chlorophenols.

The chlorophenols have a strong medicinal taste and odor; even very small amounts (at parts per billion to parts per million concentrations) can be tasted in water. Very small amounts of chlorophenols can also make fish taste bad [Toxic Substances Portal - Chlorophenols, Agency for toxic substance and disease registry, 1999]. Chlorophenols with at least two chlorines have either been used directly as pesticides or have been converted into pesticides. Also, some chlorophenols, especially 4-chlorophenol, have been used as antiseptic. Apart from being produced commercially, small amounts of some chlorophenols, especially the mono- and di-chlorophenols, may be produced when drinking water or wastewater is disinfected with chlorine, if certain contaminants like phenol are present in the raw water. Chlorophenol are also produced during the bleaching of wood pulp with chlorine when paper is being produced. The following are the nineteen different types of chlorophenols:

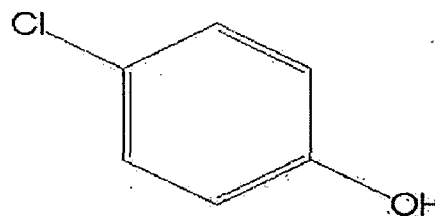
2-CP; 3-CP; 4-CP; 2,3-DCP; 2,4-DCP; 2,5-DCP; 2,6-DCP; 3,4-DCP; 3,5-DCP; 2,3,4, -TCP; 2,3,5-TCP; 2,3,6-TCP; 2,4,5-TCP; 2,4,6-TCP; 3,4,5-TCP; 2,3,4,5, -TeCP; 2,3,4,6-TeCP; 2,3,5,6-TeCP; PCP.

### 1.2.1 Properties of 4-chlorophenol

Physical properties of 4-chlorophenol are listed in table 1.1

**Table 1.1. Physical properties of 4-chlorophenol**

Property	Value
Boiling point	220 <sup>o</sup> C
Melting point	42.5 <sup>o</sup> C
Molecular weight	128.56 g/mol
Density	1.306 g/cm <sup>3</sup>
Vapour Pressure	0.9998 mm Hg at 50 <sup>o</sup> C
Flash point	115.6 <sup>o</sup> C



[ Source: <http://www.wolframalpha.com/entities/chemicals/4-chlorophenol/gw/fx/vm/>]

## **1.2.2 Discharge concentration of chlorophenol from various industries**

The majority of known environmental releases of chlorophenols are to the surface water. The principal point source of water pollution by chlorophenols is industrial waste discharge; then comes the leaching of chlorophenols from landfills. Chlorophenols enter the atmosphere through volatilization, with mono- and di-chlorophenols being the most volatile. Some typical values of phenolic compounds in chemical industry wastewaters were reported to be 50 mg/l for refineries, 400 mg/l for phenolic resin production, 200 mg/l for shale dry distillation and 12 mg/l for naphthalenic acid production [Sahinkaya and Dilek, 2006].

The primary nonpoint pollution source for chlorophenols comes from the application of pesticides made from chlorophenols and the chlorination of wastewater containing phenol. During recent years, because of the wide spread use of pesticides in agriculture, the amount of these compounds in environment has increased significantly. Pesticides, hence, constitute major pollutants of the environment, and their presence is of utmost concern owing to their potential toxicity towards animals and humans. Only few of these used pesticides are only partially eliminated by chemical and biological degradation and rest of them simply enter the biological chains. Presently, hundreds of pesticides of various chemical natures are used worldwide for agricultural and non-agricultural purposes. Besides some norms to control the emission of such highly toxic compounds, their emission in environment is still not under a complete control.

## **1.2.3 Health and related hazards of chlorophenol**

### **1.2.3.1 Effects of short-term (acute) exposure**

Chlorophenols are very hazardous in case of skin contact (irritant), or eye contact (irritant). The amount of tissue damage depends on the length of contact time. Skin contact can produce inflammation and blistering. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering. Inhalation of dust will produce irritation to or respiratory tract, characterized by coughing, sneezing or burning. Severe over-exposure can produce choking, unconsciousness, lung damage or even death. Eye contact with 4-chlorophenol can result in corneal damage or complete blindness. Inflammation of the eye is characterized by

watering, itching and redness of eyes [Material safety data sheet, 4-chlorophenol MSDS (<http://www.sciencelab.com/msds.php?msdsId=9923432>)].

### **1.2.3.2 Effects of long-term (acute) exposure**

According to some studies, risk of cancer was slightly higher among workers who had remained employed in pesticide manufacturing firms for a long time. These workers were exposed to very high levels of chlorophenols as well as some other toxic chemicals, so it is not certain whether the effects were caused by chlorophenols or the other chemicals. Animals that were given drinking water or food containing chlorophenols at high levels developed adverse or negative health effects. The major effects with exposure to high levels of chlorophenols in animals were found to be on the liver and the immune system. Also, the animals that ate or drank chlorophenols could not gain as much weight as their counterparts that ate food and drank water not containing chlorophenols [Material safety data sheet, 4-chlorophenol MSDS (<http://www.sciencelab.com/msds.php?msdsId=9923432>)].

### **1.2.4 Treatment of 4-Chlorophenol**

Many pure-culture studies conducted earlier have shown that toxic intermediates accumulate during biodegradation of chlorophenols because a single organism may not have the ability to completely mineralize these toxic substances. However, several studies have showed that mixed bacterial culture has ability to use chlorophenols as their sole carbon and energy sources. The main advantage achieved by the microbial consortium formed by the mixed culture is the interaction between different species present in these flocks [Arendrof and Focht, 1994].

Degradation of mono- and di-chlorophenols has been shown to be initiated by oxygenation of chlorophenols into chlorocatechols, and the dechlorination step occurs only after ring cleavage of the chlorocatechols. After the formation of catechols, chloroaromatic compounds are found to be mineralized via the ortho-cleavage pathway by 1,2-dioxygenases as shown in figure 1.1. The final degradation products of chlorophenol are only H<sub>2</sub>O and CO<sub>2</sub>.



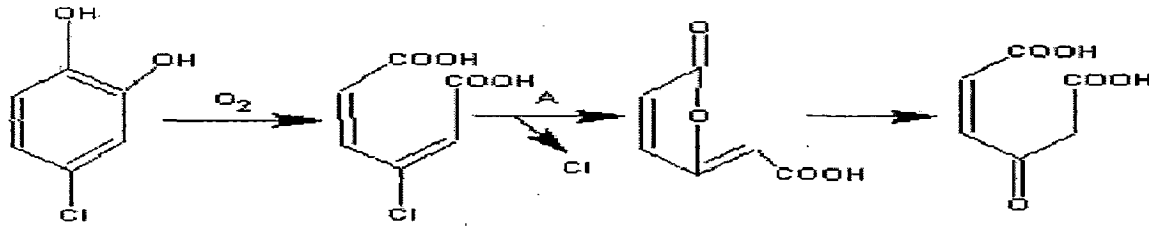


Fig. 1.1. Degradation pathway for chlorocatechol via ortho-ring fission [Source: Arendrof and Focht, 1994]

### 1.3 Sequential batch reactor

Sequential batch reactors (SBR's) are industrial processing tanks for treatment of wastewater. SBR's treat wastewater from sewage or mechanical biological treatment facilities in batches or output from anaerobic digesters. Air is bubbled through the wastewater to reduce its biochemical oxygen demand (BOD) and chemical oxygen demand (COD) to make the water suitable for its discharge into sewers or for its use on land itself [[http://en.wikipedia.org/wiki/Sequencing\\_batch\\_reactor](http://en.wikipedia.org/wiki/Sequencing_batch_reactor)].

SBR's are a variation of the activated-sludge process. They differ from activated-sludge processes in the aspect that they combine all the treatment processes and steps into a single basin, whereas in conventional activated sludge processes these steps occur in different basins. Improvements in equipment and technology, especially in aeration devices and computer control systems, have made SBRs a very viable choice over the conventional activated sludge systems. These plants are more practical for a number of reasons:

- The treatment cycle in SBR's can be adjusted to undergo aerobic and anaerobic conditions in order to achieve the biological nutrient removal, including nitrification, denitrification and phosphorus removal. BOD levels of less than 5 mg/L can be achieved consistently. Also, low phosphorus limits of less than 2 mg/L can be achieved by using a combination of biological treatment and chemical agents within the vessel and treatment cycle. Low total nitrogen limits of less than 5 mg/L can be achieved by the aerobic conversion of ammonia to nitrates (nitrification) and the anoxic conversion of nitrates to nitrogen gas (denitrification) within the same tank.
- In areas where there is a limited space, treatment takes place in a single basin instead of multiple basins, allowing a smaller footprint. Also, low total suspended solid values of less

than 10 milligrams per liter (mg/L) can be achieved if effective decanters are used that even eliminate the need for a separate clarifier.

- Wastewater discharge permits are becoming more stringent day by day and SBRs offer a very cost-effective way to achieve lower effluent limits. Note that discharge limits requiring a greater degree of treatment may necessitate the addition of a tertiary filtration unit following the SBR.
- Older wastewater treatment facilities can be retrofitted to an SBR as the basins are already present.

Regulation by a number of environmental laws related to air, land and water are imposed to petrochemical refineries because they are generally considered as a major source of pollutants in areas where they are located. Petrochemical are regarded as one of the most polluting industries by the Government of India. The components and methods used for the conventional wastewater treatment system employed in petrochemical industry are broadly divided into three i.e. Primary treatment, which basically include flow equalization unit, API oil separator; Secondary treatment, which includes chemical treatments like neutralization, flocculation and coagulation, physico-chemical treatment comprising of dissolved air floatation, biological treatment involving activated sludge process, SBR, oxidation ponds, trickling filters, rotating biological contactor, etc.; tertiary treatment includes UV disinfection, filtration, chlorination, etc.

But the heart of most of the treatment plants is the secondary treatment where removal of organic matter, suspended solids and nutrients (nitrogen, phosphorus) from the wastewater is accomplished bringing the effluent quality within the standard limit. Thus the efficiency of the secondary treatment should be as high as possible and also, it should be compatible with all possible loading with influent. At present, most of the refineries are using activated sludge process as their secondary treatment process which requires a huge installation cost, a large installation area and high maintenance thus some modification are required in the process so that all these deficiencies can be efficiently eliminated [<http://www.fao.org/docrep/t0551e/t0551e05.htm>].

Due to its toxicity, biological treatment of Wastewater containing a toxic substrate is a bit difficult, since the microorganisms are not able to treat that substance initially. Therefore, the first step to make an SBR efficiently operative is the acclimatization, i.e., the adaptation of these microorganisms to a particular toxic substrate. Several different mechanisms have been described to explain the process of acclimatization. During this process there is a selection and multiplication of some specialized microorganisms and physiological transformations occur in the metabolic system of the microorganisms [Wiggings et al., 1987], i.e., alterations taking place at the enzymatic level, regulation and production, mutations, etc. When the biomass is aerobic, the time period for acclimatization usually range from hours to days, depending on the characteristics of the Wastewater, pH, temperature, concentration and type of substrate, etc. Once acclimatized to a particular substrate, an appropriate control strategy of the SBR may avoid the negative impact of the inhibition which can be caused by the excess of toxic substrate and a high sludge activity of the biomass is maintained in the system [Andrade et al., 2006].

## 1.4 Adsorption

Adsorption is a process that occurs when a liquid or gas solute accumulates on the surface of a liquid or a solid (adsorbent), forming an atomic or molecular film (the adsorbate). The basic difference between adsorption and absorption is that, in absorption a substance diffuses into a solid or liquid to form a solution. The term sorption encompasses both processes, while desorption is just a reverse process. Adsorption is operative in most of the natural biological, physical and chemical systems, and is widely used in industrial applications.

Similar to surface tension, adsorption is the result of surface energy. In a bulk material, all the bonding requirements of the constituent atoms of the material are filled. But atoms present on the clean surface experience a bond deficiency as they are not wholly surrounded by other atoms on all sides. Thus it is energetically favorable for these surface atoms to get bonded with whatever happens to be available. The exact nature of this bonding depends on the types of the species involved. The adsorbed material is broadly classified as exhibiting physisorption or chemisorption.

[[http://www.fpharm.uniba.sk/fileadmin/user\\_upload/english/Physical\\_Chemistry/5-Adsorption.pdf](http://www.fpharm.uniba.sk/fileadmin/user_upload/english/Physical_Chemistry/5-Adsorption.pdf)].

- In *Physisorption* or physical adsorption, the adsorbate adheres to the surface only through Van-der Waals (weak intermolecular) forces, which are also responsible for the non-ideal behavior of the real gases.
- In *Chemisorption*, a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van-der Waals forces which cause physisorption.

In a batch adsorption process the feed solution and the adsorbent particles are brought into contact until equilibrium binding between the two is achieved. The spent solution, containing the impurities and used adsorbent particles, is then separated from the adsorbent by using an appropriate solid-liquid separation process which can be filtration or centrifugation. The used solid material obtained (i.e. the adsorbent with the bound solute) is frequently washed for the removal of impurities. The adsorbed solute can then be removed from the adsorbent by adding a liquid which favors desorption of the solute. The solute can then be separated from the adsorbent by using appropriate solid-liquid separation techniques. [Principles of bio-separations engineering, 2006, Raja Ghosh]

## 1.5 Objective of work

The aim of this research is to study the treatment of 4-chlorophenol bearing wastewater by biological treatment in a blank SBR and a GAC-SBR. The performance of two types of SBR's has been compared. The operating conditions, for the biodegradation of 4-chlorophenol in SBR, have been optimized and the following operating parameters for the two type of SBR's have been studied:

- Effect of initial organic loading
- Effect of dose of GAC in GAC-SBR
- Effect of cycle time, volume exchange ratio (VER) and hydraulic retention time (HRT)
- Contact time study of removal of 4-chlorophenol in two types of SBR's

In the adsorption study the main objective was to investigate the viability of GAC for the removal of 4-chlorophenol. The experiments have been carried out to study the following:

- Effect of type of adsorbent, contact time, dose, pH and initial concentration of pollutant on the removal of 4-chlorophenol from aqueous solution by batch process

- Kinetics of adsorptive removal of 4-chlorophenol in batch adsorption study
- To perform the equilibrium isotherm study for removal of 4-chlorophenol using GAC

#### **2.1 General**

This section presents various treatment technologies proposed in the literature for the treatment of phenolic wastewater, many researchers have done appreciable work in the field of phenolic wastewater treatment specifically 4-chlorophenol. While choosing any removal method, it is necessary to consider the final desired concentration and also the associated cost and feasibility of monitoring this goal. Many treatment methods are available for the removal of 4-chlorophenol; various methods have been developed to remove 4-chlorophenol from industrial effluent including photochemical precipitation, oxidation, adsorption, biological treatment, etc. The critical literature review of all these methods is discussed in the present chapter.

#### **2.2 Coagulation/co-precipitation**

Coagulation is basically the process of growth and aggregation of particles in water. In this process, the dissolved ions form an insoluble solid and then precipitate. Co-precipitation, another form of coagulation, refers to the formation of an insoluble complex formed by an inorganic compound and the coagulant. The process of coagulation includes all the reaction mechanisms and it results in particle growth, which is referred to as floc formation and particle aggregation within water being treated. It also encompasses coagulant formation, particle destabilization and physical inter-particle contacts.

Coagulation involves the removal of colloidal (size ranging from 0.001 - 1 00 microns) and settleable (size > 100 microns) particles. However, the term also sometimes refers to the removal of dissolved ions (size < 0.001 microns), which is actually precipitation. In precipitation process, the dissolved ions in solution form an insoluble solid via a chemical reaction and this solid precipitates at the bottom.

The common example of co-precipitation is, formation of precipitate of naturally occurring dissolved iron in groundwater, when exposed to oxygen. Aluminum and ferric salts are the common coagulants used in water treatment to remove particulate matter. For example, alum

and ferric sulphate are used in removing octanoic acid, phenol and benzoic acid [Mo et al., 2007]. These compounds are not efficiently removed by coagulation and in most cases the extent of removal does not depend strongly on dose of coagulant. Removal ranges between 3-20%. Chemical coagulation is mainly used to remove the compounds present in wastewater from dye manufacturing industry. Coagulation/flocculation process is used as pretreatment for purification of terephthalic acid wastewater.

### **2.3 Electro-coagulation**

Coagulation means the process of changing the particle surface charge and hence allowing suspended matter to form an agglomeration and electro means application of an electrical charge to water. As the name reflects, electro-coagulation is an advanced and economical water treatment technology. It is largely similar to the process of coagulation, as explained in section 2.3, in mechanism with an exception that metal ions are introduced into the solution. It is generally used for the removal of soluble pollutants, heavy metals, colloidal solids etc. by introduction of charged metal hydroxide species. In the beginning, the formation of metal hydroxide species by the oxidation of metal electrodes takes place. Both adsorption and electrostatic attraction are responsible for the mechanism behind pollutant removal.

Basically, this process is characterized by a compact size of the equipment, a very rapid rate of pollutant removal, simplicity in operation, energy efficiency, and low operating and equipment costs [Daneshvar et al., 2004]. In addition to reduction in the actual pollutant concentration, this process also makes the water clear, colorless, palatable and odorless which are added benefits to the actual treatment. Being mainly composed of metallic oxides and hydroxides, the sludge formed in this treatment tends to be readily settleable and easy to dewater.

Floc formed in electro-coagulation, tend to be much larger in size as compared to the floc formation in coagulation. Also floc formed here contains less bound water, is acid resistant and is more stable and hence can be separated easily by filtration technique. Since only electrodes are introduced in the water with metal hydroxides contributing towards the sludge formation, electro-coagulation has effluent with very little total dissolved solids content compared to other techniques.

## 2.4 Electrochemical oxidation

The application of electrical energy has been used to degrade chlorophenols since long [Gattrell and Krik, 1993; Tahar and Savall, 1999]. Electrochemical degradation utilizes a high redox potential at an anode and a low redox potential at a cathode to oxidize or reduce the contaminants. Most of the applications of electrochemical degradation involved cathodic reduction or anodic oxidation of the chlorinated organic contaminants. It was shown that pentachlorophenol was sequentially dechlorinated (i.e., reduced) at a carbon fiber cathode [Schmal et al., 1986]. Experiments conducted indicated that the composition of the cathode was critical for cathodic reduction of 4-chlorophenol. Reduction of 4-chlorophenol was not observed when carbon cloth or graphite rod was used as cathodes. However, a palladized carbon cloth cathode has been shown to dechlorinate 4-chlorophenol to phenol. They hypothesized three possible mechanisms for the reduction of 4-chlorophenol to phenol: 1) direct reduction at the cathode, 2) hydrogenation (i.e. reduced by hydrogen gas) at a palladium catalyst surface, and 3) adsorption of 4-chlorophenol at a cathode surface followed by hydrogenation at a palladium/electrode surface.

Some studies [Cheng et al., 2003] showed that hydrogen evolution is important for the direct dechlorination reaction and cathode made of materials that are capable of adsorbing hydrogen into its lattice tends to perform more efficiently than other materials. On the other hand, high hydroxyl ion was found to play an important role for the indirect degradation of chlorophenols [Johnson et al., 2000]. The high concentration of hydroxyl ion in the vicinity of cathode enhances the production rate of OH radicals, which oxidizes chlorophenols.

## 2.5 Adsorption

Adsorption is used in wastewater treatment plants to remove toxic organic pollutants (especially halogenated but also non-halogenated), and to an extent, inorganic contaminants, from the wastewater. It is commonly used in treatment of industrial wastewaters containing those organic compounds which cannot be easily biodegraded during secondary (biological) treatment or are highly toxic. Adsorption finds applications in tertiary wastewater treatment as a finishing step before final discharge [Kopecky et al., 1996]. The basic difference between adsorption and absorption is that absorption is that the process through which a substance, originally present in



one phase, is removed from that phase by dissolution in another (typically a liquid), as opposed to the accumulation at the interface as it is in the case of adsorption. In other words, adsorption is a surface phenomenon whereas in absorption dissolution takes place at bulk [<http://www.lenntech.com/library/adsorption/adsorption.htm>].

The most common industrial adsorbents are activated carbon, silica gel, nonporous silica and alumina because they possess enormous surface areas per unit weight. Activated carbon is prepared by roasting organic material to decompose it to granules of carbon –coconut shell, wood and bones are common sources. Silica gel is the matrix of hydrated silicon dioxide. Alumina is mined or precipitated aluminum oxide and hydroxide. Although activated carbon is a magnificent material for adsorption, its black color persists and it adds a grey tinge if even trace amount is left after treatment; however filter materials with very fine pores remove carbon quite efficiently. [Li et al., 2005]. Activated carbon is by far the most effective and common adsorbent used in wastewater treatment. Since, during the adsorption process, the pollutant is removed by accumulation of adsorbate at the interface between the adsorbent and the wastewater (liquid phase), the adsorbing capacity of activated carbon is always associated with very high surface area per unit volume.

## **2.6 Biological treatment**

Sequencing batch reactors are basically the industrial processing tanks for the treatment of wastewater. SBR treats wastewater such as sewage or output from anaerobic digesters or mechanical-biological treatment facilities in batches. Oxygen is bubbled through the wastewater to reduce chemical oxygen demand (COD) and biochemical oxygen demand (BOD) to make it suitable for its discharge into sewers or for use on land.

Biological treatment transforms, stabilizes and removes 4-chlorophenol by means of microorganism. Microorganism, primarily certain specific bacteria accomplish this by oxidation/reduction, detoxification, mineralization or methylation. SBR's can be successfully used for treating most wastewaters. It is possible to biodegrade most toxic industrial chemicals including 4-chlorophenol and other phenolic compounds in the waste water using microbial cultures under controlled laboratory conditions.

**Yu and Gu (1996)** presented the experimental results of a sequencing batch reactor (SBR) with aerated fill and an SBR with unaerated fill treating synthetic phenolic wastewater under identical conditions, both of influent phenol concentration and aeration time. The performance of the two reactors was evaluated according to waste removal efficiency, sludge settleability, phenol profiles and suspended solids concentration. It was observed that at low influent phenol concentrations (e.g. 400 mg/L), the SBR with unaerated fill performed better than the SBR with aerated fill, in which there was the tendency for some filamentous bacteria to develop. However, when the influent phenol concentration was increased (e.g. >800 mg/L), phenol accumulated during the fill period in SBR with unaerated fill became inhibitory to micro-organisms. Also, this led to a reduction in substrate removal efficiency and the growth of dispersed biomass.

They also concluded that SBRs filled with and without aeration had certain distinct advantages and disadvantages. The selection of fill strategies should be dependent not only on the wastewater composition and biodegradability, but the concentration of toxic organics in wastewaters should also be taken in consideration.

**White and Schnabel (1998)** accomplished the biological treatment of cyanide in a sequencing batch bio-film reactor (SBBR), where a mixed culture of micro-organisms on silicone tubing was provided with cyanide as the only carbon and nitrogen source. The SBBR was made to operate on a 24-hour cycle. Over the course of each cycle, 20mg/L of cyanide was degraded to almost 0.5 mg/L. The micro-organisms converted all the cyanide not used in cell growth to ammonia. It was also demonstrated that, when supplied with the glucose, the micro-organisms would readily consume excess ammonia. For each mole of ammonia added, 10 moles of  $\text{NH}_3\text{-N}$  were removed from the solution.

**Mangat and Elefsiniotis (1999)** conducted a bench-scale study using SBR's to investigate the effects of hydraulic retention time (HRT), presence or absence of supplemental substrate and the variation in feed concentration on biodegradation potential of 2,4-dichlorophenoxyacetic acid (2,4-D), one of the most commonly used phenoxy-acid herbicides. A long acclimatization period (about 120 days) was observed before 2,4-D biodegradation was established. It was found that 2,4-D can be utilized as the only source of carbon and energy by the acclimatized biomass. At steady-state operation, all reactors achieved practically complete

removal (>99%) of 2,4-D and the corresponding supplemental substrate (wherever applicable), regardless of the HRT, ranging from 12 to 48 h. A sequential utilization pattern of supplemental substrate and 2,4-D was observed throughout the entire study. The 2,4-D specific removal rates were affected by the type of supplemental substrate being used (phenol or dextrose), being significantly lower (30 to 50%) in the case of dextrose. Overall, the changes in the feed concentration of supplemental substrate or 2,4-D did not produce a significant effect on the biodegradation behavior of 2,4-D.

**Lim et al. (2001)** made a study on the application of simultaneous adsorption and biodegradation processes in the same reactor and found it to be effective in the removal of both biodegradable and non-biodegradable contaminants in various kinds of wastewater. The objective of this study was to evaluate the efficacy of the two processes under sequencing batch reactor (SBR) operation in treating the copper and cadmium-containing synthetic wastewater with powdered activated carbon (PAC) as the adsorbent.

The SBR systems were operated with fill, react, settle, draw and idle periods in the ratio 0.5:3.5:1.0:0.75:0.25 for a cycle time of 6 hours. In the presence of 10 mg/L Cu (II) and 30 mg/L Cd (II), the average COD removal efficiencies were observed to be above 85% with the PAC dosage in the influent solution at 143 mg/L compared to only around 60% without PAC addition. Cu (II) was found to exert a more pronounced inhibitory effect on bioactivity of the micro-organisms compared to Cd (II). It was observed that the combined presence of both Cu (II) and Cd (II) did not exert synergistic effects on the micro-organisms. Kinetic study conducted for the React period showed that the addition of PAC had minimized the inhibitory effect of heavy metals on the bioactivity of microorganisms.

**Vinitnantharat et al. (2001)** conducted experiments to study the effect of GAC (Granular Activated Carbon) added to Sequential Batch Reactor (SBR) in the case of phenol shock loading. The reactor was fed with phenol as the sole carbon source. Three types of shock loading namely step-up shock load, short term fluctuation and step-wise augmentation were performed to compare its performance with conventional SBR over a period of 24 days of operation.

In the step-up shock load period, the GAC loaded SBR showed a better tolerance than the conventional SBR for the increasing phenol concentration from 500 mg/l to 2000 mg/l during the first two cycles. With time going on, both the systems showed failure in degrading the phenol. In the short term fluctuation period, the GAC loaded SBR performed better removal of phenol at 3000 mg/l whereas the conventional SBR could not tolerate this concentration. Removal of phenol was also achieved in GAC loaded SBR during step-wise augmentation and was not achieved by conventional SBR with an initial phenol concentration of 2000 and 3000 mg/L. The experimental results showed that the GAC loaded SBR was superior to conventional SBR for all cases of shock loading and it played a role of a buffer through the period of shock loading without any refilling of the virgin GAC into the reactor. The point to be focused was that the GAC was loaded initially to SBR and the used GAC was not removed from time to time. Also, no more GAC was added to the system once the system was started.

**Tomei et al. (2003)** investigated the biodegradation kinetics of 4-nitrophenol in a lab-scale SBR fed with the compound as the only carbon source. The experimental results obtained, showed that the complete 4-nitrophenol removal can easily be achieved with the acclimatized biomass. Furthermore, an improvement in the removal kinetics can be obtained if the substrate concentration peak reached in the SBR at the end of the filling time, is maintained to quite a low value. Both the long feed phase and the high biomass concentration are effective in reducing the substrate concentration peak and hence improving the process efficiency.

**Kargi et al. (2005)** investigated nitrogen, phosphate, COD and para-chlorophenol (4-CP) removal from synthetic wastewater using a four-step SBR for different sludge ages and initial para-chlorophenol concentrations. The nutrient removal process consisted of anaerobic, oxic, anoxic and oxic phases with different hydraulic residence times (HRT) of 1/3/1/1 h and a settling phase of 0.75 h. Synthetic wastewater containing different concentrations of para-chlorophenol (0–400 mg/L) was treated in an SBR for nutrient removal for different sludge ages (5–25 days). Percent removals of COD,  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4\text{-P}$  and 4-chlorophenol were investigated as the functions of initial concentrations of 4-CP and the sludge age. The experimental results were then correlated with a response function. Predicted response function values were found to be in good agreement with the experimental results indicating a good fit of the data ( $R^2 = 0.93\text{--}0.99$ ).

