"BIODEGRADATION OF PHENOL BY *PSEUDOMONAS PUTIDA*"

A Dissertation Report

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Technology (Pulp & Paper)

By

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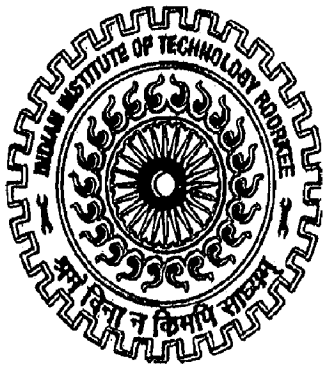

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in this dissertation report entitled "BIODEGRADATION OF PHENOL BY PSEUDOMONAS PUTIDA" in partial fulfillment of the requirements for the award of the degree of Master of Technology in pulp and paper technology, IIT Roorkee is an authentic record of my own work carried out, under the supervision of Dr.U.K.Ghosh, Asst Professor, Department of Paper Technology, IIT Roorkee, Saharanpur campus, Saharanpur.

The matter embodied in the dissertation report, has not been submitted by me for the award of any other degree.

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

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ABSTRACT

Biodegradation is the break down of a compound by a biological organism. Over the past few decades the biodegradation of compounds such as phenol has been researched extensively. Phenol research has shown that certain microorganisms are capable of utilizing it as an energy source, and a variety of methods are available for its removal. The aim of this research was to pursue the problem of phenol degradation by using agro based and low-cost adsorbents as the bed material. Removal of aromatic compounds from industrial wastewater is an environmental concern for industry. In addition, aromatics may be accumulating in lakes, unique natural systems, where the fate and toxicity of these contaminants is unknown. To determine he feasibility of aromatic compound biodegradation in such conditions the effect of pH and adsorbent size on the biodegradation of phenol as a model aromatic waste compound by the *pseudomonas putida* was examined.

Thus combining the two processes adsorption and biodegradation. Both batch and column studies were performed on phenol concentration in the range of 20-500mg/l. the system consisted of a bioreactor developed to run in continuous mode using *pseudomonas putida*. A standard method was modified to quantitatively analyze phenol concentration level. A series of experiments were performed to optimize pH, adsorbent dose, phenol concentration, particle size of adsorbent.

TABLE OF CONTENTS

CONTENTS	Page no.
ACKNOWLEDGEMENT	**i**
ABSTRACT	**ii**
Table of content	**iii**
List of tables	**vi**
List of Figures	**vii**
CHAPTER I	
INTRODUCTION	**1-9**
1.1 Phenol	1-5
1.2 Problems with Phenol	5-7
1.3 Phenol in effluent	7-9
CHAPTER 2	
PULP AND PAPER INDUSTRY- AN OVERVIEW	**10-19**
2.1 Paper Industry	11-13
2.2 Toxicity Concerns	13-19
CHAPTER 3	
LITERATURE REVIEW	**20-48**
3.1Waste Water Treatment Techniques	21
3.1.2 Filtration	21
3.1.3 Aeration	22
3.1.4 Reverse osmosis water filter system	23
3.2 Physico Chemical Process	24 - 33
3.3 Biofiltration	34 - 44
3.4 Simultaneous Adsorption and Biodegradation	45 - 47
3.5 Objective of the present work	48
CHAPTER 4	
EXPERIMENTAL WORK	**49 - 59**
4.1 Materials	49
4.1.1 Adsorbent	49
4.1.2 Adsorbent preparation	49-52

4.1.2 Adsorbent preparation 49-52
4.1.3. Stock solution 52
4.1.4. Microorganism 53
4.1.5. Growth Medium 53
4.1.6. Revival of Culture 53
4.1.7 Basal Salt Medium 54
4.2 Method for Determination of Phenol Concentration 54-55
4.3 Sterility 56
4.4 Method of Transfer 56
4.5 Acclimatization of Culture 56
4.6 Measurement of Cell Growth and Phenol Concentration in Batch System 56
4.7 pH of the Culture 57
4.8 Experiment 57
4.8.1 Preparation of the activated carbon 57
4.8.2 Batch Study 57
4.8.2.1 Biological Study 57
4.8.2.2 Adsorption Study 57
4.8.2.3 Simultaneous Adsorption and Biodegradation Study 57-59
CHAPTER 5
RESULTS AND DISCUSSIONS **60 - 90**
5.1 Physical characterization of prepared activated carbons 61
5.1.1 Properties of activated carbon prepared from bagasse pith and bottom ash 61
5.1.2 Proximate analysis of bagasse pith [wt. %] for different particle size 62
5.1.3 Proximate analysis of bottom ash [wt. %] for different particle size 62
5.1.4 Effect of variation of particle size on analysis of methyl blue and iodine no. 63
5.2 Batch Study 64
5.2.1 Adsorption of phenol on activated carbon 65
5.2.2 Phenol adsorption capacity of bottom ash 66 - 67
5.2.3 Effect of pH 68
5.2.4 Effect of particle size of adsorbent (activated bagasse pith carbon) 69
5.2.5 Effect of Adsorbent Dose on percent phenol Removal 70

5.3 Biodegradation of phenol through *Pseudomonas Putida* 71-72
5.4 Simultaneous Adsorption Biodegradation 73 - 75
5.5 Comparative study of Adsorption, Biodegradation and Simultaneous Adsorption and Biodegradation 76-77
5.5.1 Effect of Adsorbent Dose 76
5.5.2 Effect of Particle Size of Adsorbent 77
5.5.3: Effect of pH 77
5.6 Breakthrough Curve for phenol in batch study 78
5.7 Column Study 79
5.7.1 Adsorption of phenol on bagasse pith carbon in biodegradation column 79 - 80
5.7.2 Adsorption of phenol on bottom ash carbon in biodegradation column 81 - 82
5.7.3 Simultaneous adsorption and biodegradation of phenol on bagasse pith carbon in biodegradation column 83 - 84
5.7.4 Simultaneous adsorption and biodegradation of phenol on bottom ash carbon in biodegradation column 85 - 86
5.7.5 Biomass curve of phenol at different concentration 87
5.8 Comparative study of Adsorption, and Simultaneous Adsorption and Biodegradation 88
5.8.1 Effect of pH (with bagasse pith carbon as bed material) 88
5.8.2 Effect of adsorbent dose for 300mg/l phenol concentration 89
5.8.3 Effect of Flow Rate for 300mg/l phenol concentration (SAB) 90
5.9 Breakthrough Curve for phenol in column study 90
CHAPTER 6
CONCLUSION AND FUTURE SCOPE **91 – 92**
REFERENCES **93 - 95**
APPENDIX A

List of Tables

Table 1.1: Some physical and chemical properties of phenol 4

Table1.2: Sources of phenols and other related aromatic compounds in wastewater.....8

Table 1.3: Discharge standards of phenol/phenolic compounds for different industries (CPCB 1995).....9

Table2.1: Common Water Pollutants From Pulp and Paper Processes.....14

Table2.2: Common Air Pollutants From Pulp and Paper Processes.....14

Table 2.3: Kraft Chemical Pulped-Chlorine Bleached Paper Production.....16

Table 2.4 : Kraft Chemical Pulped-Chlorine Bleached Paper Production.....17

Table 2.5: Kraft Chemical Pulped-Chlorine Bleached Paper Production.....18

Table 2.6: Pollutant Releases (short tons/ year).....19

Table 3.1: Characteristics Associated with Physical/Chemical Adsorption.....28

Table 3.2: Classification of pores.....29

Table 3.3: A comparison of different types of reactors with biofilm reactors.....44

Table 4.1: Optimum Conditions of Growth for Microbial Culture.....53

Table 4.2: Composition of Nutrient Agar Medium.....53

Table 4.3: Composition of B.S.M.....54

Table 4.4: Volumes and Concentrations of Assay Reagents for the Standard Method for Phenol Detection (APHA, 1992) and the Modified Assay Method for Phenol Detection.....55

Table 4.5: Specifications of biological tower.....58

Table 5.1: Physical properties of activated carbon with and without binder.....61

Table 5.2: Effect of particle size on analysis of bagasse pith 62

Table 5.3: Effect of particle size on analysis of bottom ash.....62

Table 5.4: Iodine and methyl blue adsorption figures for activated carbon from bagasse pith for different particle size.....63

Table 5.5: Iodine and methyl blue adsorption figures for activated carbon from bottom ash for different particle size.....63

List of Figures

Fig.3.1: Osmosis and Reverse Osmosis.....23
Fig. 3.2: Structure of activated carbon 24
Fig. 3.3: Diagrammatic Representation of Isotherm Classification.....32
Fig. 4.1: Photograph of Biodegradation Column.....59
Fig. 5.1: Calibration curve for phenol.....64
Fig. 5.2: Adsorption of phenol on bagasse pith carbon.....65
Fig. 5.3: Percent removal of phenol by bagasse pith carbon.....66
Fig. 5.4: Adsorption of phenol on bottom ash.....66
Fig. 5.5: Percent removal of phenol by bottom ash.....67
Fig. 5.5: Percent removal of phenol by bottom ash.....67
Fig. 5.6: phenol removal by bagasse pith carbon at varying pH.....68
Fig.5.7: Percent removal of phenol at varying pH.....68
Fig.5.8: Effect of particle size of adsorbent on phenol adsorption.....69
Fig. 5.9: Effect of particle size of absorbent on percent phenol removal.....69
Fig. 5.10: Effect of adsorbent dose on percent phenol removal.....70
Fig.5.11: Biodegradation of phenol through *pseudomonas putida*.....71
Fig. 5.12: Percent removal of phenol by *Pseudomonas putida*.....72
Fig. 5.13 phenol removal by simultaneous adsorption and biodegradation when bed material is activated carbon from bagasse pith.....73
Fig. 5.14: Percent phenol removal by simultaneous adsorption and biodegradation when bed material is activated carbon from bagasse pith.....74
Fig. 5.15: Phenol removal by simultaneous adsorption and biodegradation when bed material is activated carbon from bottom ash.....74
Fig. 5.16: Percent phenol removal by simultaneous adsorption and biodegradation when bed material is activated carbon from bottom ash.....75
Fig. 5.17: Biomass curve for bagasse pith carbon.....75
Fig.5.18: Effect of Adsorbent Dose.....76
Fig.5.19:Effect of Particle Size of Adsorbent.....77
Fig.5.20: Effect of pH.....77
Fig. 5.21: Breakthrough curve for phenol removal in batch study.....78

Fig. 5.22: Adsorption of phenol on bagasse pith carbon in biodegradation column.....79
Fig.5.23: Percent removal of phenol by Bagasse Pith Carbon.....80
Fig. 5.24: Adsorption of phenol on bottom ash carbon.....81
Fig. 5.25: Percent removal of phenol by Bottom ash Carbon 82
Fig. 5.26: Variation of conc. of phenol during Simultaneous adsorption and biodegradation of phenol on bagasse pith carbon in biodegradation column.....83
Fig. 5.27: Percent removal of phenol during Simultaneous adsorption and biodegradation of phenol on bagasse pith carbon in biodegradation column.....84
Fig.5.28: Variation of conc. of phenol during Simultaneous adsorption and biodegradation of phenol on bottom ash carbon in biodegradation column.....85
Fig. 5.29: Percent removal of phenol during Simultaneous adsorption and biodegradation of phenol on bagasse pith carbon in biodegradation column.....86
Fig. 5.30: Biomass curve for bagasse pith carbon.....87
Fig. 5.31: Effect of pH for 300 mg/l phenol concentration.....88
Fig. 5.32: Effect of adsorbent dose for 300mg/l phenol concentration.....89
Fig. 5.33: Effect of Flow Rate for 300mg/l phenol concentration (SAB).....90
Fig. 5.34: Breakthrough curve for 300mg/l phenol (column).....90

CHAPTER 1

INTRODUCTION

concentration of phenols in wastewater varies from 10 mg/i to 3000 mg/i phenol and its compounds impart taste and odour to water and are toxic to aquatic life. Phenols and phenolic compounds are among most common organic pollutants of wastewater that requires careful treatment before being discharged into the receiving stream of water.

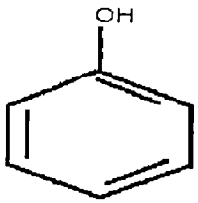
The permissible limits for phenol in industrial effluents before being discharged into municipal sewers and surface waters are specified as *5.0* and 1.0 mg/i respectively by the regulatory agencies in India .The phenol concentration in the effluents from coke ovens and steel plants varies in a wide range from 110 to 5000 mg/i. Continuous ingestion of phenol for a prolonged period of time causes mouth sore, diarrhea, excretion of dark urine and impaired vision at concentration levels ranging between 10 and 240 mg/l .Lethal blood concentration of phenol is around 4.7 to 130 mg /100 ml. Significant amount of phenol can be adsorbed through the skin of the human forearm if present in concentrations of *2.5-10* gm/i in aqueous solutions. Ingestion of large amounts can cause a burning sensation in the body, abdominal pain, sweating, cyanosis, lowering of body temperature, decreased respiration, loss of reflux activity and it may lead to death due to respiratory failure . Chronic poisoning effects reported in human include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, faintness and other mental disturbances.

1.1 Phenol

Phenol is an aromatic compound consisting of a benzene ring with a hydroxyl group (-OH) attached. It is toxic at low concentrations and unlike single chain carbon molecules , phenol is highly stable and difficult to degrade . (Autenreith et al., 1991). Phenol is a white crystalline solid which melts at 43 °C and liquefies upon contact with water. It has a characteristic acrid odour and a sharp burning taste. It is soluble in most organic solvents; its solubility in water is limited at room temperature; above 68 °C it is entirely water-soluble. Phenol is moderately volatile at room temperature. It is a weak acid, and in its ionized form very sensitive to electrophile substitution reactions and oxidation.

1.1.1 IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES

Chemical formula: C_6H_6O
Chemical structure:



Relative molecular mass: 94.11
Common name: phenol

1.1.2 Physical and chemical properties

Some physical and chemical properties of phenol are given in Table 1.

Table 1.1 Some physical and chemical properties of phenol[a]

Boiling point (101.3 Pa)	181.75 °C
Melting point	43 °C 40.9 °C (ultrapure material)
Relative density (20 °/4 °)[b]	1.071
Relative vapour density (air = 1)	3.24
Vapour pressure (20 °C)	0.357 mmHg
(50 °C)	2.48 mmHg
(100 °C)	2.48 mmHg
Saturation concentration in air (20°C)	0.77 g/m^3
Log n-octanol/water partition coefficient (log P_{ow})	1.46d
Solubility in water (16 °C)	67 g/litre[c]
Dissociation constant in water at 20 °C (K_a)	1.28 x 10^{-10}
Flash-point (closed cup)	80 °C
(open cup)	79 °C
Flammability limits	1.3-9.5%

[a] From: Kirk-Othmer (1980); RIVM (1986)
[b] Weast (1987)
[c] Above 68.4 °C phenol is entirely soluble in water
[d] The P_{ow} of phenol is very much dependent on pH; pH at log P_{ow} = 1.46 was not given
[e] Budavari *et al.* (1989)

Phenol has a melting point of 43 °C and forms white to colourless crystals (Budavari *et al.,* 1989). It has also been described as a colourless to pink solid or thick liquid (NIOSH, 1985a). Phenol has a characteristic acrid smell and a sharp burning taste. In the molten state, it is a clear, colourless liquid with a low

viscosity. A solution with approximately 10% water is called phenolum liquefactum, as this mixture is liquid at room temperature. Phenol is soluble in most organic solvents (aromatic hydrocarbons, alcohols, ketones, ethers, acids, halogenated hydrocarbons). The solubility is limited in aliphatic solvents.

The chemical properties of phenol are affected by the resonance stabilization possibilities of phenol and, in particular, of the phenolate ion. Because of this, phenol reacts as a mild acid. In the presence of electrophilic groups (meta-indicators), the acidic properties are emphasized.

Phenol is sensitive to oxidizing agents. Splitting of the hydrogen atom from the phenolic hydroxyl group is followed by resonance stabilization of the resulting phenyloxy radical. The radical formed can easily be further oxidized. Depending on the oxidizing agent applied and the reaction conditions, various products, such as dihydroxy- and trihydroxybenzenes and quinones are formed. These properties make phenol suitable as an antioxidant functioning as a radical trapping agent. Phenol undergoes numerous electrophilic substitution reactions, such as halogenation and sulfonation. It also reacts with carbonyl compounds in both acidic and alkaline media. In the presence of formaldehyde, phenol is readily hydroxymethylated with subsequent condensation to resins.

1.2 Problems with Phenol

The toxicity of phenol has been widely doccumented and there is a greaty concern over the disastrous effects phenol has upon both humans and the environment. Phenol is formed during the natural decomposition of organic materials. The major part of phenol present in the environment, however, is of anthropogenic origin. The effects on aquatic life are destructive at low concentrations , and the danger for humans is just as great as 1gm of phenol is lethal (Bond and Straub,1974). Solutions of phenol are corrosive to skin and eyes. Phenol vapours can irritate the respiratory tract. There is evidence that

phenol is not a skin sensitizer.

Continued exposure to phenol for humans is quite damaging . the literature to date strongly points out the high toxicity of phenol, not only to human beings but to the aquatic life. For fish, 5-25 mg/l is lethal, and as low as 0.1 mg/l leaves an odour and an after taste (Kirk-Othmar, 1982). For humans the allowed exposure is 20 mg/day for people working with phenol(Bond and Straub, 1974) . it was also stated that small doses to humans are damaging causing dangerous and painful burns and adsorption through the skin may occur (Windholtz, 1983). Ingestion of phenol can cause vomiting, paralysis, lung failure and cardiac arrest(Windholtz,1983). Although effluent can be diluted and then discharged into the waterways, this approach is not feasible for a chemical toxic at 5-25 mg/l.

No data are available on atmospheric phenol levels. Background levels are expected to be less than 1 ng/m^3. Urban/suburban levels vary from 0.1 to 8 μg/m^3, while concentrations in source-dominated areas (industry) were reported to be up to two orders of magnitude higher. Phenol has been detected in rain, surface water and ground water, but data are very scarce. Elevated phenol levels have been reported in sediments and ground waters due to industrial pollution. Occupational exposure to phenol may occur during the production of phenol and its products, during the application of phenolic resins (wood and iron/steel industry) and during a number of other industrial activities. The highest concentration (up to 88 mg/m^3) was reported for workers in the ex-USSR quenching coke with phenol-containing waste water. Most other reported concentrations did not exceed 19 mg/m^3.

Exposure by way of drinking-water and inadvertently contaminated food products should be low; phenol has an objectionable smell and taste.

1.2.1 Effects on humans

A wide range of adverse effects has been reported following well-documented human exposure to phenol by the dermal, oral or intravenous routes. Gastrointestinal irritation has been reported following ingestion. Local effects following dermal exposure range from painless blanching or erythema to corrosion and deep necrosis. Systemic effects include cardiac dysrhythmias, metabolic acidosis, hyperventilation, respiratory distress, acute renal failure, renal damage, dark urine, methaemoglobinaemia, neurological effects

(including convulsions), cardiovascular shock, coma and death. The lowest reported dose resulting in a human death was 4.8 g by ingestion; death occurred within 10 min.

The potential for poisoning through inhalation of phenol vapours has long been recognized, but no cases of death following this route of exposure have been reported. Symptoms associated with inhalation of phenol included anorexia, weight loss, headache, vertigo, salivation and dark urine.

Phenol is not a sensitizing agent.

The human odour threshold for phenol has been reported to range from 0.021 to 20 mg/m^3 in air. The odour threshold for phenol in water has been reported to be 7.9 mg/litre, and the taste threshold 0.3 mg/litre in water.

1.3 Phenol in Effluent

Phenol is commonly found in effluent and in waste particularlyfrom petroleum sites. It is also produced in coking plants, oil refineries and chemical industries involved with the production of paper, pesticides resins, dyes and pharmaceuticals (Autenrith et. al 1991). Effluent waters can contain as low as10 mg/l to greater than 5000 mg/l of phenol

The toxicity of phenol has found to cause problems during treatment. Treatment plants consist of treating tanks such as settlement or activated sludge tanks and these consists of a wide range of bacteria and protozoa(Forster and Johnson, 1987). Many substrates are essential for the growth of effluent treating organisms, although as the concentration of certain chemicals increases above an optimum level activity will decrease and if levels are too high activity may cease completely.

Phenol is a major concern in effluent treatment as there are few organisms that grow in treatment tanks able to degrade the substance. Even at low concentrations the cell populations within the tank is unable to degrade phenol due to inhibition. Cell death can occur if conditions are limiting and this can lead to irreversible changes in the cell populations within treating tanks (Barnes and Fitzgerald, 1987). To overcome the problem of toxicity effluent containing phenol is commonly treated through separate methods.

Table1.2: Sources of phenols and other related aromatic compounds in wastewater

Sources	**Pollutants**
Petroleum refining	Hydrocarbons (alkanes, cycloalkanes, polyaromatic hydrocarbons), benzenes, substituted benzenes, toluene, noctanes, n-decanes, naphthalene, biphenyls, phenol, cyanide, suiphide and ammonia Naphthalene, heptanes, benzenes, butadiene,C-4 alcohols, phenol and resorcinol.
Petrochemicals and basic orgamc chemical manufacture	rn-amino phenol, phenol, resorcinol, dinitrophenol, pnitrophenol, trinitrophenol benzene sulphonic acids, aniline, chlorobenzenes, toluene.
Coal refining	Phenol, catechol, o-, m-, p-cresols, resorcinol, hydroquinone, pyrogallol, polyaromatic hydrocarbons, pyridines, pycolines, lutidines, xylenes, toluene, benzoic acid,
pharmaceutical	Toluene, benzyl alcohols, phenyl acetic acid, chlorinated products of benzene, chloroform, ether, ethyl alcohol.
Tannery	Tannin, catechin, pbenol, chiorophenol, nitro phenols
Pulp and paper mill	Lignin. vanillin, vanillic acid, dehydrodivanillian, ferulic acid, cinnamic acid, synringic acid, vieratic acid, protocatechuic acid, gentisic acid, benzoic acid, catechol, coniferyl alcohol, dehydrodihydroconiferyl alcohol, phenyl propioic acid, phenols and chiorophenols.

The National Institute of Occupational Safety and Health (NIOSH) recommends a limit of 5 ppm phenol in workroom air over a 10 hr work shift and not more than 16 ppm during 15 min period, WHO recommends the permissible phenolic concentration of 0.000 1mg/l in potable water (WHO 1963).

Table 1.3: Discharge standards of phenol/phenolic compounds for different industries (CPCB 1995)

S.No	Industry	Parameters	Maximum allowable concentration, mg/I
1	Oil	Phenol	1.0
2	Cotton and textiles	Phenolic compounds (as phenol)	5.0
3	Coke ovens	Phenolic compounds (as phenol)	5.0
4	Composite & woolen mills	Phenolic compounds (as phenol)	1.0
5	Dye and dye intermediates	Phenolic compounds (as phenol)	1.0
6	Integrated iron and steel plants	Phenol	1.0
7	Petrochemicals	Phenol	5.0
8	Pharmaceutical manufacturing and formation	Phenolic (as phenol)	1.0
9	Paint	Phenolics (as phenol)	1.0
10	Common effluent treatment plants	Phenolics (as phenol)	5.0
11	Pesticides manufacturing and formulation	Phenolics (as phenol)	1.0

Recovery of phenols is normally intended in cases of liquid wastes with flow rates larger than 10m3/h and phenol concentration of at least 2000mg/i. In some of the industries phenol removal as a pretreatment operation involves the treatment of highly concentrated phenolic water prior to dilution by other process waste streams.

CHAPTER 2

PAPER INDUSTRY- AN OVERVIEW

2.1 Pulp and Paper Industry

World paper and pulp production is estimated to be about 261 million tons yr−1, with a generation of wastewater discharges between 20 and 350 m3 ton−1 (Field *et al.*, 1992). The organic load of this effluent (measured as COD) ranges between 30 and 180 kg ton−1 of the final product and the chlorinated organic compounds load range between 1 and 10 kg ton−1 (Field *et al.*, 1992). Pulp and paper effluent is toxic and has a brown color. Toxicity has always been associated with wood resin, phenols (Walden *et al.*, 1986) and tannins (Temmink *et al.*, 1989). The color of the effluent results from the presence of high molecular weight phenolic compounds, some products from lignin degradation (Field *et al.*, 1992) and polymerized tannins (Crookes and Sikes, 1990).

Aerobic treatments have commonly been used in the pulp and paper industry (Strehler and Welander, 1994). Aerated lagoons remove between 30 and 40% of the organic-linked chlorine and about 50% of the chlorinated phenolic compounds (Briant and Barkley, 1991), while activated sludge treatments remove around 50% of the chlorinated organic compounds and about 60% of the chlorinated phenolic compounds (Briant and Barkley, 1991). Nevertheless, neither treatment is able to remove the color present in the pulp industry effluent (Paice and Jurasek, 1984).

The pulp and paper industry is one of India's oldest and core industrial sector. The socio-economic importance of paper has its own value to the country's development as it is directly related to the industrial and economic growth of the country. Although paper has many uses, its most important contribution to modern civilization is its use as a medium to record knowledge. Paper manufacturing is a highly capital, energy and water intensive industry. It is also a highly polluting process and requires substantial investments in pollution control equipment. In India, around 905.8 million m3 of water is consumed and around 695.7 million m3 of wastewater is discharged annually by this sector. India's current average fresh specific water consumption of about 150 m3/tonne of product is far above the global best specific water consumption of 28.66 m3/tonne (for large scale wood based pulp and paper mill) and this large gap is primarily attributed to the use of obsolete technology equipments and poor water management practices. The large water requirements and consumption by the Indian pulp and paper industries has led to, water fast becoming a scarce commodity and lowering of the groundwater table and thus

increased pumping costs and more importantly water shortage in many regions. Realizing the importance of water and excessive usages of water by pulp and paper sector, Central Pollution Control Board (CPCB) has taken initiative to develop the water conservation guidelines and water consumption standards and entrusted National

Productivity Council to undertake the study to address these issues. India produces 5.96 million tones of paper per year (2003 – 2004) through 309 paper manufacturing mills at a capacity utilization of approximately 60 percent. The number of paper manufacturing mills has increased consistently from just 17 in 1951 to around 600 in Year 2002 with an annual installed capacity of 6.2 million to meet the increasing demand.

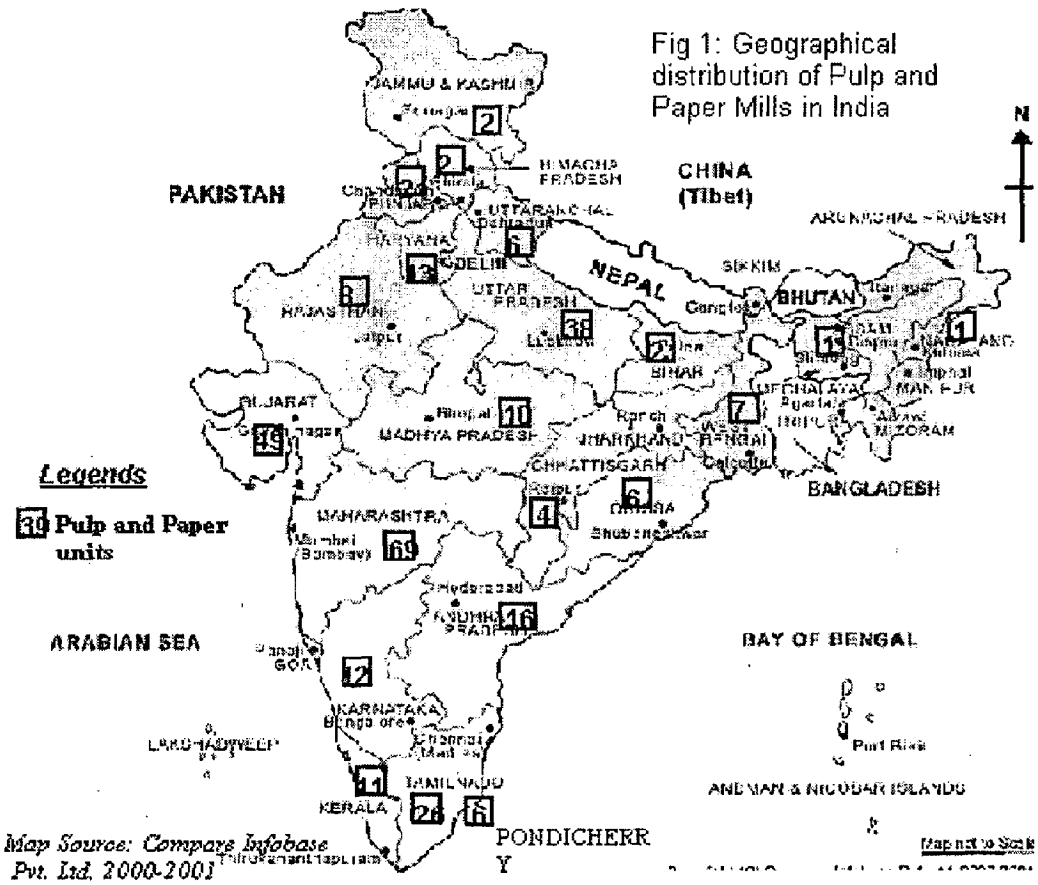


Fig 1: Geographical distribution of Pulp and Paper Mills in India

Adsorption operations have been commonly used in advanced wastewater treatments. Activated carbon is one of the most useful adsorbent materials for the removal of trace organic compounds, such as mutagenic and toxic compounds (Suzuki, 1997). Phenolic compounds are adsorbed strongly in activated carbon (Montgomery, 1985), but due to the high cost, new research regarding cheaper adsorption materials has been carried out in the last few years (Middeldorp *et al.*, 1990; Streat *et al.*, 1995; Cox *et al.*, 1997).

TABLE I

Characteristics of the bleached Kraft mill untreated wastewater

Parameter	Unit	Untreated wastewater[a]	
		Range	Average
pH		3.5–10.6	5.1
Color	U Pt/Co	592–1400	951
BOD_5	$mg\ L^{-1}$	242–513	318
COD	$mg\ L^{-1}$	823–1942	1208
Phenolic compounds UV_{215}	$mg\ L^{-1}$	190–350	322
Tannin-lignin	$mg\ L^{-1}$	44–64	52

[a] Values are the average of eleven determinations.

2.2 Toxicity concerns: arise from the presence of phenols, chlorinated organic compounds such as dioxins, furans, and others (collectively referred to as adsorbable organic halides, or AOX) in wastewaters after the chlorination/extraction sequence.

Due to the large volumes of water used in pulp and paper processes, virtually all U.S. mills have primary and secondary wastewater treatment systems installed to remove particulate and biochemical oxygen demand (BOD) produced in the manufacturing processes. These systems also provide significant removals (e.g., 30-70 percent) of other important parameters such as adsorbable organic halides (AOX) and chemical oxygen

demand (COD). The major sources of effluent pollution in a pulp and paper mill are presented in table 2.1 below:

Table2.1: Common Water Pollutants From Pulp and Paper Processes

Source	*Effluent characteristics*
Water used in wood handling/debarking and chip washing	Solids, BOD, color
Chip digester and liquor evaporator condensate	Concentrated BOD, can contain reduced sulfur
"White waters" from pulp screening, thickening, and cleaning	Large volume of water with suspended solids, can have significant BOD
Bleach plant washer filtrates	BOD, color, chlorinated organic compounds
Paper machinewater flows	Solids, often precipitated for reuse
Fiber and liquor spills	Solids, BOD, color

Source: Smook, G.A. *Handbook for Pulp & Paper Technologists*. Second edition. Vancouver: Angus Wilde Publications, 1992.

Wastewater treatment systems can be a significant source of cross-media pollutant transfer. For example, waterborne particulate and some chlorinated compounds settle or absorb onto treatment sludge and other compounds may volatilize during the wastewater treatment process. The following table 2.2 is an overview of the major types and sources of air pollutant releases from various pulp and paper processes:

Table2.2: Common Air Pollutants From Pulp and Paper Processes

Source	*Type*
Kraft recovery furnace	Fine particulates
Fly ash from hog fuel and coal-fired burners	Course particulates
Sulfite mill operations	Sulfur oxides
Kraft pulping and recovery processes	Reduced sulfur gasses
Chip digesters and liquor evaporation	Volatile organic compounds
All combustion processes	Nitrogen oxides

Source: Smook, G.A. *Handbook for Pulp & Paper Technologists*. Second edition. Vancouver: Angus Wilde Publications, 1992.

Pulp and paper mills have made significant investments in pollution control technologies and processes. According to industry sources, the pulp and paper industry spent more than $1billion per year from 1991-1994 on environmental capital expenditures. In 1991 and 1992, this represented 20 percent of total capital expenditures. Chemical recovery and recycling systems in the chemical pulping process significantly reduce pollutant outputs while providing substantial economic return due to recovery of process chemicals. Chemical recovery is necessary for the basic economic viability of the kraft process. According to EPA sources, all kraft pulp mills worldwide have chemical recovery systems in place. Some sulfite mills, however, still do not have recovery systems in place. Scrubber system particulate "baghouses" or electrostatic precipitators (ESPs) are are often mill air pollution control components. The significant residual waste streams from pulp and paper mills include bark, wastewater treatment sludges, lime mud, lime slaker grits, green liquor dregs, boiler and furnace ash, scrubber sludges, and wood processing residuals. Because of the tendency for chlorinated organic compounds (including dioxins) to partition from effluent to solids, wastewater treatment sludge has generated the most significant environmental concerns for the pulp and paper industry. With the exception of bark, wastewater treatment sludge is the largest volume residual waste stream generated by the pulp and paper industry. Sludge generation rates vary widely among mills. For example, bleached kraft mills surveyed as part of EPA's 104-Mill Study reported sludge generation that ranged from 14 to 140 kg sludge per ton pulp. Total sludge generation for these 104 mills was 2.5 million dry metric tons per year, or an average of approximately 26,000 dry metric tons per year per plant. Pulpmaking operations are responsible for the bulk of sludge wastes, although treatment of papermaking effluents also generates significant sludge volumes. For the majority of pulp and integrated mills that operate their own wastewater treatment systems, sludges are generated onsite. A small number of pulp mills, and a much larger proportion of papermaking establishments, discharge effluents to publicly-owned wastewater treatment works (POTWs). Potential environmental hazards from wastewater sludges are associated with trace constituents (e.g. phenol and its compounds, chlorinated organic compounds) that partition from the effluent into the sludge.

Table2.3 below presents the process steps, material inputs, and major pollutant outputs (by media) of a kraft pulp mill practicing traditional chlorine bleaching. The following resources are recommended for pollutant production data (e.g., pounds of BOD per ton of pulp produced) for those pollutants presented in table 2.3 below:

Table 2.3: Kraft Chemical Pulped-Chlorine Bleached Paper Production

Process Step	Material Inputs	Process Outputs	Major Pollutant Outputs*	Pollutant Media
Fiber Furnish Preparation	Wood logs Chips Sawdust	Furnish chips	dirt, grit, fiber, bark	Solid
			BOD	Water
			TSS	
Chemical Pulping Kraft process	Furnish chips	Black liquor (to chemical recovery system), pulp (to bleaching/processing)	resins, fatty acids	Solid
			color	Water
			BOD	
			COD	
			AOX	
			VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	
			VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	Air
	Cooking chemicals: sodium sulfide (Na_2S), NaOH, white liquor (from chemical recovery)		reduced sulfur compounds (TRS)	
			organo-chlorine compounds (e.g., 3,4,5- trichloroguaiacol)	

Table 2.4 : Kraft Chemical Pulped-Chlorine Bleached Paper Production

Process Step	Material Inputs	Process Outputs	Major Pollutant Outputs*	Pollutant Media
Bleaching	Chemical pulp	Bleached pulp	dissolved lignin and carbohydrates	Water
			color	
			COD	
			AOX	
			inorganic chlorine compounds (e.g., chlorate (ClO_3^-))[1]	
	Elemental chlorine (Cl_2), chlorine containing compounds		organo-chlorine compounds (e.g., dioxins, furans, chlorophenols)	
	Hypochlorite (HClO, NaOCl, $Ca(OCl)_2$) Chlorine dioxide (ClO_2)		VOCs (acetone, methylene chloride, chloroform, MEK, carbon disulfide, chloromethane, trichloroethane)	Air / Water
Papermaking	Additives, Bleached/ Unbleached pulp	Paper/paperboard product	particulate wastes	Water
			organic compounds	
			inorganic dyes	
			COD	
			acetone	
Wastewater Treatment Facilities	Process wastewaters	Treated effluent	sludge	Solid
			VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	Air
			BOD	Water
			TSS	
			COD	
			color	
			chlorophenolics	
			carbon disulfide	
			VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	

Table 2.5: Kraft Chemical Pulped-Chlorine Bleached Paper Production

Process Step	Material Inputs	Process Outputs	Major Pollutant Outputs*	Pollutant Media
Power Boiler	Coal, Wood, Unused furnish	Energy	bottom ash; incombustible fibers	Solid
			SO_2, NO_x, fly ash, coarse particulates	Air
Chemical Recovery System				
Evaporators	Black liquor	Strong black liquor	evaporator noncondensibles (TRS, volatile organic compounds: alcohols, terpenes, phenols)	Air
			evaporator condensates (BOD, suspended solids)	Water
Recovery Furnace	Strong black liquor	Smelt	fine particulates, TRS, sulfur dioxide	Air
		Energy		
Recausticizing	Smelt	Regenerated white liquor	dregs	Solids
		Lime mud	waste mud solids	Water
Calcining (Lime Kiln)	Lime mud	Lime	fine and coarse particulates	Air

Table 2.6 below summarizes annual releases of carbon monoxide (CO), nitrogen dioxide (NO_2), particulate matter of 10 microns or less (PM10), total particulates (PT), sulfur dioxide (SO_2), and volatile organic compounds (VOCs).

Table 2.6: Pollutant Releases (short tons/year)

Industry Sector	CO	NO_2	PM_{10}	PT	SO_2	VOC
Metal Mining	5,391	28,583	39,359	140,052	84,222	1,283
Nonmetal Mining	4,525	28,804	59,305	167,948	24,129	1,736
Lumber and Wood Production	123,756	42,658	14,135	63,761	9,419	41,423
Furniture and Fixtures	2,069	2,981	2,165	3,178	1,606	59,426
Pulp and Paper	**624,291**	**394,448**	**35,579**	**113,571**	**541,002**	**96,875**
Printing	8,463	4,915	399	1,031	1,728	101,537
Inorganic Chemicals	166,147	103,575	4,107	39,062	182,189	52,091
Organic Chemicals	146,947	236,826	26,493	44,860	132,459	201,888
Petroleum Refining	419,311	380,641	18,787	36,877	648,155	369,058
Rubber and Misc. Plastics	2,090	11,914	2,407	5,355	29,364	140,741
Stone, Clay and Concrete	58,043	338,482	74,623	171,853	339,216	30,262
Iron and Steel	1,518,642	138,985	42,368	83,017	238,268	82,292
Nonferrous Metals	448,758	55,658	20,074	22,490	373,007	27,375
Fabricated Metals	3,851	16,424	1,185	3,136	4,019	102,186
Computer and Office	24	0	0	0	0	0
Electronics and Other Electrical	367	1,129	207	293	453	4,854
Motor Vehicles, Bodies, Parts	35,303	23,725	2,406	12,853	25,462	101,275
Dry Cleaning	101	179	3	28	152	7,310

CHAPTER 3

LITERATURE REVIEW

3.1WASTE WATER TREATMENT TECHNIQUES

Various treatment processes used for the rernoal and recovery of phenol are described in following paragraphs.

3.1.1Coagulation, flocculation and sedimentation

Natural and wastewater containing small particulates. They are suspended in water forming a colloid. These particles carry the same charges, and repulsion prevents them from combining into larger particulates to settle. Thus, some chemical and physical techniques are applied to help them settle. The phenomenon is known as coagulation. A well known method is the addition of electrolyte. Charged particulates combine with ions neutralizing the charges. The neutral particulates combine to form larger particles, and finally settle down.

Sedimentation let the water sit around to let the floculated or coagulated particles to settle out. It works best with relatively dense particles (e.g. silt and minerals), while flotation works better for lighter particles (e.g. algae, color). Sedimentation is used in pre-treatment and wastewater treatment.

3.1.2 Filtration

Filtration is the process of removing solids from a fluid by passing it through a porous medium. Coarse, medium, and fine porous media have been used depending on the requirement. The filter media are artificial membranes, nets, sand filter, and high technological filter systems. The choice of filters depends on the required filtering speed and the *cleanness* requirement. The flow required for filtration can be achieved using gravity or pressure. In pressure filtration, one side of the filter medium is at higher pressure than that of the other so that the filter plane has a pressure drop. Some portion of this filter type must be enclosed in a container.

The process of removing the clogged portion of the filter bed by reversing the flow through the bed and washing out the solid is called back washing. During this process,

the solid must be removed out of the system, but otherwise the filters must be either replaced or taken out of service to be cleaned.

3.1.3 Aeration

Bringing air into intimate contact with water for the purpose of exchanging certain components between the two phases is called aeration. Oxygenation is one of the purposes of aeration. Others are removal of volatile organic substances, hydrogen sulfide, ammonia, and volatile organic compounds.

A gas or substance dissolved in water may further react with water. Such a reaction is called hydration. Ionic substance dissolve due to hydration.