Percentage COD and nutrient ( $\text{NH}_4\text{-N}$ ,  $\text{PO}_4\text{-P}$ ) removals decreased with an increase in 4-CP contents at a constant sludge age because of the inhibitory effects of 4-CP on microorganisms. However, improved nutrient removals were obtained at high sludge age operations due to the high biomass concentrations. Also, high 4-CP contents adversely affected the percent 4-CP removals and the sludge settling characteristics (as per the values of calculated SVI). Increasing 4-CP contents resulted in a decrease in percentage 4-CP removals and an increase in the sludge volume index (SVI) values. Adverse effects of high 4-CP concentrations can be partially overcome by operating the system at high sludge ages. The system should be operated at low 4-CP concentrations of less than 100 mg/L and high sludge ages of above 20 days in order to obtain high percentage nutrient removals and good settling sludge with low SVI values.

He et al. (2007) conducted two types of operation means “SBR reactor alone (control reactor)” and “adding zeolite powder into the SBR reactor (test reactor)” to treat municipal wastewater. The test results revealed that addition of zeolite powder could improve the activity of the activated sludge. It was investigated that the specific oxygen utilization rate (SOUR) of the tested zeolite sludge were about double times as compared to the control activated sludge, and the nitrification rate and settling property of zeolite-activated sludge were both improved. Due to combination of zeolite adsorption for  $\text{NH}_4^+\text{-N}$  and the enhanced simultaneous nitrification and de-nitrification (SND), a higher nitrogen removal was observed in the test reactor as compared to the control reactor, and the addition of zeolite powder is also helpful to inhibit sludge bulking. In addition, through long-term parallel shock load test, it was observed that the zeolite powder addition could enhance the ability of activated sludge in resisting the shock load of organics and ammonium. Compared to control activated sludge, zeolite powder added activated sludge could remove COD,  $\text{NH}_4^+\text{-N}$ , Total Nitrogen (TN) and Total Phosphorus (TP) significantly in a shorter cycle time. At the same operational time period, the test SBR could treat wastewater quantity of 1.22 times compared to that treated in control SBR.

Mun et al. (2007) successfully induced the dechlorination of 2,4,6-trichlorophenol to p-chlorophenol under acidogenic conditions (pH 5.6–6.5) by manipulating the start-up procedure of an acidogenic SBR. A stepwise pH reduction from neutral to acidic level during the start up was crucial for inducing dechlorination. Once induced, the dechlorination can proceed at pH as low as 5.6 before the inhibition occurs. Optimum pH for maximum dechlorination rate was

found to range from 6.0 to 6.3. High primary (sucrose) to secondary (2,4,6-trichlorophenol) substrate ratio failed to induce any dechlorination.

**Lim et al. (2008)** performed a study to compare the performance of two sequencing batch reactors (SBR) added with ethylenediamine-modified rice husk (MRH) and powdered activated carbon (PAC), respectively, as adsorbents for the removal of COD and ammoniacal nitrogen (AN) from a mixture of landfill leachate and domestic wastewater at various mixing ratios. The performances of the two reactors were evaluated by monitoring the effluent COD, AN, nitrite nitrogen and nitrate nitrogen concentrations as well as the concentration profiles of these parameters during the react phase of the operating cycle.

The results showed that at the combined wastewater strength of 170 mg AN/L, a 70% COD removal and almost complete AN removal were achieved in the SBR added with PAC for a dosage of 1.5 g PAC/cycle being used. In comparison, a 70% COD removal and almost complete AN removal were achieved in the SBR added with MRH at the higher wastewater strength of 215 mg AN/L on the application of a lower dosage of 0.5 g MRH/cycle. Overall, the activated rice husk proved to have a good potential of being used as an alternative adsorbent to PAC in the leachate treatment.

**Wang et al. (2008)** developed aerobic granules for biological degradation of 2,4-dichlorophenol (2,4-DCP) in an SBR. A key strategy was to involve the addition of glucose as a co-substrate and a step-wise increase in the influent 2,4-DCP concentration. After operation of 39 days, stable granules with a diameter ranging between 1–2 mm and having a clearly defined shape and appearance were obtained. After granulation, the effluent 2,4-DCP and chemical oxygen demand (COD) concentrations were 4.8 mg/L and 41 mg/L, with high removal efficiencies of 94% and 95%, respectively. Efficient degradation of 2,4-DCP by these aerobic granules suggests their potential application in treatment of industrial wastewater containing chlorophenols and other inhibitory chemicals.

**Sharma et al. (2010)** reported the optimization of parameters for the biodegradation of resorcinol bearing aqueous solution in a sequencing batch reactor (SBR). Various parameters studied include mixed liquor suspended solid (MLSS) concentration, initial concentration of resorcinol and the fraction of fill phase used as the aerated phase. Increases in the MLSS

concentration and the aeration time were found to induce a positive effect on resorcinol removal efficiency. The settling characteristic of the sludge was measured in terms of sludge volume index (SVI).

The aim of this work was to determine the effect of different parameters namely mixed liquor suspended solids (MLSS) concentration, initial resorcinol concentration and the ratio of aeration phase to fill phase for the removal of resorcinol from the aqueous solution in SBR.

The experimental setup consisted of two identical well-mixed SBR's. Both the reactors worked as individual reactors. Aeration was achieved by using an air pump with sintered-sand diffusers at the bottom of the each tank/reactor. The feeding and the decanting operations were performed using peristaltic pumps. Dissolved oxygen (DO) concentration inside the reactor was maintained above 2 mg/L during all the experiments by controlling the flow of air through air-rotameter. The reactors were operated at a temperature of  $28 \pm 2^{\circ}\text{C}$ . The reactor was operated on a fill-and-draw basis, with a cycle time of 5 hours consisting of 2.5 hours fill time. Remaining 2.5 hours were divided into react phase and settle phase. To maintain an appropriate level of MLSS concentration within the reactor, some amount of sludge was wasted after every cycle which helped in preventing the problem of sludge bulking and excessive growth of filamentous bacteria. For this purpose, sludge retention time (SRT) was maintained constant at 10 day.

The effect of the fraction of fill phase aeration during the fill phase on the efficiency of SBR was studied by varying time of aeration. The removal efficiency was found to be higher for larger values of aeration time, while the final concentration at intermediate values of aeration time was observed to be high. This showed that relatively higher removal efficiencies are obtained for SBR having a longer aeration time.

In a part of the study, fill and settle times were kept constant. The total fill phase was also kept aerated. The effect of the influent concentration on the performance of SBR was studied under different loadings. The amount removed and the removal efficiencies after the treatment in the SBR with varying initial resorcinol loading were observed. The results obtained showed that the removal efficiency first increased and then decreased with an increase in initial concentration. However, the amount of resorcinol removed kept on increasing with an increase in the initial concentration.

**Chiavola et al. (2010)** studied the technical feasibility of an SBR for the biological treatment of sediments contaminated by polycyclic aromatic hydrocarbons (PAHs). In this study, a bench-scale Sediment Slurry Sequencing Batch Reactor (SS-SBR) was fed with the river sediments contaminated by a PAH mixture made by pyrene, fluorene, anthracene and crysene. The performance was evaluated under various operating conditions, obtained by modification of the influent organic load, the feed composition and the hydraulic residence time (HRT).

The best performance was observed for 3-rings compounds with respect to the 4-rings PAHs. Particularly, the highest removal was obtained for fluorene, whereas the lowest one for crysene. Crysene seemed to be preferably biodegraded in the presence of other PAHs, suggesting that co-metabolism took place during the react phase.

**Farabegoli et al. (2010)** investigated the biological de-colorization of RR-195 (Reactive Red 195) under alternate anaerobic aerobic conditions in a laboratory scale SBR containing a mixed culture, fed with a biodegradable carbon source. Different values of Sludge Retention Time (SRT), Hydraulic Retention Time (HRT), organic carbon loadings and influent color were adopted during the experimental activity and their effects on color and chemical oxygen demand (COD) removal efficiencies and process kinetics determined.

By their study they demonstrated the suitability of an alternating anaerobic aerobic SBR for biological treatment of the azo-dye RR 195-containing wastewater. A biodegradable carbon source in the influent to the plant was found to play a key role for the process to be highly efficient. The results herewith obtained suggested that the influent COD/dye ratio must be properly selected to provide the electron equivalents needed for the oxidation of dye molecule. Furthermore, the value of the COD/dye ratio must be increased when nitrates are present at the beginning of anaerobic react phase.

**Sarti and Zaiat (2011)** studied the biological sulfate reduction in a laboratory-scale anaerobic sequential batch reactor containing mineral coal for biomass attachment. The reactor was fed with industrial wastewater with increasingly high sulfate concentrations to establish its application limits. Special attention was paid to use of butanol in the sulfate reduction that originated from melamine resin production. This product was used as the main organic



amendment to support the biological process. In this study the reactor was operated for 65 cycles (48 h each).

The application of butanol (electron donor) for biological treatment of effluent containing high sulfate concentrations significantly reduced the sulfate concentration. The anaerobic sequential batch reactor filled with mineral coal achieved high sulfate reduction efficiencies (99%) in a short period of operation at different initial sulfate concentrations. Based on the results from anaerobic SBR, it was concluded that the anaerobic configuration can be used for combined removal of sulfate and organic matter at sulfate influent concentrations below 1.0 g  $\text{SO}_4^{2-}$  per liter, if butanol is used as the electron donor. At influent sulfate concentrations higher than this, highly volatile fatty acids concentrations (residual COD) and sulfur-reduced compounds were generated. In this case, the simultaneous methanogenesis and sulfidogenesis suppression were observed.

**Badiei et al. (2011)** evaluated the feasibility of the hydrogen generation from palm oil mill effluent (POME), a high strength wastewater with very high solid content in an anaerobic sequencing batch reactor (ASBR) using enriched mixed micro-flora, under a mesophilic digestion process at 37°C. Four different hydraulic retention times (HRT's), ranging from 96 h to 36 h at constant cycle length of 24 h and different organic loading rate (OLR) concentrations were tested to evaluate the hydrogen productivity and the operational stability of ASBR. The results showed the higher system efficiency was achieved at HRT of 72 h with maximum hydrogen production rate of 6.7 L  $\text{H}_2/\text{d}$  and a hydrogen yield of 0.34 L  $\text{H}_2/\text{g COD}_{\text{feeding}}$ , while in longer and shorter HRTs, hydrogen productivity decreased. Organic matter removal efficiency was also affected by HRT; accordingly, the total and soluble COD removal reached more than 37% and 50%, respectively. Sludge retention time (SRT) of 4-19 days was achieved at these wide ranges of HRTs. Low concentration of volatile fatty acid (VFA) confirmed the state of stability and efficiency of sequential batch mode operation was achieved in this ASBR. Results also suggested that ASBR had the potential to offer high digestion rate and good stability of operation for POME treatment.

**Ding et al. (2011)** conducted a study to evaluate the domestic sewage treatment using a special sequencing batch bio-film reactor (SBBR). To optimize the operation of traditional

SBBRs and reduce the aeration phase, a newly devised intelligent controlling system (ICS) was adopted to control the SBBR.

In this study, one typical operation cycle contained three procedures i.e. fill (instantaneous), react (7 h), and draw (10 min). The experimental system included two parts, the reactor and the ICS. A laboratory scale reactor with a working volume of 20 L was fabricated using polymethyl methacrylate, because polymethyl methacrylate is not so easy to be broken or deformed, and it is easy to observe the bio-film carriers and sludge in the reactor.

The SBBR, controlled by an ICS installed in a computer, employed intermittent aeration. Temperature and DO, which had a remarkable effect on the respiratory rate of the microorganisms, were used as the controlling factors in the ICS. At the beginning of each reaction phase, a minimum DO value was required before switching on the ICS. The first hour was divided into two phases according to the ICS, an aeration phase (0.5 hours) and a non-aeration phase (0.5 hours). Next, the ICS produced a schedule of aeration and non-aeration time based on the temperature and the respiratory rate of microorganisms in the reactor, which were measured after every 2 hours. According to the schedule, the reactor was aerated initially for a space ( $t_1$ ) and then non-aerated for another space ( $t_2$ ), the total time was 2 hours. After that, a new schedule of 2 hours was produced based on the temperature and the respiratory rate of micro-organisms in the reactor. The process will be carried on again and again until the ICS was switched off. However, the  $t_1$  and  $t_2$  varied with the temperature and respiratory rate of micro-organisms in different schedules. At the end of each aeration phase, if DO concentration in the reactor was lower than the minimum DO value set in the system, reactor would still be aerated for another 10 minutes until the DO concentration reached the minimum DO value. Conversely, if DO concentration in the reactor was higher than the minimum DO value at the end of non-aeration phase, the reactor would not be aerated for another 10 minutes until the DO concentration decreased to the minimum DO value.

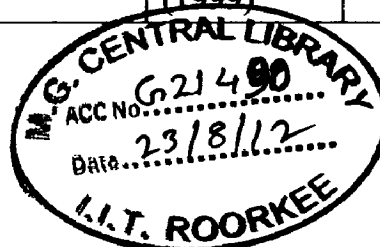
During the aeration phase, the air compressor was operated but the circulating pump was switched off. While, during the non-aeration phase, the air compressor was switched off and the circulating pump was put on. As a result, the SBBR functioned automatically. Air was introduced into the reactor using a porous diffuser at a flow rate of 300 L/h, which was controlled by a flow meter.

Based on the high specific area and economical price, a sponge was cut into 315 small pieces (cuboids of 2 cm×2 cm×5 cm) with a specific surface area of 290 m<sup>2</sup>/m<sup>3</sup> and a porosity of 98% and they were fixed in a frame made of polypropylene that was placed in the reactor as the bio-film carrier.

Stable performance was achieved in the SBBR at a hydraulic retention time (HRT) of 7 hours, at which point the removal efficiencies of NH<sub>3</sub>-N, TP and COD reached 99%, 100% and 96%, respectively. When compared with conventional SBBRs, the SBBR controlled by ICS reduced the HRT and total aeration time by 56% and 50%, respectively, and achieved a better performance at removing COD. In addition, the optimal carbon nitrogen (COD/N) ratio for the simultaneous removal of nitrogen and COD in this SBBR was found to be 12.5, and no accumulation of NO<sub>3</sub>-N or NO<sub>2</sub>-N was detected at this ratio, indicating an efficient simultaneous nitrification and denitrification (SND) occurring in the reactor. The SND efficiency reached 98%. The results from various literatures have been briefly presented in table 2.1.

**Table 2.1. Important remarks and results from various literatures**

Type of Pollutant	Culture of Bacteria	Cycle time (hours)	% Removal	Author	Remarks
Synthetic Phenolic Waste-water	Mixed culture	24 hours	-	Yu and Gu (1996)	At low influent concentration, unaerated fill dominated in terms of performance while at high influent concentration, aerated fill dominated.
Cyanide waste	Mixed culture	24 hours	-	White and Schnabel (1998)	Achieved using Sequential Batch Bio-film Reactor (SBBR). IT was observed that bacteria became more active on addition of glucose.
2,4-dichlorophenoxyacetic acid	Mixed culture	Varying from 12 h to 48 h	>99%	Mangat and Elefsiniotis (1999)	No apparent trend was observed during the HRT variation study.



Cu (II) and Cd (II)	Mixed culture	6 hours	85% for SBR loaded with adsorbent, 60% otherwise	Lim et al. (2001)	SBR's with and without adsorbent were compared and it was observed that adding adsorbent increased the efficiency of SBR.
Phenol	Mixed culture	-	-	Vinitnanthart et al. (2001)	Adding GAC to SBR improved the performance and removal efficiency of SBR against shock loadings.
4-nitrophenol	Mixed culture	8 hours	Almost 100 %	Tomei et al. (2003)	Complete 4NP removal can be easily achieved with acclimatized biomass, even if inhibition kinetics is observed.
Synthetic para-chlorophenol waste water	-	7 hours	Varied with influent concentration	Kargi et al. (2004)	Percent COD and nutrients removal decreased with increasing 4-CP contents.
2,4,6-trichlorophenol	Anaerobic bacteria	12 hours	-	Mun et al. (2007)	Dechlorination to 4-CP was achieved. Optimum pH ranged from 6.0-6.3.
Landfill leachate and domestic wastewater	Mixed culture	-	70 % COD removal and complete Ammonical nitrogen removal	Lim et al. (2008)	Adding modified rice husk as adsorbent in SBR could treat wastewater with more strength as compared to adding powdered activated carbon.
2,4-dichlorophenol	Aerobic bacteria	4 hours	94%	Wang et al. (2008)	COD removals upto 95%
Resorcinol	Mixed culture	5 hours	-	Sharma et al. (2010)	Increases in MLSS concentration and aeration time were found to induce positive effect on resorcinol removal efficiency

Polycyclic aromatic hydrocarbons (PAHs)	-	-	>80%	Chiavola et al. (2010)	The best performance was observed for the 3-rings compounds with respect to the 4-rings PAHs
Reactive Red 195	Mixed culture	-	-	Farabegoli et al. (2010)	Different pollutant removal % for different HRT.
Sulphate	Anaerobic bacteria	48 hours		Sarti and Zaiat (2011)	The application of butanol for the biological treatment of effluent containing high sulfate concentrations significantly reduced the sulfate concentration.
Palm oil mill effluent(P.O.M.E.)	Anaerobic bacteria	36 h – 96 h	-	Badiei et al. (2011)	Highest system efficiency was achieved at HRT of 72 h with maximum hydrogen production rate
Domestic Sewage	Aerobic Bacteria	7 hours	99%	Ding et al. (2011)	To optimize the operation of traditional SBBRs and reduce the aeration phase, a newly developed intelligent controlling system (ICS) was adopted to control the SBBR.

### 3.1 Sequential Batch Reactor (SBR)

#### 3.1.1 SBR process description

The unit processes of the SBR and conventional activated sludge systems are the same. The SBR is just an activated sludge system which operates in time rather than in space. The difference between these two technologies is that the SBR performs equalization, biological treatment, and secondary clarification in the same tank using a timed control sequence. This type of reactor also performs primary clarification in some cases. Whereas, in a conventional activated sludge system, these unit processes are accomplished by using separate tanks. The operation of an SBR is basically based on a fill-and-draw principle, which broadly consists of five steps — fills, react, settle, decant, and idle. [Sequencing batch reactor design and operational considerations, 2005, New England interstate water pollution control commission] These steps can be altered for different operational applications.

**Fill:** During the fill phase, influent wastewater is fed to the basin. This influent acts as food to the microbes in the activated sludge, which creates an environment for biochemical reactions to take place. Aeration and mixing can be varied during this phase to create the following three different scenarios:

- *Static Fill* – Under a static-fill scenario, while the influent wastewater is entering the tank, there is no mixing or aeration. Static fill is mainly used during the initial start-up phase of any facility, at plants where nitrification or denitrification is not needed, and during low flow periods to save power. As the mixers and aerators remain off, this scenario reflects an energy-savings component.
- *Mixed Fill* – Under a mixed-fill scenario, mechanical mixers are active, but the aerators still remains off. The mixing action here, produces a uniform blend of influent wastewater and biomass. As there is no aeration, an anoxic condition is present, which promotes denitrification. Anaerobic conditions may also be achieved during the mixed-

fill phase. Under anaerobic conditions the biomass releases phosphorous. This release is reabsorbed by the biomass itself, once aerobic conditions are reestablished. This phosphorous release does not happen with anoxic conditions.

- *Aerated Fill* – Under an aerated-fill scenario, both the mechanical mixing unit and aerators are activated. The contents of the basin are aerated to convert the anoxic or anaerobic zone over to an aerobic zone. No adjustments to the aerated-fill cycle are needed to achieve nitrification and reduce organics. But, to achieve denitrification, it is necessary to switch the oxygen off to promote anoxic conditions for denitrification. By switching the oxygen on and off during this phase with the blowers, oxic and anoxic conditions are achieved, allowing for nitrification and denitrification.

**React:** During this phase, no influent wastewater enters the basin and the mechanical mixing and aeration units are on. As there are no additional volume and organic loadings, the rate of organic removal increases dramatically.

Most of the carbonaceous BOD removal occurs in this phase. Further nitrification occurs by allowing the aeration and mixing to continue—the majority of denitrification takes place in the mixed-fill phase. The phosphorus released during mixed fill, plus some additional phosphorus, is consumed during the react phase.

**Settle:** During this phase, activated sludge is allowed to settle under steady conditions—no flow enters the basin and no mixing or aeration takes place. The activated sludge settles as a flocculent mass and forms a distinctive interface with the clear supernatant.

The sludge mass is called the sludge blanket. This phase is a very critical part of the cycle, because if the solids don't settle rapidly, some sludge may be drawn off during the subsequent decant phase degrading effluent quality.

**Decant:** During this phase, a decanter is used to remove the clear supernatant effluent. Once the settle phase is complete, decanter is made to initiate the opening of an effluent-discharge valve. There are fixed-arm and floating decanters. Fixed-arm decanters are comparatively less expensive and can be designed to allow the operator to lower or raise the level of the decanter. Floating decanters maintain the inlet orifice slightly below the water surface to minimize the removal of solids (sludge particles) in the effluent removed during the decant phase. Also,

floating decanters offer the operator flexibility to vary fill and draw volumes. It is optimal that the decanted volume is the same as the volume entering the basin during the fill phase. It is also important that no surface foam or scum is decanted during this phase. The vertical distance from the decanter to the bottom of the tank should be maximized to avoid disturbing the settled biomass.

**Idle:** This step occurs between the 'decant' and the 'fill' phases. The time varies, based on the influent flow rate and the operating strategy. During this phase, a small but fixed amount of activated sludge at the bottom of the SBR basin can be pumped out as per need, a process called wasting.

### **3.1.2 Continuous flow systems**

SBR facility usually consists of two or more basins, all of them operating in parallel. In this modified version of SBR, the flow enters each basin on a continuous basis. The influent wastewater flows into the influent chamber, which further has inlets to the react basin at the tank bottom to control the entrance speed so as not to agitate the settled solids [EPA 932-F-99-073, Wastewater Technology Fact Sheet, Sequencing Batch Reactors, 1999]. Continuous-flow systems are not exactly true batch reactions as the influent is constantly entering the basin. The design configurations of continuous-flow systems and SBR are otherwise very similar in almost all aspects. Plants operating under continuous flow mode should operate this way as the standard mode of operation, reason being that wastewater continuously enters the treatment plant. Ideally, a true batch reaction SBR must operate under continuous flow only. Plants that have already been designed as continuous-inflow systems have shown to have relatively poor operational conditions during the peak flows. Some of the major problems of the continuous-inflow systems have been poor effluent, overflows, permit violations and washouts.

### **3.2 Design criteria of SBR**

The very first step, for any wastewater treatment plant design, is to have knowledge about the influent characteristics of the wastewater and the effluent requirements for the proposed system. The influent parameters typically include TSS, pH, alkalinity, design flow, maximum daily flow BOD<sub>5</sub>, wastewater temperature, ammonia nitrogen and total phosphorus. For industrial and domestic wastewater, some other site-specific parameters may also be



required. The effluent discharge parameters from the system are generally dictated by the state and central pollution control board [Sequencing batch reactor design and operational considerations, 2005, New England interstate water pollution control commission]. The parameters typically defined for the municipal systems are BOD5, TSS, flow rate and fecal coli forms. It is imperative to establish effluent requirements because they will impact the operating sequence of the SBR.

### 3.2.1 Design parameters of SBR

After determining the influent and effluent characteristics of the system, SBR manufacturers are consulted by the design engineer for a recommended design. A unified approach to design an SBR is in a development phase; however, the approach needed to design the nitrification and denitrification facilities in a single anoxic system, such as flow or loadings, can safely be applied with some modifications [Wastewater engineering, 4th edition, 2003, Eddy and Metcalf]. The most important factor to be considered specifically for the SBR design is the flow volume that basically determines whether a reactor will serve the need or there is a need of two or more vessel system. The feed volume/total volume ratio, typically known as volume exchange ratio (VER), must be determined by the desired effluent quality which in turn decides reactor sizing for the engineer.

### 3.2.2 Determination of SBR operating cycle time

Total Cycle Time ( $T_C$ ) can be calculated by adding fill time ( $T_f$ ), react time ( $T_r$ ), settle time ( $T_s$ ) and decant time ( $T_d$ ). An idle time ( $T_i$ ) can also be added. Hence, the total cycle time is given by

$$T_C = T_f + T_r + T_s + T_d + T_i \quad (3.1)$$

The total cycle time and fill time are used to determine the required number of reactors,  $N$ . The relation is described by the following equation: [Lee et al., 1999].

$$N = T_C / T_f \quad (3.2)$$

In case,  $N$  is not an integer, the number of tanks decided for the design would be the next integer. Although in theory it is possible to operate tanks of different sizes, it would be more practical to have all the tanks in the system of same size.

### **3.2.3 Decanting system**

No more than one-third of the volume contained in the basin should be decanted after each cycle in order to prevent disturbance of the settled sludge, during the decant phase. The decanting should never interfere with the settled sludge. Also, decanters should avoid vortexing. The main problem with decanting more than the above specified volume is that it can bring with it the settled solids into the effluent, hence, compromising with the effluent quality. For any SBR plant to run optimally, the most important consideration is that the decant volume is the same as the volume fed during the fill phase. The flux (upward forces) caused during the decant phase creates an upward force that can pull the poorly settled sludge particles up and out in the effluent. [Norcross, 1992].

### **3.2.4 Blower requirement**

Usually during the design of SBR designs, several small blowers are preferred in spite of one high capacity blower. The main reason behind this choice is the uniform aeration of complete basin. However, it is common for some SBR designs to put a single high capacity blower per tank to provide aeration facility, but the operational efficiency can be substantially improved when plants utilize several smaller blowers, instead of a single high capacity blower. Apart from uniform air distribution, also, in a plant designed with only one blower per tank, it is somewhat difficult to scale back on the aeration provided [Schroeder, 1982]. With multiple smaller blowers, there is an option to shut down some aeration units off line when maximum aeration is not required. Hence it also contains a cost saving component.

Secondly, fine-bubble membrane diffusers are preferred over coarse-air bubble aeration for the reason that fine-bubble diffusers have more oxygen transfer capability to the water due to the increased surface area in contact. However, the amount of surface area in contact with water is proportional to the amount of oxygen transferred into water but the same amount of air contained in a bigger bubble has lesser surface area in contact with water as compared to an equal amount of air divided into many smaller bubbles. Depth of aerators also plays an important part in the oxygen transfer, due to contact time. The deeper the aerator lies in the basin, the longer it takes for the air bubble to reach the surface. Obviously, aerator depth is deepest when a tank is filled to the highest possible water level.

### 3.2.5 Bottom slope

Slope rectangular basins slightly to any one corner allows for hosing down the unit, therefore, all the basins should have a downward sloped bottom with a drain and sump for routine basin maintenance and ease of cleaning. Circular basins should be sloped toward the center for the maintenance. All SBR designs should necessarily include a means for completely emptying each basin of all sludge, debris, grit and liquid. [Chambers, 1993]

## 3.3 Adsorption

### 3.3.1 General

Adsorption is a process in which a substance, originally present in one phase, is removed from that phase by its accumulation at the interface between that phase and a separate solid phase. In principle adsorption can occur at any solid fluid interface. Examples of adsorption include:

- Liquid-solid interface (the adsorption of an organic pollutant on the surface of activated carbon);
- Gas-solid interface (the adsorption of a Volatile organic compound on the surface of activated carbon).

The driving force for adsorption is the reduction in interfacial (surface) tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid [<http://www.energy-concepts.com/process>]. The basic difference between adsorption and absorption is that absorption is the process through which a substance, originally present in one phase, is removed from that phase by dissolution in another (typically a liquid), as opposed to the accumulation at the interface as in the case of adsorption. In other words, adsorption is a surface phenomenon whereas in absorption, dissolution takes place at bulk [<http://www.lenntech.com/library/adsorption/adsorption.htm>].

Adsorption process is thought to take place in three broad stages, as the adsorbate concentration increases.

*Stage I:* At the start, a single layer of molecules builds up over the surface of the adsorbent. The formation of a monolayer is associated with a change in free energy which is a characteristic of the force that holds it.

*Stage II:* With the increasing fluid concentration second, third etc., layers are formed by the physical adsorption. The number of layers which may form in this stage are limited by the size of the pores and the size of the adsorbate.

*Stage III:* Finally, for adsorption from gas phase, the capillary condensation may occur in which the capillaries become filled with the condensed adsorbate, when its partial pressure reaches a critical value relative to size of the pore.