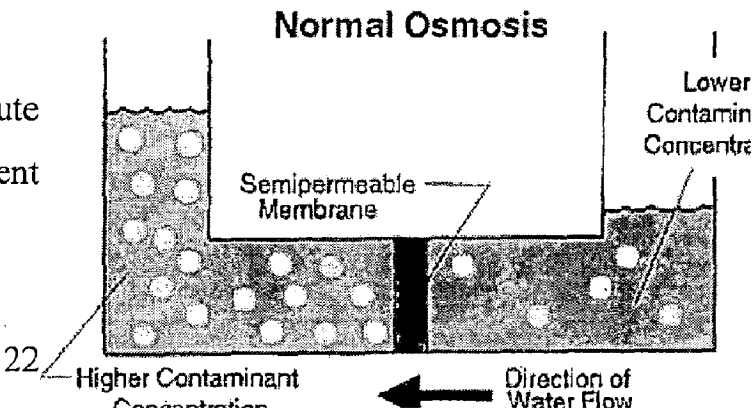
These reactions are reversible, and aeration may also causes dehydration resulting in releasing the gas from water. Henry's law is applicable to this type of equilibrium for consideration. Methods of aeration are

- Diffused aeration - Air bubbles through water.
- Spray aeration - Water is sprayed through air.
- Multiple-tray aeration - Water flows through several trays to mix with air.
- Cascade aeration - Water flows downwards over many steps in the form of thin water falls.
- Air stripping - A combination of multiple tray and cascade technique plus random packed blocks causing water to mix thoroughly with air.

3.1.4 Reverse osmosis water filter system

In the following discussion, a dilute solution and a concentrated solution are considered. The dilute solution can be a clean water whereas the concentrated solution contains undesirable solute (electrolyte or others).

When a compartment containing a dilute solution is connected to another compartment



containing a concentrated solution by a semipermeable membrane, water molecules move from the dilute solution to concentrated solution. This phenomenon is called osmosis. Pig bladders are natural semipermeable membranes. As the water molecules migrate through the semipermeable membrane, water level in the solution will increase until the (osmotic) pressure prevents a net migration of water molecules in one direction. A pressure equivalent to the height difference is called the osmotic pressure. By applying pressure in the higher concentration solution, water molecules migrate from a high concentration solution to a low concentration solution. This method is called reverse osmosis water filter system. The concept of reverse osmosis is illustrated in the diagram .

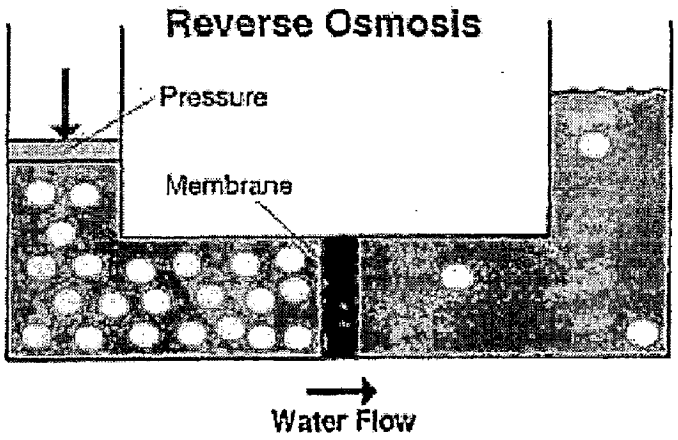


Fig.3.1: Osmosis and Reverse Osmosis

In this technique, the membrane must be able to tolerate the high pressure, and prevent solute molecules to pass through. Regarding membranes, PurePro made the following statement: Semipermeable membranes have come a long way from the natural pig bladders used in the earlier osmosis experiments. Before the 1960's, these membranes were too inefficient, expensive, and unreliable for practical applications outside the laboratory. Modern advances in synthetic materials have generally solved these problems, allowing membranes to become highly efficient at rejecting contaminants, and making them tough enough to withstand the greater pressures necessary for efficient operation.

3.2 Physico Chemical Process

This class of waste water treatment includes hot gas or steam stripping, adsorption, using activated carbon, silica gel, saw dust, boiler ash etc., ion exchange, and oxidation and phase transfer catalysis

3.2.1 Treatment by activated carbon

Treatment by activated carbon is mostly due to adsorption or absorption. When a chemical species is adhered to the surface of a solid, it is an adsorption. When partial chemical bonds are formed between adsorbed species or when the absorbate got into the channels of the solids, we call it absorption. However, these two terms are often used to mean the same, because to distinguish one from type from the other is very difficult.

Application of activated charcoal for the removal of undesirable odour and taste in drinking water has been recognized at the dawn of civilization. Using bone char and charred vegetation, gravel, and sand for the filtration of water for domestic application has been practiced for thousands of years. Active research and production of activated charcoal was accelerated during the two world wars. The use of poison gas prompted the development of masks. They are still in use today. The structure of the activated carbons is shown in fig. 3.2.

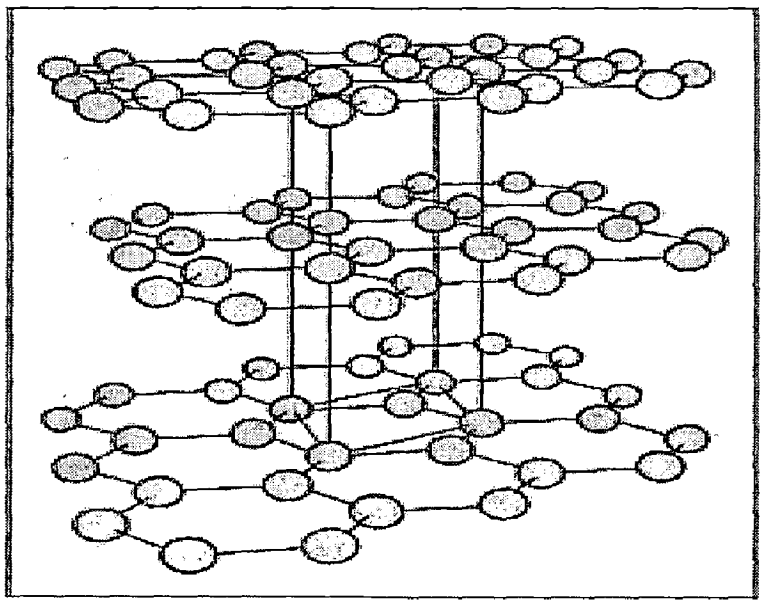


Fig. 3.2: Structure of activated carbon

Charcoal absorbs many substances, ranging from colored organic particulates.phenols to inorganic metal ions. Charcoal has been used to remove the colour of raw sugar from various sources.

Charcoal consists of microcrystallites of graphite. The particles are so small in charcoal that they were considered amorphous. The crystal structure of graphite consists of layers of hexagonal networks, stacked on top of each other. Today, making activated carbon is a new and widely varied industry. Other molecules attach themselves to the porous surface and dangling carbons in these microcrystallites.

Carbon containing substances are charred at less than 900 K to produce carbon in the manufacture of activated carbon. However, the carbon is activated at 1200 K using oxidizing agent to selectively oxidize portions of the char to produce pores in the material. Because of the special process to produce used, these materials with high surface to mass ratio, they are called activated carbon rather than activated charcoal. Factors affecting the absorption are particle size, surface area, pore structure, acidity (pH), temperature, and the nature of the material to be absorbed. Usually, adsorption (absorption) equilibria and rate of adsorption must be considered for effective applications.

3.2.1.1POROSITY AND SORPTION BEHAVIOUR

An understanding of the processes involved in adsorption is vital to gaining an insight of the mechanisms involved. The principles of adsorption onto porous adsorbents, in particular activated carbons, are considered with reference to gas and vapour adsorption processes.

3.2.1.2 Principles of Adsorption

The term adsorption is said to have been first used by Kayser [Kayser, H., 1881] in 1881 in order to explain the condensation of gases on surfaces, in contrast to gas absorption in which gas molecules penetrate the bulk phase of the absorbing solid. The term 'sorption' was proposed by McBain [McBain ,et.al. 1909] as a complete

description of mass transport into a solid, encompassing surface adsorption, absorption by penetration into the solid and condensation within pores.

Adsorption is described as the enrichment of one or more components in the interfacial layer,[Sing, K.S.; Al.,1985] i.e. an excess of molecules exists at the adsorbate/adsorbent interface, upon exposure of an adsorbing solid to a gas or vapour. It is the selective collection and concentration onto solid surfaces of certain molecules contained in a vapour or gas stream. Hence, vapours or gases referred to as adsorbates when adsorbed, even of mixed systems and at low concentrations, may be captured, often selectively, and removed from the effluent stream using a material of the category of adsorbents. Adsorption is divided into the two sub-categories of physical adsorption (physisorption) or van der Waals adsorption and chemical adsorption (chemisorption) and the adsorption process can be determined whether chemical bonds are formed during the process. Physisorption is applicable to all adsorbate-adsorbent systems provided the conditions of pressure and temperature are suitable whereas chemisorption may only occur if the system is capable of making a chemical bond.

3.2.2 Physical Sorption (Physisorption)

The process is a dynamic one where an equilibrium state exists with molecules and the interaction between the adsorbent and adsorbate.

No chemical bonds are formed during physical adsorption; attraction between the adsorbate and adsorbent exists by the formation of intermolecular electrostatic, such as London dispersion forces, or van der Waals forces from induced dipole-dipole interactions, or may be dependent on the physical configuration of the adsorbent such as the porosity of activated carbons. Dispersion forces are the result of rapid fluctuations in the electronic density of one adsorbent molecule inducing an electrical moment in a second atom.[Gregg, S.J.; et.al.1982] If the adsorbate possesses a permanent dipole, or even a multipole, then additional interactions may occur, as charge distributions are induced in the adsorbent and interactions of these moments with any permanent field of thesolid. The process is a very general one and is analogous with that of condensation.

Physisorption occurs to varying extents for all adsorbates, gases and vapours, with all adsorbing solids and the effect increases with decreasing temperature or increasing pressure. Physical adsorption is based on certain basic considerations and adsorption on a heterogeneous surface, that is a surface on which the sites are different, occurs at the sites of highest adsorption potential. The process of physical adsorption into the microporous structure of activated carbon follows the theory of dubinin.

The mechanism of adsorption is dependent upon the size of the admolecule in comparison with the pore width due to the energetic interactions between the chosen adsorbate and the pores. Admolecules initially adsorb into the pores with the highest energy, ignoring activated diffusion effects, then adsorption proceeds via filling of progressively larger, or decreasing energy, porosity. Some pores are capable of accommodating two or three admolecules and, therefore, may undergo co-operative adsorption effects by reducing the volume element thus increasing the energy and adsorptive potential of the pore.

The process of adsorption is always exothermic due to the increased ordering of the adsorbate on the adsorbent surface, reducing the entropy, as:

$\Delta G = \Delta H - T\Delta S$

Thus the amount adsorbed should decrease with increasing temperature as a reduction in the thermal energy supplied to the process, by Le Chatelier's principle, favours the exothermic process of adsorption increasing the equilibrium uptake, except in the case of activated diffusion.

It has been proposed by Lamond and Marsh,[Lamond, T.G.; Marsh, H. ,.1964] by the interpretation of data for physical adsorption of nitrogen on both polar and non-polar surfaces that physical adsorption is independent of the surface chemistry of the adsorbent.

3.2.3 Chemical Adsorption (Chemisorption)

Chemisorption involves the transfer of electrons between the adsorbent and the adsorbate with the formation of chemical bonds, by chemical reaction, between the two species causing adhesion of the adsorbate molecules. Chemical adsorption is far less common than physical adsorption and due to the chemical bonds formed regeneration of the

adsorbent for subsequent re-use is often difficult or impossible.[Cheremisinoff, N.P.; et.al.1993]

Due to the fact that chemical bonds are formed during the adsorption process, desorption of the adsorbed phase may yield products which are chemically different to the original adsorbate. For example oxygen may chemically bond to the surface of a carbon, which upon desorption may evolve CO and CO2 as products.

Table 3.1: Characteristics Associated with Physical/Chemical Adsorption

[Cheremisinoff, N.P.;et.al.1993]

	Physical Adsorption	Chemical Adsorption
Heat of Adsorption / kJmol-1	20-40c.f. heats of liquefaction	>80c.f.bulk-phase chemical reactions
Rate of Adsorption (at 273K)	Fast	Slow
Temperature Dependence of Uptake (with Increasing T)	Decreases	--- Increases
Desorption	Easy- by reduced pressure or increased temperature	Difficult - high temperature required to break bonds
Desorbed Species	Adsorbate unchanged	May be different to original adsorptive
Specificity	Non-specific	Very Specific
Monolayer Coverage	Mono or multilayer condition dependent	Monolayer

3.2.4 Classification of Pores

Porosity has a classification system as defined by IUPAC,[IUPAC ; et.al.1972] which gives a guideline of pore widths applicable to all forms of porosity The widely accepted I.U.P.A.C. classification is as follows:

Table 3.2: Classification of pores

Micropores	Width less than 2 nm
Mesopores	Width between 2 and 50 nm
Macropores	Width greater than 50 nm

Microporosity may then be subdivided into three subsequent categories:

Ultramicropores	Width less than 0.5 nm
Micropores	Width between 0.5 - 1.4 nm
Supermicropores	Width between 1.4 - 2.0 nm

3.2.4.1 Origin of Porosity

The total classification of porosity is tri-modal, as outlined previously, although not all adsorbents will contain all classes of pores, and the three types of pores are formed in different ways.

Microporosity

The micropores are formed as the result of imperfect stacking of constituent molecules and packing arrangements of the bulk material, producing a lack of crystallite alignment, and small pseudo-graphitic crystallites.[Walker, P.L. et.al. 1986] The easiest way to imagine the microporosity, in keeping with the model outlined for general porosity, is that it exists as a series of interconnecting volume elements, rather like zeolites, but with each volume

element of a different size and shape, connected in a completely random manner, with exception to precursor retention, three-dimensional structure. No two micropores will ever be identical and up to, although often much less than, 90% of adsorption in activated carbons takes place in the micropores. Their shape has been shown, by TEM studies

[Thomas, J.M. and Thomas, W.J., et. al. 1967] to be either slit-like or convoluted in shape.

The class of micropores may be subdivided into three separate groups: i) ultramicroporosity (diameter < 0.5 nm)[IUPAC, et.al. 1985] - usually responsible for activated diffusion the pore diameter is comparable to that of the admolecule. ii) Microporosity (diameter ~ 0.5 –1.4 nm)[IUPAC, et.al.1985] - fill quickly, within the first few minutes of adsorption. Overlap of the pore wall potentials results in a pore filling mechanism for

Adsorption in micropores

iii) supermicroporosity (size - 1.4 - 2.0 nm)[IUPAC, et.al.1985] - co-operative pore filling is usually associated with a ratio of approximately 4:1 adsorbate molecule to pore diameter, as is typically found in the supermicropores. Monolayer formation occurs and the pore diameter is effectively reduced enhancing the adsorption potential of the pore hence increasing adsorption and completing the pore filling at low relative pressure. This class of porosity was proposed by Dubinin [Dubinin,1979] who originally purposed the classification system.

The micropores provide sites of maximum adsorption potential for an admolecule/atom and within the pore an admolecule is usually influenced by approximately twelve adsorbent atoms. Due to the close proximity of the walls of micropores an interaction of the Polyani potentials, the result of overlapping of the dispersion fields, may occur resulting in a relatively deep potential energy well and enhanced adsorption at a given pressure. Hence, diffusion into the ultramicropores has a significant activation energy associated with it.

During the adsorption process an admolecule will wait until the vibration sequence of the pore wall opens up the porosity and then it will move 'into' the pore. Once inside the pore the admolecule has the ability to move 'out' but concentration gradients established within the porosity during the adsorption process should prevent such a situation. The pore filling process may be divided into three steps:

1. Monolayer formation
2. Pore filling by co-operative effects
3. Completion of the pore filling process

Adsorption into micropores is completely reversible and no hysteresis loop is observed because of the inability for the adsorbate to condense in such narrow volume elements.

3.2.4.2 Mesoporosity

Mesopores are the result of major defects in the structure of a solid and serve as passages, providing a transport system, to the micropores. These are the pores which give rise to the phenomenon of capillary condensation with the adsorption/desorption isotherm, which is observed by the existence of an inherent hysteresis loop.. The pore diameters, greater than 2 nm but less than 50 nm according to IUPAC definition, are so large that at low relative pressures monolayer coverage occurs followed by further layers and the adsorbed film acts as a nucleus upon which capillary condensation may take place.

3.2.4.3 Macroporosity

The micro pores are considered important in the process of adsorption whereas the meso- and macro pores primarily act as transport pores Major lattice structure defects, such as racks, fissures and etching channels, within a solid lead to the formation of macro pores which may be treated as an open surface. It is possible to observe macro porosity by optical microscope and scanning electron microscopy as they are of the order 50 nm and greater. There is no actual upper limit to the diameter of the pores but it is usually 1-2mm.

Adsorption is via the layer by layer mechanism typical of non-porous solids and they act as transport pores allowing access to the internal surfaces and microporosity. These pores do not contribute considerably to the surface area of the adsorbent, typically less than 2 m2/g.

3.2.4.4 Classification of Adsorption Isotherms

Adsorption isotherms should conventionally be plotted on the basis of relative pressure, p/po (x-axis) versus amount adsorbed expressed as a molar quantity (y-axis) in mmolg-1, to allow comparisons to be made. The experimental procedure involves the use of partial pressure, where the actual pressure is expressed with respect to the saturation vapour pressure at a constant temperature of adsorption, hence the process is isothermal. Adsorption data may alternatively be expressed in terms of an isobar, the variation in uptake with temperature at constant pressure, or an isostere, the change in temperature with pressure at a constant surface coverage. Isotherms provide a significant amount of

information about the adsorbent used and the interaction with the adsorbate in the system, including:

i) assessment of the surface chemistry and fundamentals involved in the adsorption process;

ii) estimates of the surface area, pore volume and pore size distribution;

iii) efficiency profiles for carbons used in industrial processes.

The interpretation of adsorption isotherms can yield a large amount of information about the processes involved, as outlined above, but this is only possible upon careful analysis of the data obtained and this can often lead to confusion in the interpretations made.

The extent of adsorption on a surface, usually denoted n, is generally a function of the temperature, pressure and nature of the adsorbent and adsorbate:

n = f(P, T, adsorbate, adsorbent)

For isothermal adsorption of a particular system this simplifies to

n = f(P)T, adsorbent, adsorbate)

By working within the limits of vacuum and the saturation vapour pressure, the pressure may be expressed in terms of relative vapour pressures, i.e. p/po:

n = f(p/po)T, adsorbent, adsorbate

This gives a universal basis upon which all isotherms may be displayed in order to make the comparison of results easier. The above relationship may be used to graphically represent uptake profiles in the form of an 'adsorption isotherm'.

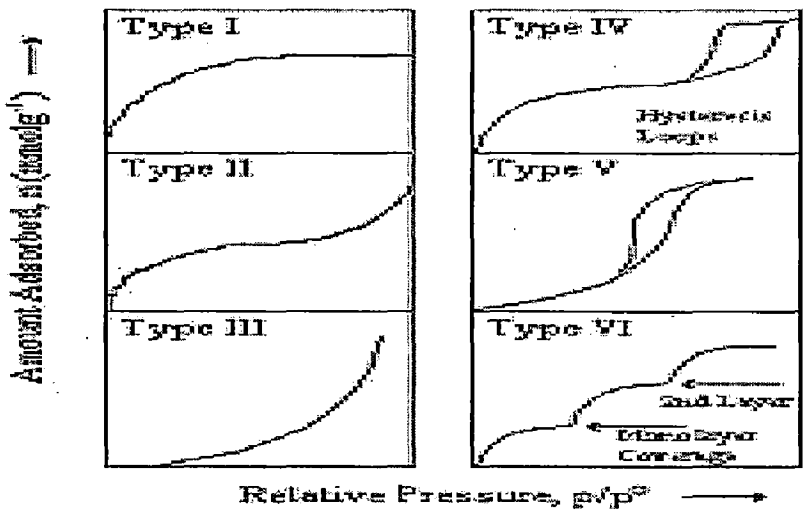


Fig. 3.3: Diagrammatic Representation of Isotherm Classification

The figure above shows the possible shapes and information which may be drawn from them is outlined below.

Type I Isotherm - these are typical of adsorbents with a predominantly microporous structure, as the majority of micropore filling will occur at relative pressures below 0.1. The adsorption process is usually complete at a partial pressure of ~0.5. Examples include the adsorption of nitrogen on carbon at 77K and ammonia on charcoal at 273K.

Type II Isotherm - physical adsorption of gases by non-porous solids is typified by this class of isotherm. Monolayer coverage is followed by multilayering at high relative pressures. Carbons with mixed micro- and meso-porosity produce Type II isotherms.

Type III Isotherm - the plot obtained is convex to the relative pressure axis. This class of isotherm is characteristic of weak adsorbate-adsorbent interactions [Kiselev,et.al.1968] and is most commonly associated with both non-porous and microporous adsorbents. The weak interactions between the adsorbate and the adsorbent lead to low uptakes at low relative pressures. However, once a molecule has become adsorbed at a primary adsorption site, the adsorbate-adsorbate interaction, which is much stronger, becomes the driving force of the adsorption process, resulting in accelerated uptakes at higher relative pressure. This co-operative type of adsorption at high partial pressures is known as cluster theory and examples include the adsorption of water molecules on carbon where the primary adsorption sites are oxygen based.

Type IV Isotherm - A hysteresis loop, which is commonly associated with the presence of mesoporosity, is a common feature of Type IV isotherms, the shape of which is unique to each adsorption system. Capillary condensation gives rise to a hysteresis loop[Sing, K.S.W.; Everett, D.H.; Haul et.al.1985] and these isotherms also exhibit a limited uptake at high relative pressures.

Type V Isotherm - these isotherms are convex to the relative pressure axis and are characteristic of weak adsorbate-adsorbent interactions. These isotherms are indicative of microporous or mesoporous solids. The reasons behind the shape of this class of isotherm are the same as those for Type III and again water adsorption on carbon may exhibit a Type V isotherm.

Type VI Isotherm - introduced primarily as a hypothetical isotherm, the shape is due to the complete formation of monomolecular layers before progression to a subsequent

layer. It has been proposed, by Halsey, that the isotherms arise from adsorption on extremely homogeneous, non-porous surfaces where the monolayer capacity corresponds to the step height. One example known to exist is the adsorption of krypton on carbon black (graphitised at 3000 K) at 90K.

3.3 BIOFILTRATION

Organic solvent emissions result in a variety of challenges for both formulators and applicators of paint and coatings, petrochemical and pulp and paper. Workers and nearby residents can also be affected by health threats and unwanted effluents from these industries. In addition, regulatory requirements affect product formulations, application methods, and even set production limits. Great progress has been made through pollution prevention efforts and incorporating new products and processes that emit less solvent; however, more cost-effective methods, such as biofiltration, are needed to control solvent emissions.

3.3.1 BASICS

So, what is a biofilter? "Filter" suggests a physical mesh that removes particles from the air, but this is misleading. Biofiltration is actually an effluent treatment process based on concepts that are literally as old as dirt. Nature has provided bacteria and fungi that are capable of using almost any organic material as a food source. These microbes are plentiful in organic soils and decaying vegetable matter. Biofilters are a controlled environment where the organic solvents and odor compounds are brought in contact with the natural microorganisms that can use them as a food source. The end products of this degradation are carbon dioxide and water vapor. The concept, then, is to pass the contaminated effluent through garden mulch where the microbes will capture and eat the solvents and odors (see figure 1) .

Traditional biofilters have successfully used these principles for decades, with more widespread use in Europe than the United States. They have typically been very large, single-layer units that rely on a loose bed of organic media to control conditions for treatment. There have been significant limitations in handling high or variable concentrations of solvents. Engineered biofilters use a variety of advances to increase their efficiency of treatment and reduce their size from something like a parking lot to a parking space. First, the contaminated effluent is conditioned to maintain temperature and

humidity levels ideal for the metabolism of the microbes. Second, the compost or organic media that supports the microbes is structured to increase the effective surface area and allow multiple layers. In brief, it is an engineered ecosystem where the microorganisms think they are in Miami on Spring Break with the buffet always open and consisting of the organic solvents and odors. The contaminated effluent is conditioned through water contact in the biotrickling filter, followed by full treatment through the layers of the compost biofilter.

3.3.2WHAT IS BIOFIFLTRATION?

Biofiltration is a relatively new pollution control technology. It is an attractive technique for the elimination of malodorous gas emissions and of low concentrations of volatile organic compounds (VOCs).

The most common style biofilter is just a big box. Some can be as big as a basketball court or as small as one cubic yard. A biofilter's main function is to bring microorganisms into contact with pollutants contained in effluent stream. The box that makes up this biofilter contains a filter material, which is the breeding ground for the microorganisms. The microorganisms live in a thin layer of moisture, the "biofilm", which surrounds the particles that make up the filter media. During the biofiltration process, the polluted air stream is slowly pumped through the biofilter and the pollutants are absorbed into the filter media. The contaminated stream is diffused in the biofilter and adsorbed onto the biofilm. This gives microorganisms the opportunity to degrade the pollutants and to produce energy and metabolic byproducts in the form of CO_2 and H_2O.

This biological degradation process occurs by oxidation, and can be written as follows:

Organic Pollutant + O_2 □ CO_2 + H_2O + Heat + Biomass

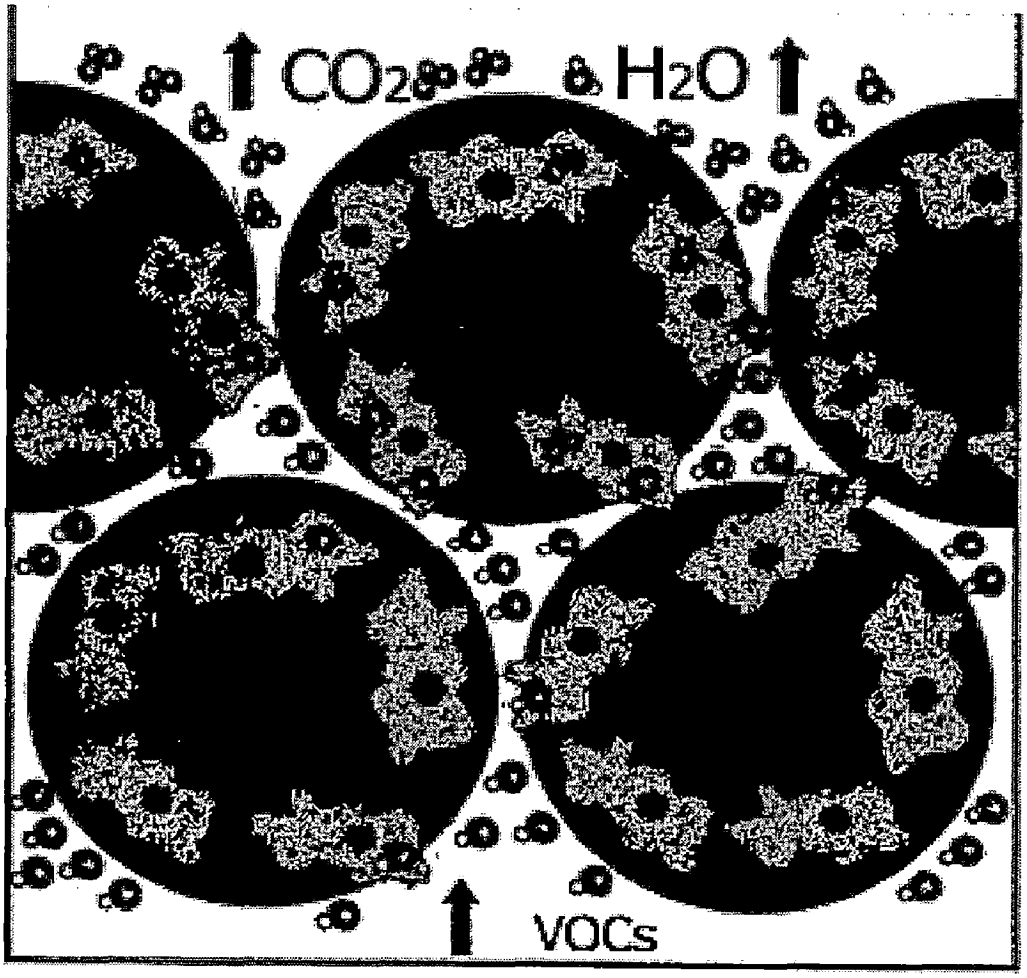


Figure 1. Biofiltration process.

3.3.3 BACKGROUND

While the use of biofiltration in the United States is not wide spread, hundreds of these systems are successfully operating in Europe, Netherlands, New Zealand, Germany, and Japan. Biofilters have been designed primarily for odor control at wastewater treatment plants, rendering plants, and composting operations. However, biofilters are becoming more popular in the treatment of VOCs and other organic compounds (et.al. Selvi B. Anit , Robert J. Artuz).

The following is a brief timeline of the development of biofilters:

1923 -- Biological methods were proposed to treat odorous emissions.

1955 -- Biological methods were applied to treat odorous emissions in low concentrations in Germany.

1960's -- Biofiltration was used for the treatment of pollutants both in Germany and US.

1970's -- Biofiltration is used with high success in Germany.

1980's -- Biofiltration is used for the treatment of toxic emissions, effluent and volatile organic compounds (VOCs) from industry.

1990's -- Today, there are more than 500 biofilters operating both in Germany and Netherlands and it is widely spreading in US.

Applications for odor control have occurred since the 1950s and ranged from soil filters to large biological trickling filter plants. Odorous air emissions generally can be characterized as having relatively low pollutant concentrations that include hydrogen sulfide, mercaptons, and other reduced sulfur compounds. In addition, applications for VOC control have just become popular in the past decade and are still being researched extensively. For example, research has shown that biofilters can be used to remove a variety of airborne contaminants, including aliphatic and aromatic hydrocarbons, alcohols, aldehydes, organic acids, phenols, acrylate, carbolic acids, amines and ammonia.

3.3.4 PROCESS DESCRIPTION

Biofiltration utilizes a supported media for microbial growth to remove odors and organic contaminants from air streams and liquid effluent. The filter consists of a closed chamber containing contaminant degrading microbes and absorbed water suspended in a filter medium. The filter medial is designed to provide a high capacity for water uptake, have a long working life, and provide a low pressure drop for the effluent passing through the media.

3.3.4.1 Biofilter media:

The moist filter medium provides physical and chemical conditions appropriate for the transfer of contaminants from the effluent to the liquid phase and the biodegradation of the contaminants in the biofilm layer. The mechanism of the biofiltration process

includes a combination of adsorption, absorption and microbial degradation. Microorganisms contained in the biofilm layer continually metabolize the contaminants, as they are absorbed, converting them ultimately to water, carbon dioxide and salts.

Typical biofilter media material includes compost-based materials, earth, heather, plastic, or wood-product based material. The purpose of the biofilter media is to provide a large surface area for the absorption and adsorption of contaminants. The media also serves as a nutrient source for the microbial population. In fact, some types of media lack proper nutrients and will require the manual addition nutrients (e.g. nitrogen and phosphorous compounds) in order to sustain microbial life. Most biofilters will operate for 5-7 years before it is necessary to renew the filter media.

Major considerations when determining the appropriate filter material include:

1. Ability to retain moisture to sustain biofilm layer;
2. Large surface area, both for contaminant absorption and microbial growth;
3. Ability to retain nutrients and supply them to microbes as required;
4. Low resistance to effluent flow;
5. Physical characteristics, such as physical stability and ease of handling

3.3.5 DESIGN PARAMETERS

3.3.5.1 *Space Constraints:*

Space at a site is the greatest concern during design of a biofiltration system. A small biofiltration unit can be designed to handle approximately 30 cubic-feet-per-minute in as little space as 25 square feet, similarly, a biofiltration system designed to treat large volumes of effluent and require space as large as a basketball court.

3.3.5.2 *Chemical Constituents and Concentrations:*

Analysis of chemical constituents and their concentrations are required to determine if biofiltration is a plausible alternative. Biofilters performed best when treating hydrophilic compounds in low concentrations (<1000 ppm). Some chemicals biologically degrade at low rates, such as chlorinated compounds, which require units to be oversized.

3.3.5.3 *Residence Time:*

Residence Time represents the amount of time the microbes are in contact with the contaminated air stream, and is defined by (Void Volume/Volumetric Flow Rate). Consequently, longer residence times produce higher efficiencies; however, a design

must minimize residence time to allow the biofilter to accommodate larger flow rates. For most biofilters, residence times range between 30 seconds to 1 minute.

3.3.5.4 *Humidity:*

The humidity of gas stream is important for maintaining the moisture content of the biofilter media. Gas streams introduced to the biofiltration system are usually pumped through a humidifier prior to entering the biofilter. The gas entering the biofilter should be humidified to greater than 95% relative humidity.

3.3.5.5 *Ph-Control:*

The by-products of microbial degradation are organic acids. In order to maintain the pH of the vessel around neutral, or a pH of 7, buffering material may be added to the organic media.

3.3.5.6 *Biofilter Media:*

The media used in biofilters can include peat, heather, bark, composted sewage sludge, granular carbon or other suitable materials. Generally, the media should be capable of providing nutrients to the microorganisms and minimizing pressure drop. In addition, the moisture content of the biofilter media must be maintained between 30% and 60% in order to support the microbial population. In addition to humidifying the airflow, sprinkler systems are frequently installed inside the biofilter that can be controlled to maintain a suitable bed moisture.

3.3.5.7 *Pressure Drop:*

Pressure drop across the biofilter reactor vessel should be minimized since an increase in pressure drop requires more blower power and can result in air channeling through the media. Pressure drop is directly related to the moisture content in the media and the media pore size. Increased moisture and decreased pore size result in increased pressure drop. Consequently, media filter selection and watering is critical to biofilter performance and energy efficiency. For a typical biofilter pressure drops range between 1 and 10 kPa.

Maintenance:

The operation and maintenance of the biofiltration system would require weekly site visits during initiation of operations for maintenance. However, after acclimation and all system problems are resolved the frequency of site visits could be reduced to the biweekly or monthly.

3.3.6 ADVANTAGES AND DISADVATAGES OF BIOFILTRATION

3.3.6.1 Advantages of Biofiltration:

1. The main advantage of using biofiltration over other more convention control methods are lower capital costs, lower operating costs, low chemical usage, and no combustion source.
2. Biofiltration units can be designed to physically fit into any industrial setting. A biofiltration unit can be designed as any shape, size or as an open field with the piping and delivery system underground. In addition, biofilters can be designed with stacked beds to minimize space requirements and multiple units can be run in parallel.
3. Biofiltration is versatile enough to treat odors, toxic compounds, and VOCs. The treatment efficiencies of these constituents are above 90% for low concentrations of contaminants (<1000 ppm).
4. Different media, microbes and operating conditions can be used to tailor a biofilter system for many emission points.

3.3.6.2 Disadvantages of Biofiltration:

1. Biofiltration cannot successfully treat some organic compounds, which have low adsorption or degradation rates. This is especially true for chlorinated VOCs.
2. Contaminant sources with high chemical emissions would require large biofilter units or open areas to install a biofiltration system.
3. Sources with emissions that fluctuate severely or produce large spikes can be detrimental to the of a biofilter's microbial population and overall performance.
4. Acclimation periods for the microbial population may take weeks or even months, especially for VOC treatment.

3.3.7 COMMERCIAL APPLICATIONS

There have been over 50 commercial biofilters using compost-type material installed in Europe and the United States over the past 15 years.

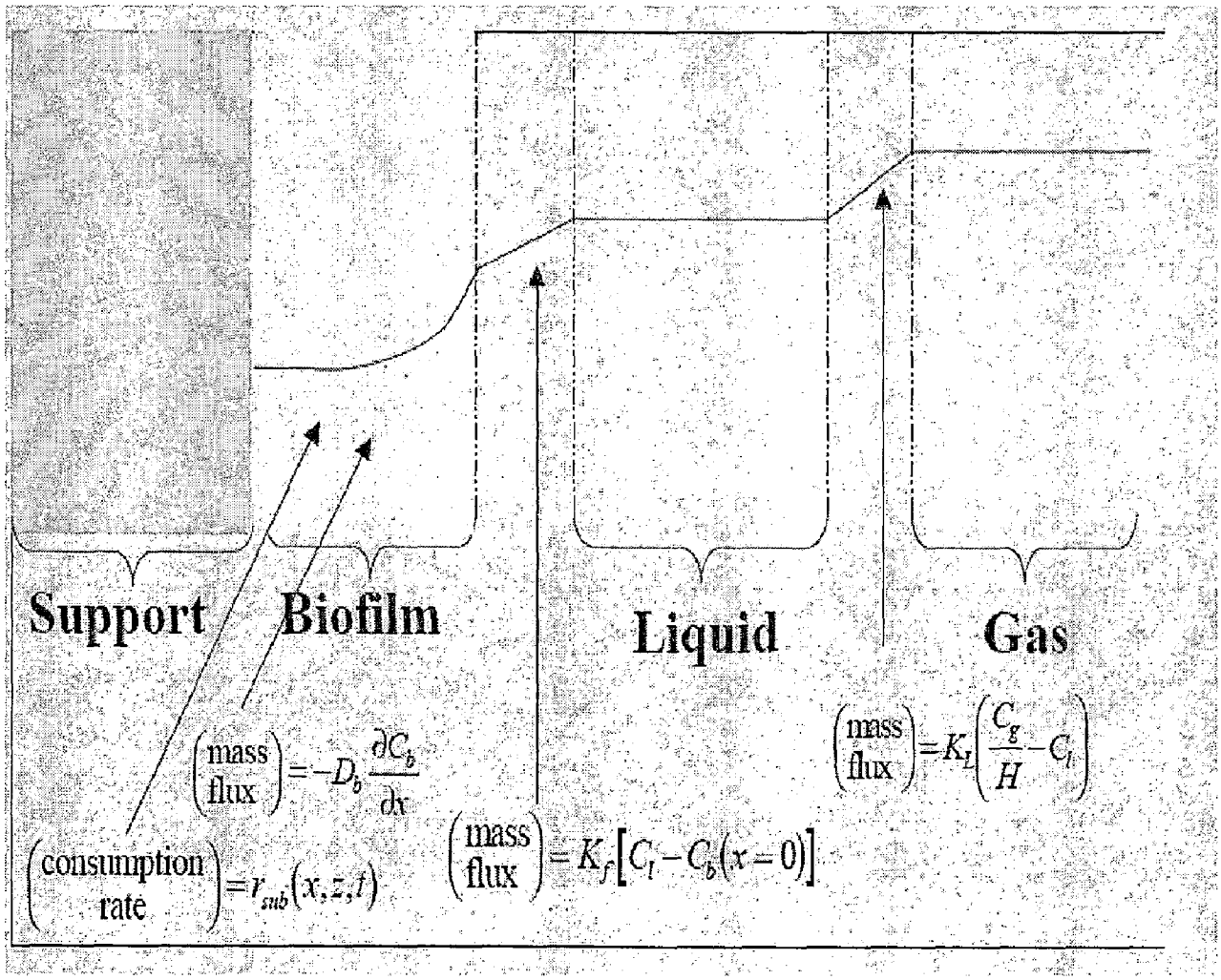
VOC applications to date have included the following industries:

- Chemical and petrochemical industry
- Oil and gas industry
- Synthetic resins
- Paint and ink
- Pharmaceutical industry
- Waste and wastewater treatment
- Soil and Groundwater remediation
- Pulp and Paper industry

Odor abatement applications to date have included the following industries.

- Sewage treatment
- Slaughter houses
- Rendering
- Gelatin and glue plants
- Agricultural and meat processing
- Tobacco, cocoa and sugar industry
- Flavor and fragrance

3.3.8 SCHEMATICS OF A BIOFILTER



3.3.8.1 Mathematical model

3.3.8.2 *Material balances in gas phase*

The plug flow model without dispersion is applied as follows:

$$\frac{\partial C_g}{\partial t} = -U\frac{\partial C_g}{\partial h} + R_x \qquad (1)$$

Consider steady state system with the solid phase in equilibrium, and with the assumption that the contaminant and water are only exchanged between biofilm and gas phase. For the contaminant and water movement, the following equations apply:

$$U\frac{\partial C_g}{\partial h} = R_x \qquad (2)$$

*R*x is the overall reaction rate per unit biofilter volume which is equal to the volumetric rate across gas/biofilm interface (fluxB). Hence,

$$U\frac{\partial C_g}{\partial h} = \text{fluxB} \qquad (3)$$

where fluxB can be defined in terms of a partial differential equation as follows:

$$\text{fluxB} = D_s A_s \left(\frac{\partial C_s}{\partial r}\right)_{r=R_c+\delta} \qquad (4)$$

with the initial condition;

$Cg = Cgi$ at $h = 0$ (5)

where U is the superficial velocity (m s−1), Cg the concentration in the gas phase (gm−3), e.g. pollutant and water, Cgi the initial concentration in the gas phase (gm−3), e.g. pollutant and water, h is the bed height (m), As the specific area of the biofilm per unit biofilter volume (m2 m−3), Ds the diffusivity in the biofilm phase (m2 s−1), Cs the concentration in the biofilm phase (gm−3), r the distance in biofilm phase (m), δ the biofilm thickness (m) and Rc is the particle radius (m).

3.3.8.3. *Material balance in biofilm phase*

For each of the species involved (contaminant and water), the following equations apply:

$$D_s\left[\frac{\partial^2 C_s}{\partial r^2} + \frac{S}{r}\frac{\partial C_s}{\partial r}\right] - r_x = 0 \qquad (6)$$

where S is the shape factor which equals 0 for planar shape, 1 for cylindrical shape, and 2 for spherical shape; c and w are the subscripts for contaminant and water, respectively; rx can be either rc or rw, as given by

$$r_c = r_m \frac{C_s}{K_m + C_s} \qquad (7)$$

$$r_w = -\upsilon\left(r_m \frac{C_s}{K_m + C_s}\right) \qquad (8)$$

where rx is the volumetric rate of consumption for pollutant (rc) and production for water (rw) (gm−3 s−1), υ the g of water produced by conversion of 1 g of methanol, rm the maximum rate of reaction per unit biofilm volume (gm−3 s−1), and Km is the Monod constant (gm−3). Considering the boundary conditions, the material balance across the gas/ biofilm interface requires that

$$D_s A_s \left(\frac{\partial C_s}{\partial r}\right)_{r=Rc+\delta} = k_g A_s [C_g^* - C_g]_{r=Rc+\delta} \qquad (9)$$

where *k*g is the mass transfer coefficient in the gas phase (m s−1), *m* the distribution coefficient between gas and biofilm phase, and C□g is the contaminant concentration in the gas phase at equilibrium which is defined as follows:

$C\square g = mCs$ at $r = Rc + \delta$ *(gas/biofilm interface)* (10)

Where *m* is the distribution coefficient between gas phase and biofilm phase.