### **3.3.2 Adsorption in wastewater treatment**

Adsorption is used in wastewater treatment plants to remove toxic organic pollutants (especially halogenated but also non-halogenated), and to an extent, inorganic contaminants, from the wastewater. It is commonly used in treatment of industrial wastewaters containing those organic compounds which cannot be easily biodegraded during secondary (biological) treatment or are highly toxic. Adsorption finds applications in tertiary wastewater treatment as a finishing step before final discharge [Kopecky et al., 1996]. The main motivation for the use of adsorption process in wastewater treatment lies in the fact that many industrial wastewaters contain substances that:

- are very volatile and cannot be transferred to the atmosphere directly;
- have the potential to create noxious vapors or odors, or for imparting color to the wastewater;
- are hazardous or toxic;
- are difficult to remove via conventionally used secondary treatment processes;
- are present in very small concentrations that make their removal via other methods practically difficult.

### 3.3.3 Adsorption as a physical process

In the adsorption process the material being adsorbed (adsorbate) is simply but very effectively removed from one phase (e.g. a wastewater) and transferred to another phase (adsorbent) which basically means that adsorption is a physical separation process which doesn't alter the adsorbed material chemically [<http://en.wikipedia.org/wiki/Adsorption>]. As the chemical characteristics or properties of the adsorbed material do not change, the use of adsorption process in wastewater treatment is associated with the removal of these hazardous materials from the wastewaters and their transfer to the adsorbent. This implies that the adsorbent now contains the hazardous material. Hence, appropriate actions must be taken to treat this spent adsorbent at the end of every cycle [Sankar et al., 1999]. The adsorbent can be regenerated (i.e., the hazardous material may be removed via stripping), disposed of (together with the pollutants it contains) in a landfill or destroyed (together with the pollutants it contains) in an incinerator as per the requirement and on the basis of optimization of different economic factors.

### 3.3.4 Activated carbon as an Adsorbent

Activated carbon is by far the most common and effective adsorbent used in wastewater treatment. Since, during the adsorption process, the pollutant is removed by accumulation of adsorbate at the interface between the adsorbent and the wastewater (liquid phase), the adsorbing capacity of activated carbon is always associated with very high surface area per unit volume. In activated carbon the high surface area per unit volume characteristic is obtained with a two-step process used in carbon manufacturing [Li et al., 2005]. First step includes the pyrolysis of the raw material (typically a very high carbon source such as coal, nut shells or wood) to remove the lighter fraction producing a charred, highly carbonaceous solid residue; second step includes the activation of this charred residue via oxidation (typically with air or steam) to form a network of pores and passages with high surface area.

Pores in activated carbon usually range from 10 to 10,000 Å in diameter. While, pores having a diameter larger than 1000 Å are called macropores, the pores having a diameter smaller than 1000 Å are called micropores. Out of these two types, micropores are primarily responsible

for the adsorption characteristics of activated carbon. Typical surface areas in activated carbons range from 500 to 1500 m<sup>2</sup>/g of carbon.

Activated carbon is usually produced in particle sizes up to a few millimeters. The total surface area available for the adsorption process is not significantly affected by the particle size for the reason that the micropore structure responsible for adsorption doesn't change significantly with changing particle size [Bystrzejewski et al., 2010]. This fact implies that the total adsorption capacities of small and large particles are not very different. The activated carbon having larger particle sizes, i.e. of the order of 1 mm or more, is termed as granular activated carbon (GAC). This can be packed in columns through which a liquid can be passed, and the adsorbent can be regenerated after use. On the other hand, carbon having smaller particle sizes i.e. of the order of tens of mm is termed as powdered activated carbon (PAC) [Yener et al., 2008], [Tancredi et al., 2004]. This material can only be used by its direct addition to a liquid and it must be removed after use (e.g., by filtration or centrifugation) and disposed off. In general, the larger the particle size the more expensive is the carbon. Bulk dry density of GAC is 0.22-0.5 kg/L while bulk dry density of PAC is 0.34-0.74 kg/L.

### 3.3.5 Adsorption Equilibrium

Adsorption takes place upon contacting a particular amount of GAC with wastewater containing the adsorbate. Adsorption continues until equilibrium is achieved between the substance in solution and the same substance in adsorbed state. At equilibrium, a relationship exists between the concentration of the species in solution and concentration of the same species in the adsorbed state i.e., the amount of species adsorbed per unit mass of adsorbent.

### 3.4 Adsorption Isotherms

The adsorption equilibrium basically relates  $q$  to  $C$ . The adsorption equilibrium is a function of the temperature [Liu et al., 2010]. Therefore, the adsorption equilibrium relationship at a given temperature is typically referred to as an *adsorption isotherm*, i.e.:

$$q = f(C) \tag{3.3}$$

Where,  $q$  is the mass of species adsorbed/mass of adsorbent (i.e., equilibrium concentration of the adsorbable species in solid adsorbent) and  $C$  is the equilibrium concentration of adsorbable species in solution.

Different adsorbates-adsorbents exhibit different types of equilibrium relationships (i.e., equation 3.1 may take different mathematical forms) [Qi and Schideman, 2008]. It has been found that for most of the cases of importance in wastewater treatment the equation takes either the form of a Langmuir isotherm or Freundlich isotherm. Both of these isotherms are explained in the subsequent sections.

### 3.4.1 Langmuir Isotherm

The Langmuir adsorption model is assumed to be a dynamic process. It is assumed that at equilibrium the number of molecules being adsorbed will be equal to the number of molecules leaving the adsorbed state [Liu, 2006]. This equation is based on the following assumptions:

1. Adsorbed molecules don't interact with each other.
2. Only monolayer adsorption is taking place.
3. Adsorbed molecules do not migrate on the adsorbent surface.
4. Adsorbent surface is uniform in terms of energy of adsorption.

The Langmuir isotherm is given by the following equation:

$$Q_e = \frac{Q_m K_A C_e}{1 + K_A C_e} \quad (3.4)$$

Where  $Q_e$  is the amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium,  $Q_m$  is the amount of adsorbate adsorbed per unit amount of adsorbent required for monolayer adsorption (limiting adsorbing capacity)  $K_A$  is the constant, related to enthalpy of adsorption and  $C_e$  is the concentration of adsorbate solution at equilibrium.

### 3.4.2 Freundlich Isotherm

The Freundlich isotherm doesn't indicate any adsorption limit when coverage reaches sufficient to fill a monolayer. The heat of adsorption declines in magnitude with an increase in extent of adsorption in many instances. This decrease in the heat of adsorption is logarithmic,

implying that the adsorption sites are distributed exponentially with respect to the adsorption energy [Losso et al., 2002]. The equation describing such isotherm is the Freundlich Isotherm which is given by:

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (3.5)$$

Where  $K_F$  and  $n$  are the constants and  $C_e$  is the concentration of adsorbate solution at equilibrium.

Thus a plot between  $\ln Q_e$  and  $\ln C_e$  gives a straight line if the adsorbate and adsorbent are following Freundlich isotherm. . This isotherm is frequently applied to the adsorption of impurities or pollutants from a liquid solution onto the activated carbon.

The Freundlich equation is found to be useful for dilute solutions over a small concentration range [Qi and Schideman, 2008]. A high adsorption throughout the concentration range is indicated by a high  $K_F$  and high 'n' value whereas, a low  $K_F$  and a high 'n' indicates a low adsorption throughout the concentration range. Adsorption taking place at strong solute concentration is indicated by a low 'n' value.

The basic differences between Langmuir and Freundlich isotherms [Mesquita and Silva, 2004] are listed in Table 3.1.

**Table 3.1. Comparison of Langmuir and Freundlich Adsorption**

Sl. No.	Langmuir Isotherm	Freundlich Isotherm
1.	The Langmuir isotherm has a theoretical justification.	The Freundlich isotherm represents an empirical model.
2.	The Langmuir isotherm assumes reversible adsorption and desorption of the adsorbate molecules.	No assumption is made for the Freundlich isotherm
3.	The Langmuir isotherm typically represents well data for single components.	The Freundlich isotherm can be used also for mixtures of compounds



### 3.4.3 Redlich-Peterson (R-P) isotherm

Redlich and Peterson incorporated three parameters to devise an empirical isotherm. This isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It approaches the Freundlich model at high concentration and Langmuir model at low concentrations. Furthermore, the R-P equation incorporates three parameters into an empirical isotherm, and therefore, it can be applied either in homogenous or heterogeneous systems due to the high versatility of equation. It can be described as follows:

$$q_e = \frac{K_R C_E}{1 + \alpha_R C_E^\beta} \quad (3.6)$$

Where,  $K_R$  is R-P isotherm constant (L/g),  $\alpha_R$  is R-P isotherm constant (L/mg) and  $\beta$  is the exponent which lies between 0 and 1.

## 3.5 Adsorption Practices

In all the adsorption processes the powdered activated carbon (PAC) is added to wastewater for a fixed period of time to allow the pollutants to be adsorbed. The adsorption process can be carried out once (in a single stage) or repeated (in several stages). The possible processes can be classified as:

- Batch adsorption (single stage)
- Multistage crosscurrent adsorption
- Multistage countercurrent adsorption

### 3.5.1 Batch Adsorption

In batch adsorption finely divided activated carbon is contacted with the wastewater for a given period of time in a mixing vessel. The activated carbon used in this process is typically supplied in a powdered form (PAC) or in Granular form (GAC). After the process is complete (typical contact time: 2 to 5 hours) the spent carbon is separated from the wastewater (e.g., by filtration) and then regenerated or disposed off.

### 3.5.2 Multistage Crosscurrent Adsorption

In this case fresh carbon is added to each stage of the adsorption process. Equilibrium is assumed to be achieved in each stage.

### 3.5.3 Multistage countercurrent adsorption

In multistage countercurrent adsorption, the streams leaving each stage are assumed to be in equilibrium with each other. The rates of wastewater and activated carbon moving from stage to stage are constant. In wastewater applications typically no more than two stages are used.

### 3.6 Factors Affecting Adsorption

There are several factors which affect the adsorption of a substance on an adsorbent [**Manual for laboratory practice in physical chemistry for students of pharmacy, 2007**]. The most important of them are:

- *Contact time or residence time*: The longer the contact time, the more complete the adsorption would be.
- *Surface area of the adsorbent*: Larger surface area implies a greater adsorption capacity.
- *Degree of ionization of the adsorbate molecule*: Neutral molecules are adsorbed to a higher extent than highly ionized molecules.
- *Particle size of the adsorbent*: Smaller particle sizes reduce the internal diffusional and limits the mass transfer i.e. the penetration of the adsorbate inside the adsorbent (equilibrium is more easily achieved in this case and nearly full adsorption capacity can be utilized). However, pressure drop across the columns packed with powdered material is too high for its use in packed beds. Also, Addition of powdered adsorbent must be followed by their subsequent removal.
- *Solubility of adsorbate in liquid (wastewater)*: Substances having less solubility in water are more easily removed from water (i.e., adsorbed) than the substances with relatively higher solubility. Also, non-polar substances will be removed more easily than polar substances since the former have a lesser affinity for water.
- *pH*: Degree of ionization of any species is affected by the pH of solution. This, in turn, affects adsorption.

- *Size of the molecule with respect to size of the pores:* Large molecules may not be able to enter small pores which can reduce the adsorption.
- *Affinity of the solute for the adsorbent (carbon):* The surface of the activated carbon is negligibly polar. Hence non-polar substances will be picked up more easily by the carbon than the polar ones.

## CHAPTER IV

### *EXPERIMENTAL STUDIES ON SBR AND ADSORPTION*

---

#### 4.1 General

In the present work, detailed studies have been performed to compare the performance of two SBR's, one without adsorbent (control SBR) and one with adsorbent (test SBR), for the removal of 4-chlorophenol. The effect of organic loading, cycle time, volume exchange ratio (VER), hydraulic retention time (HRT) and adsorbent dosage have been used as performance parameters for the two SBR's. Same compound has been removed using adsorption for the adsorption study. During this, effect of pH, effect of adsorbent dosages and batch kinetics were studied. Granular Activated Carbon (GAC) was used as the adsorbent in the study. Synthetic wastewater for the study was prepared by adding appropriate quantities of 4-chlorophenol to distilled water.

#### 4.2 Experimental setup for SBR

The experimental set-up composed of a well-mixed SBR, having 5L working volume. An aquarium-type air pump with sintered-sand diffusers was fixed at the bottom of the reactor for the purpose of aeration. The decanting operation was done with peristaltic pump and wasting operation was done using the tap at the bottom of the reactor. Concentration of dissolve oxygen (DO) inside the reactor was monitored continuously and was maintained between 2 mg/l and 4 mg/l during the experiments by controlling the flow of air using an air regulator. Mixed Liquor Suspended Solids (MLSS) concentration was controlled around 3000 mg/L. Excess sludge, which grew during the react phase, was drawn out at the end of every operating cycle, and hence a proper MLSS concentration was maintained [Sharma et al., 2010]. The reactor was operated in an open atmosphere with temperature ranging between 28<sup>0</sup>C to 32<sup>0</sup>C. Fig. 4.1 shows the SBR setup used for the present study and Fig. 4.2 shows the SBR from different views and at different stages of operation. Figure 4.3 shows the schematic diagram of the reactor. Table 4.1 lists the operating conditions for the reactor.

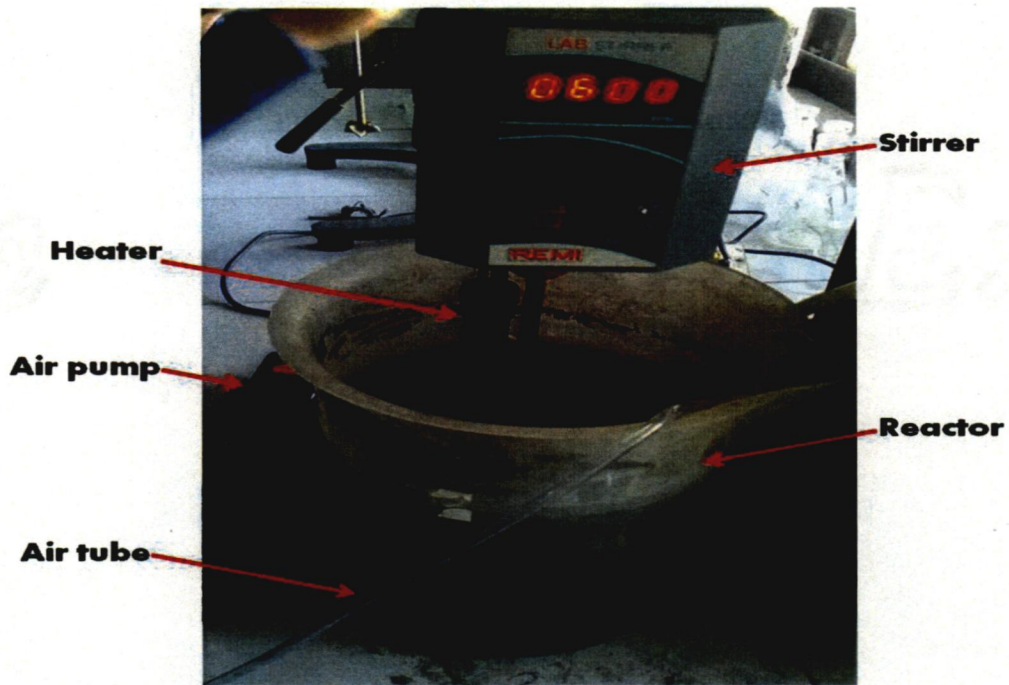


Fig. 4.1. SBR used for the present study

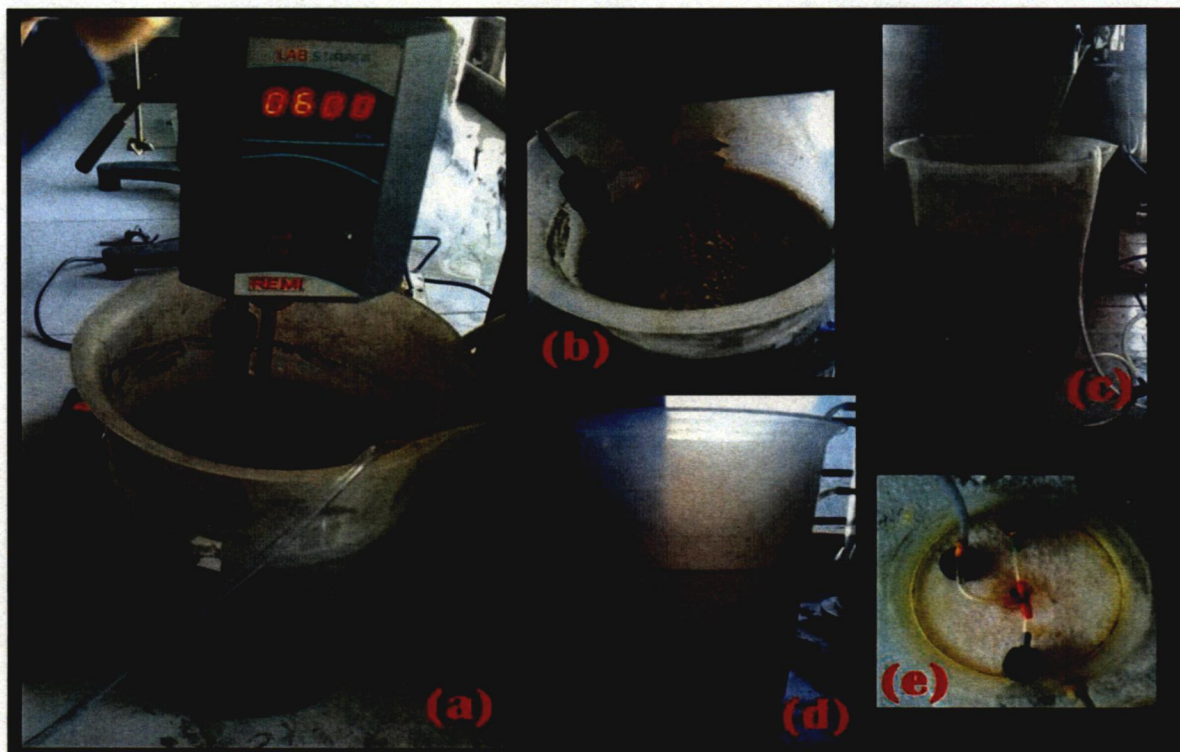


Fig. 4.2. a) SBR used for the present study, b) SBR from top view showing aeration, c) SBR from side view, d) Settled sludge in reactor, e) Aerators at bottom of reactor

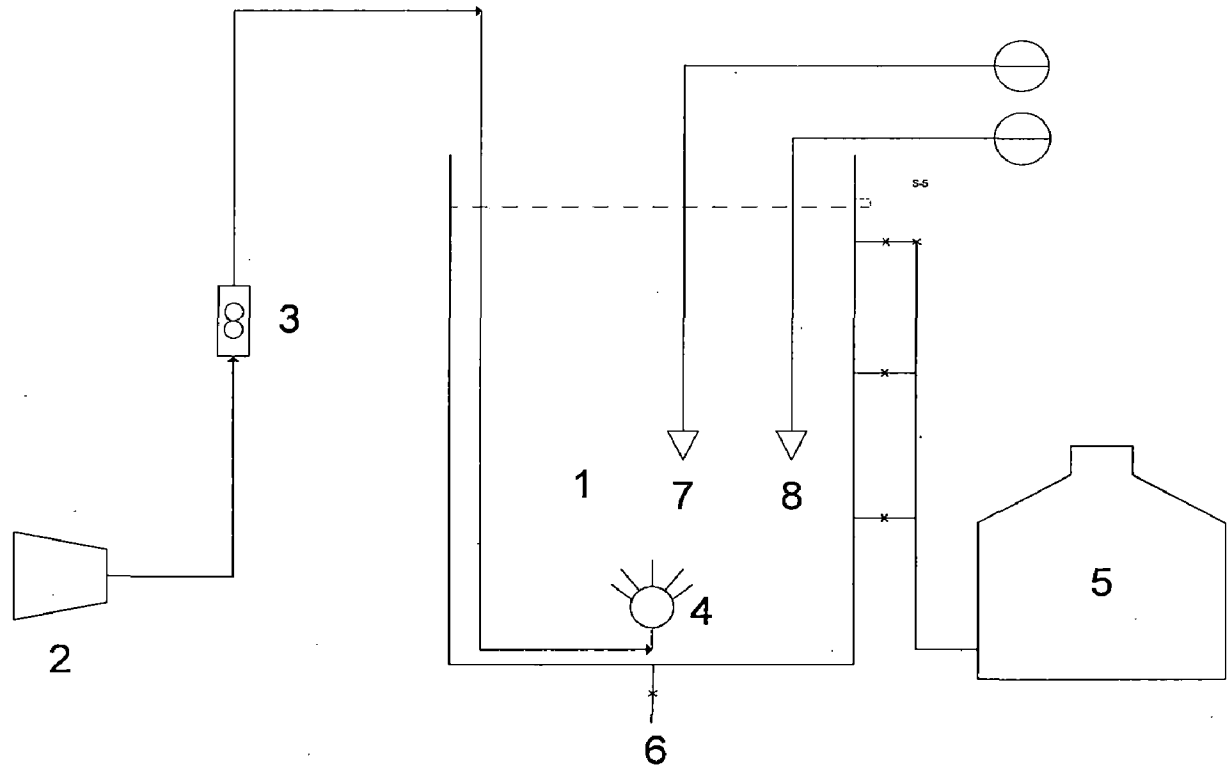


Fig.4.3. Schematic diagram of the experimental system 1. reactor; 2. air compressor; 3. air regulator; 4. air diffuser; 5. storage tank; 6. drainage valve; 7. thermostat; 8. dissolved oxygen meter.

**Table 4.1. Operating conditions of the two reactors**

Parameter	Blank SBR	GAC-SBR
Temperature ( $^{\circ}\text{C}$ )	30 $^{\circ}\text{C}$	30 $^{\circ}\text{C}$
Dissolved oxygen (mg/L)	2 - 4	2 - 4
pH	6.5 to 7	6.5 to 7
Fill phase	Instantaneous fill	Instantaneous fill
Agitator speed (rpm)	600	600
Cycle time (h)	8	6
MLSS (mg/L)	3000	3000

#### 4.2.1 Influent characteristics for SBR

The synthetic wastewater composition used was prepared as per the different concentrations of 4-chlorophenol (LR grade, Sd fine chemicals limited) in distilled water. For studying the effect of variation of concentration, the range of 4-chlorophenol concentration used for blank SBR was 50–350 mg/l and the range of 4-chlorophenol concentration used for GAC-SBR was 200 – 1500 mg/l.

## 4.2.2 Sludge characteristics

The synthetic wastewater prepared is first seeded with bacteria, which is responsible for the biodegradation of the organic matter present in the wastewater, by activated sludge collected from Haridwar (Kankhal) sewage treatment plant. Figure 4.4 shows the pictures of sequential batch reactor (SBR) taken at this treatment plant. The first step was the screening of sludge for the removal of coarse and bigger particles. The screened sludge was transferred into the reactor and was aerated for 10 days in presence of proper nutrition for micro-organisms for acclimatization of the sludge with the synthetic wastewater. This acclimatized sludge is further used for treatment of wastewater.

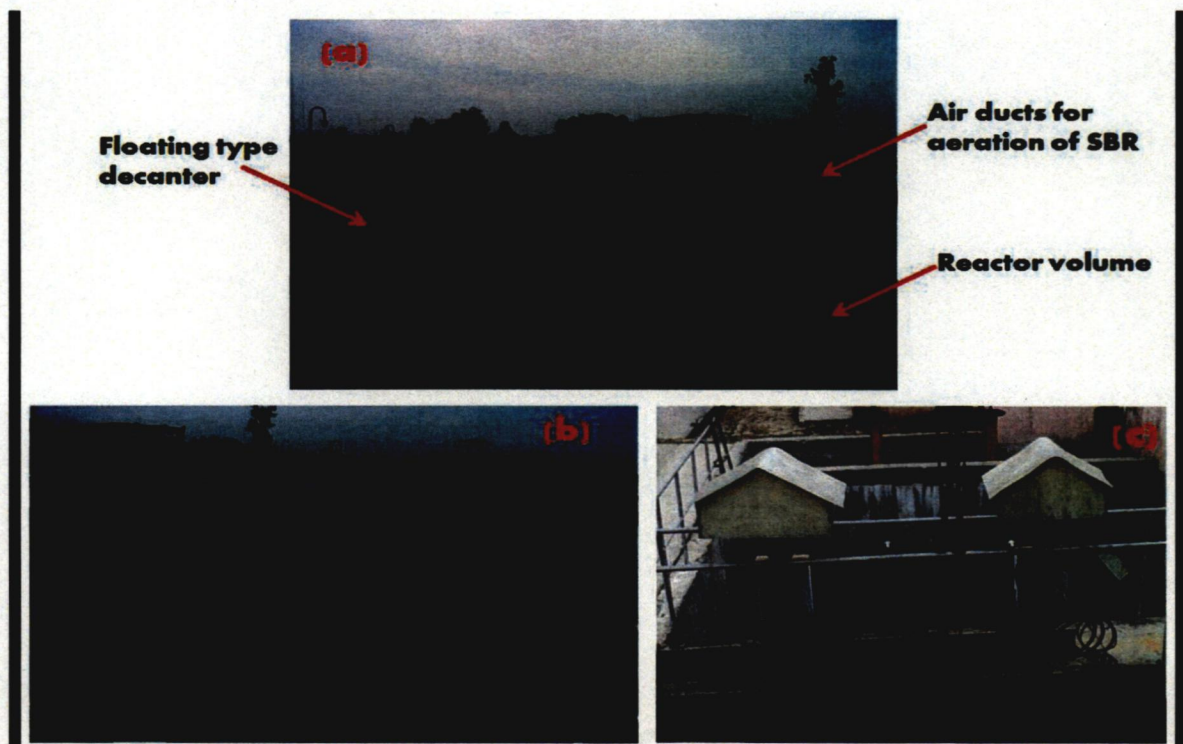


Fig. 4.4. a) Reactor volume showing decanter and aerator, b) SBR at sewage treatment plant in react phase, c) Control system for dissolved oxygen (D.O.) levels in SBR

Acclimatization is a process in which the culture of bacteria is made to survive and grow in pollutant's environment hence degrading the pollutant [Betancur et al., 2009]. Dissolved oxygen concentration was maintained between 2 mg/l to 4 mg/l using an aquarium type air blower with a regulator. Temperature was maintained between 28°C and 32°C using an aquarium

heater with temperature control. Set point of temperature was fixed to 30°C. The concentration of 4-chlorophenol used for acclimatization was 50 mg/l for blank SBR and 200 mg/l for GAC-SBR.

The nutrition provided during the course of acclimatization consisted of anhydrous glucose, ammonium chloride and disodium phosphate to supply the required carbon, nitrogen and phosphorus demand of the sludge. During first 5 days of acclimatization 100 mg/L of each of these nutrients were supplied and during the remaining 5 days the quantity of each if these nutrients was gradually decreased to zero. Settling of the sludge before and after acclimatization was observed and recorded to study the change in the settling characteristics. Also the filterability data of a 100 ml sample of sludge was recorded.

### 4.2.3 Adsorbent in SBR

Granular Activated Carbon (GAC) was selected as adsorbent for SBR. Other adsorbents, considered for the study, were RHA (rice husk ash), BFA (bagasse fly ash) and activated alumina [He et al., 2007]. The removal efficiencies of these adsorbents were compared and it was found that GAC and BFA are suitable for the removal of 4-chlorophenol. GAC was preferred over BFA for the reason that it could be easily separated from sludge after every cycle [Vinitnantharat et. al, 2001], [Lim et al., 2002], [Lim et al., 2008]. 16 g/L of adsorbent was used for each cycle in the reactor and was separated at the end of each cycle using a sieve. Table 4.2 shows the size analysis of the adsorbent particles used in SBR. The synthetic wastewater composition used was made as per the different concentrations of 4-chlorophenol. For studying the effect of variation of concentration, the range of 4-chlorophenol concentration used for reactor with adsorbent was 200 – 1500 mg/l.