When the mass transfer rate in the gas phase is very large, *k*g approaches infinity. Eq. (10) becomes the boundary condition at gas/biofilm interface and is arranged as follows:

$$C_s = \frac{C_g}{m} \quad \text{at} \quad r = R_c + \delta \qquad (11)$$

When the solid phase is in equilibrium,

$$\frac{\partial C_s}{\partial r} = 0 \quad \text{at} \quad r = R_c \qquad (12)$$

Table 3.3: A comparison of different types of reactors with biofilm reactors

Reactor Type	Comments
Membrane reactor	
Advantages	High productivities, high cell concentration can be achieved inside the reactor, clear permeates for further separation
Disadvantages	Fouling with cells, cost prohibits their use in low cost large volume chemical production
Immobilized cell reactors	
Covalent bond formation	
Advantages	High cell concentration may be achieved, high productivity
Disadvantages	Cell growth inside matrix may be restricted, cells leach out of the matrix and hence centrifugation of effluent may be required, chemical may affect the cells
Entrapment	
Advantages	High cell concentration may be achieved, high productivity
Disadvantages	Matrix often starts disintegration with time, cells leach out of matrix, centrifugation of reactor effluents is required for further separation
Biofilm	
Advantages	Comparatively high reactor productivities and high cell concentrations are achieved, reactors run longer and are economic to operate
Disadvantages	Effluent centrifugation is required

3.4 Simultaneous Adsorption and Biodegradation

Adsorption is widely used in the treatment of wastewater now a day. Granular powered carbon is the most widely used adsorbent, as it has a good capacity for the adsorption of organic molecules. A typical activated carbon particl, whether in a powdered or granular form, has a porous structure consisting of a network of inter connected macropores and mesopores that provide a good capacity for the adsorption of organic molecules due to its high surface area. The surface chemistry of activated carbon and the chemical characteristics of adsorbate, such as polarity, ionic nature, functional groups, and solubility, determine the nature of bonding mechanisms as well as the extent and strength of adsorption .A variety of physicochemical forces, such as vanderwaals, H-bonding, dipole-dipole interactions, ion exchange, covalent bonding, cation bridges and water binding can he responsible for the adsorption of organic compounds in activated carbon. In spite of these characteristics, activated carbon suffers from a number of disadvantages. It is quite expensive and the higher the quality, the greater is the cost.

However, high cost of activated carbon and 10-15% loss during conventional regeneration has been the disadvantage in the utilization of activated carbon in the developing countries. Thermal regeneration and chemical regeneration are expensive and time consuming.

Several methods of treatment of wastewater with high phenol content have been used. These include physico-chemical treatment processes, chemical oxidation and biological degradation processes. The biological treatment methods include activated sludge process and its modified form i.e. trickling filters, aerated lagoons and waste stabilization ponds.

Biological treatment for phenol removal is practiced in a number of industries at which the combined plant effluent is treated biologically for the removal of biochemical oxygen demand in addition to phenol reduction. Phenolic wastewaters from cooking plant, steel mills, aircraft manufacturing units, herbicide manufacturing, petroleum refineries etc have been treated for many years by adopting activated sludge process and trickling filter [2j.Until now, the most used technique for biological treatment is activated sludge process with adequate retention times in the aerating tank. But for high strength and low volumes of wastewaters, adsorption is widely used. Granular and powdered activated carbon is used as adsorbate.

However, high cost of activated carbon, 10-15% loss during regeneration and high cost of regeneration have been the deterrents in the utilization of activated carbon directly. This leads investigators to search for effective utilization of adsorption as well as biological treatment investigated the combination of adsorption and biodegradation of phenol on activated carbon. They used different type of cultures and some mixed cultures.

Attempts have been made to remove phenols from wastewater. Recently developed methods dealing with the removal of such compounds are adsorption and biological treatment, either operated separately or simultaneously in one unit. In most cases, the presence of hotly processes in one unit results in a better removal and process performance. Microbial mass can, in some extent, adsorb the substances, but at the same time it also degrades them. On the other band, adsorption of the substances onto adsorbent reduces the inhibitory effect of the substances for microbial mass. Accordingly, the process is expected to be more stable and the toxic compounds may be converted into less harmful substances.

With respect to process operation, simultaneous adsorption and biological, treatment is commonly applied in a conventional activated sludge process added with powder or granular activated carbon. The presence of adsorbent shows an increase in the removal efficiency. The use of biological process is also found in fluidized and fixed bed reactors having microbial film on the solid surface. In the presence of microbial film, the removal of substances is mechanistically complex involving (i) transport of substances from the bulk liquid to the surface of microbial film, (ii) simultaneous mass transfer, adsorption, and biochemical reaction within microbial film, and (iii) simultaneous mass transfer and adsorption within adsorbent. The complexity increases due to dynamic nature of the microbial film. As biochemical reaction of substances may occur on the adsorbent and in bulk suspension, the presence of biomass in adsorption process could also be expected, in some extent, to regenerate the adsorbent and thus long life operation of adsorption process may be expected.

Biological treatment for phenol removal is practiced in a number of industries. But phenol is not readily biodegradable. It is toxic to most types of microorganisms at sufficiently high concentrations and at low concentrations it can be inhibitory to the growth rate of even those species which have 'the metabolic capacity of using it as a

substrate for growth. Immobilization technology has been used in the biotreatment of wastewater.

Among the major limitations on the use of only biological system alone to degrade organic pollutants in water, are the variation in concentration and spectrum of the toxicants, which makes it difficult to maintain biological reactors under steady conditions for long periods of time. This effect is some times amplified when biological system deals with mixed microbial population. Suspended growth is ineffective for the treatment of toxic materials because the contact between the microorganisms and the contaminants is frequently limited. Hydraulic resident times often forecast the slower biodegradation rates.

But in the combination of adsorption and biodegradation the presence of activated carbon increases the liquid-solid surfaces, on which microbial cells, enzymes, organic materials and oxygen are adsorbed providing an enriched environment for microbial metabolism. Surface catalysis of physico-chemical reactions is also possible on the surface of activated carbon. The carbon adsorption capacity, controlled by the bioregeneration, is highly increased and the carbon adsorption column cycle is prolonged as compared to pure adsorption system alone. As a result, when simultaneous adsorption and biodegradation occurs, the organic contaminants removal efficiency and the final water quality are substantially improved.

Biologically treated wastewater is finally cleaned by carbon filter. Inversely the activated carbon adsorption can possibly allow the removal of toxic contaminants from the wastewater and thus ensures a stable biological post-treatment of the wastewater.

The most important advantage of simultaneous adsorption and biodegradation in reactor is the stable performance during peak loads because of the adsorption capacity reserve created by activated carbon bioregeneration. For continuous operation with granular activated carbon or immobilized biomass the most convenient configuration is that of a packed bed reactor.

3.5 Objective of the present work

1. To study the performance of biologically activated carbon reactor at different input parameters.
2. To optimize design parameter for best performance of the reactor.
3. To make a comparative study of specific uptakes for fresh activated carbon (GAC) and bio-regenerated granular activated carbon and to compare their characteristics.
4. To calculate the % bioregeneration of adsorption capacity of the prepared activated carbon of column for phenol removal and to compare the efficiency of the reactors.
5. The main aim of present work is to find out the biodegradation capacity of removal of phenol from waste water and to compare the performance of adsorption, biodegradation of phenol by pseudomonas putida, and bio sorption.
6. Another objective of the project work is to investigate the physical and chemical characteristics of low cost activated carbons prepared from bagasse pith and bottom ash.
7. Further more the work has been extended to find out the optimum conc., pH and flow rate
8. Also work has been done to find the phenol removal capacity of these adsorbents.

CHAPTER 4

EXPERIMENTAL PROCEDURE

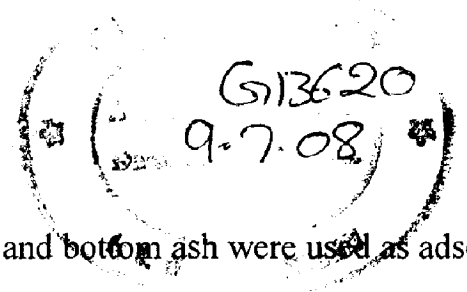
Batch studies and column (filtration tower) studies were carried out to understand the effect of different adsorbent dose, adsorption capacity of different activated carbons, initial concentration, pH, particle size of the adsorbent on the removal of phenol was performed for adsorption and, simultaneous adsorption & biodegradation (SAB).

Further studies were carried out to find the properties and phenol adsorption capacities of various agro base activated carbons prepared from bottom ash and bagasse pith.

Bioregenerated granulated activated carbon was used to study the percentage regeneration of carbon.

4.1 Materials

The compounds namely, phenol and other chemicals were all AR grade and were supplied by M/s. S.d fine-chem. Ltd.



4.1.1 Adsorbent

The activated carbon prepared from baggasse pith and bottom ash were used as adsorbent in the size range of 2-5mm. These particles were sieved into three fractions of 1.4-2 mm, 2-4 mm, and 4- 5 mm particle sizes, of which only 2-4mm were used in the present study. Initially, the, carbon particles were cleaned with distilled water to remove the fines and then dried in the oven for 24 hrs at 110°C.

4.1.2 Adsorbent preparation

The bagasse pith collected from a sugar industry, the Co-operative Sugars Ltd., Palakkad, Kerala, India was washed several times with distilled water and left to dry. The carbonisation of the bagasse pith was performed in a Matri-made muffle furnace (India) at 200°C for 2 h (C-200). Steam activation (SA) of the carbon (C-200) was carried out using the method described by the earlier workers (Warhurst et al., 1997). About 50 g of the carbon was placed in a Silica crucible and positioned at the centre of the furnace. The sample was heated at a rate of 10°C/min to 400°C and held at this temperature for 1 h. After allowing the furnace to cool to room temperature, the product was removed and washed with 1 M HCl and distilled water. The material was then washed with sulfuric acid and phosphoric acid for acid activation of the burnt up carbon particles along with

stirring. Then the activated carbon is again washed with distilled water and kept in oven for 20 hrs.

4.1.2.1 Physical and surface characteristics of Adsorbent:

Burn-off and carbon yield: Both burn-off and activated carbon yield were calculated. Burn-off is the weight loss of pyrolyzed char, determinedon a dry weight basis, that occurs during the activation process. Yield is the amount of original precursor remaining after pyrolysis and activation.

Burn-off =[(Wb – Wa)*100/Wb]

And

Yield = (Wa/Wc) x 100

Where:

Wb = dry weight before activation

Wa= dry weight after activation

Wc = dry weight of precursor before pyrolysis

Surface area measurement

One hundred to 200 mg of both commercial and experimental carbons were dried under vacuum at 110°C for 3 h to remove moisture from the carbon pores. Surface area (SBET) measurements were obtained from nitrogen adsorption isotherms at 77K using a Micromeritics Gemini III 2375 Surface Area Analyzer (Micromeritics, Inc., Norcross, GA).

Bulk density

The procedure of Ahmedna et al. (1997) was used. A weighed amount of 12-40 mesh granular carbon was added to a 10 ml graduated cylinder. The cylinder was tapped constantly until there was no Volume change and the bulk density was calculated.

Bulk density = wt. of dry sample / volume of packed dry sample

Hardness number

Hardness determinations were conducted by the method of Ahmedna et al. (1997): 3 g of 12-40 mesh granular carbon was placed in a 250 ml Erlenmeyer flask. Ten glass marbles of about 5 g each were added to the flask, which was then continuously agitated at

200 rpm in an Aquatherm water bath shaker (New Brunswick Scientific Co., Edison, NJ) for 15 min at 25°C. The carbon retained by a 40 mesh sieve was weighed and the hardness number calculated.

Hardness number = (weight of carbon retained x 100) / initial sample weight

pH and Bulk Density Determinations

The pH of each carbon sample was determined by immersing 1.0 g sample in 100 ml of de-ionized water and stirring for 1 hour.

Ash content

A weighed quantity of carbon was placed in a porcelain crucible and set in a circulating air oven at 115°C for 16 h. The samples were then weighed and placed in a muffle furnace and heated at 950°C for 1.5 h with constant air circulation. The crucibles were cooled in a dessicator and reweighed. The residue weight was calculated and reported as percent ash.

Particle size

The particle size distribution of bottom ash was determined by sieving the samples manually shaking with stainless steel mesh screens with openings.

Iodine Number

The iodine number of the prepared activated carbon was measured by titration at 30 °C based on the standard method (ASTM Designation D 4607-94).This parameter was used to evaluate the activated carbon adsorption capacity [15].

Conductivity Measurement

Conductivity measurements were carried out by the method of Ahmedna (1998). A 1% (wt/wt) solution of GAC in water was stirred at room temperature for 20 min. Electrical conductivity was measured using an EDT instrument BA380 conductivity meter with values micro Siemens (ls) [21].

4.1.3. Stock solution

Stock solution of phenol with a concentration of 10 gm/l was prepared by dissolving 10 gm of the compound in 1 liter distilled water respectively.

4.1.4. Microorganism

A pure culture of Pseudomonas putida was procured from IMTECH, Chandigarh and was further grown.

4.1.5. Growth Medium

Apart from the carbon source, the bacteria require many macro and micronutrients for their Nutrient agar medium was used whose composition is given in table 3.1

4.1.6. Revival of Culture

As the freeze- dried culture lyophilized culture can't be used directly for the degradation studies, this obtained culture from IMTECH was revived according to the procedure prescribed by the, IMTECH, Chandigarh, India.

Table 4.1 : Optimum Conditions of Growth For Microbial Culture

Culture	*Pseudomonas Putida(MTCC1194)*
Growth Condition	Aerobic
Temperature	25^0C
Incubation Time	24 Hours
Subculture	30 days

Table 4.2: Composition of Nutrient Agar Medium

Nutrient	Concentration(gm/l)
Beef Extract	1.0
Yeast Extract	2.0
Peptone	5.0
NaCl	5.0
Agar(for solid medium)	15.0

Agar is a complex poly saccharide (carbohydrate), consists of 3, 6- anhydro- L- glactose and D-galacto pyranose, free of nitrogen.

4.1.7 Basal Salt Medium

The composition of basal salt medium used for the present research work is given in the table 4.3 below.

Table 4.3: Composition of B.S.M.

K_2HPO_4	1.5 (g/l)
KH_2PO_4	0.5
$(NH_4)_2PO_4$	0.5
NaCl	0.5
Na_2SO_4	3
Yeast Extract	2
Glucose	0.5
Ferrous Sulphate	0.002
Calcium Chloride	0.002

4.2 Method for Determination of Phenol Concentration

The concentration of the phenol in the solutions was measured by using UV/VTS spectrophotometer. [Model Perkin Elmer]

Procedure for determination of phenol concentration:

The method most commonly used for the detection and quantification of phenol in water and wastewater is the Direct Photometric Method as outlined in the Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 1992) (APHA), This method relies on phenol reacting with 4- aminoantipytine with potassium ferricyanide present, thus forming a coloured antipyrine dye. The absorbance of aminoantipyrine is then measured at a wavelength of 500 nm in a 40 mm cuvette. The volume of sample required by this method to detect the minimum detectable concentration of phenol (0.1 mg/l) is 100 mL (Standard Method in Table 2), A 100 mL sample size would be too large to collect (about 40 mm.) from a 300 mL to 400 mL bioreactor during a fermentation, and therefore would not be representative of that time. To overcome this problem a small sample size of 4-5 mL would be used, as this would be a more reasonable sample volume to collect from the bioreactor, and would give an adequate sample volume for use with a 40 mm cuvette (16 nmL capacity). However,

scaling the assay reagent volumes down by this ratio (1:19) would cause errors in absorbencies, as the volumes of sample and reagents required would be too small to be dispensed precisely and repeatedly. Thus, a dilution in reagent concentration was to be used leaving all reagent volumes the same, but allowing a smaller sample size to be used. In the modified method a 40 mm cuvette was used with a sample size of 5 mL, It was anticipated that this would give increased absorbencies over a wider range,

Reagent/Sample Type	Standard Method (APHA, 1992)				Modified Method
	Original Values		Sample size 4 mL		
	Conc.	Volume*	Conc.	Volume*	Volume*
Sample	–	100 mL	–	4.0 mL	5.0 mL
Ammonium Hydroxide	0.5 N	2.5 mL	0.5 N	0.1 mL	2.5 mL
Phosphate Buffer pH 6.8	0.56M	~2.5 mL	0.56M	~0.1 mL	~2.5 mL
4-amino antipyrine	2%	1.0 mL	2%	0.04 mL	1.0 mL
Potassium ferricyanide	8%	1.0 mL	8%	0.04 mL	1.0 mL
Total Volume		107 mL		4.28 mL	12.0 mL

~ approximate volume (reagent is added until a pH of 6.5 is reached)

Volume* = Reactant Volumes

Table 4.4: Volumes and Concentrations of Assay Reagents for the Standard Method for Phenol Detection (APHA, 1992) and the Modified Assay Method for Phenol Detection.

4.3 Sterility

All the glass wares along with the solid and liquid medium were sterilized in an autoclave at 120 °c forl5 mm holding time.

4.4 Method of Transfer

Liquid medium containing of nutrient growth medium was prepared in distilled water in two 250 ml conical flasks. For solid medium appropriate quantity of agar was added to one of the flask containing liquid medium. Both were autoclaved for 20 mm at 1.05 Kg/cm^2 while hot, the conical flask containing agar was solidified. Inoculation was done in the laminar hood.

4.5 Acclimatization of Culture

Acclimatization of the culture is done to bring the phenol degrading bacteria to the phenol environment. The acclimatization of culture was performed in the batch mode in a 250 ml conical flask. The stock solution of phenol was added to the flask along with the apropriate quantity of BSM salt and the culture so as to give 10 mg/l concentration of phenol. The culture which is used for the experiment to find out the effect of initial concentration was kepr aside with acclimatization of phenol at 10mg/l only. Once the growth was observed, the phenol was added till the concentration reached 100 mg/I. Now this culture, containing 100 mg/l phenol, along with the varying adsorbent dose of the prepared activated carbon was used to degrade different concentration of phenol i.e. from 10-500 mg/l of phenol.

4.6 Measurement of Cell Growth and Phenol Concentration in Batch System

The cell growth was monitored by the optical density in a UV spectrophotoineter at a wave length of 610 nm. For the separation of biomass the samples were first filtered and centrifuged at approximately 12000 rpm for 20 mm .The supernatant was decanted and used for the determination of the phenol.

4.7 pH of the Culture

The pH of the culture was periodically measured by digital pH meter

4.8 Experiment

4.8.1 Preparation of the activated carbon

Activated carbons were prepared from agro base raw material such as bagasse pith and determination of the properties of the activated carbon for different size range.

4.8.2 Batch Study

4.8.2.1 Biological Study

The batch study has been performed for determination of the optimum concentration and the percent removal of phenol with time .

4.8.2.2 Adsorption Study

Batch studies were conducted to find out the effect of mass of adsorbent, on percentage removal of phenol.

4.8.2.3 Simultaneous Adsorption and Biodegradation Study

Batch studies were conducted by using various adsorbent doses, initial concentration pH on percentage removal of phenol.

4.8.3 Details of Biofilter Tower

Column studies have been done firstly for adsorption then biodegradation. The

specifications of the biological tower are given in table 4.4.

Table no. 4.5: Specifications of biological tower

Height of the Reactor	110 cm
Internal Diameter of the Reactor	1.95 cm
Size of the Particle	1.4-4 mm
Amount of Activated Carbon Loaded	30 gm
Total Volume	0.248 ltr
Void Volume	0.98 ltr

Start up of reactor was done by firstly making the column biologically active. Well developed inoculum (by using 400mg/l initial phenol concentration) was added to the column at flow rate of 10ml/min, until the column was filled completely. It was kept for 6 hr and then outlet is opened and inlet is introduced at the flow rate of 10 ml/min with 500 ml of inoculum in the receiver. The inoculum was recirculated to form bioactive film on the granular surface.

The phenol was introduced from the top of the biological activated tower and at outlet degraded solution of phenol samples were collected and filtered with whattman filter paper. Since the cells were immobilized on the surface of the granules, the outlet did not contain cell population, the samples were further analyzed for phenol concentration by using UV spectrophotometer.

The bioregeneration capacity was calculated by conducting another experiment with the exhausted bed. The BAC column was kept for 12hrs with out any activity after the above experiment. The break through curve is found out to calculate the percentage regeneration.

The setup used for the column experiments in the present study is shown in the Fig.4.1

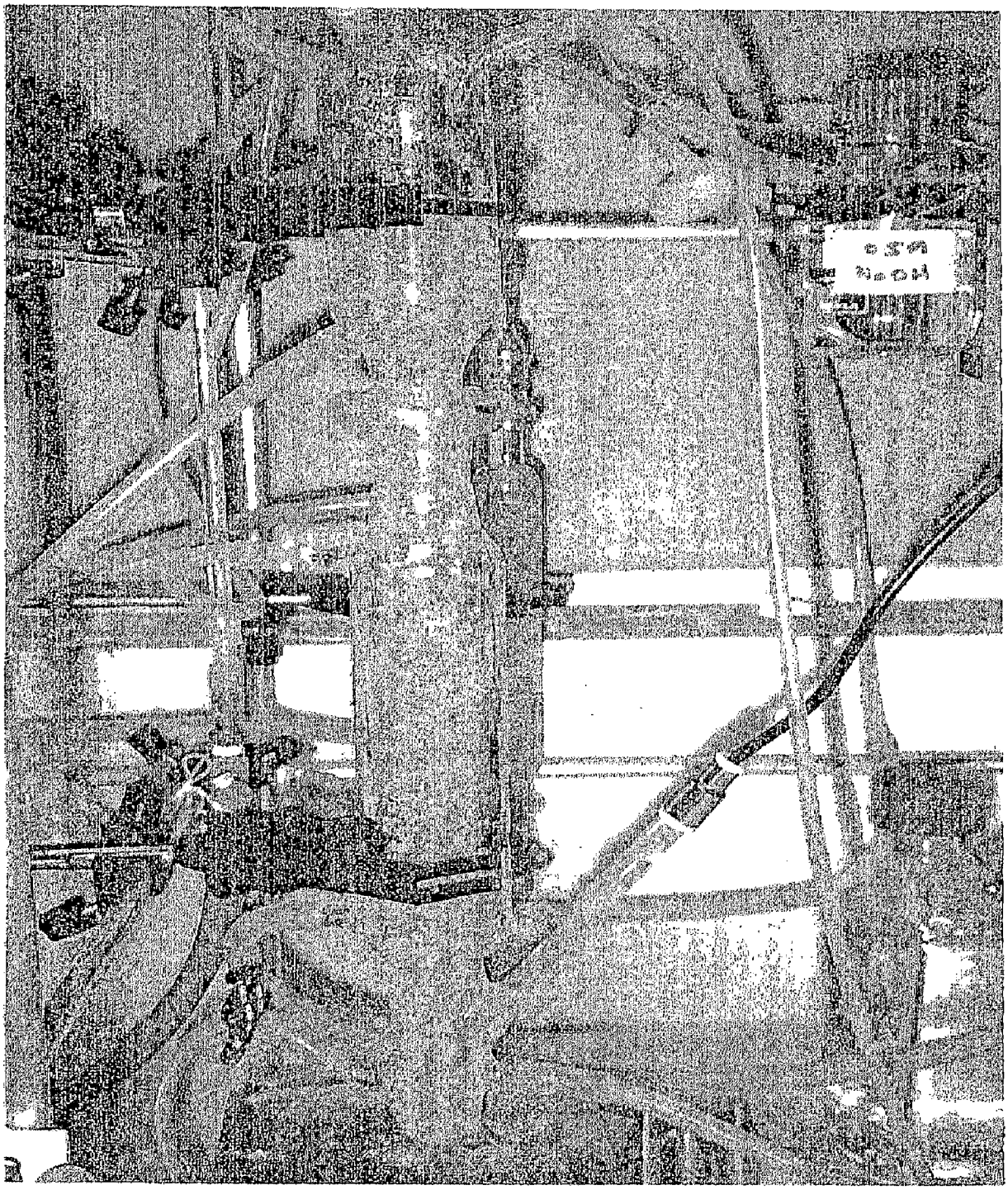


Fig. 4.1 : Photograph of Biodegradation Column

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Physical characterization of prepared activated carbons

5.1.1 Properties of activated carbon prepared from bagasse pith and bottom ash

Physical and surface properties of the prepared activated carbon were investigated and then phenol removal efficiency of both the carbon were studied. Also the effect of addition of binder for granulation of the carbon particles on the properties was studied and is shown in fig. 5.1.

Table 5.1: Physical properties of activated carbon with and without binder

S. No	Properties	Activated carbon from Bagasse pith		Activated carbon from Bottom Ash	
		Without binder	With binder	Without binder	With binder
1	Surface area(S) [m^2/gm]	607	465	543	356
2	Ash content	8.3	7.2	18.2	15.6
3	Pore Volume [cm^3/gm]	0.52	0.48	0.38	0.32
4	Moisture content	14.2	8.45	6.4	5.2
5	Iodine [mg/g]	782	760	542	580
6	Methylene Blue [mg/g]	35.12	32.4	24.56	22.66
7	pH	8.6	7.4	9.04	8.2
8	Bulk Density[g/cc]	.68	0.64	1.4	1.2

5.1.2 Proximate analysis of bagasse pith [wt. %] for different particle size

Analysis of activated carbon prepared from bagasse pith was done and the effect of variation of particle size on volatile matter and carbon was studied and is shown in fig. 5.2.

Table 5.2: Effect of particle size on analysis of bagasse pith

Particle size	>4.75mm	2.38-4.75mm	1.40-2.38mm
Volatile matter (%)	18.63	23.1	18.3
Fixed carbon (%)	65.15	63.60	63.20
Ash (%)	7.8	8.6	9.8
Moisture (%)	8.20	9.6	12.4

5.1.3 Proximate analysis of bottom ash [wt. %] for different particle size

Analysis of activated carbon prepared from bottom ash was done and the effect of variation of particle size on volatile matter and carbon content was studied and is tabulated in fig.5.3.

Table 5.3: Effect of particle size on analysis of bottom ash

Particle size	>4.75mm	2.38-4.75mm	1.40-2.38mm
Volatile matter (%)	18.63	23.1	18.3
Fixed carbon (%)	72	70.4	70.8
Ash (%)	18.8	20.6	22.6
Moisture (%)	4.2	6.8	9.65

5.1.4 Effect of variation of particle size on analysis of methyl blue and iodine no.

Table 5.4 :Iodine and methyl blue adsorption figures for activated carbon from bagasse pith for different particle size

Range[mm]	I[mg/g]	MB[mg/g]
>4.75	582	34.86
2.38-4.75	708	40.11
1.40-2.38	803	72.57

Table 5.5 :Iodine and methyl blue adsorption figures for activated carbon from bottom ash for different particle size

Range[mm]	I[mg/g]	MB[mg/g]
>4.75	512	22.4
2.38-4.75	562	27.2
1.40-2.38	598	30.8

5.2 Batch Study

Phenol biodegradation was studied in batch experiments at 20 – 500 mg/l concentration by free cells and immobilized phenol adapted by pseudomonas putida. The phenol concentration in the medium decreased clearly when the adsorbed microorganism started to grow.

The main aim of present work is to find out the biodegradation capacity of removal of phenol from waste water and to compare the performance of adsorbtion , biodegraditon of phenol by pseudomonas putida, and bio sorption. Another objective of the project work is to investigate the physical and chemical characteristics of low cost activated carbons preparet from bagasse pith and bottom ash.

Further more the work has been extended to find out the optimum conc., pH and flow rate Also work has been done to find the phenol removal capacity of these adsorbents.

For determination of phenol concentration for unknown solutiona calibration curve is drawn for known solution. The calibration curve is shown in fig. 5.1 data for which is enclosed in Appendix.

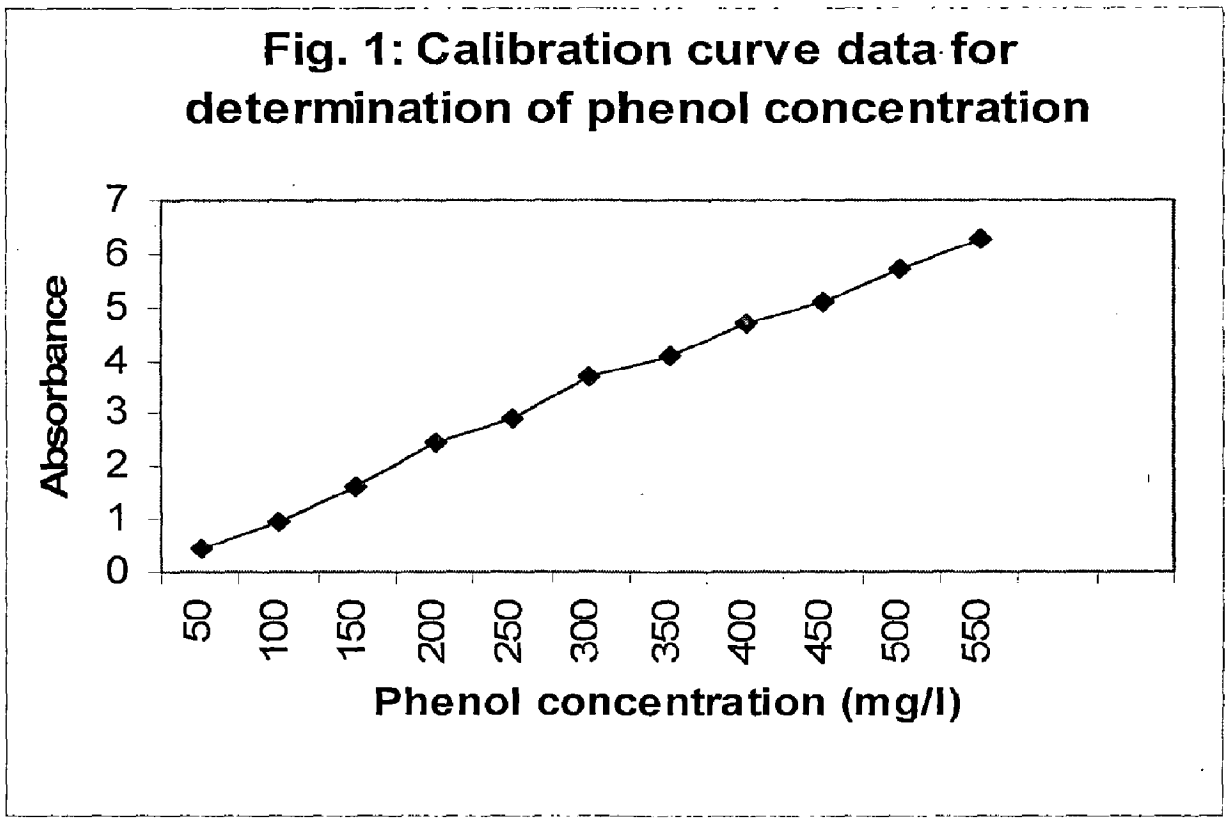


Fig. 5.1: Calibration curve for phenol

5.2.1 Adsorption of phenol on activated carbon

Phenol of varying conc. from 20 mg/l to 500mg/l was kept in conical flask along with the bed material i.e activated carbon and phenol adsorbtion was recorded at regular intervals for both activated carbons prepared from bagasse pith and bottom ash.

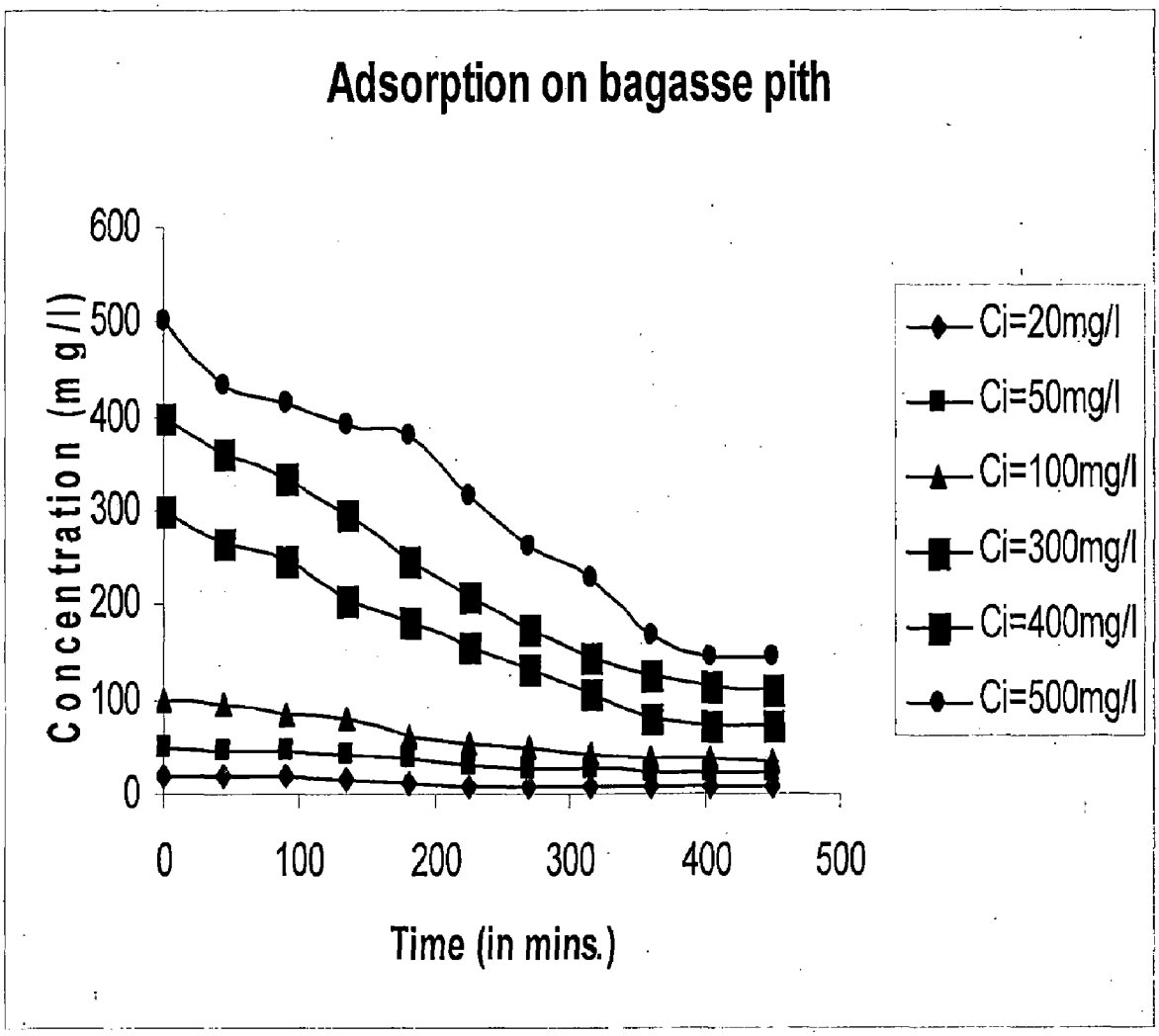


Fig. 5.2: Adsorption of phenol on bagasse pith carbon

Maximum phenol absorbed was recorded for 500 mg/l, but the adsorption of phenol for 300 mg/l, 400mg/l and 500mg/l was nearly same but adsorption for 300 mg/l take place earlier so it was considered as optimum concentration as shown in fig. 5.2.

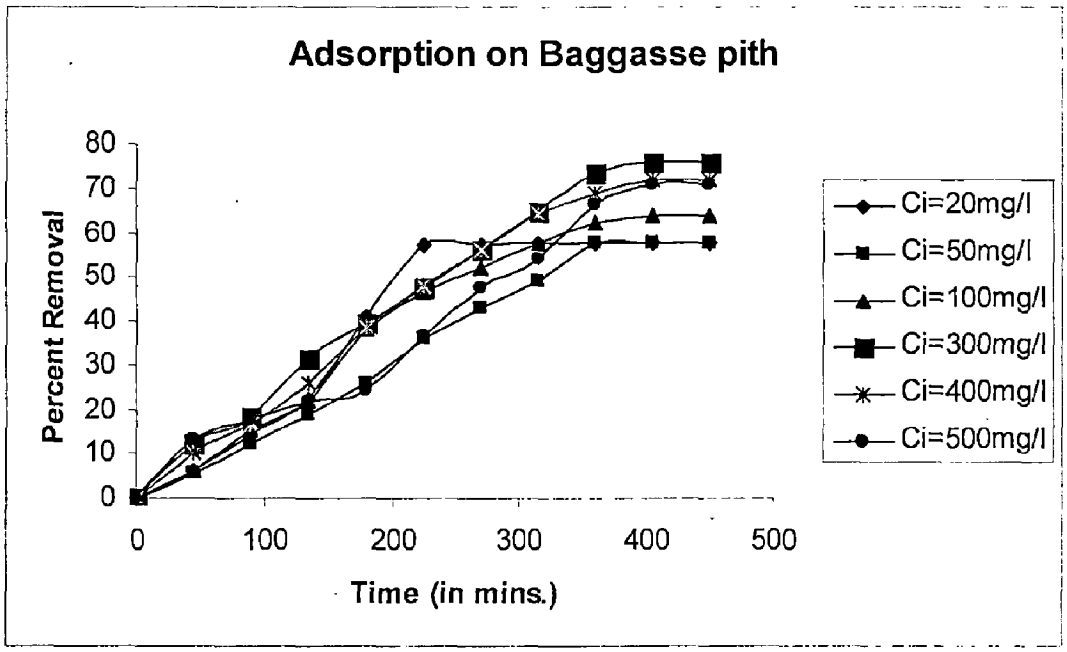


Fig. 5.3: Percent removal of phenol by bagasse pith carbon

Percent removal of phenol by bagasse pith carbon for 300 mg/l was the best. 76% of phenol was adsorbed from water as shown in fig. 5.3.

5.2.2Phenol adsorption capacity of bottom ash

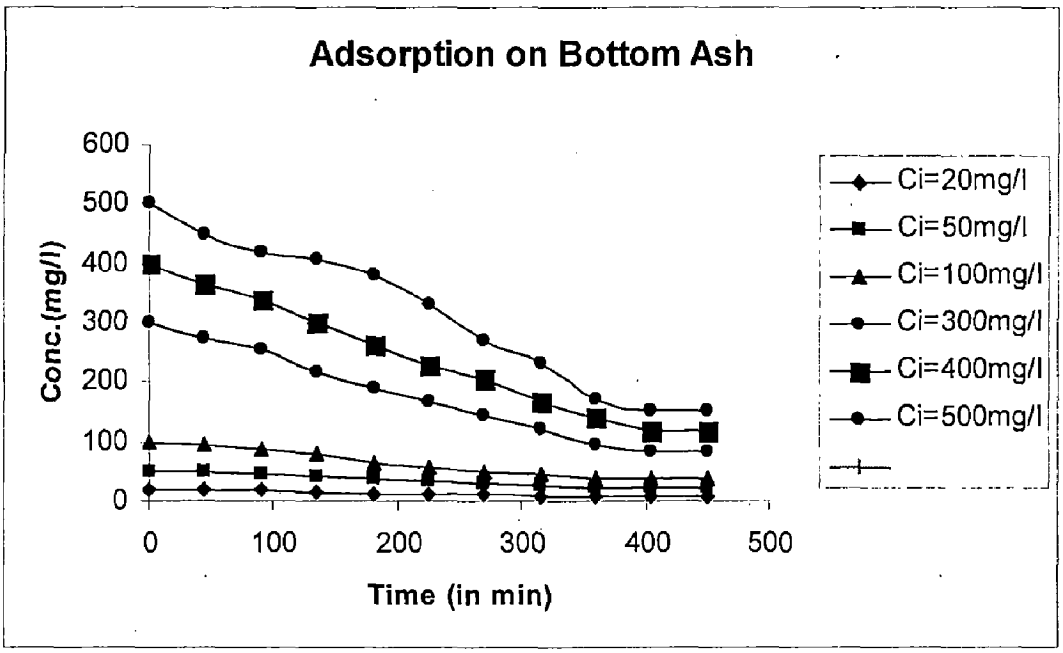


Fig. 5.4: Adsorption of phenol on bottom ash

Maximum phenol absorbed was recorded for 300 mg/l, but the adsorption of phenol for 300 mg/l, 400mg/l and 500mg/l was nearly same but adsorption for 300 mg/l take place earlier so it was considered as optimum concentration as observed from fig. 5.4.

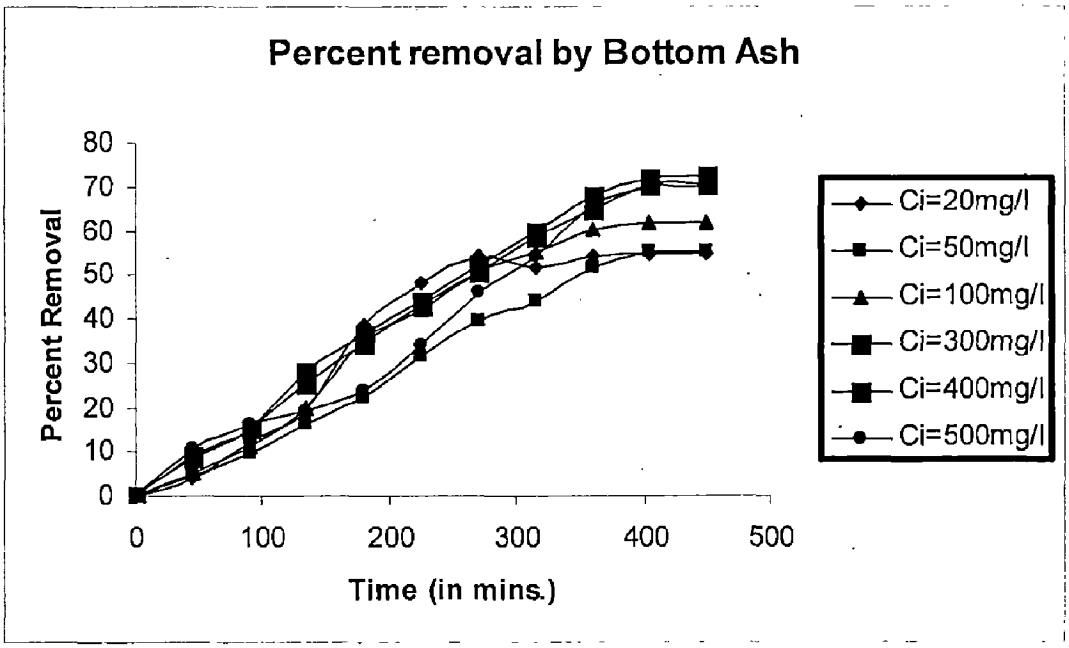


Fig. 5.5: Percent removal of phenol by bottom ash

By comparing the phenol adsorption tendency of bottom ash and activated carbon from bagasse pith, it was found that bagasse pith removes 76% of phenol from waste water while bottom ash removes only 72% of phenol when initial concentration of phenol fed was 300 mg/l as observed from fig. 5.3 and fig.5.5.