**Table 4.2. Size pattern of the adsorbent particles used in SBR**

Size of sieve (mm)	Weight % of oversize particles
2.36	3 %
2	5 %
1.7	14 %
1.4	32 %
1	44 %
0.85	1 %
0.71	0 %



### 4.3 Experimental procedure

After the acclimatization was done, the acclimatized sludge was added to wastewater. The concentration of bacterial cell in the reactor was varied by varying the volume of the sludge. The microbial concentration was measured in terms of MLSS (mg/l). The batch reactor was operated on a fill-and-draw basis. At the start of experiment, the reactor was filled with synthetic wastewater and sludge. The contents were made to react for a particular span of time using the stirrer and aeration was done to maintain the D.O. between 2 to 4 mg/L. Then the contents were allowed to settle. After the completion of settle phase the samples were taken from the effluent port and filtered with filter paper (Whatman filter paper no. 42 pore size of ca. 2.5  $\mu\text{m}$ ) and then tested for final 4-chlorophenol concentrations. Experimental procedure for the operation of 2 reactors i.e. blank SBR and GAC-SBR were same except the fact that, in GAC-SBR appropriate amount of GAC was added at the start of each cycle and the used adsorbent was removed at the end of every cycle using sieves.

#### 4.3.1 Analytical methods

Analysis of the wastewater was done as per standard methods. The concentration of 4-chlorophenol was determined by finding out the absorbance of the solution at 225 nm, using UV-spectrophotometer (Shimadzu 1800). A linear variation of absorbance was obtained against concentration of 4-chlorophenol up to 10 mg/l as per the calibration plot. For this reason, the samples with higher concentration of 4-chlorophenol were diluted to lower concentrations with distilled water, whenever necessary, for accurate determination of the concentration using the linear portion of the calibration curve. Figure 4.5 shows the calibration curve for 4-chlorophenol on UV- spectrophotometer.

The peaks for maximum absorbance were detected for both, the 4-chlorophenol solution and the sludge using UV spectrophotometer. It was found that maximum absorbance for chlorophenol was obtained at a wavelength of 225 nm and sludge did not show any absorbance at 225 nm. So UV spectrophotometer can be safely used for determining the concentration of 4-chlorophenol. Figure 4.6 and figure 4.7 show the snapshots of the absorbance curves of 4-chlorophenol and sludge respectively on UV spectrophotometer.

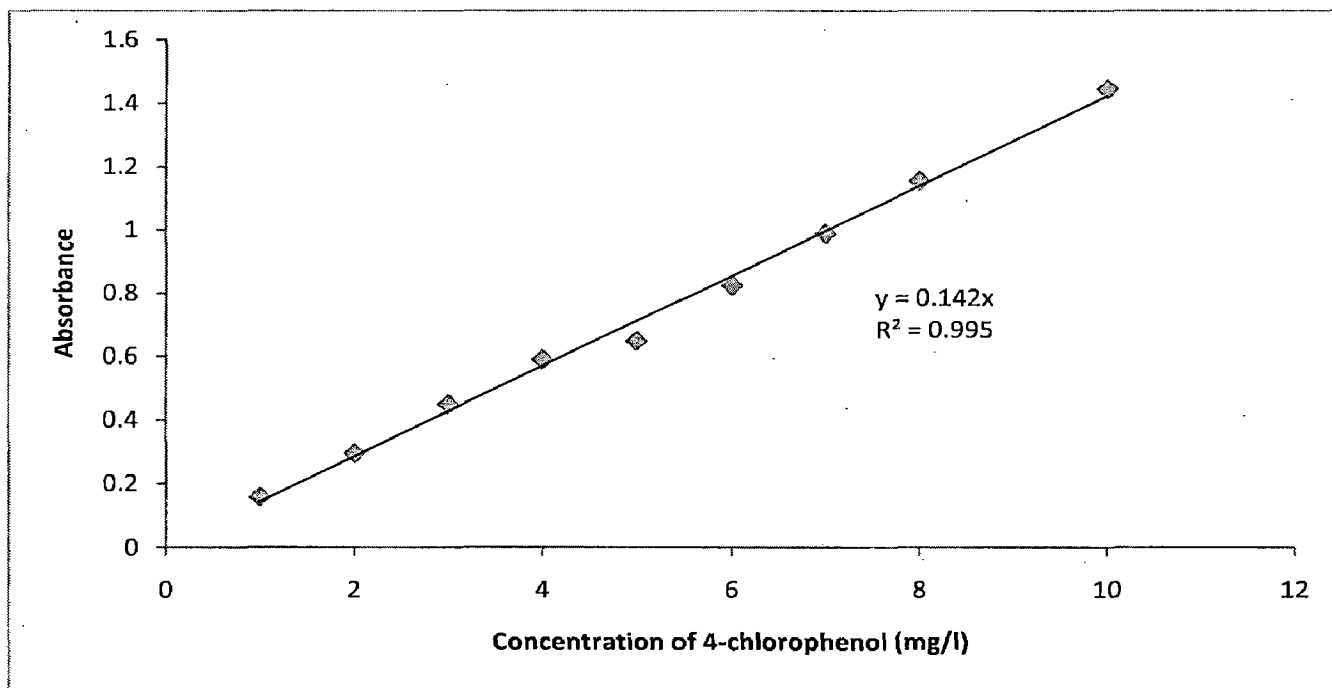


Fig 4.5. UV-spectrophotometer Calibration for 4-chlorophenol, wavelength used = 225 nm

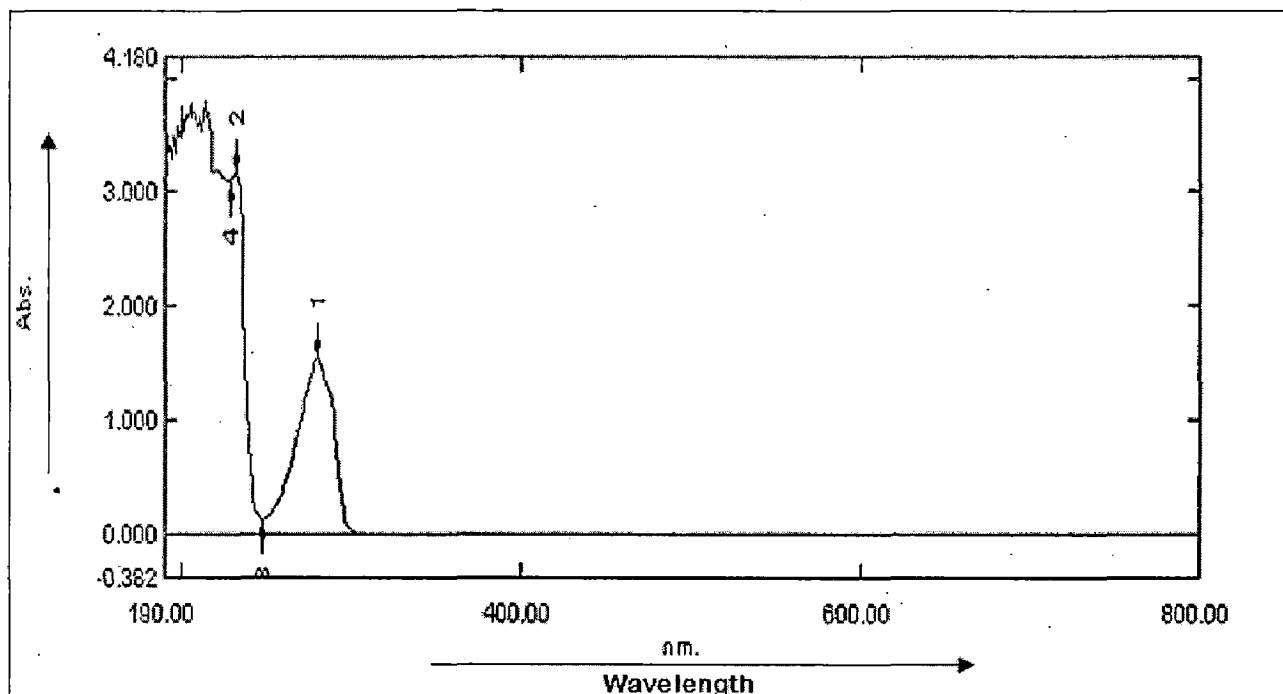


Fig 4.6. Absorbance of 4-chlorophenol at different wavelengths

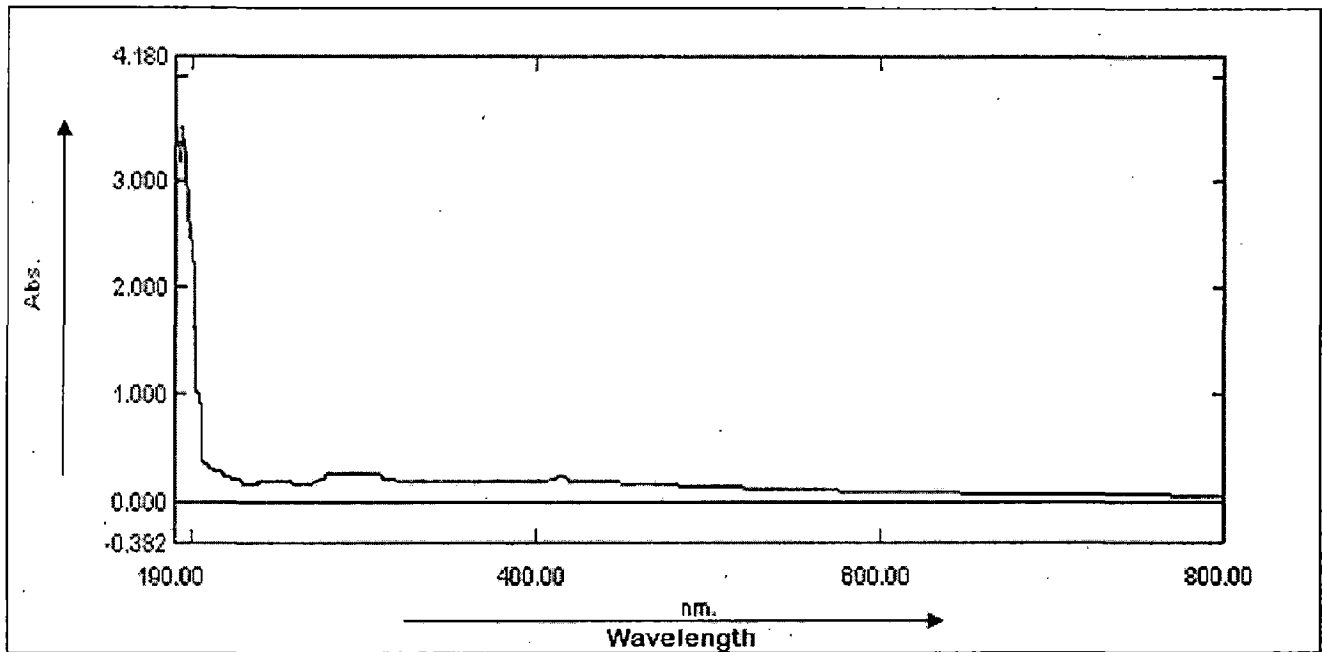


Fig 4.7. Absorbance of sludge at different wavelengths

### 4.3.2 Cycle time for SBR

Samples were taken from the reactor at different intervals of time for different concentrations of 4-chlorophenol. They were filtered using filter paper and then were tested for the concentration of 4-chlorophenol using U-V spectrophotometer. Cycle time ( $T_c$ ) was optimized for maximum 4-chlorophenol removal. In case of GAC-SBR the samples taken were centrifuged after filtration. Total Cycle Time ( $T_C$ ) can be calculated by adding fill time ( $T_f$ ), react time ( $T_r$ ), settle time ( $T_s$ ) and decant time ( $T_d$ ). An idle time ( $t_i$ ) can also be added. Hence, the total cycle time is given by :

$$T_C = T_f + T_r + T_s + T_d + T_i \quad (4.1)$$

### 4.3.3 Effect of volume exchange ratio (VER) and hydraulic retention time (HRT)

VER (Volume Exchange Ratio) is given by following formula:

$$VER = \frac{V_F}{V_T} \quad (4.2)$$

In this formula  $V_F$  is fill volume (L) and  $V_T$  is total volume (L).

HRT is the time the wastewater takes to pass through the system. The theoretical amount of time required for a given flow to pass through a unit process. HRT (Hydraulic Retention Time) is given by following formula:

$$HRT = \frac{V_T}{V_F} * \frac{1}{N_C} = \frac{1}{VER} * \frac{T_C}{24} \quad (4.3)$$

In this formula  $N_c$  is number of cycles per day and  $T_c$  is time of one cycle in hours.

Concentration of 4-chlorophenol was fixed to 100 mg/L for blank SBR and 500 mg/L for GAC-SBR and removal efficiencies for both the reactors were studied at different VER's. Hence VER for the two reactors was optimized for maximum removal of 4-chlorophenol. The optimized value of  $T_c$  was used to calculate the HRT at different VER's and the HRT of reactor was also optimized at the same time.

#### **4.3.4 Effect of adsorbent dosage in SBR**

To find the optimum adsorbent dosage for GAC-SBR the analysis was done at the different amount of adsorbent ranging from 4 to 14 g/L with initial adsorbate concentration 500 mg/L of 4-chlorophenol [Sirianuntapiboon and Ungkaprasatcha, 2007]. VER and HRT were fixed to their optimum values for this purpose.

### **4.4 Influent characteristics for adsorption**

#### **4.4.1 Batch experiments**

The effect of important parameters like adsorbent dose, initial concentration, pH and contact time on the adsorptive removal of 4-chlorophenol was studied using batch experiment. For each experiment run 50 ml of 4-chlorophenol solution (in distilled water) of known concentration, pH and the known amount of the adsorbent dose were taken in 100 ml Stoppard conical flask. This solution of 4-chlorophenol was agitated continuously in controlled orbital shaking incubator (manufactured by REMI) at a constant agitation speed of 150 rpm at a fixed temperature i.e. 30°C. Upon completion of the experiment each solution was filtered and centrifuged for the removal of spent adsorbent. The supernatant was analyzed for the amount of 4-chlorophenol. The percentage removal of 4-chlorophenol and equilibrium adsorption uptake in

solid phase  $q_e$  (mg of solute adsorbed/g of adsorbent) was calculated by using the following relationship:

$$\text{Percentage Removal} = 100(C_o - C_e)/C_o \quad (4.4)$$

$$\text{Amount of adsorbed 4-chlorophenol per g of solid, } q_e = (C_o - C_e) V/w \quad (4.5)$$

where,  $C_o$  is the initial concentration (mg/L),  $C_e$  is the equilibrium concentration (mg/L),  $V$  is the volume of the solution and  $w$  is the mass of adsorbent (g).

#### **4.4.2 Effect of type of adsorbent**

To find the effect of type of adsorbents, experiments were conducted with 4 different types of adsorbents namely RHA, BFA, GAC and activated alumina. 50 ml of aqueous solution containing 200 mg/L of 4-chlorophenol was taken in four different 100 ml flasks, 1 g of each adsorbent were added to each flask. The temperature was maintained at 30°C and % removal for each adsorbent was calculated.

#### **4.4.3 Effect of adsorbent dosage**

To find the optimum adsorbent dosage, analysis was done at the different amount of the adsorbent ranging from 8 to 26 g/L with initial adsorbate concentration 200 mg/L of 4-chlorophenol.

#### **4.4.4 Effect of pH**

To find the effect of pH, experiments were conducted at different concentration of 4-chlorophenol. The tests were conducted at different pH's of solution ranging from 2 to 10 g/L for initial concentration of 200 mg/L of 4-chlorophenol. The amount of adsorbent was fixed to the optimum as found before. The temperature was maintained at 30°C.

#### **4.4.5 Batch kinetics and isotherm study**

To determine the cycle time for maximum adsorptive removal of 4-chlorophenol, 50 ml of aqueous solution containing 200 mg/L of 4-chlorophenol was taken in many flasks, 1 g of adsorbent were added to different flasks of 4-chlorophenol. The flasks were kept in a temperature controlled shaker and they were agitated at 150 rpm. Flasks were withdrawn at

different time intervals, the contents of the flask were filtered, centrifuged and supernatant was analyzed. The adsorption kinetics was followed for 6 hours. To study the kinetics of adsorption of 4-chlorophenol various kinetic models, like pseudo-first order, pseudo-second order, intra-particle diffusion model and Bangham's models were analyzed. To find the equilibrium nature of adsorption of 4-chlorophenol, Langmuir and Freundlich isotherms were studied.

## 4.5 Studies on GAC and wasted sludge

### 4.5.1 Settling and filterability of sludge

Sludge was allowed to settle in a 1000 mL calibrated measuring cylinder and the height of the solid-liquid interface as the function of settling time during the settling of sludge for activated sludge (before acclimatization) and acclimatized sludge was observed and plotted against time.

SVI, a simple parameter for characterizing sludge thickening properties, was used to quantify the settling characteristics of the sludge. SVI is defined as volume (in L) occupied by 1 g of settled sludge after 30 min of settling. The SVI was calculated from the following relation:

$$\text{SVI (mL/g)} = \frac{\text{Volume of settled sludge (mL/L)} * 1000(\text{mg/g})}{\text{MLSS (mg/L)}} \quad (4.6)$$

Gravity filtration was used for generating experimental data. In gravity filtration the hydrostatic head is assumed to be constant neglecting the effect of height of the liquid on the total pressure as it is very less as compared to atmospheric pressure. A long thin vertical graduated cylinder of 100 mL was used to collect the filtered liquid from sludge and its height was recorded against time. Filter paper and Buchner funnel were used for performing this experiment and the following force balance equation was used for calculation:

$$\frac{\Delta t}{\Delta V} = \frac{\mu}{A\Delta P} \left( \frac{\alpha C V}{A} + R_m \right) \quad (4.7)$$

where,  $\Delta t$  is the time interval of filtration (s),  $\Delta V$  is the filtrate volume collected in  $\Delta t$  time interval ( $\text{m}^3$ ),  $\alpha$  is the specific cake resistance,  $\mu$  is viscosity of the filtrate (Pa.s),  $C$  is the MLSS

concentration in the slurry,  $A$  is the filtration area ( $\text{m}^2$ ),  $R_m$  is the resistance of the filter medium ( $\text{m}^{-1}$ ), and  $\Delta P$  is the pressure drop across the filter (Pa) [Sharma et al., 2011].

#### **4.5.2 BET surface area for GAC**

Brunauer, Emmett, Teller (BET) analysis of GAC was done using Surface Area and Porosity Analyzer (Micromeritics ASAP 2020). In this part of the study the BET surface area of GAC, Barrett, Joyner and Halenda (BJH) adsorption/desorption surface area of pores, single point total pore volume and the cumulative BJH adsorption/desorption pore volume of pores ( $17 \text{ \AA} < d < 3000 \text{ \AA}$ ) was observed.

#### **4.5.3 Physicochemical characterization**

Morphology of the sludge before and after the treatment of 4-chlorophenol containing wastewater and distribution of different elements in the sludge was studied using a scanning electron microscope (SEM) Quanta, Model 200 FEG, USA. Firstly, the samples were gold coated using Sputter Coater, Edwards S150, which basically provides conductivity to the samples, then the SEMs and energy dispersive X-ray (EDX) spectra were taken. Same was done to study the morphology of GAC before and after treatment with 4-chlorophenol.

#### **4.5.4 EDAX**

The qualitative elemental composition of the sludge before and after treatment with 4-chlorophenol was determined using an Energy Dispersive X-ray (EDAX) analyzer/Spectrometer (Model ECON-149-10, country). Firstly, the samples were eluted with milli-Q water until the electrical conductivity of the supernatant of these samples was almost equal to that of the milli-Q water. The scanning energy for the EDAX analysis ranged from 0-10 KeV with an elapsed time of 100 s. Same was done to study the elemental composition of GAC before and after treatment with 4-chlorophenol.

# CHAPTER V

## *RESULTS AND DISCUSSIONS*

---

### 5.1 Introduction

The performances of the sequential batch reactor (SBR) with and without granular activated carbon (GAC), hereby denoted as blank SBR and GAC-SBR respectively, for biodegradation of 4-chlorophenol were studied. Influent having different concentrations of 4-chlorophenol was used and contact-time study for these concentrations was performed. For the GAC-SBR, the dose of adsorbent was optimized for maximum removal of 4-chlorophenol. Cycle time, volume exchange ratio (VER) and hydraulic retention time (HRT) were optimized for both the SBR's. The removal efficiencies of the two reactors were compared at optimum conditions. A brief study of adsorptive removal of 4-chlorophenol using GAC was also made.

### 5.2 Treatment of 4-chlorophenol bearing wastewater using blank SBR

#### 5.2.1 Cycle time optimization

Total cycle time ( $T_C$ ) consists of fill ( $T_f$ ), react/aerate ( $T_r$ ), settle ( $T_s$ ) and decant ( $T_d$ ). An idle time ( $T_i$ ) can also be added. Thus, the total cycle time is given by:

$$T_C = T_f + T_r + T_s + T_d + T_i \quad (5.1)$$

As can be seen from the figure 5.1 (initial concentration of 4-chlorophenol = 100 mg/L), the removal of 4-chlorophenol almost stopped after 6 h. This point was the point of maximum removal of 4-chlorophenol and the removal obtained was about 75%. Hence, the optimum react time for the blank SBR was 6 h. Fill time for the reactor was 0 (instantaneous fill was used). Time given for settle phase, decant phase and idle phase were 40 min, 20 min and 60 min respectively. Hence the total cycle time for the reactor was calculated to be 8 h ie. 480 min.



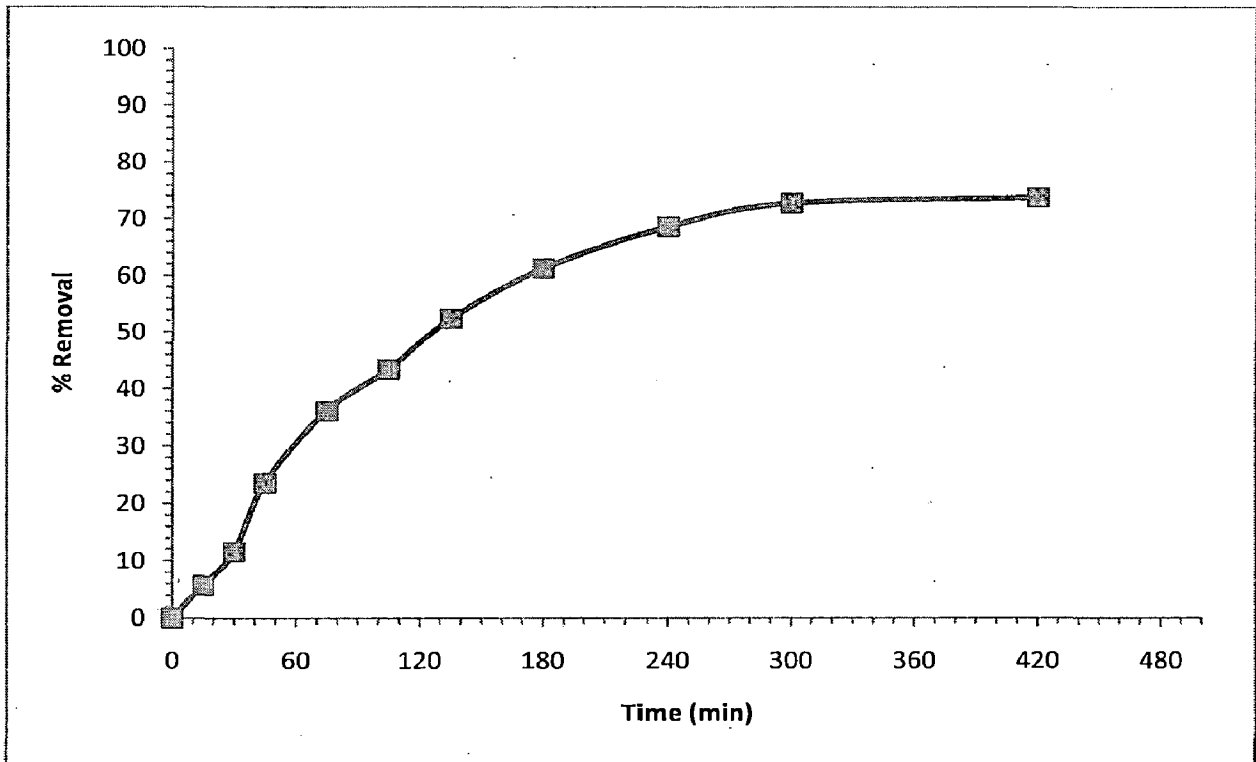


Fig. 5.1. % removal of 4-chlorophenol with time,  $C_0 = 100 \text{ mg/l}$ ,  $T = 30^\circ\text{C}$ ,  $\text{MLSS} = 3000 \text{ mg/L}$

### 5.2.2 Effect of VER and HRT

Different fill volumes were used to vary the VER of blank SBR. Values of VER were ranging from 0.2 to 0.7 as can be seen from table 5.1. Taking the value of  $T_c$  as 8 h, the values of HRT were ranging from 0.47 d to 1.67 d and values of percentage removal for each of these were recorded and the same were plotted against HRT as shown in figure 5.2. Hence the VER of SBR was optimized to 0.2 and HRT was optimized to 1.67 d. The initial concentration of 4-chlorophenol used for all these experiments was taken as 100 mg/L and these experiments were carried out at  $30^\circ\text{C}$ .

**Table 5.1. Removal efficiencies of blank SBR at different VER and SBR**

$V_t$	$V_{\text{sludge}}$	$V_f$	$\text{VER} = V_f/V_t$	$\text{HRT} = (1/\text{VER}) * (T_c/24)$	% removal
5	4	1	0.2	1.67	71.9
5	3.5	1.5	0.3	1.11	68.4
5	3	2	0.4	0.83	50.8
5	2.5	2.5	0.5	0.67	38.1
5	2	3	0.6	0.56	30.0
5	1.5	3.5	0.7	0.48	24.1

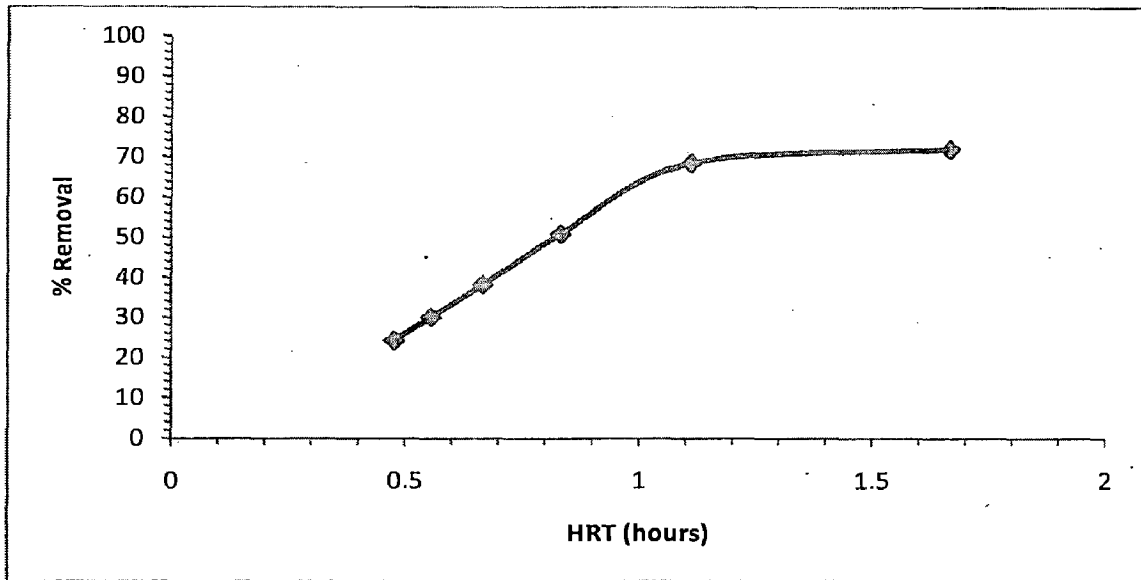


Fig. 5.2. % removal of 4-chlorophenol in blank SBR at different HRT,  $C_0 = 100 \text{ mg/l}$ ,  $T = 30^\circ\text{C}$ ,  $MLSS=3000 \text{ mg/L}$

### 5.2.3 Kinetic study and effect of initial concentration on removal of 4-chlorophenol using blank SBR

The removal efficiency also gets affected by variation in the initial 4-chlorophenol loading. So, in order to study the tolerance of 4-chlorophenol loading on blank SBR, the effect of varying initial concentration of 4-chlorophenol was studied. In this part of study, VER is kept constant at 0.2 and cycle time is fixed to 8 h. The effect of initial 4-chlorophenol loading on the performance of blank SBR was studied for different loading of 50, 100, 200, 250 and 350 mg/L. The removal efficiencies after the treatment in blank SBR with varying initial 4-chlorophenol loading are shown in figure 5.3. The results obtained from the experiment reflect that the highest removal efficiency achieved was almost 75% for initial 4-chlorophenol loading of 50 mg/L. With an increase in initial 4-chlorophenol loading, the removal efficiency decreased and the blank SBR failed to work for initial 4-chlorophenol loading of 200 mg/L or more. The removal efficiency achieved for initial 4-chlorophenol loading of 350 mg/L was merely 20.5 %. Figure 5.4 shows the contact-time data for the removal efficiency of blank SBR for three different values of initial 4-chlorophenol loading. Removal of 4-chlorophenol using blank-SBR was found to follow second order kinetics. The values of constants for were calculated and these values are shown in table 5.2 along with the regression coefficients,  $R^2$  and MPSD (Marquardt's percent standard deviation) [Ho et al., 2001].