By studying the adsorbent characteristics and their tendency to remove phenol, it was found that the activated carbon prepared from baggase pith ha better adsorption properties and could remove higher percent of phenol from waste water. The best concentration level found for adsorption was 300 mg/l.

5.2.3 Effect of pH

As the pH is increased the adsorbtion capacity adsorbent increase and the adsorbent shows maximum phenol adsorption efficiency at pH 7.8 as shown in fig. 5.6 and it is easy to maintain the pH around neutral solution. The effect of pH was observed for the phenol of concentration 300 mg/l. As this concentration shows the best adsorption efficiency .

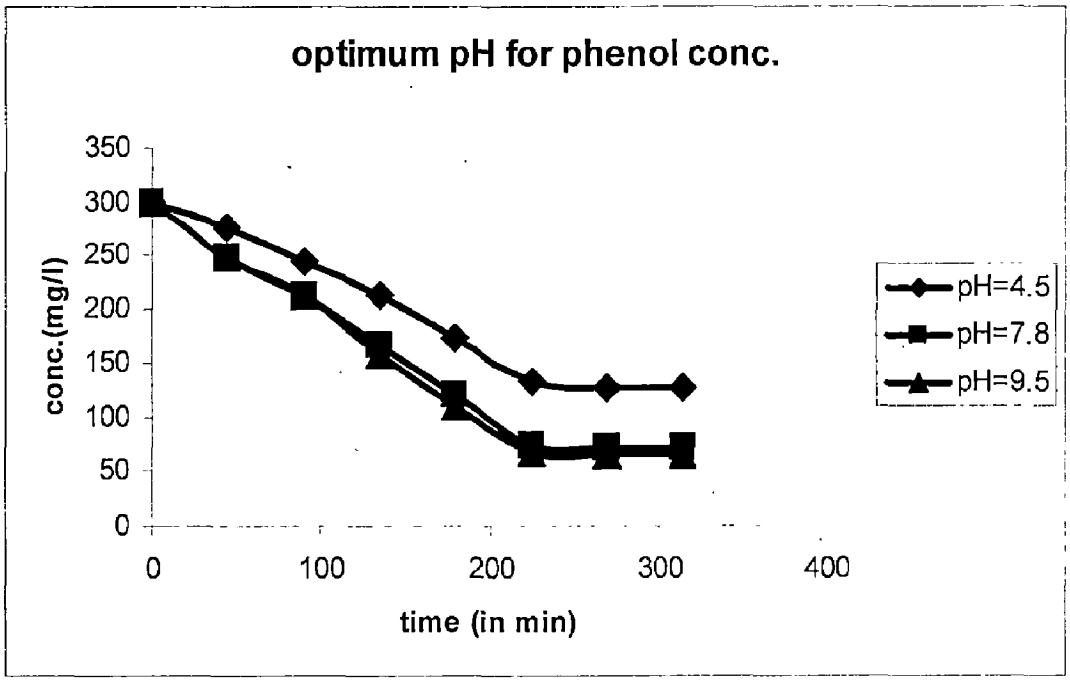


Fig. 5.6: phenol removal by bagasse pith carbon at varying pH

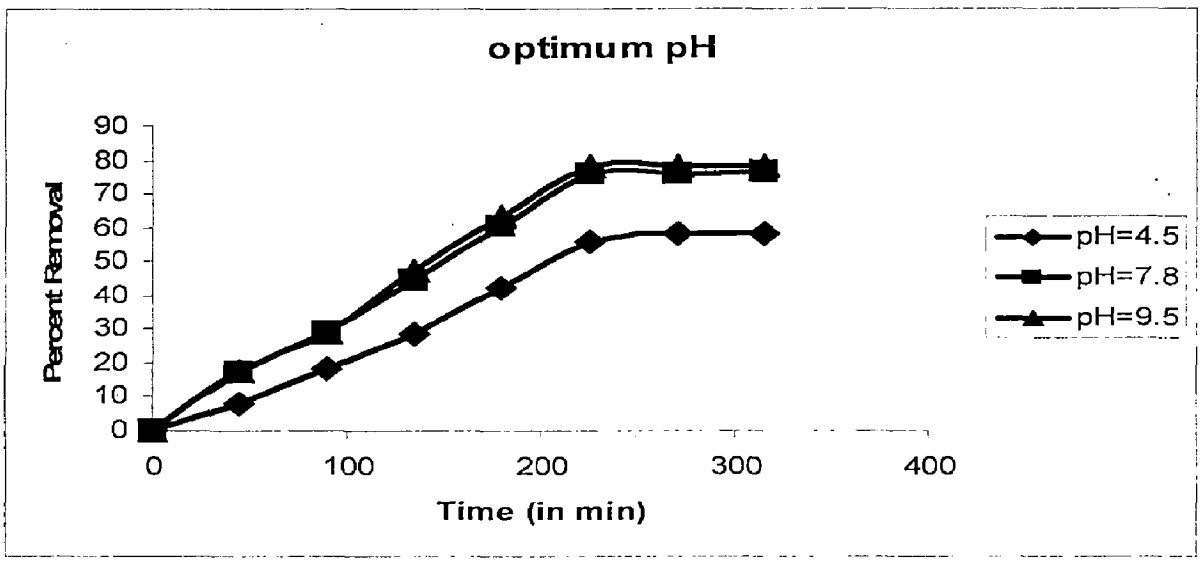


Fig.5.7: Percent removal of phenol at varying pH

The optimum pH at which maximum removal of phenol was observed is supposed to be 7.8 as observed from fig.5.7 Percent removal of phenol was found to be favored at pH around neutral conditions

5.2.4 Effect of particle size of adsorbent (activated bagasse pith carbon)

It is clear from the graph5.8 and 5.9 that as the particle size of the adsorbent decreases the percent removal of phenol is increasing. But for producing very fine activated carbons the cost for processing is very high. So the optimum particle size for adsorption of phenol is 2-4 mm.

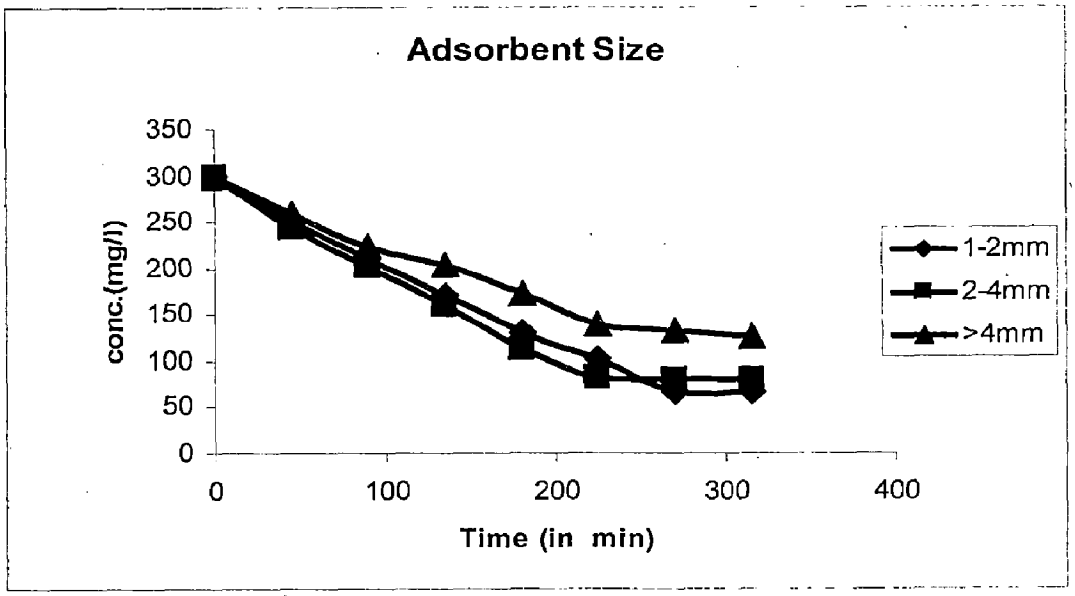


Fig.5.8 : Effect of particle size of adsorbent on phenol adsorption

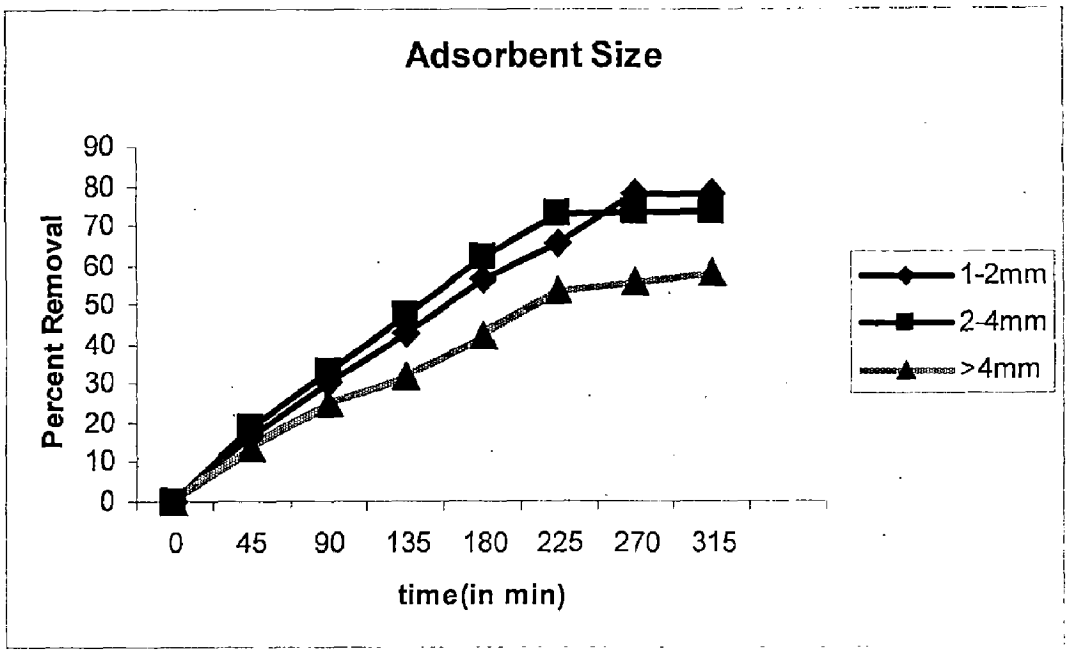


Fig. 5.9: Effect of particle size of absorbent on percent phenol removal

5.2.5 Effect of Adsorbent Dose on percent phenol Removal

From the graph 5.10 below it is clear that the optimum dose for phenol removal from waste water is 6 gm/l. as the amt. of adsorbent dose increases the percent removal of phenol increases and at certain extent it becomes constant.

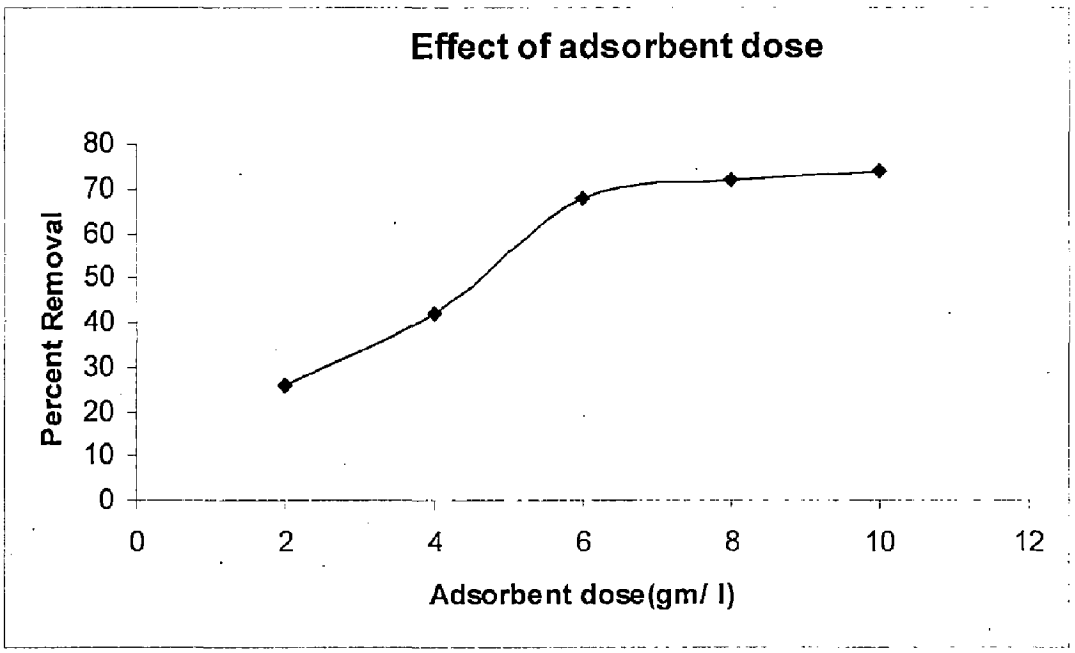


Fig. 5.10: Effect of adsorbent dose on percent phenol removal

5.3 Biodegradation of phenol through *Pseudomonas Putida*

Phenol was fed at varying concentrations from 50mg/l to 500mg/l into the flasks along with the well grown culture acclimatized in the phenol environment and was kept in shaker at 172 rpm . Regular readings were taken at time interval of 90 mins as shown in fig. 5.11.

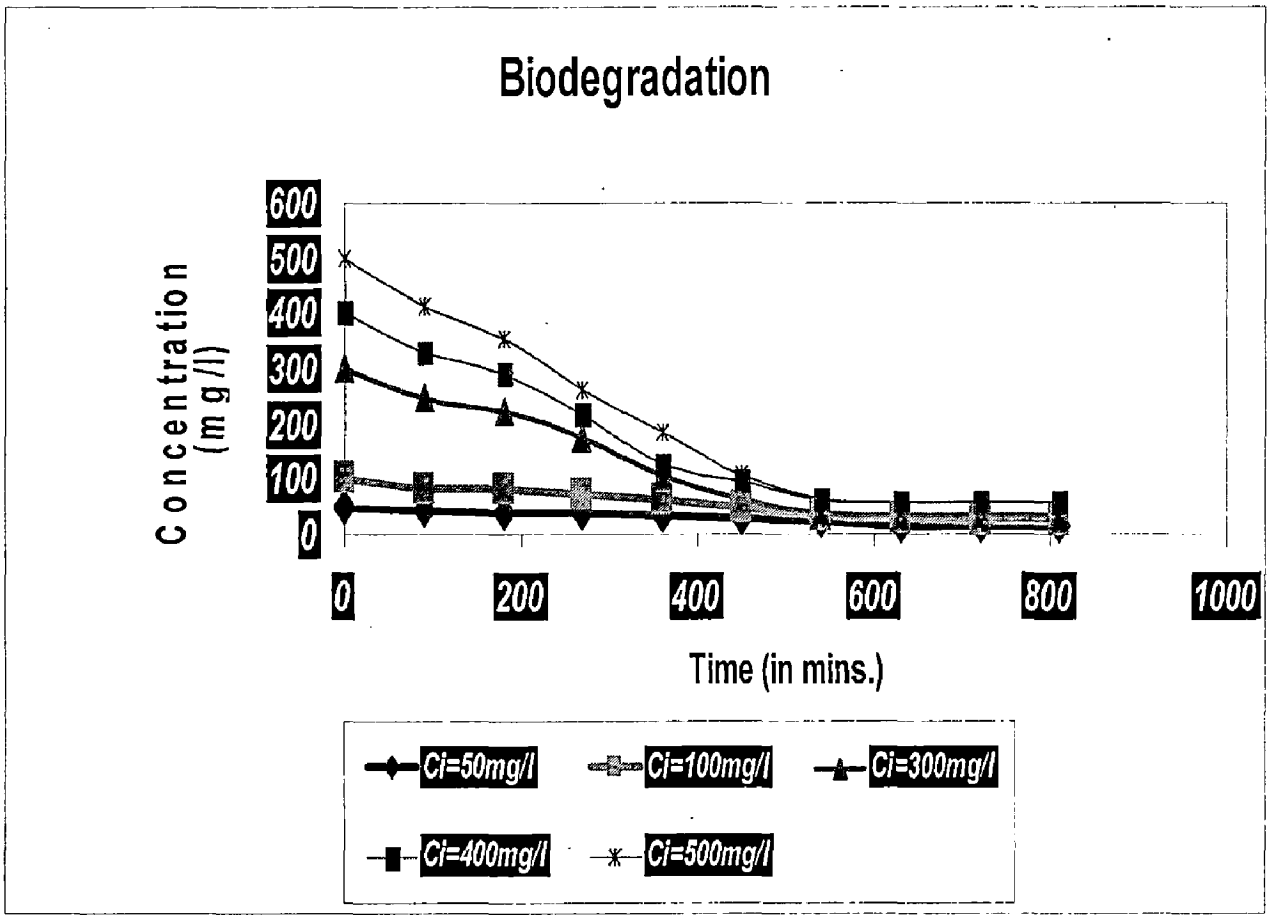


Fig.5.11: Biodegradation of phenol through *pseudomonas putida*

From the results of biodegradation experiment and as observed form fig. 5.12 it was found that around 88% of phenol was removed from the wastewater for the 300 mg/l phenol concentration. Although at high concentration the percent removal efficiency was nearly same.

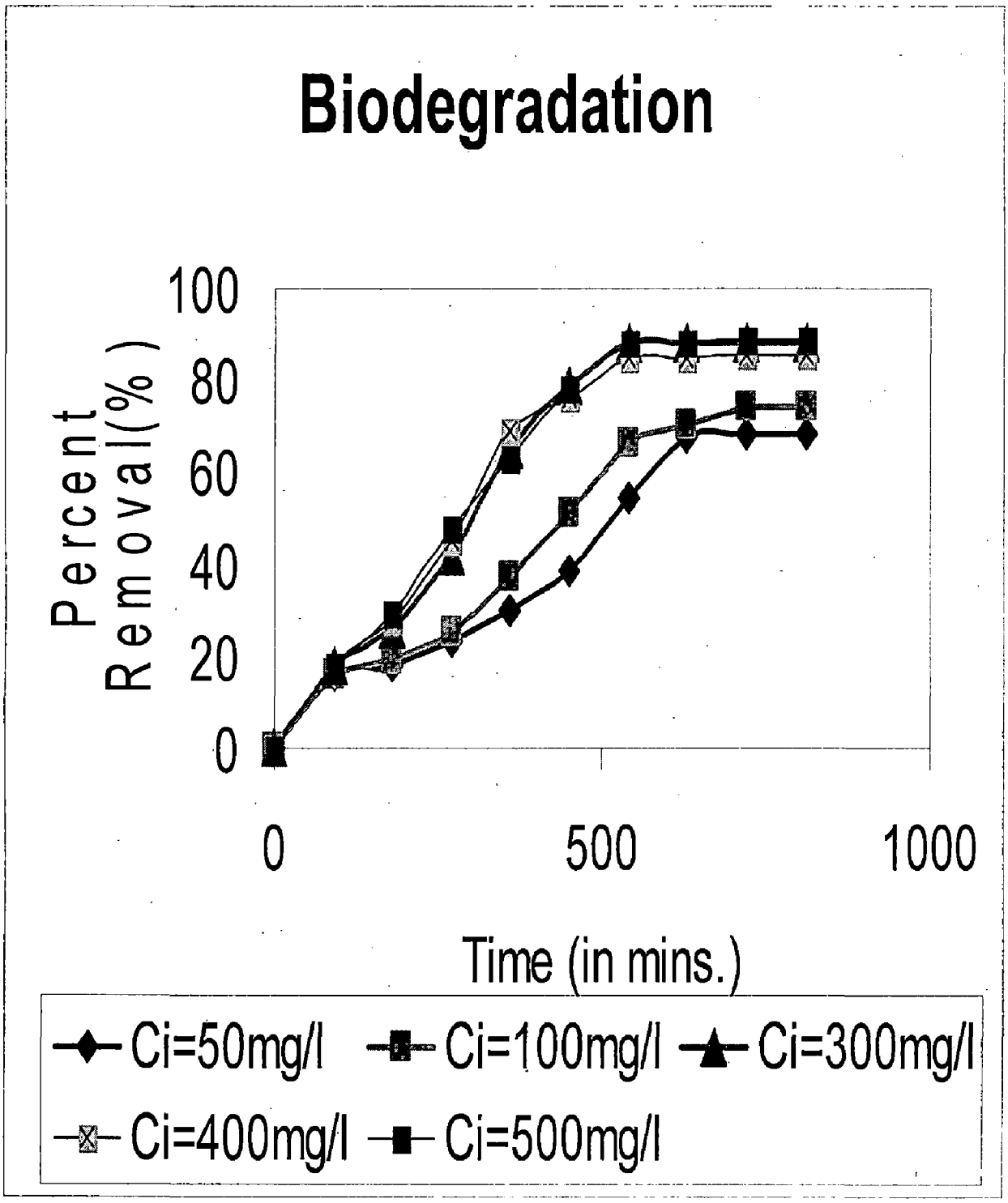


Fig. 5.12: Percent removal of phenol by *Pseudomonas putida*

5.4 Simultaneous Adsorption Biodegradation

Experiments were conducted at different phenol concentrations by using simultaneous adsorption and biodegradation. This process gives best phenol removal when activated carbon prepared from bagasse pith was used as bed material. The best percent removal was observed for phenol of concentration 300mg/l.Around 94% of phenol was removed from 300mg/l phenol concentration when bed material was bagasse pith carbon as indicated in fig. 5.13 and 5.14 while for bottom ash around 88% of phenol was removed for 300mg/l concentration as observed from fig. 5.15 and 5.16.