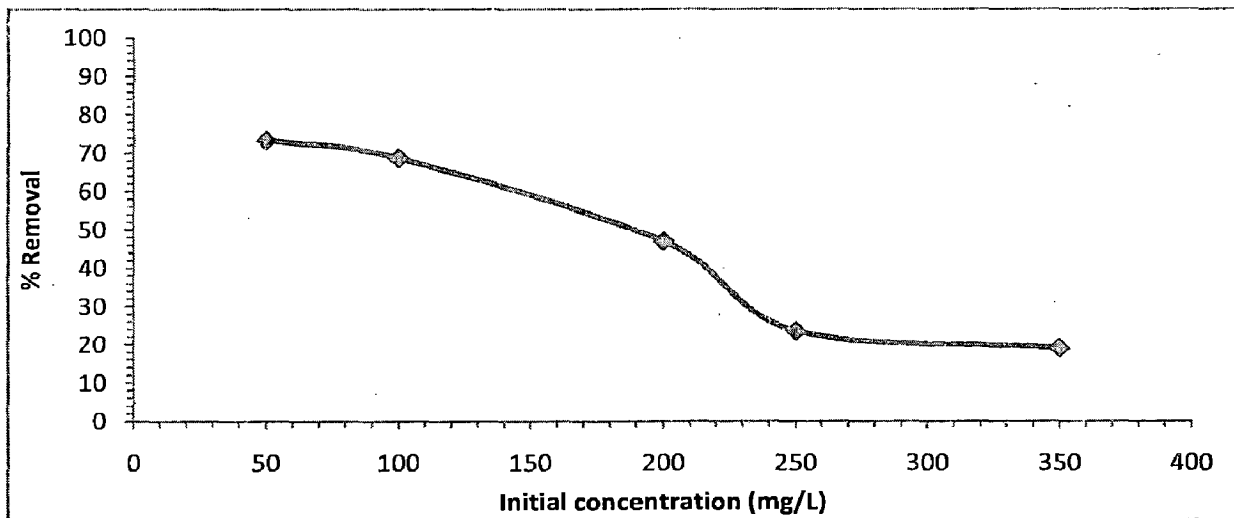


Fig. 5.3. % removal of 4-chlorophenol at different initial concentrations of 4-chlorophenol in blank SBR,  $T = 30^{\circ}\text{C}$ , natural pH,  $VER = 0.2$ ,  $MLSS = 3000 \text{ mg/L}$

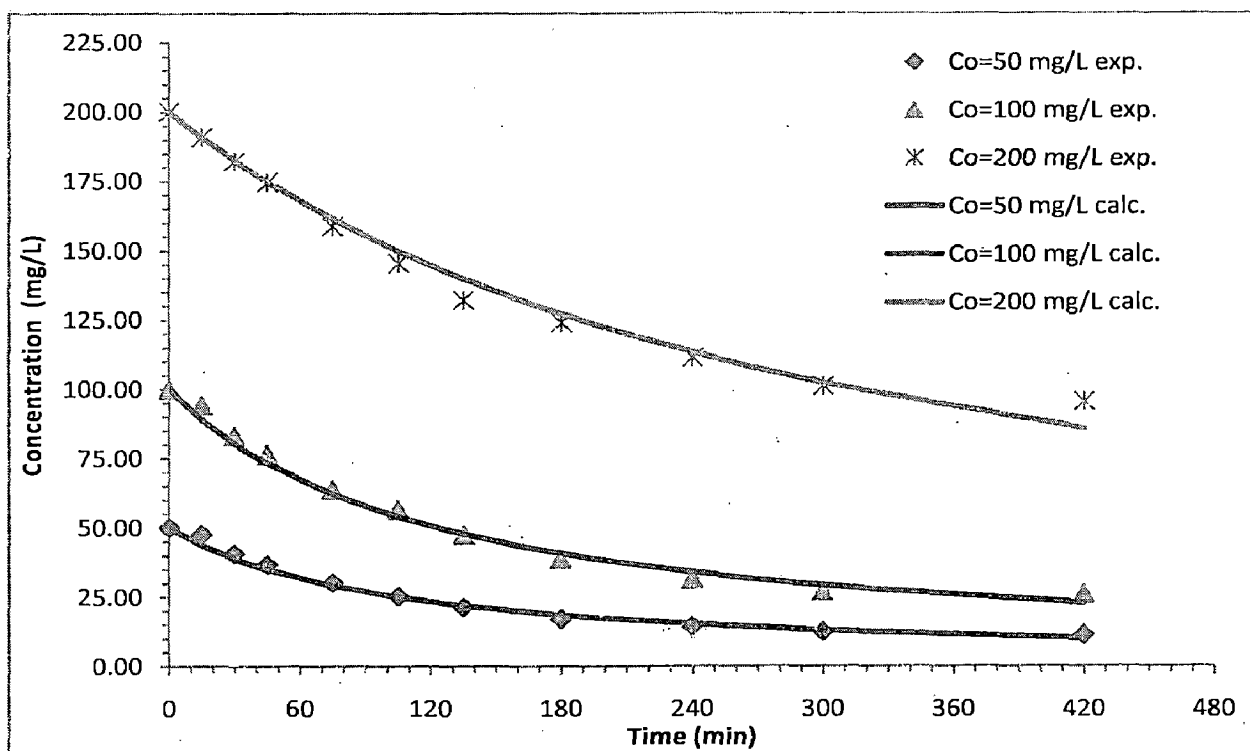


Fig. 5.4. Contact-time data for removal of 4-chlorophenol for different initial concentrations of 4-chlorophenol in blank SBR,  $T = 30^{\circ}\text{C}$ , natural pH,  $VER = 0.2$ ,  $MLSS = 3000 \text{ mg/L}$

Table 5.2. Kinetic parameters values for the removal of 4-chlorophenol by blank SBR

Initial concentration (mg/L)	k	n	$R^2$	MPSD
50	$1.92 \times 10^{-4}$	2	0.992989	6.136448
100	$8.11 \times 10^{-5}$	2	0.993145	6.029485
200	$1.59 \times 10^{-5}$	2	0.984576	3.87297

## 5.3 Treatment of 4-chlorophenol using adsorption

### 5.3.1 Selection of Adsorbent

Various adsorbents were tested for their adsorption efficiency towards 4-chlorophenol using batch experiments. For all the experiments, the initial concentration of 4-chlorophenol used was 200 mg/L. All the experiments were carried out at natural pH. The adsorption was carried out in 100 ml flasks containing 50 mL of 4-chlorophenol solution of desired concentration. The agitating speed of the shaker was 150 rpm and temperature was 30<sup>0</sup>C and the experiments were carried out for 6 h. Figure 5.5 shows the relative adsorption capacity of Rice Husk Ash (RHA), Bagasse Fly Ash (BFA), GAC and activated alumina for 4-chlorophenol. GAC and BFA showed similar removal efficiencies of about 98% but GAC was selected for further study as it could be easily separated from sludge when used in SBR whereas BFA got dissolved in the SBR-sludge and it could not be separated.

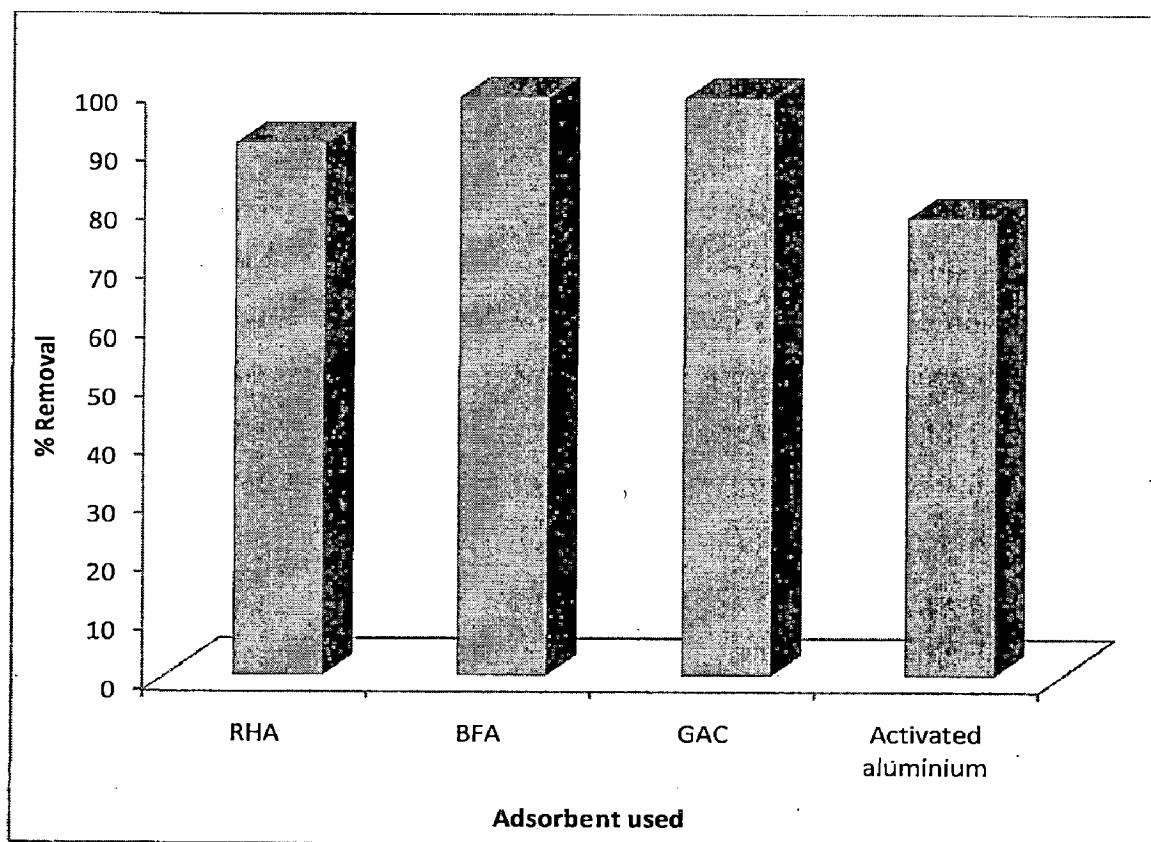


Fig. 5.5. Removal of 4-chlorophenol by different adsorbents  $T = 30^{\circ}\text{C}$ , natural pH,  $C_0 = 200 \text{ mg/L}$

### 5.3.2 Effect of adsorbent dosage

Adsorption of 4-chlorophenol was carried out at different doses of GAC. It was observed that the removal efficiency of 4-chlorophenol increased with an increase in adsorbent dose. This trend was followed up to 20 g/L of adsorbent and beyond that the removal efficiency attained a constant value which means increasing the adsorbent dose further did not increase the removal efficiency. Hence the adsorbent dose was optimized to 20 g/L. All the experiments were carried out at 30<sup>0</sup>C and natural pH conditions. Figure 5.6 represents the removal efficiencies at various doses of adsorbent.

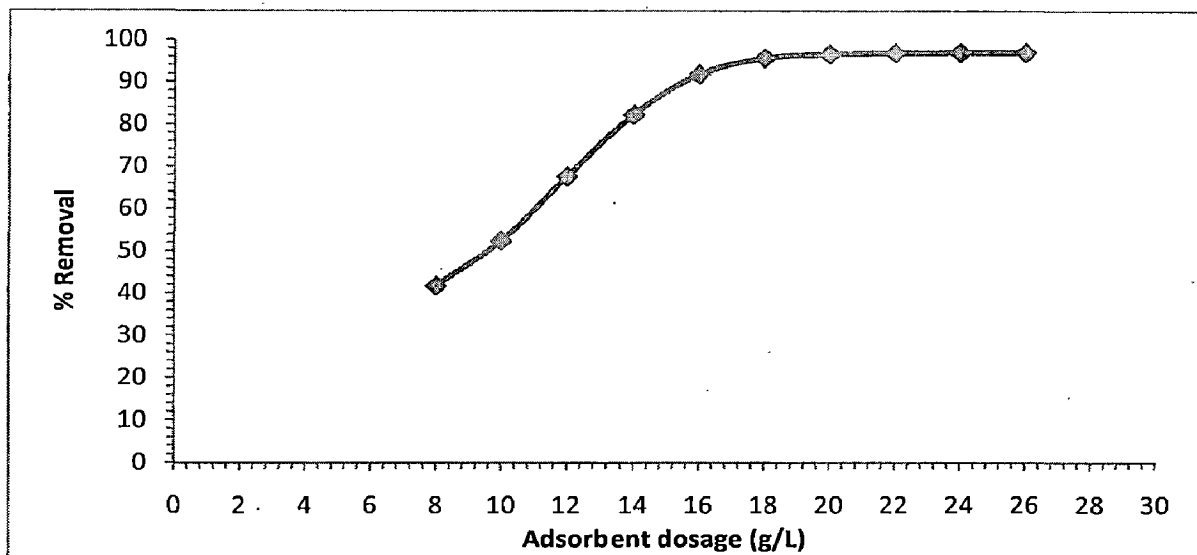


Fig 5.6. Removal of 4-chlorophenol at different adsorbents dosages  $T = 30^{\circ}\text{C}$ , natural pH,  $C_0 = 200$  mg/L

### 5.3.3 Effect of pH

To study the effect of pH over adsorption of 4-chlorophenol, solutions of various pH were prepared using buffer solutions and experiments were carried out at 30<sup>0</sup>C and 150 rpm shaker speed. Adsorbent dose was fixed to 20g/L and the initial concentration of 4-chlorophenol for all the experiments was 200 mg/L. The pH of the solutions taken in consideration were 2, 4, 6, 6.5 (natural pH), 7 (neutral), 8, 10. It was observed that removal efficiency of 4-chlorophenol was almost same in acidic region and it decreased as the medium of solution turned basic. Natural pH of the solution is found to be 6.5 (slightly acidic), hence the further study is done at natural pH of 4-chlorophenol solution. Figure 5.7 shows the adsorptive removal efficiency of 4-

chlorophenol at different pH conditions. The justification for this trend comes from the fact that GAC is slightly negatively charged. At higher pH values of the solution, 4-chlorophenol dissociates to liberate anions which are repelled by the negatively charged GAC and hence the adsorption capacity of GAC decreases at higher pH. While in acidic medium, 4-chlorophenol does not liberate  $H^+$  ions and anions, resulting in their adsorption on the surface of GAC [Hameed et al., 2008].

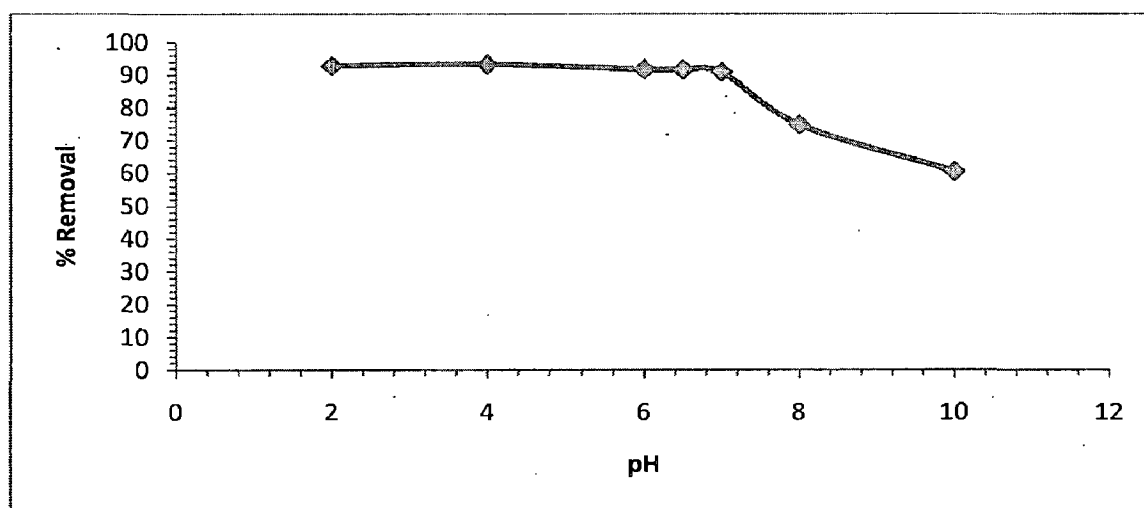


Fig 5.7. Removal of 4-chlorophenol at different pH  $T = 30^{\circ}C$ ,  $C_o = 200 \text{ mg/L}$

### 5.3.4 Kinetic study and effect of initial concentration on adsorptive removal of 4-chlorophenol

Initial 4-chlorophenol loading also affects the adsorptive removal efficiency. In this part of study, adsorbent dose was kept constant at 20 mg/L and natural pH of 4-chlorophenol solution was used. The effect of initial 4-chlorophenol concentration was studied for different loading of 100, 200, 300, 500, 800, 1200 mg/L. The results obtained from the experiment show that the highest removal efficiency achieved was 97% for initial 4-chlorophenol concentration of 100 mg/L. With an increase in initial 4-chlorophenol concentration, the removal efficiency decreased the removal efficiency achieved for initial 4-chlorophenol concentration of 1200 mg/L was merely 40%. Figure 5.8 shows time data of the adsorptive removal efficiency for various values initial 4-chlorophenol concentration while figure 5.9 shows the plot between  $q_t$  and time, where  $q_t$  is the amount of adsorbate adsorbed at time  $t$  (mg/g) for three different values of initial 4-chlorophenol loading. Removal of 4-chlorophenol using adsorption was found to follow first

order kinetics. The values of constants for were calculated and these values are shown in table 5.3 along with the regression coefficients,  $R^2$  and MPSD.

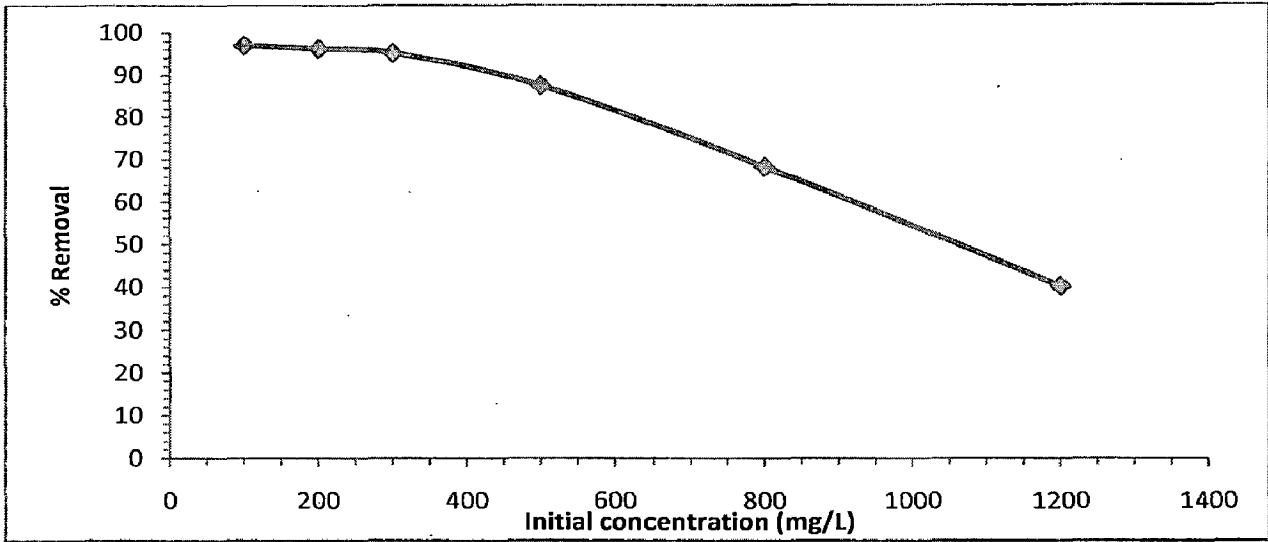


Fig. 5.8. % removal of 4-chlorophenol at different initial concentrations of 4-chlorophenol  $T = 30^{\circ}C$ , natural pH

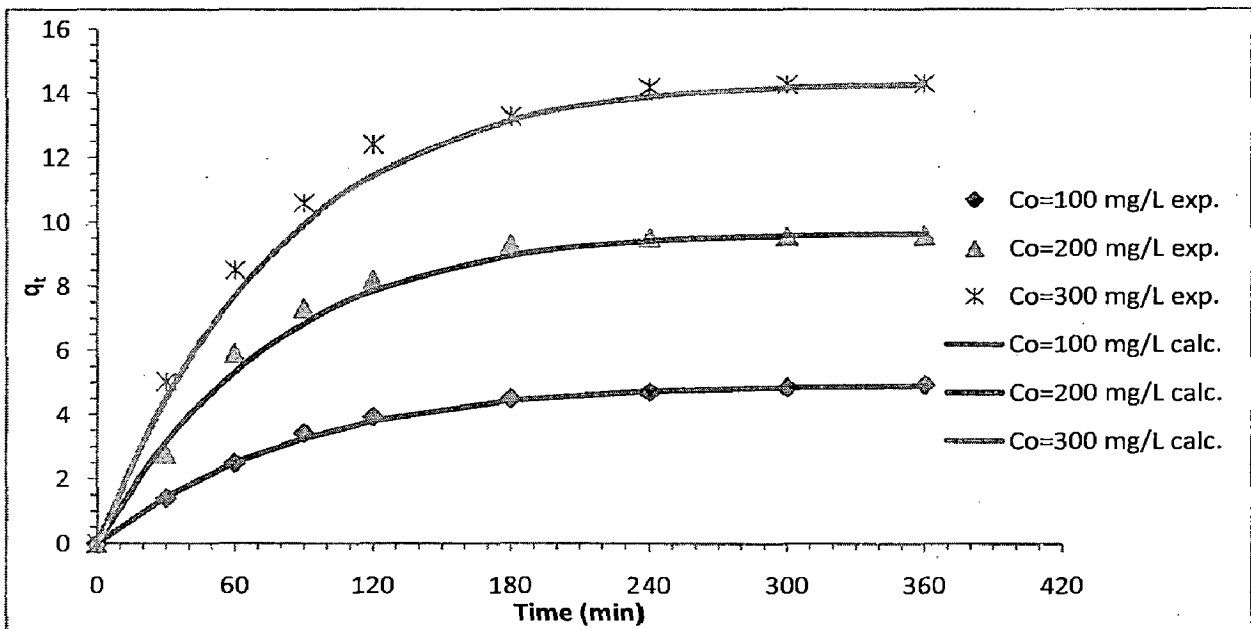


Fig. 5.9. Contact-time data for the % removal of 4-chlorophenol at different initial concentrations of 4-chlorophenol,  $T = 30^{\circ}C$ , natural pH

Table 5.3. Kinetic parameters values for the adsorptive removal of 4-chlorophenol

Initial concentration (mg/L)	k	n	$R^2$	MPSD
100	0.011941	1	0.9978699	192.3769
200	0.015168	1	0.9938864	278.5608
300	0.014606	1	0.9987675	339.4972

### 5.3.5 Study of adsorption isotherms

Freundlich isotherm, Langmuir isotherm and Redlich-Peterson isotherm were used for the adsorption study. Figure 5.10 shows the plot between  $q_e$  and  $C_e$ . The values of constants for all the isotherms were calculated and these values are shown in table 5.4. The equilibrium adsorption data for adsorption of 4-chlorophenol on GAC was best represented by Langmuir and Redlich-Peterson isotherms with  $R^2$  values of 0.9961 and 0.9963 respectively.

The single-component Langmuir constant,  $q_m$ , is the monolayer saturation at equilibrium and the other single-component Langmuir constant,  $K_L$ , corresponds to the concentration at which the amount of 4-chlorophenol bound to the GAC is equal to  $q_m/2$ . This indicates the affinity of the 4-chlorophenol molecules to bind with GAC. A low  $K_L$  value indicates a lower affinity and hence a weak bonding of 4-chlorophenol molecules to GAC.  $K_F$  and  $n$ , the single-component Freundlich isotherm constants, indicate the adsorption capacity and adsorption intensity, respectively. Higher the value of  $n$ , the higher will be the affinity and the heterogeneity of the adsorbent sites. Since  $n > 1$ ; 4-chlorophenol molecules are not favorably adsorbed by RHA. For favorable adsorption, the Redlich-Peterson constant,  $\beta$  normally lies between 0 and 1.

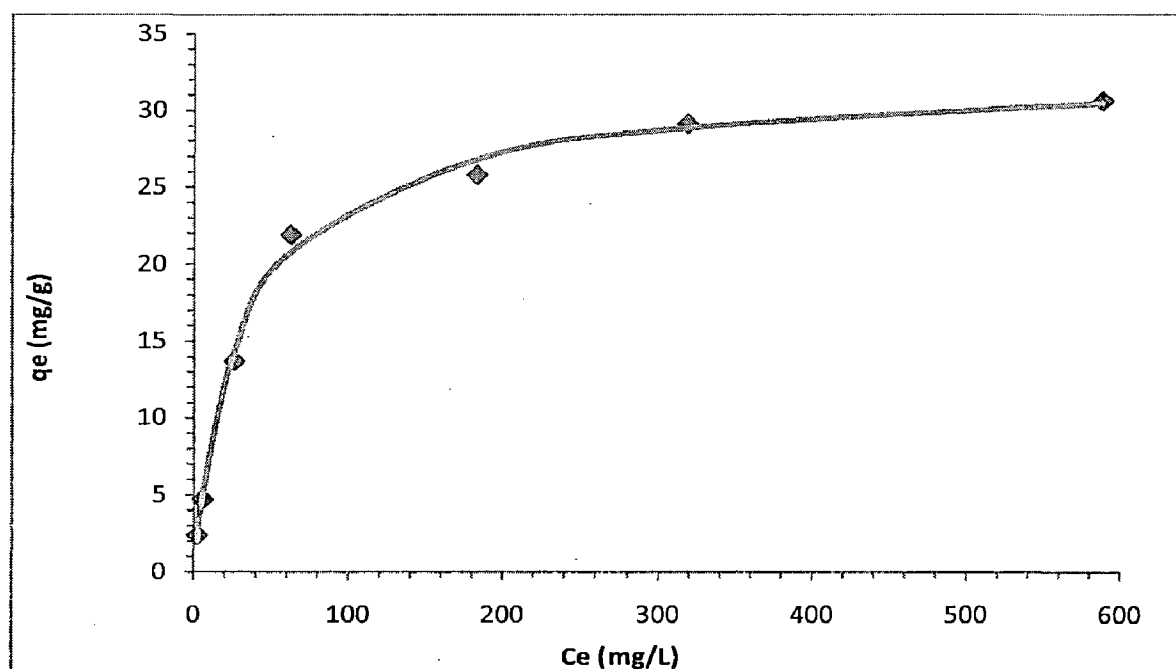


Fig. 5.10  $q_e$  v/s  $C_e$  plot for adsorption of 4-chlorophenol,  $T = 30^\circ\text{C}$ , natural pH,  $T_C = 5$  h



**Table 5.4. Isotherm parameters values for the removal of 4-chlorophenol by GAC**

Langmuir constants				
$K_L$ (L/mmol)	$q_m$ (mmol/g)	$R^2$	SSE	
0.031	31.81	0.9961	3.196	
Freundlich isotherm				
$K_F$	n	$R^2$	SSE	
4.97	0.33	0.9244	64.381	
Redlich-Peterson Isotherm				
$K_R$	$\alpha_R$	$\beta$	$R^2$	SSE
1.064	0.039	0.974	0.9963	2.92

## 5.4 Treatment of 4-chlorophenol bearing wastewater using GAC-SBR (SBR with adsorbent)

### 5.4.1 Effect of adsorbent dose in SBR

The setup of SBR was made to work in a similar way with the exception that a certain amount of adsorbent was added to the influents of SBR in each cycle. This adsorbent was completely removed from SBR using sieves. The adsorbent used was GAC. Various amounts of GAC were added to SBR during each cycle and the removal efficiency for each of the cycle was recorded. The initial concentration of 4-chlorophenol used for each experiment was 500 mg/L. All the experiments were done at 30°C and at natural pH. Time given for each cycle was 8 h which allowed 6 h of react period. It was observed that as the adsorbent dose was increased, the removal efficiency of SBR also increased. As it can be seen from figure 5.11, this trend continued up to a dose of 16 g/L of adsorbent and beyond this the removal efficiency of SBR became almost constant. Hence, the adsorbent dose was optimized to 16 g/L for the SBR loaded with GAC as adsorbent and 4-chlorophenol as pollutant.

### 5.4.2 Cycle time optimization

As can be seen from the figure 5.12 (initial concentration of 4-chlorophenol = 100 mg/L), the removal of chlorophenols almost stopped after 4 h. Hence the optimum react time for the GAC-SBR was 4 h. Fill time for the reactor was 0 (Instantaneous fill). Times given for settling, decanting and idle phase were 40 min, 20 min and 60 min respectively. Hence the total cycle time for the GAC-SBR was calculated to be 6 h i.e. 360 min.

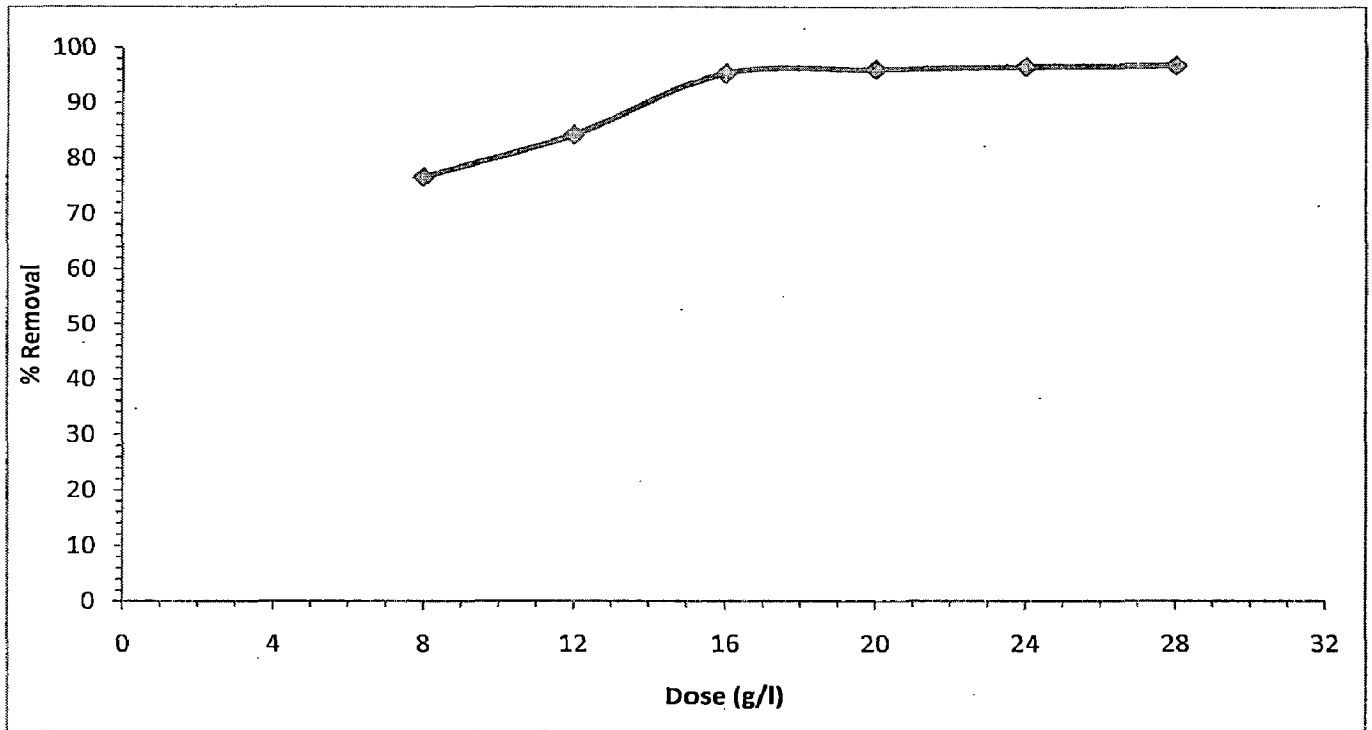


Fig. 5.11. % removal of 4-chlorophenol at different doses of GAC in GAC-SBR  $C_0 = 500$  mg/l,  $T = 30^\circ\text{C}$ , natural pH, MLSS = 3000 mg/L

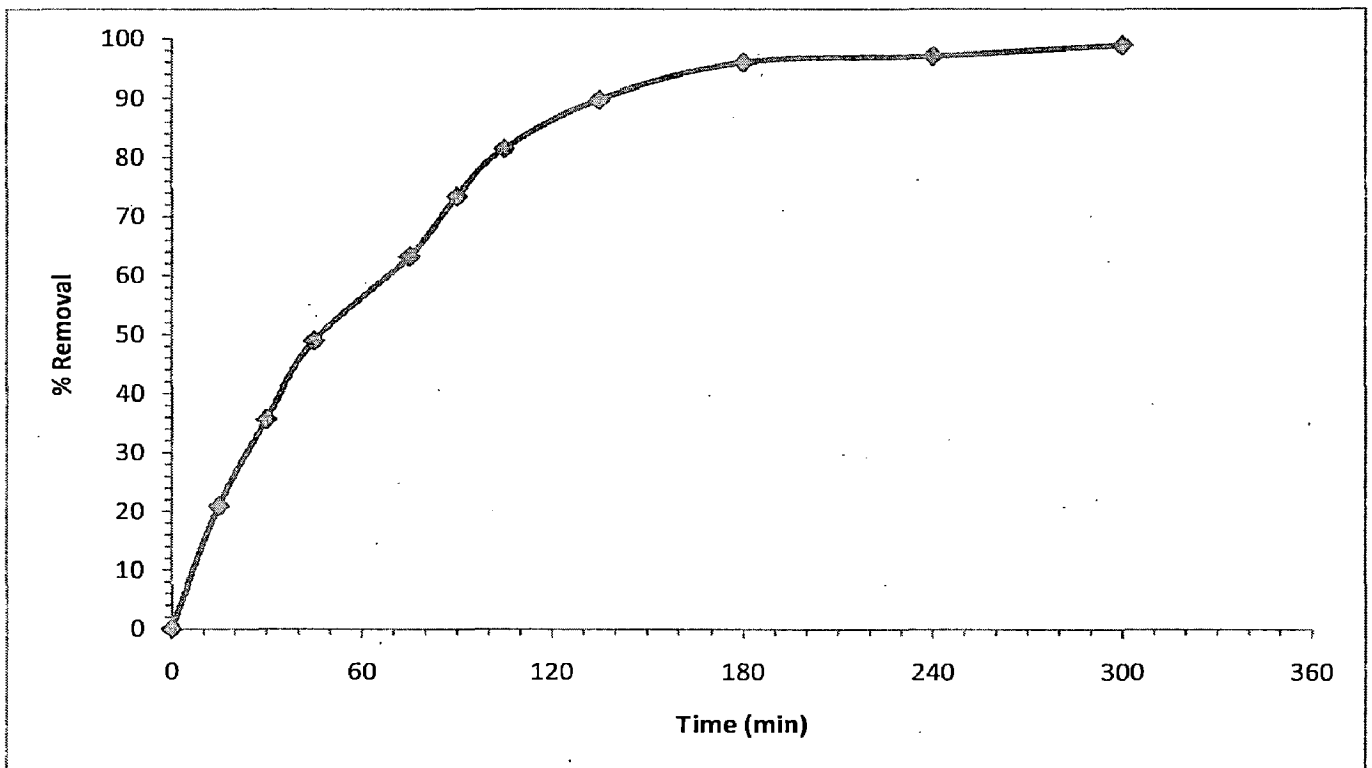


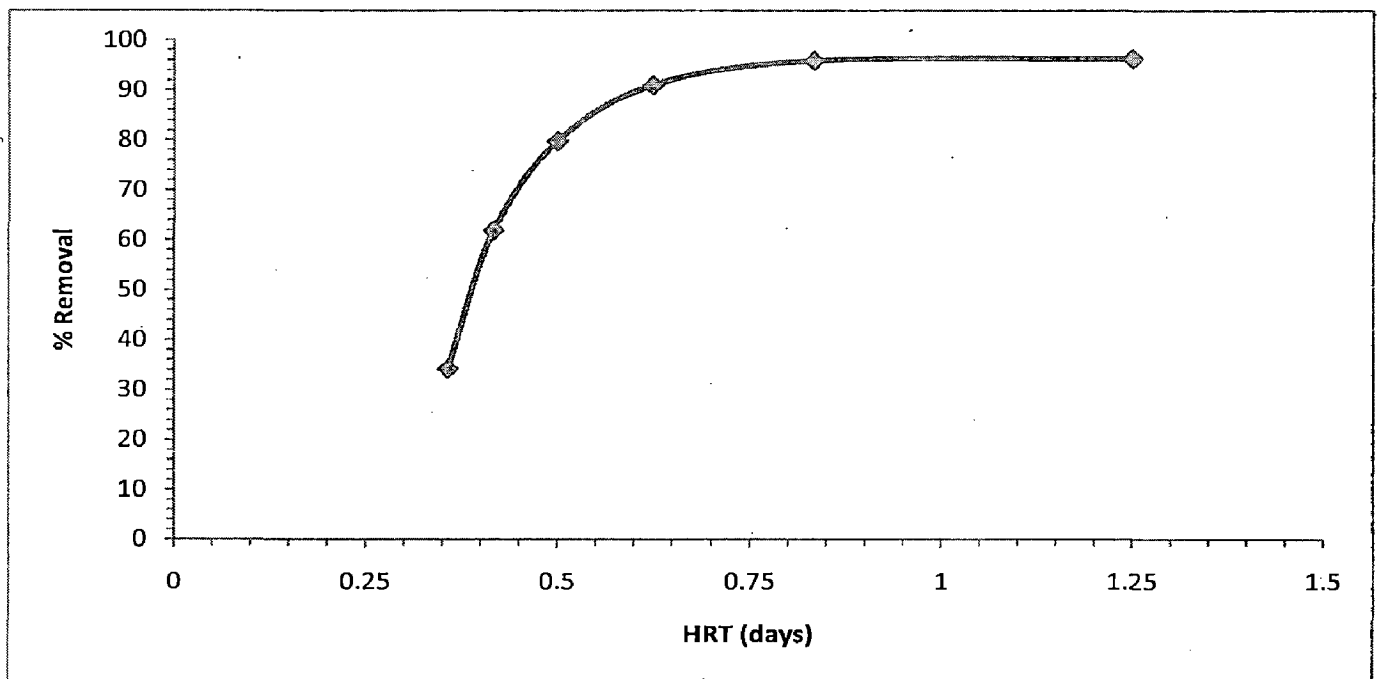
Fig. 5.12. % removal of 4-chlorophenol with time in GAC-SBR,  $C_0 = 500$  mg/l,  $T = 30^\circ\text{C}$ , natural pH, MLSS = 3000 mg/L

### 5.4.3 Effect of VER and HRT

Different fill volumes were used to vary the VER of SBR as was done in section 5.2.2. Values of VER were ranging from 0.2 to 0.7 as can be seen from table 5.5. Taking the value of  $T_c$  as 6 h, the values of HRT were ranging from 0.35 d to 1.25 d and values of percentage removal for each of these were recorded and the same were plotted against HRT as shown in figure 5.13. Hence the VER of SBR was optimized to 0.2 and HRT was optimized to 1.25 d. The initial concentration of 4-chlorophenol used for all these experiments was taken as 500 mg/L and these experiments were carried out at 30°C.

**Table 5.5. Removal efficiencies of SBR at different VER and HRT**

$V_t$	$V_{\text{sludge}}$	$V_f$	$VER = V_f/V_t$	$HRT = (1/VER) * (T_c/24)$	% removal
5	4	1	0.2	1.25	96.11
5	3.5	1.5	0.3	0.83	95.74
5	3	2	0.4	0.625	90.85
5	2.5	2.5	0.5	0.5	79.63
5	2	3	0.6	0.42	61.75
5	1.5	3.5	0.7	0.36	34.12



*Fig. 5.13. % removal of 4-chlorophenol at different values of HRT in GAC-SBR,  $C_0 = 500$  mg/l,  $T = 30^\circ\text{C}$ , natural pH, MLSS = 3000 mg/L*

#### 5.4.4 Kinetic study and effect of initial concentration on removal of 4-chlorophenol using GAC-SBR

The effect of initial concentration of 4-chlorophenol on SBR (GAC-SBR) was studied in a similar way as it was done in section 5.2.3. Fixing the cycle time to 6 h, VER value to 0.2 and adsorbent dosage to 16 g/L the effect of initial 4-chlorophenol loading on the performance of SBR was studied for different loading of 200, 500, 750, 1000, 1250 and 1500 mg/L.

The removal efficiencies after the treatment in GAC-SBR with varying 4-chlorophenol loading are shown in figure 5.14. The results obtained from the experiment show that the highest removal efficiency achieved was about 98% for initial 4-chlorophenol loading of 200 mg/L. With an increase in initial 4-chlorophenol loading, the removal efficiency achieved for initial 4-chlorophenol loading of 1500 mg/L was merely 52 %. Figure 5.15 shows the contact-time data for the removal efficiency of GAC- SBR for three different values of initial 4-chlorophenol loading. Removal of 4-chlorophenol using GAC-SBR was found to follow first order kinetics. The values of constants for were calculated and these values are shown in table 5.6 along with the regression coefficients,  $R^2$  and MPSD.

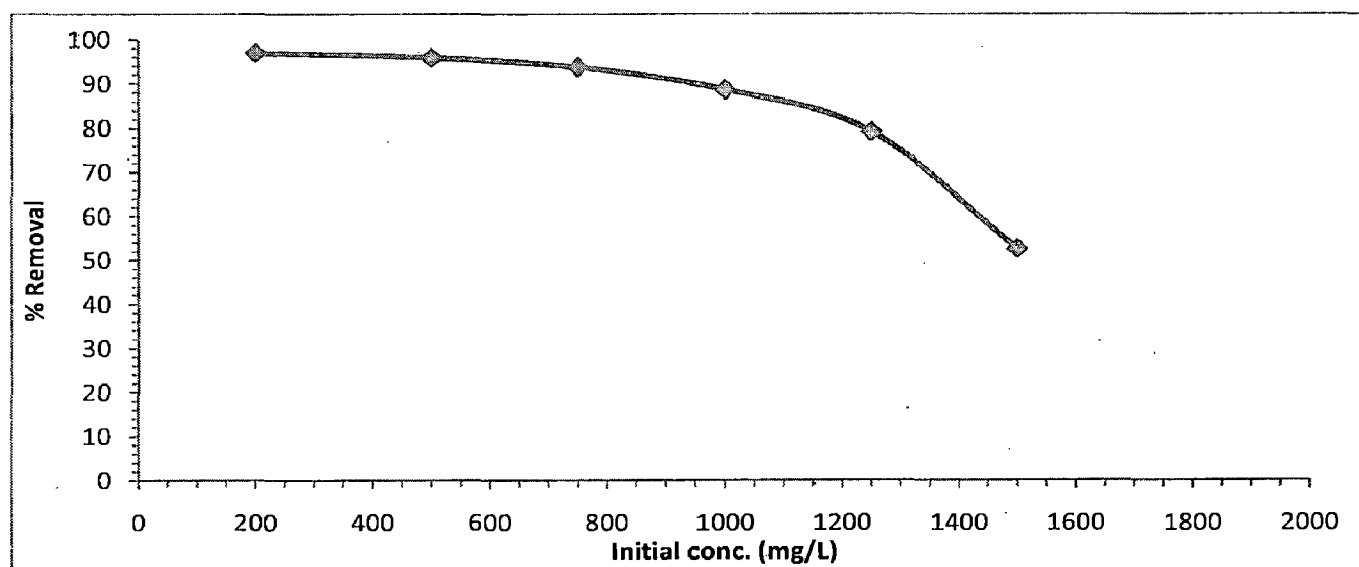


Fig. 5.14. % removal of 4-chlorophenol at different initial concentrations of 4-chlorophenol in GAC-SBR,  $T = 30^{\circ}\text{C}$ , natural pH, VER = 0.2, MLSS = 3000 mg/L

Table 5.6. Kinetic parameters values for the adsorptive removal of 4-chlorophenol

Initial concentration (mg/L)	k	n	$R^2$	MPSD
500	0.015824	1	0.995569	18.56086
750	0.012546	1	0.995978	19.65712
1000	0.009927	1	0.989602	19.57886

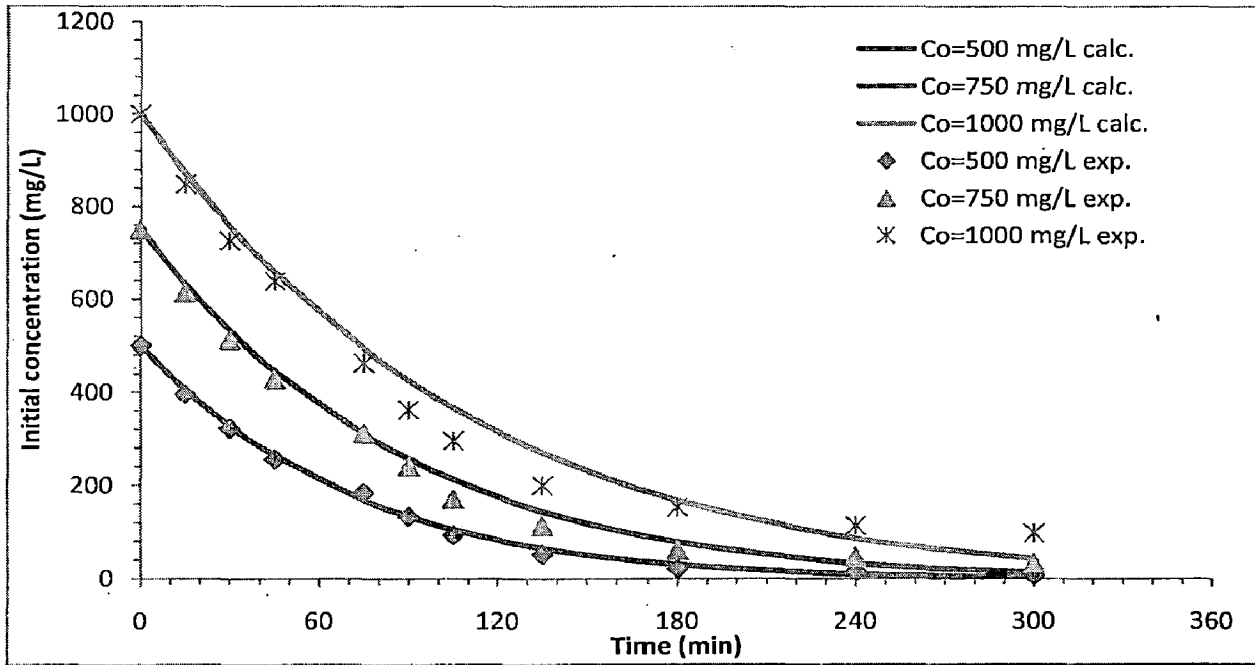


Fig. 5.15. Contact-time data for removal of 4-chlorophenol for different initial concentrations of 4-chlorophenol in GAC-SBR,  $T = 30^{\circ}\text{C}$ , natural pH,  $VER = 0.2$ ,  $MLSS = 3000 \text{ mg/L}$

## 5.5 Study on sludge

The liquid-solid suspension of SBR was mixed and the resultant was tested for its various characteristics like SVI, settling and filterability characteristics.

### 5.5.1 Calculation of sludge retention time (SRT) and sludge wasting rate (SWR)

SRT is the time the sludge takes to pass through the system. SRT for the two SBR systems (blank SBR and GAC-SBR) were calculated using the following equations:

$$SRT = \frac{V_T * X_R * 24}{SWR * T_C * X_{SS}} \quad (5.2)$$

where,  $V_T$  is the total working volume of reactor (L),  $X_R$  is MLSS after react phase (mg/L),  $X_{SS}$  is MLSS of settled sludge (mg/L),  $T_C$  is time of cycle (h) and SWR is Sludge wasting rate (L/cycle). SWR can be calculated using the formula:

$$SWR = \frac{(X_R - X_{initial})}{X_{SS}} * V_T \quad (5.3)$$

where,  $X_{initial}$  is MLSS at the start of react phase .Putting the formula for SWR in the formula for SRT, we get,

$$SRT = \frac{X_R}{X_R - X_{initial}} * \frac{T_C}{24} \quad (5.4)$$

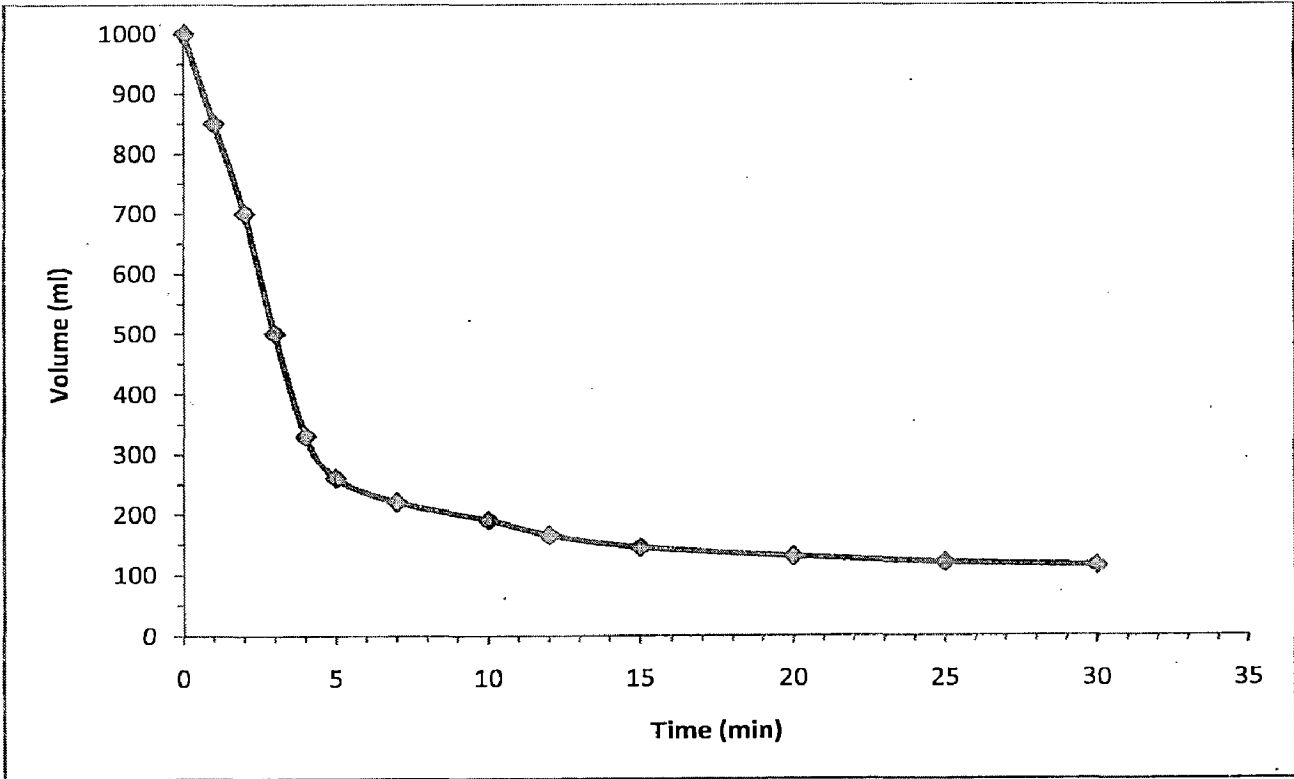
here,  $T_C$  is time of one cycle in hours. Value of  $X_{initial}$  was kept constant at 3000 mg/L by wasting the desired amount of sludge from the reactor from time to time. Values of  $X_R$  and  $X_{SS}$  were observed daily for 7 days after each cycle and this value was observed to be around 3100 mg/L and 8350 mg/L. Using the value of  $T_C$  as 8 h for blank SBR (section 5.2.1) and 6 h for GAC-SBR (section 5.4.2) the values of SRT were calculated to be 10.3 days and 7.75 days for blank SBR and GAC-SBR respectively. Value of SWR was calculated to be 60 mL per cycle (same for both the SBR's as value of SWR does not depend on  $T_C$ ).

### 5.5.2 Settling and sludge volume index (SVI)

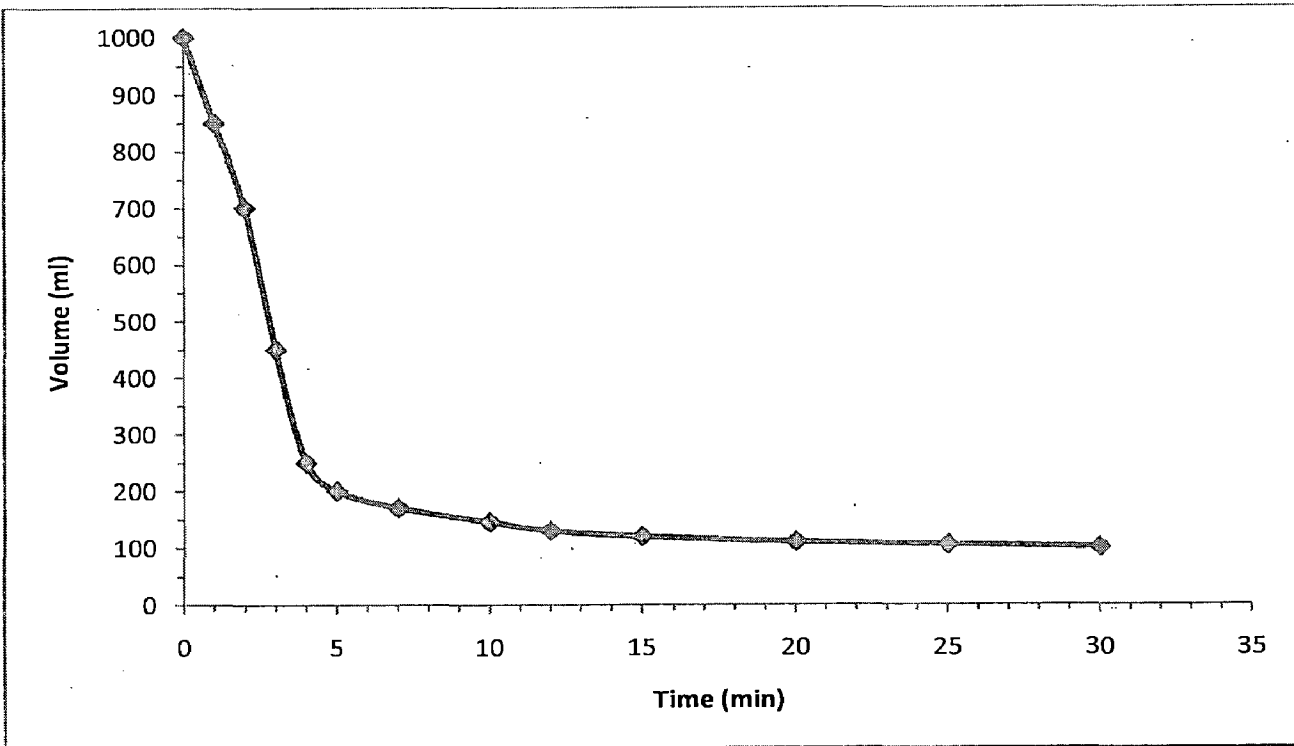
Figure 5.16 and figure 5.17 show the height of the solid-liquid interface as the function of settling time during the settling of sludge for activated sludge (before acclimatization) and acclimatized sludge respectively. The SVI was calculated from the following relation:

$$SVI \text{ (mL/g)} = \frac{\text{Volume of settled sludge after 30 min (mL/L)} * 1000(\text{mg/g})}{MLSS(\text{mg/L})} \quad (5.5)$$

Volume of settled sludge before and after acclimatization was found to be 115 mL and 100 mL respectively. MLSS was fixed to 3000 mg/L. By calculation, it was observed that settling of the sludge improves with time and sludge volume index (SVI) of the sludge was decreased from 38.33mL/g to 33.33mL/g. Sludge having  $SVI < 100$  is considered to be well settling sludge; for  $100 < SVI < 200$ , sludge is considered to be light sludge; and for  $SVI > 200$ , sludge is considered to be bulky in nature [Sharma et al., 2010]. Hence for the present case, sludge was found to be well settling sludge.



*Fig 5.16. Settling curve of sludge before acclimatization*



*Fig 5.17. Settling curve of sludge after acclimatization*

### 5.5.3 Filterability

The following force balance equation was used for calculation:

$$\frac{\Delta t}{\Delta V} = \frac{\mu}{A\Delta P} \left( \frac{\alpha CV}{A} + R_m \right) \quad (5.6)$$

where,  $\Delta t$  is the time interval of filtration (s),  $\Delta V$  is the filtrate volume collected in  $\Delta t$  time interval ( $m^3$ ),  $\alpha$  is the specific cake resistance,  $\mu$  is viscosity of the filtrate (Pa.s),  $C$  is the MLSS concentration in the slurry,  $A$  is the filtration area ( $m^2$ ),  $R_m$  is the resistance of the filter medium ( $m^{-1}$ ), and  $\Delta P$  is the pressure drop across the filter (Pa) [Sharma et al., 2011]. In the filterability study the volume of filtrate collected in a very thin and long graduated vertical cylinder was recorded at regular time interval neglecting the filtrate volume obtained in the first 1 min and value of  $\alpha$  and  $R_m$  was calculated from the  $dt/dV$  versus  $V$  plot (not shown here). For MLSS concentration of  $3.00 \text{ kg/m}^3$ , viscosity of  $0.959 \text{ cP}$  and density of  $1025 \text{ kg/m}^3$ , the values of  $\alpha$  and  $R_m$  were  $3.6 \times 10^{10}$  and  $2.298 \times 10^{11}$  respectively. Figure 5.18 simply shows the amount of filtered volume collected against time.

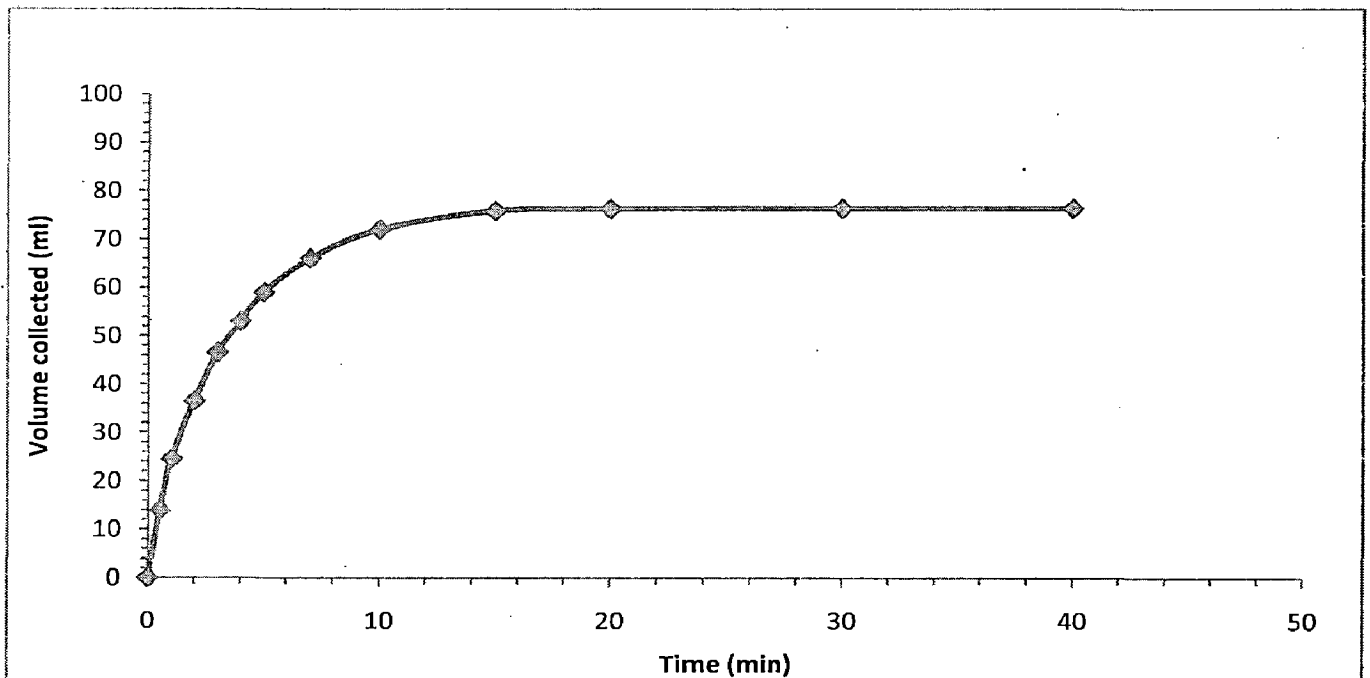


Fig 5.18. Filterability of sludge

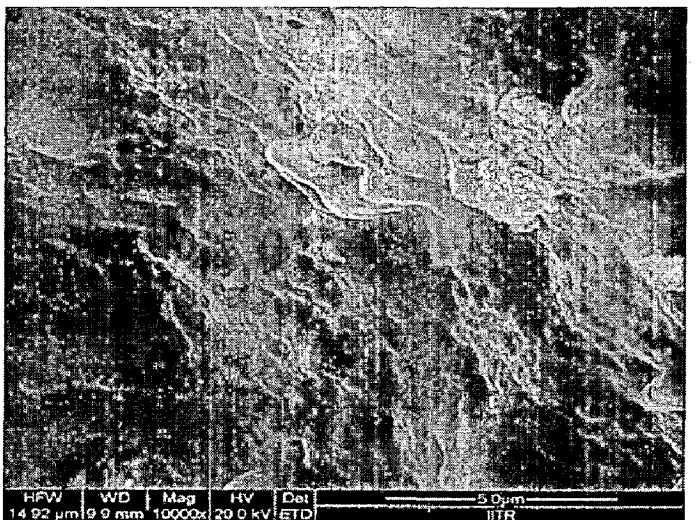
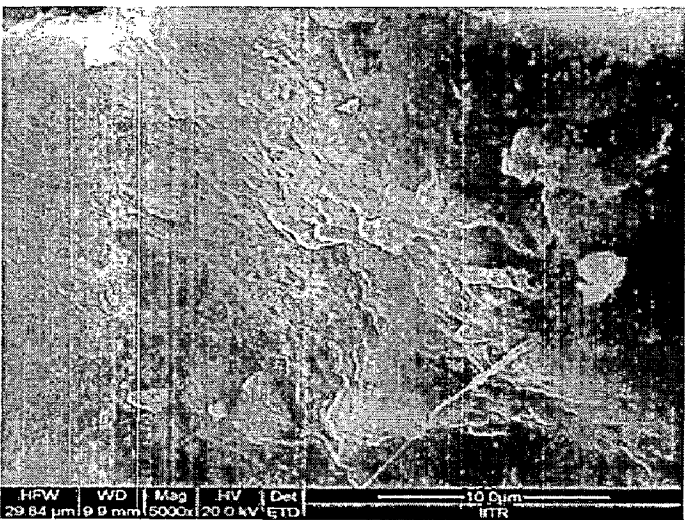
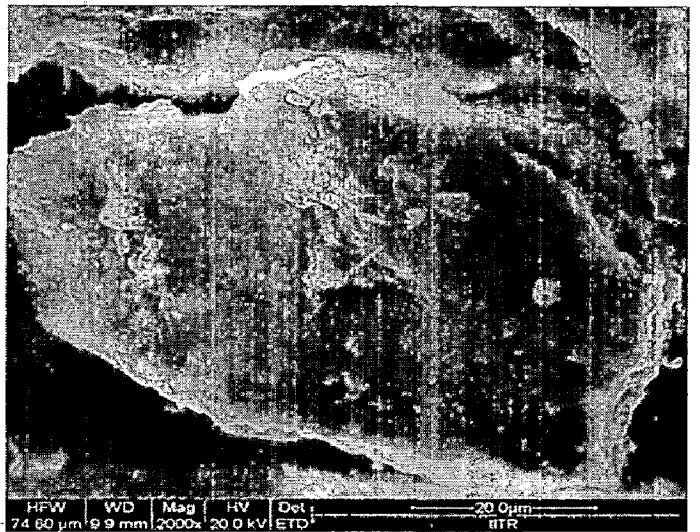
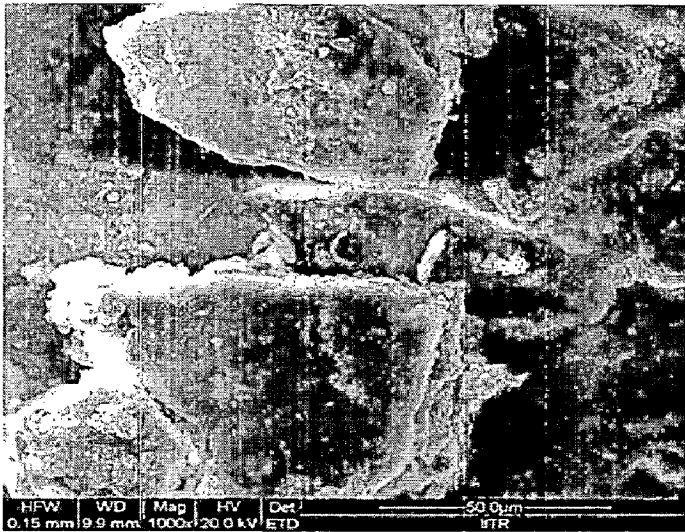
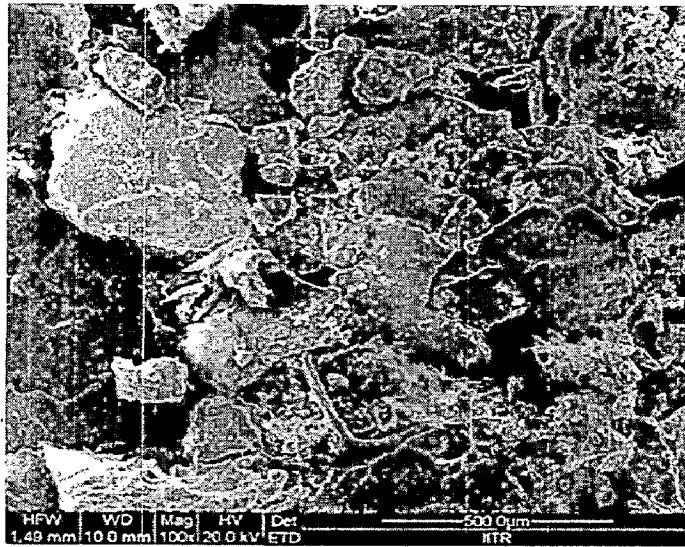


### 5.5.4 SEM and EDX analysis

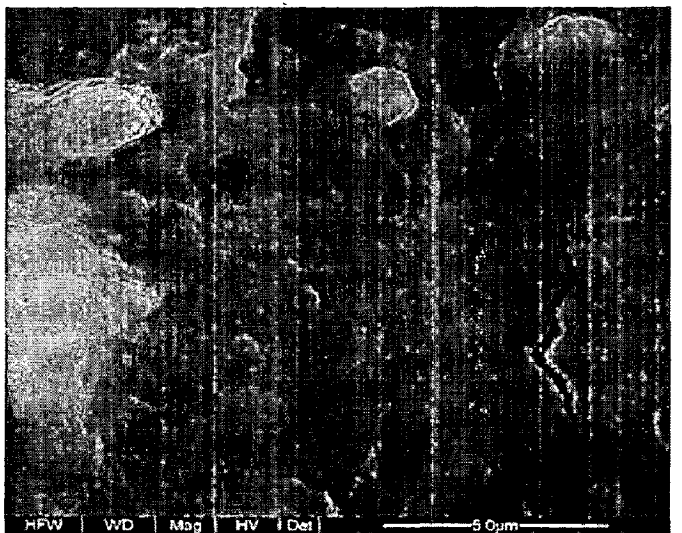
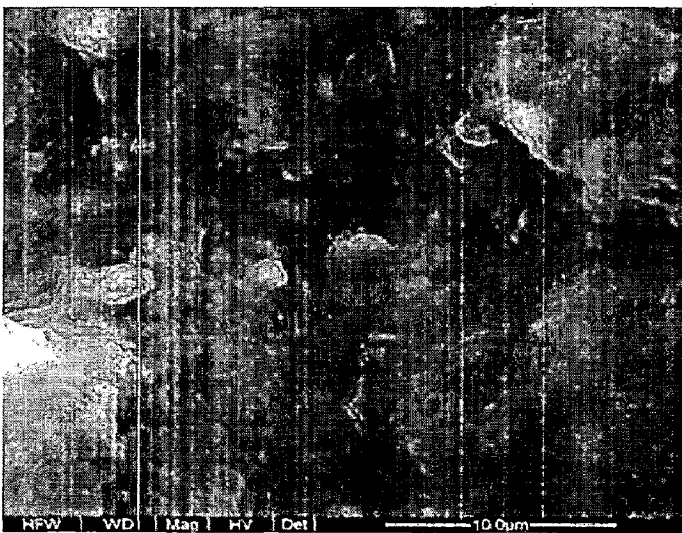
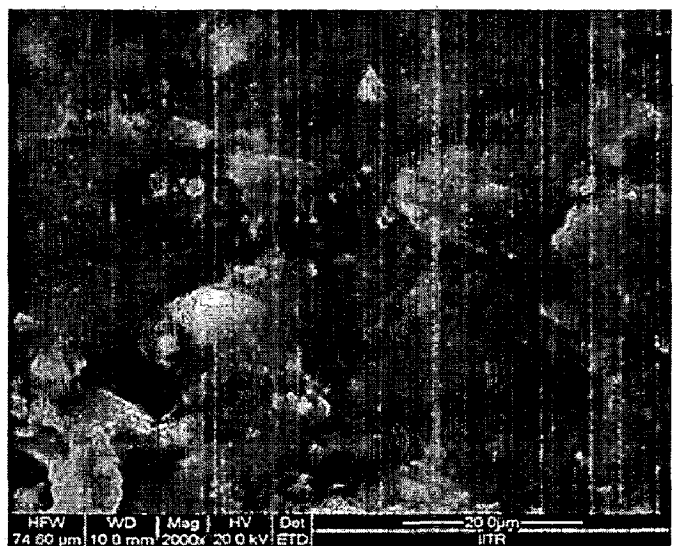
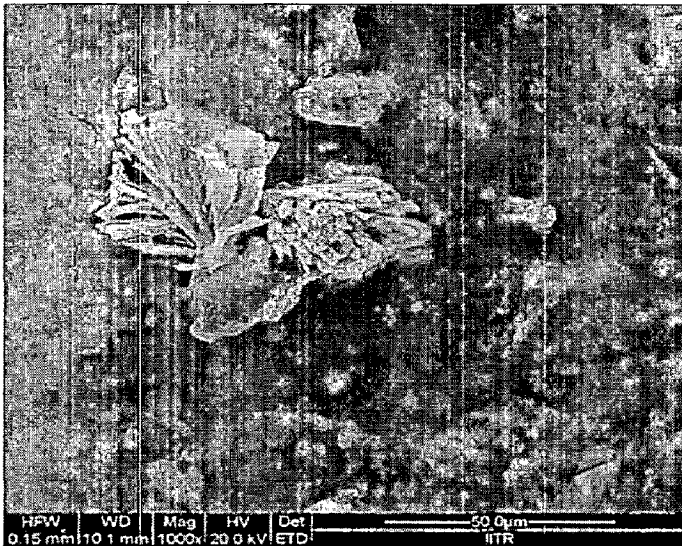
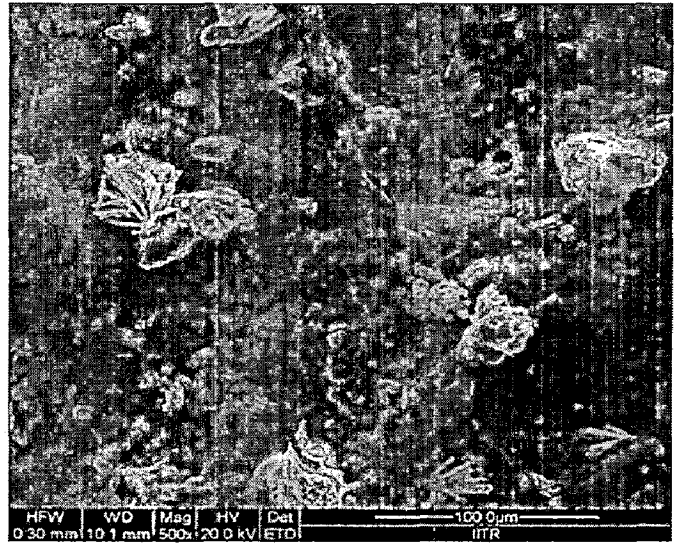
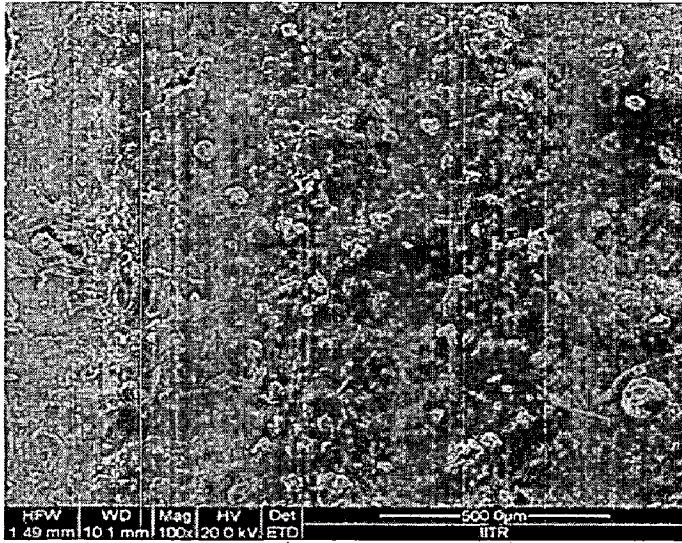
The SEM's of the non acclimatized and acclimatized sludge are shown in figure 5.19 and 5.20 respectively. The texture surface of sludge before and after treatment is revealed by these figures. The elemental composition of sludge was determined using EDX analyzer. Activated sludge mainly contained carbon and oxygen. The relative weight percentage of elements in non-acclimatized sludge and acclimatized sludge are presented in table 5.7. Figure 5.21 displays the EDX spectra of non-acclimatized sludge while figure 5.22 displays the EDX spectra of acclimatized sludge. Both of these were found to contain about 63% of carbon and 16% of oxygen by weight. The amounts of phosphorus and chlorine changed significantly. Also there were deposits of phosphorus found on the surface. Metals like sodium, potassium, magnesium, aluminum, calcium and iron were found in traces.

**Table 5.7. Relative % of elements in non-acclimatized and acclimatized sludge**

Element	Non-acclimatized sludge		Acclimatized sludge	
	Wt %	At %	Wt %	At %
C	63.89	76.17	63.16	76.39
O	16.46	14.74	15.67	14.23
Na	00.53	00.33	01.44	00.91
Mg	00.81	00.48	00.32	00.19
Al	02.51	01.33	01.55	00.83
Si	07.81	03.98	03.05	01.58
P	01.96	00.90	03.69	01.73
S	01.04	00.46	01.00	00.46
Cl	00.38	00.15	04.04	01.66
K	01.28	00.47	00.64	00.24
Ca	01.23	00.44	03.63	01.32
Fe	02.11	00.54	01.80	00.47



*Fig 5.19. SEM of sludge before acclimatization*



*Fig 5.20. SEM of sludge after acclimatization*

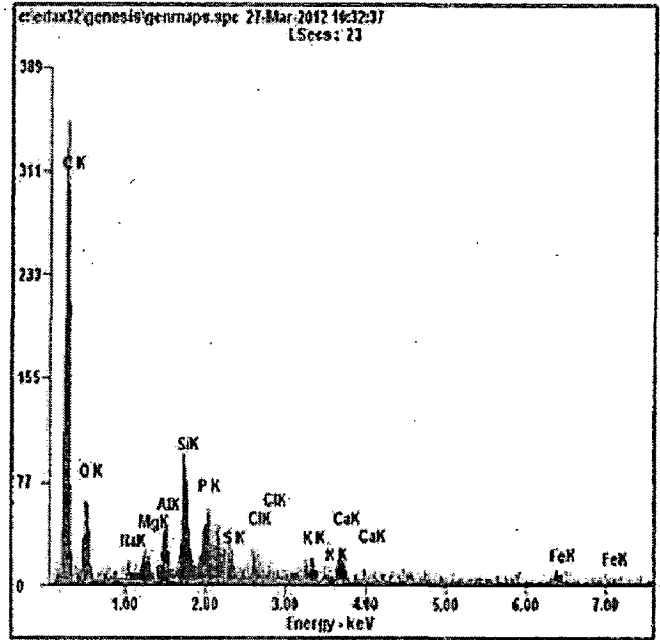
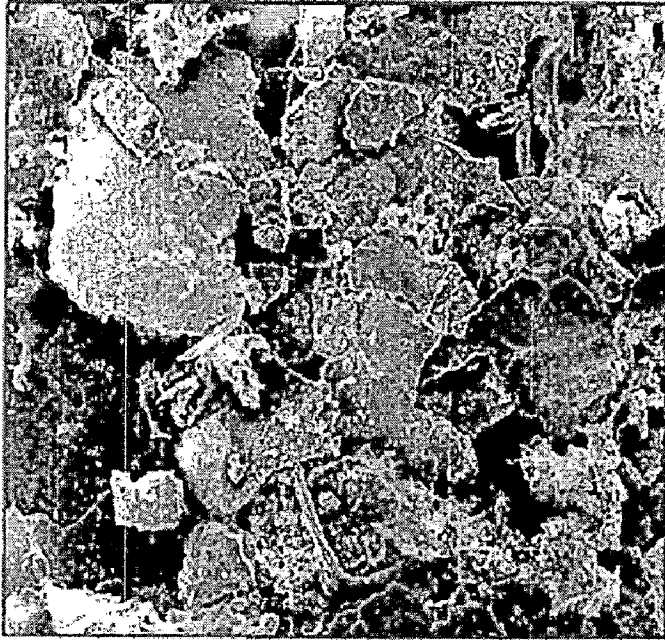


Fig 5.21. EDX of non-acclimatized sludge

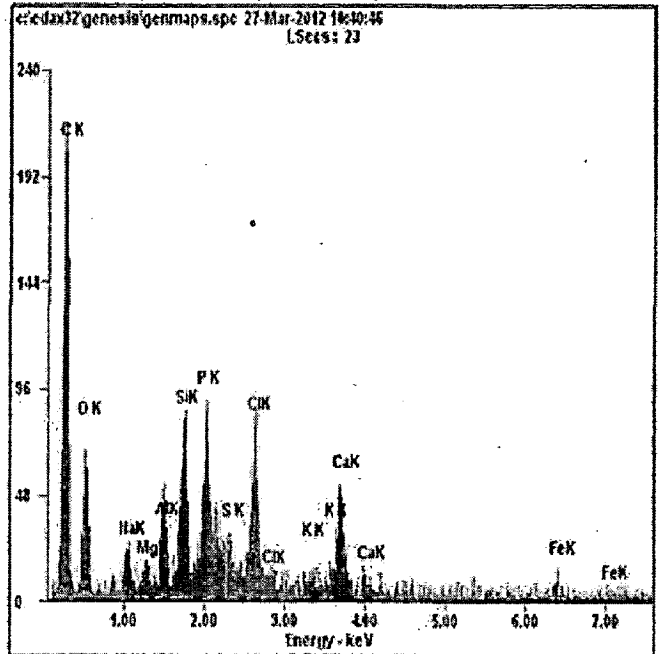
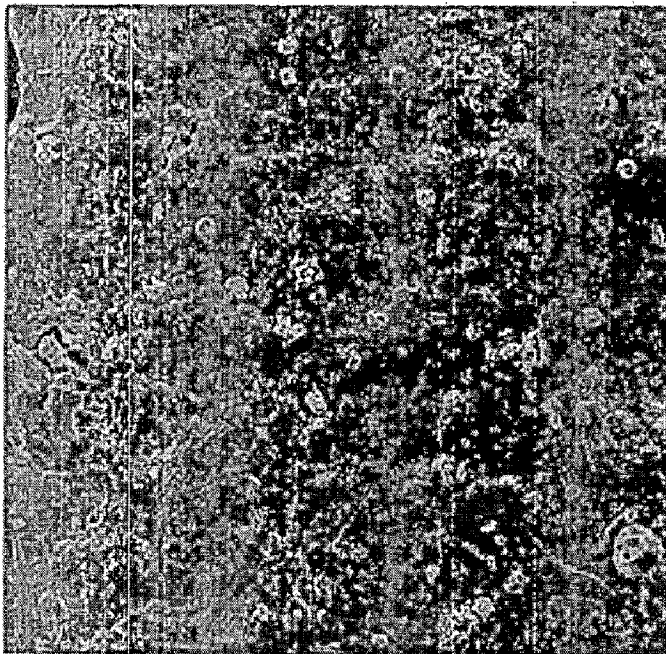


Fig 5.22. EDX of acclimatized sludge

## 5.6 Study on adsorbent

### 5.6.1 BET surface area analysis

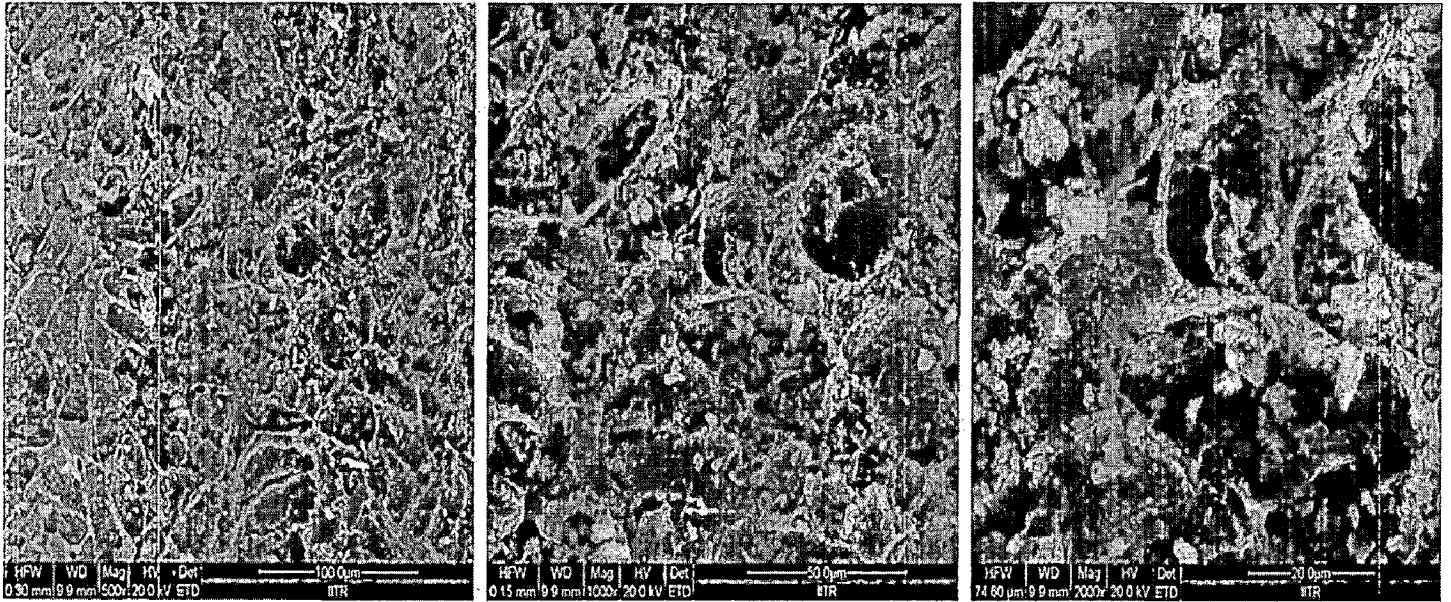
The BET surface area of GAC was found to be 137.4693 m<sup>2</sup>/g. Barrett, Joyner and Halenda (BJH) adsorption/desorption surface area of pores was 45.487/25.3814 m<sup>2</sup>/g in GAC. For GAC the single point total pore volume was found to be 0.082946 cm<sup>3</sup>/g. The cumulative BJH adsorption/desorption pore volume of pores (17 Å < d < 3000 Å) was obtained as 0.035819/0.015281 cm<sup>3</sup>/g in GAC.

### 5.6.2 SEM and EDX analysis

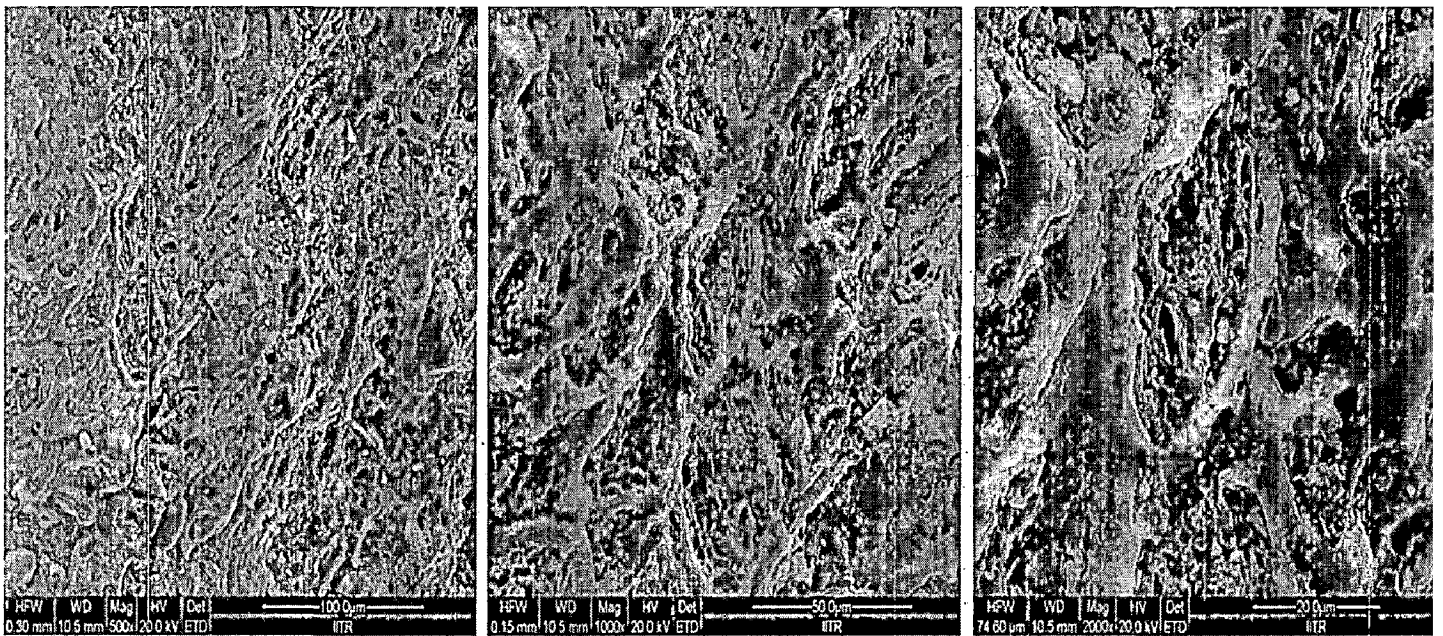
The SEM's of the GAC before and after treatment with 4-chlorophenol are shown in figure 5.23 and 5.24 respectively. The texture surface of the adsorbent before and after treatment is revealed by these figures. It was observed that porosity of the adsorbent decreased after the treatment with wastewater as active sites were covered by the anions of 4-chlorophenol. The elemental composition of adsorbent was determined using EDX analyzer. As expected, GAC analysis showed a carbon peak with very high relative percentage of carbon. GAC contained 91% carbon before treatment and 85% carbon after treatment. The amount of Chlorine changed significantly after treatment. Initially, no chlorine was present in GAC, but after treatment, the % of chlorine increased to 4% which must be due to the deposition of 4-chlorophenol anions on the surface of GAC. Nitrogen and oxygen were found to be present in reasonable amounts. Traces of sodium, aluminum and sulfur were present. The relative weight percentage of elements in non-treated and treated GAC are presented in table 5.8. Figure 5.25 displays the EDX spectra of non-treated GAC while figure 5.26 displays the EDX spectra of treated GAC.

**Table 5.8. Relative % of elements in non-treated and treated GAC**

Element	Non-treated GAC		Treated GAC	
	Wt %	At %	Wt %	At %
C	90.90	93.20	84.89	90.64
N	02.70	02.37	02.45	02.25
O	04.81	03.70	05.05	04.05
Na	00.38	00.20	00.25	00.14
Mg	-	-	00.42	00.22
Al	00.79	00.36	00.49	00.23
Si	-	-	01.55	00.71
S	00.43	00.16	00.30	00.12
Cl	-	-	04.04	01.46
K	-	-	00.56	00.18



*Fig 5.23. SEM of GAC before treatment*



*Fig 5.24. SEM of GAC after treatment*

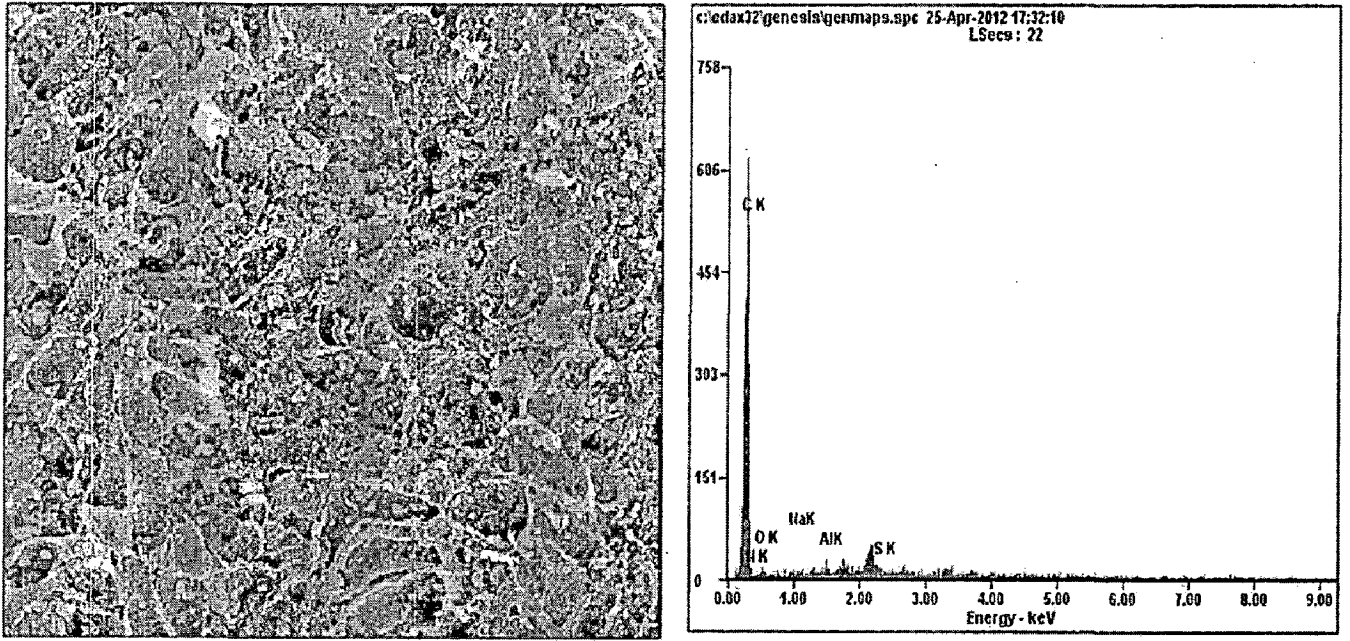


Fig 5.25. EDX of non-treated GAC

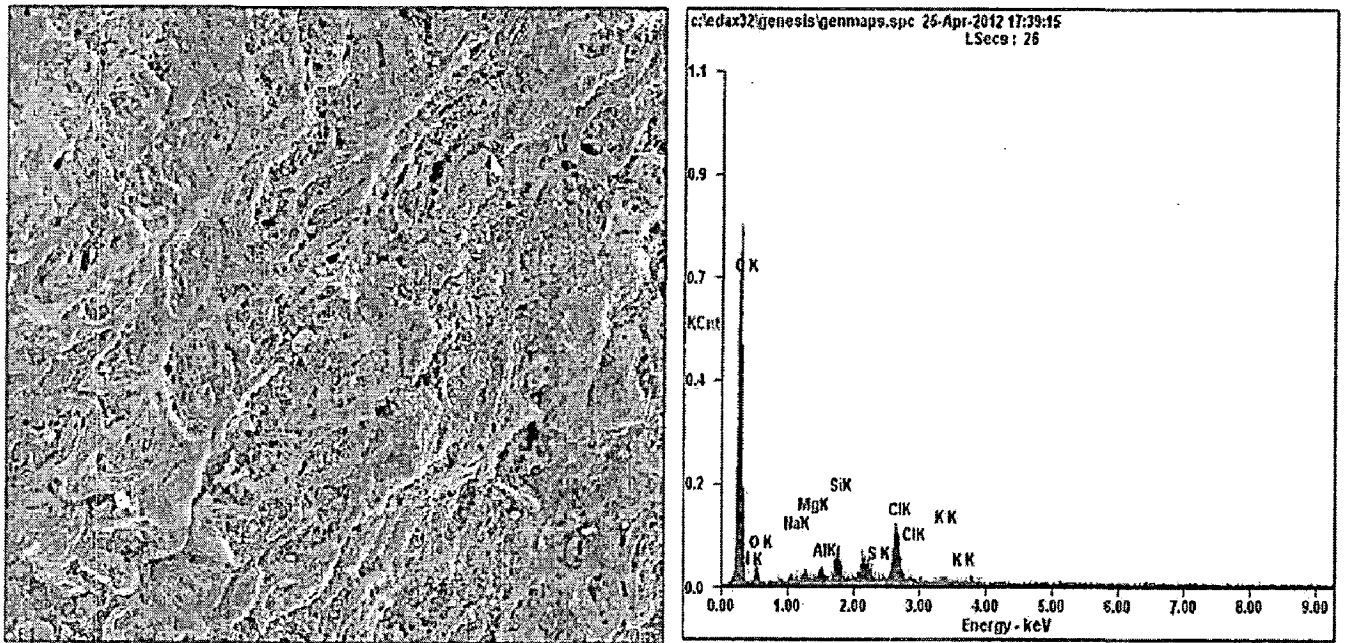


Fig 5.26. EDX of treated GAC

## **CHAPTER VI**

### **CONCLUSIONS AND RECOMMENDATIONS**

---

#### **6.1 Conclusions**

In the present study, the performance of two SBR's, one without adsorbent (blank SBR) and one with adsorbent (GAC-SBR) were compared in terms of percentage removal of 4-chlorophenol and their tolerance for shock loading. A brief study was made on removal of 4-chlorophenol using adsorption on GAC. Following conclusions can be made from the present study:

##### **6.1.1 Conclusions on adsorption of 4-chlorophenol**

A brief study was made on removal of 4-chlorophenol using adsorption. GAC was observed to be the best adsorbent for the treatment of 4-chlorophenol. Removal efficiency of 4-chlorophenol increased with an increase in adsorbent dose up to 20 g/L of adsorbent, after which the removal efficiency became almost constant. Hence, 20 g/L was decided to be the optimum adsorbent dose and was used for the present study. The removal efficiency of 4-chlorophenol remained almost constant at different pH's in acidic medium; however, it decreased significantly with an increase in basicity of the medium. Natural pH of 4-chlorophenol was found to be 6.5 which is slightly acidic and hence optimum for adsorptive removal of 4-chlorophenol. The adsorptive removal efficiency of 4-chlorophenol decreased with an increase in its initial concentration. For an initial concentration of 100 mg/L, the removal efficiency was about 97% which decreased to merely 40% for an initial concentration of 1200 mg/L. Adsorption of 4-chlorophenol using GAC followed first order kinetics. In addition, Langmuir isotherm and Redlich-Peterson isotherm represented a better fit of experimental data than the Freundlich isotherm.

##### **6.1.2 Comparison of two SBR's**

The performance of two types of SBR's (blank SBR and GAC-SBR) was compared. GAC-SBR was observed to be a better choice for 4-chlorophenol removal in almost every aspect. By addition of GAC, the cycle time of SBR decreased from 8 h to 6 h, hence more



wastewater can be treated in the same time by this improvisation in SBR. Also, due to a change in cycle time the SRT decreased from 10.3 d to 7.75 d. However, same amount of sludge (60 mL) was withdrawn from both the SBR's after every cycle. The maximum removal efficiency for SBR was increased from 73% to 97% by the addition of GAC in SBR, also, GAC-SBR could treat wastewater with 1250 mg/L of initial concentration of 4-chlorophenol as compared to just 200 mg/L for blank SBR. In addition, the tolerance for shock loading was increased by the addition of GAC. However, for both the SBR's the removal efficiency decreased with an increase in initial concentration of 4-chlorophenol. The VER for both the SBR's was optimized at 0.2, however, due to a decrease in cycle time, the HRT decreases from 1.67 days to 1.25 days after addition of GAC. 16 g/L of fresh GAC was added to GAC-SBR at the beginning of each cycle and removed at the end of the cycle. Blank SBR followed second order kinetics for removal of 4-chlorophenol while GAC-SBR followed second order kinetics for the same. The performance comparison of blank SBR and GAC-SBR has been shown in table 6.1.

**Table 6.1. Performance comparison of blank SBR and GAC-SBR**

Parameter	Blank SBR	GAC-SBR
Cycle time (hours)	8	6
VER	0.2	0.2
HRT (days)	1.67	1.25
SRT (days)	10.3	7.75
SWR (mL/cycle)	60	60
Maximum removal efficiency	73% ( $C_0 = 50$ mg/L)	97% ( $C_0 = 200$ mg/L)
	67% ( $C_0 = 100$ mg/L)	96% ( $C_0 = 500$ mg/L)
	45% ( $C_0 = 200$ mg/L)	94% ( $C_0 = 750$ mg/L)
Maximum initial concentration tolerable	200	1250
Kinetic model	Pseudo-second order	Pseudo-first order

### 6.1.3 Sludge

Sludge volume index (SVI) was decreased from 38.33 to 33.33 after the acclimatization of sludge showing that the settling characteristics of the sludge have improved after acclimatization. EDX of the sludge suggested that the amount of phosphorus and chlorine increased significantly after acclimatization of sludge. The sludge was tested for its filterability.

The values of specific cake resistance and the resistance of filter medium were calculated to be  $3.6 \times 10^{10}$  and  $2.298 \times 10^{11}$ .

## 6.2 Recommendations

- Experiments may be carried out with different reactor volumes and with different phenolic compounds.
- Experiment may be carried out with other type of adsorbents so as to check their efficacy for removal of phenolic compounds in SBR.
- If possible, all the lab scale experiments on SBR should be carried out in automated setups to avoid any change in the operating conditions throughout the procedure.

## REFERENCES

---

- Andrade I.M., Buitrón G., Betancur M.J., Moreno J.A., Optimal degradation of inhibitory wastewaters in a fed-batch bioreactor, *Journal of Chemical Technology and Biotechnology* 81 (4), pp. 713–720, 2006
- Arendorf J.J. and Focht D.D., Formation of chlorocatechol-meta cleavage product by *Pseudomonas* during metabolism of monochlorophenyl, *Appl. Envir. Microbiol* 60, pp. 2884-2889, 1994
- Badiei T., Jahim J.M., Anuar N., Abdullah S.R.S., Effect of hydraulic retention time on biohydrogen production from palm oil mill effluent in anaerobic sequencing batch reactor, *International journal of hydrogen energy* volume 36, pp. 5912-5919, 2011.
- Betancur M.J., Martínez F., Ocampo C., Moren J.A., Buitron X., Andrade I.M., Acclimatization model of an aerobic bioreactor for the treatment of toxic wastewater, *Simulation Modelling Practice and Theory* 17, pp. 680–691, 2009.
- Betancur M.J., Moreno J.A., Andrade I.M., Buitron G., Practical optimal control of fed-batch bioreactors for the waste water treatment, *International Journal of Robust and Nonlinear Control* 16 (3), pp. 173–190, 2005.
- Chambers B., Batch Operated Activated Sludge Plant for Production of High Effluent Quality at Small Works, *Water Science and Technology*. vol. 28, no. 10, 1993.
- Cheng H., Scott K., Christensen P.A., Engineering aspects of electrochemical hydrodehalogenation of 2,4-dichlorophenol in a solid polymer electrolyte reactor, *Appl. Catal., A*, 261, pp. 1-6, 2004
- Chiavola A., Baciocchi R., Gavasci R., Biological treatment of PAH-contaminated sediments in a Sequencing Batch Reactor, *Journal of Hazardous Materials*, pp. 97–104, 2010.

- Daneshvar N.; Ashassi-Sorkhabi H.; Kasiri M.B., Decoloration of dye wastewater by electrocoagulation with a comparative investigation of different electrode connections, *Journal of Hazardous Materials B* 112, pp. 55 – 64, 2004
- Ding D., Feng C., Jin Y., Hao C., Zhao Y., Suemura T., Domestic sewage treatment in a sequencing batch biofilm reactor (SBBR) with an intelligent controlling system, *The International Journal on the Science and Technology of Desalting and Water Purification*, pp. 238-244, 2011.
- Edwards J.D.. *Industrial Wastewater Treatment: A guidebook*. CRC Press, Boca Raton, 1995
- Farabegoli G., Chiavola A., Rolle E., Naso M., Decolorization of Reactive Red 195 by a mixed culture in an alternating anaerobic–aerobic Sequencing Batch Reactor, *Biochemical Engineering Journal* Vol. 52, pp. 220–226, 2010.
- Gattrell M. and Kirk D.W., Study of electrode passivation during aqueous phenol electrolysis, *J. Electrochem. Soc.*, 140, pp. 903-911, 1993
- He.S.B., Xue. G., Kong. H.N., Li. X., Improving the performance of sequencing batch reactor (SBR) by the addition of zeolite powder, *Journal of Hazardous Materials* 142, pp. 493–499, 2007.
- Johnson D.C., Feng J., Houk L.L., Direct electrochemical degradation of organic wastes in aqueous media, *Electrochim. Acta*, 46, pp. 323-330, 2000
- Kargi F., Uygur A., Baskaya H.S, para-Chlorophenol inhibition on COD, nitrogen and phosphate removal from synthetic wastewater in a sequencing batch reactor, *Bioresource Technology* 96, pp. 1696-1702, 2005.
- Kopecky F., Kaclik P., Fazekas T., *Laboratory manual for physical chemistry*, Farmaceutical faculty of Comenius University, Bratislava, 1996
- Kushwaha J.P., X Srivastava V.C., Mall I.D., Treatment of dairy wastewater by commercial activated carbon and bagasse flyash: Parametric, kinetic and equilibrium modelling, disposal studies, *Bioresource Technology* 101, pp. 3474–3483, 2010.

- Lee T.T., Wang F.Y., Newell R.B., Dynamic modelling and simulation of activated sludge process using orthogonal collocation approach, *Water Research*, Volume 33, Issue 1, pp.73-86, 1999
- Levin M., Gealt M., *Biotreatment of Industrial and Hazardous Waste*, McGraw-Hill, New York, USA, 1993.
- Li J.J., Cui J., Zhao N.Q., Shi C.S., Du X.W., The properties of granular activated carbons prepared from fly ash using different methods, *Carbon* Volume 44, Issue 7, pp. 1346–1348, 2006.
- Lim. P.E., Ong. S.A., Seng. C.E., Simultaneous adsorption and biodegradation processes in sequencing batch reactor (SBR) for treating copper and cadmium-containing wastewater, *Water Research* 36, pp. 667–675, 2002.
- Lim. S.P., Ahmad. M.N., Seng. C.E. and Lim. P.E., Activated rice husk addition in sequencing batch reactor for the co-treatment of landfill leachate and domestic wastewater, *GMSARN International Conference on Sustainable Development*, 2008.
- Lisovskii A., Semiat R., Aharoni C., Adsorption of sulfur dioxide by active carbon treated by nitric acid: I Effect of the treatment on adsorption of SO<sub>2</sub> and extractability of the acid formed, *Carbon*, 35 (10–11), pp. 1639–1643, 1997.
- Liu Q.S., Zheng T., Wang P., Jiang J.P., Li N., Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers, *Chemical Engineering Journal* Volume 157, Issues 2–3, pp. 348–356, 2010.
- Liu Y., Some consideration on the Langmuir isotherm equation, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Volume 274, Issues 1–3, pp. 34–36, 2006. Material safety data sheet, 4-chlorophenol MSDS
- Losso J.N., Ng C., Marshall W.E., Rao R.M., Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin–water system, *Bioresource Technology* Volume 85, Issue 2, pp. 131–135, 2002.

- Mangat S.S., Elefsiniotis P., Biodegradation of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-d) in sequencing batch reactors, *Water Research* Volume 33, No. 3, pp. 861-867, 1999.
- Mesquita M.E., Silva J.M.V., Preliminary study of pH effect in the application of Langmuir and Freundlich isotherms to Cu-Zn competitive adsorption, *Geoderma* Volume 106, Issues 3-4, pp. 219-234, 2002
- Mo J., Hwang J.E., Jegal J., Kim J., Pretreatment of a dyeing wastewater using chemical coagulants, *Dyes and Pigments* 72, pp. 240-245, 2007.
- Mohan S.V., Sarma P.M., *Advanced Bioremediation Processes in Chemical Industries*, Scientific and Technical Report (10), IWA Publishing, London, p. 76, 2001
- Mun C.H., Ng W.J., He J., Acidogenic sequencing batch reactor start-up procedures for induction of 2,4,6-trichlorophenol dechlorination, *Water Research* Vol. 42, pp. 1675-1683, 2008.
- NEIWPCC, New England Interstate Water Pollution Control Commission, sequencing batch reactor design and operational considerations, pp. 6-27, 2005
- Norcross K.L., *Sequencing Batch Reactors-An Overview*, *Water Science and Technology*. vol. 26, pp. 9-11, 1992.
- Oremusova J., *Manual for laboratory practice in physical chemistry for students of pharmacy*, Department of Physical Chemistry, Faculty of Pharmacy, Comenius University, Bratislava, 2007,
- Pitchard. P.H, Neill. E.J., Spain. C.M. and Ahem. D.J., Physical and biological parameters that determine the fate of p-chlorophenol in laboratory test systems, *Applied and Environmental Microbiology* 53, 1987.
- Rao. K.R., *Pentachlorophenol: chemistry, pharmacology and environmental toxicology*. Newyork, Plenums Press, 1978.

- Rochkind M.L., Blackburn. J.W., Sayler.G.S., Microbial Decomposition of Chlorinated Aromatic Compounds, EPA/600/2-86/090, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1986
- Sahinkaya E., Dilek F.B., Effect of biogenic substrate concentration on the performance of sequencing batch reactor treating 4-CP and 2,4-DCP mixtures, Journal of Hazardous Materials B128, pp. 258–264, 2006
- Sankar M., Sekaran G., Sadulla S., Ramasami T., Removal of diazo and triphenylmethane dyes from aqueous solutions through an adsorption process, Journal of Chemical Technology and Biotechnology, 1999.
- Sarti A., Zaiat M., Anaerobic treatment of sulfate-rich wastewater in an anaerobic sequential batch reactor (AnSBR) using butanol as the carbon source, Journal of Environmental Management Vol. 92, pp. 1537-1541, 2011.
- Schmal D., Erkel J.V., Duin P.J.V., Electrochemical reduction of halogenated compounds in process waste water, The Institution of Chemical Engineers Symposium Series No. 98, Electrochemical Engineering, pp. 281-291, 1986
- Schroeder E.D., Design of sequencing batch reactor activated sludge process, In civil engineering for practicing and design engineers 2, pp 33-34
- Shaoying Q., Schideman L. C., An overall isotherm for activated carbon adsorption of dissolved natural organic matter in water, Water Research Volume 42, Issue 13, pp. 3353–3360, 2008.
- Sharma. V., Srivastava. V.C., Kushwaha J.P. and Mall. I.D., Studies on biodegradation of resorcinol in sequential batch reactor, International Biodeterioration & Biodegradation, pp. 764-768, 2010.
- Sirianuntapiboon. S., Ungkaprasatcha. O., Removal of Pb<sup>2+</sup> and Ni<sup>2+</sup> by bio-sludge in sequencing batch reactor (SBR) and granular activated carbon-SBR (GAC-SBR) systems, Bioresource Technology 98, pp. 2749–2757, 2007.

- Sittig. M., Hand book of toxic and hazardous chemicals, Park Ridge, NJ, Noyes Publications, 1981.
- Strous M., Heijnen J.J., Kuenen J.G., Jetten M.S.M., The sequencing batch reactor as a powerful tool for the study of slowly growing anaerobic ammonium-oxidizing microorganisms, *Applied Microbiol Biotechnol* vol. 50, pp. 589-596, 1998.
- Tahar N.B., Savall A., Electrochemical degradation of phenol in aqueous solution on bismuth doped lead dioxide: a comparison of the activities of various electrode formulations, *J. Appl. Electrochem.*, 29, pp. 277-283, 1999
- Tancredi N., Medero N., Moller F., Piriz J., Plada C., Cordero T., Phenol adsorption onto powdered and granular activated carbon, prepared from Eucalyptus wood, *Journal of Colloid and Interface Science* Volume 279, Issue 2, pp. 357-363, 2004.
- Tomei M.C., Annesinib M.C., Bussolettib S., 4-nitrophenol biodegradation in a sequencing batch reactor: kinetic study and effect of filling time, *Water Research* 38, pp. 375-384, 2004.
- Tomei M.C., Annesini M.C., Luberti R., Cento G., Senia A., Kinetics of 4-nitrophenol biodegradation in a sequencing batch reactor, *Water Research* volume 37, pp. 3803-3814, 2003.
- Vinitnantharat S., Woo-Suk C., Ishibashi Y., Ha S.R., Stability of Biological Activated Carbon-Sequencing Batch Reactor (BAC-SBR) to Phenol Shock Loading, *Thammasat Int. J. Sc. Tech.*, Vol.6, No.2, 2001
- White D.M., Schnabel William, Treatment of Cyanide Waste in a Sequential Batch Biofilm Reactor, *Water Research* Volume 32, No. 1, pp. 254-257, 1998.
- Wiggings B.A., Jones S.H., Alexander M.A., Explanations for the acclimation period preceding the mineralization of organic chemicals in aquatic environments, *Applied and Environmental Microbiology* 53 (4), pp.791-796, 1987
- Wilderer P.A., Irvine R.L., Goronszy M.C., Sequencing batch reactor technology, *Chemical Business* 5, 2006.



Yu H.Q, Gu G.W., Treatment of phenolic wastewater by sequencing batch reactors with aerated and unaerated fills, Waste Management, Vol. 16. No. 7, pp. 561-566, 1996.

EPA 932-F-99-073, Wastewater Technology Fact Sheet, Sequencing Batch Reactors, 1999

Material safety data sheet, 4-chlorophenol MSDS (<http://www.sciencelab.com/msds.php?msdsId=9923432>)

Principles of bio-separations engineering, 2006, Raja Ghosh.

Sequencing batch reactor design and operational considerations, New England interstate water pollution control commission, 2005

Toxic Substances Portal - Chlorophenols, Agency for toxic substance and disease registry, 1999.

<http://www.chemvirocarbon.com>

<http://www.energy-concepts.com/process>

[<http://www.fao.org/docrep/t0551e/t0551e05.htm>].

[http://www.fpharm.uniba.sk/fileadmin/user\\_upload/english/Physical\\_Chemistry/5Adsorption.pdf](http://www.fpharm.uniba.sk/fileadmin/user_upload/english/Physical_Chemistry/5Adsorption.pdf)

<http://www.lenntech.com/library/adsorption/adsorption.htm>

<http://en.wikipedia.org/wiki/Adsorption>