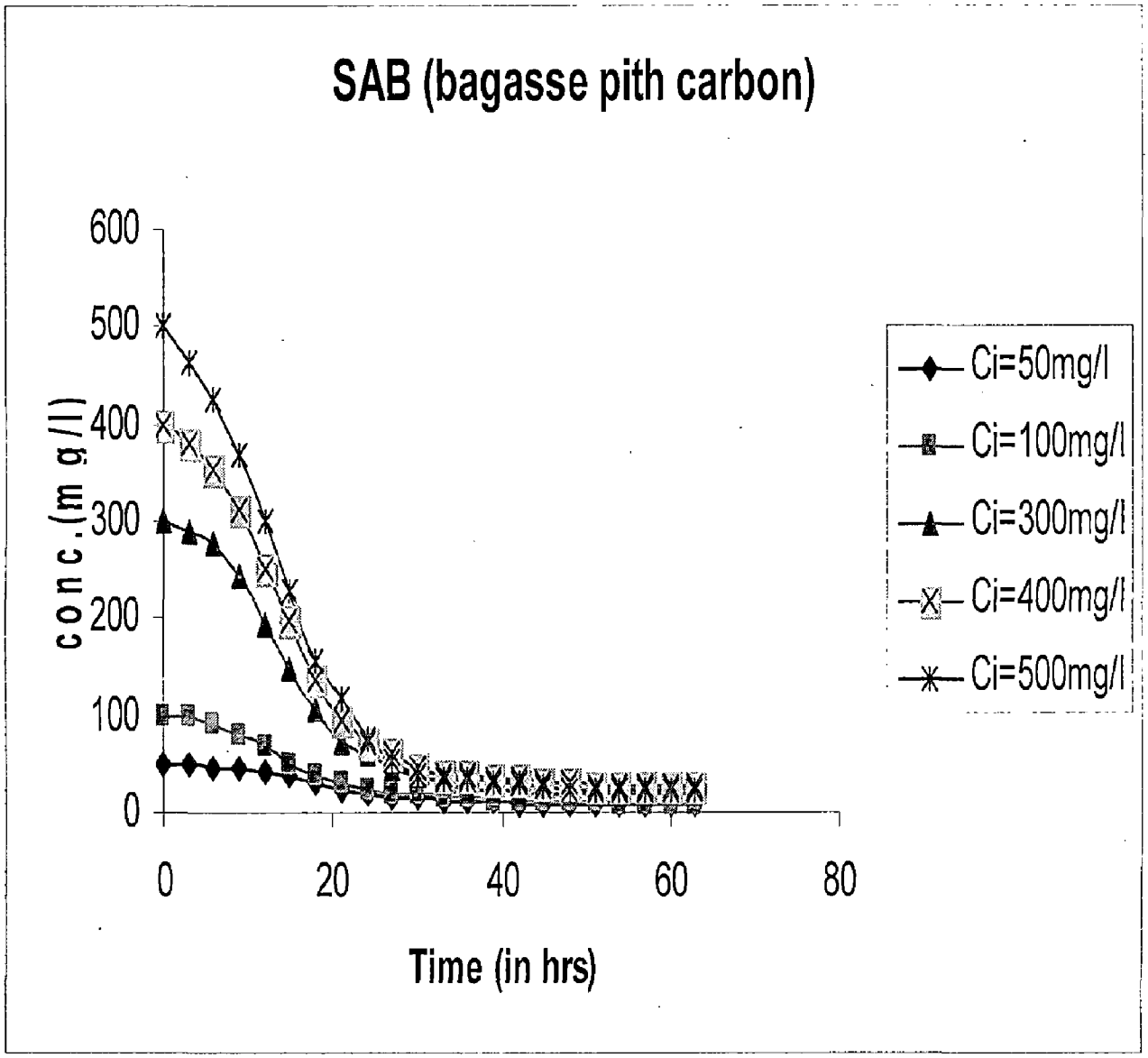


Fig. 5.13 phenol removal by simultaneous adsorption and biodegradation when bed material is activated carbon from bagasse pith

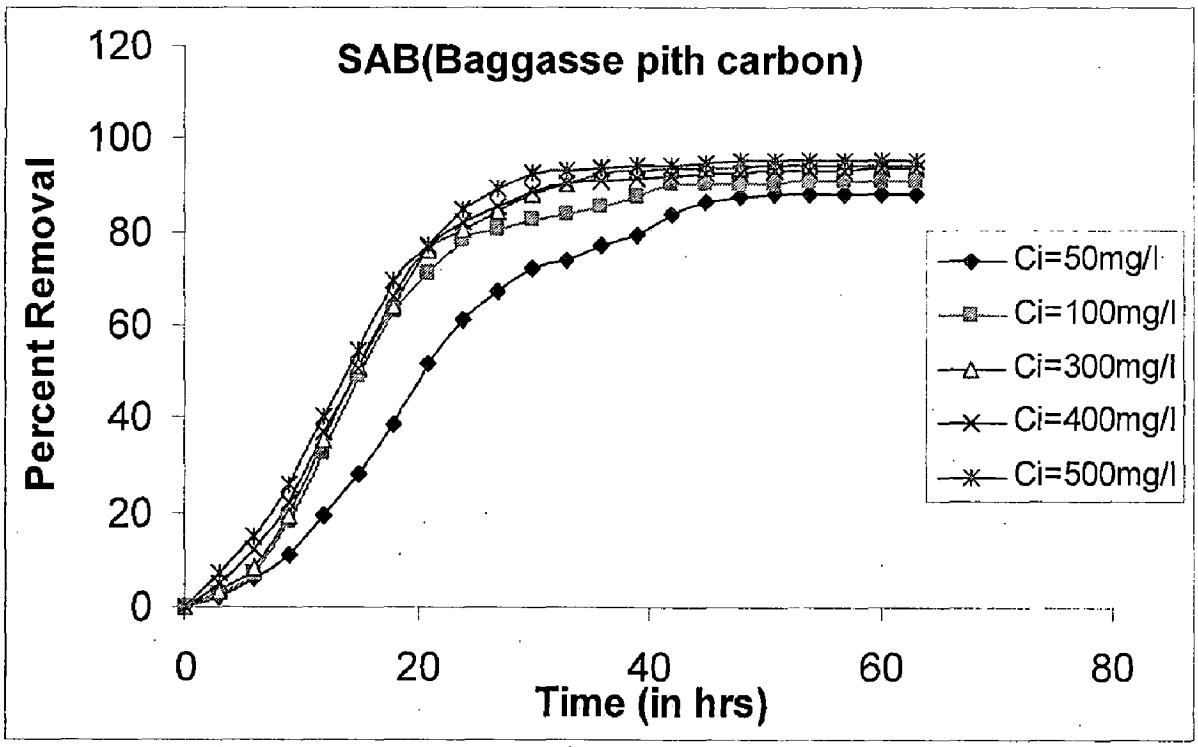


Fig. 5.14: Percent phenol removal by simultaneous adsorption and biodegradation when bed material is activated carbon from bagasse pith

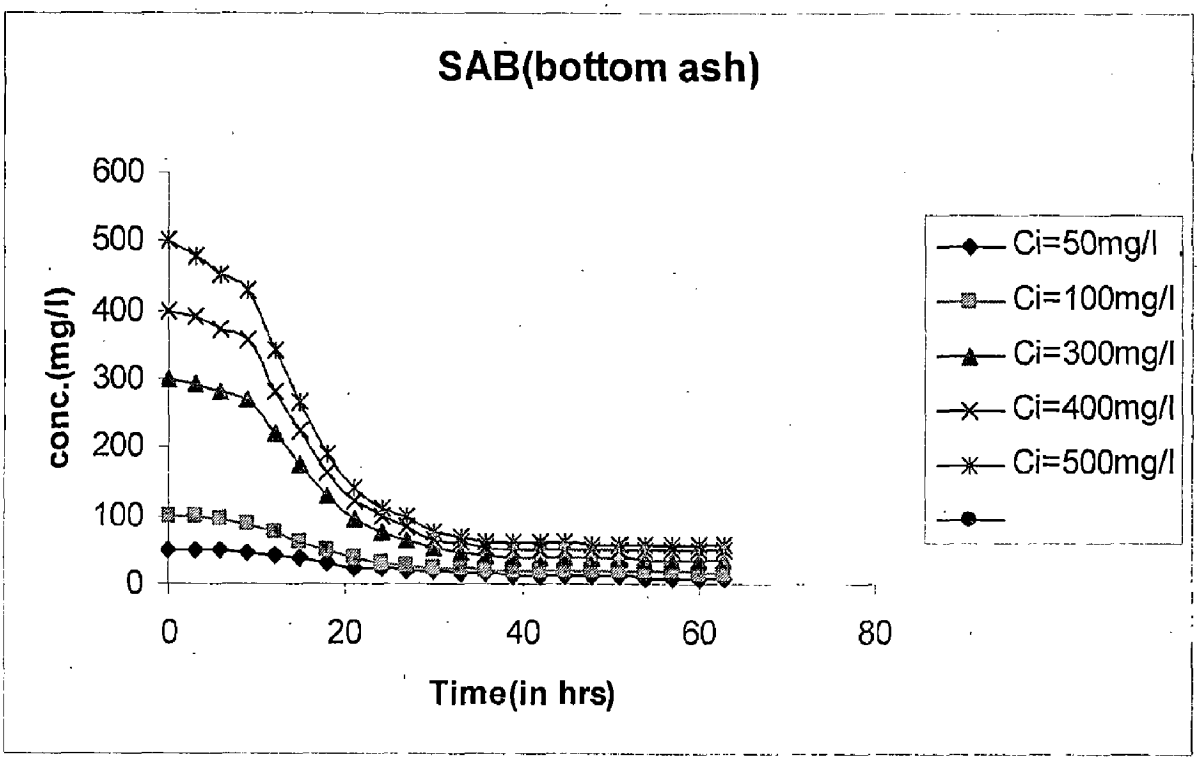


Fig. 5.15: Phenol removal by simultaneous adsorption and biodegradation when bed material is activated carbon from bottom ash

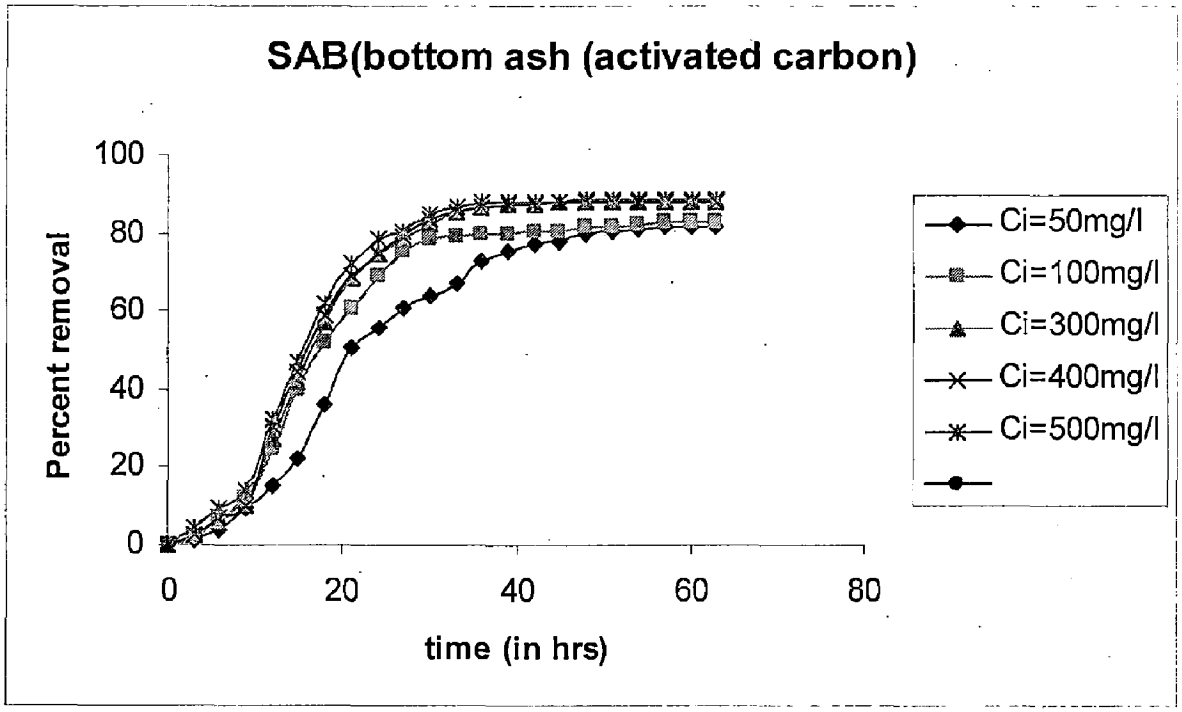


Fig. 5.16: Percent phenol removal by simultaneous adsorption and biodegradation when bed material is activated carbon from bottom ash

The graph 5.17 below shows the rate of increase in biomass for different concentration levels of phenol. The dry cell growth concentration (biomass) was observed maximum for 500mg/l phenol concentration level when the test was run for simultaneous adsorption biodegradation.

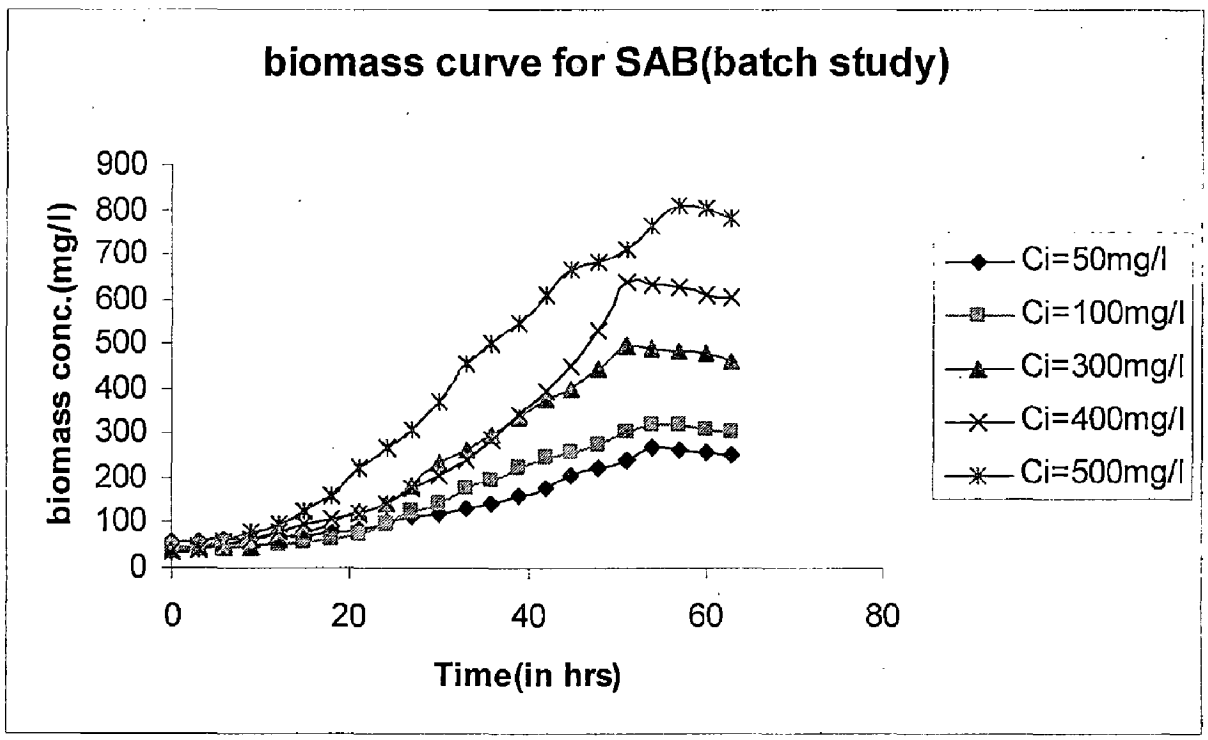


Fig. 5.17: Biomass curve for bagasse pith carbon

5.5Comparative study of Adsorption, Biodegradation and Simultaneous Adsorption and Biodegradation

A comparative study of all the three processes viz. adsorption , biodegradation and simultaneous adsorption and biodegradation was done for 300 mg/l phenol concentration level as for this concentration the optimum removal was observed and the experiments were run on the activated carbon produced from bagasse pith. Batch Experiments were conducted for studying the percent removal of phenol on variation of the amount of adsorbent dose, change in the particle size, and change in pH.

5.5.1 Effect of Adsorbent Dose

Fig. 5.18 below shows the effect of change of adsorbent dose on the percent phenol removal and from the graph it is clear from the curve that the optimum amount of adsorbent dose is 6 gm/l.

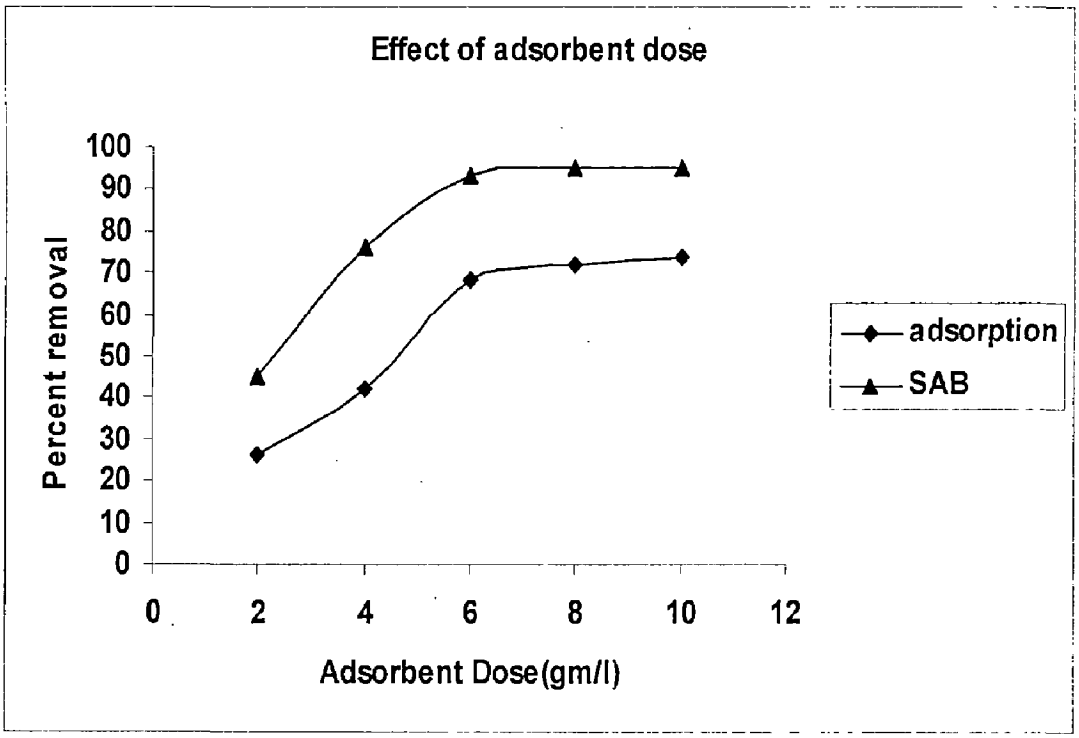


Fig.5.18: Effect of Adsorbent Dose

5.5.2 Effect of Particle Size of Adsorbent

As observed from fig. 5.19 the optimum particle size of the adsorbent which can be used as a bed material for the biosorption process. The optimum size range found for the bed material is 2-4 mm.Although it is clear from the graph that as the particle size decreases the percent phenol removal increases but producing fine activated carbon particles is a costly process.

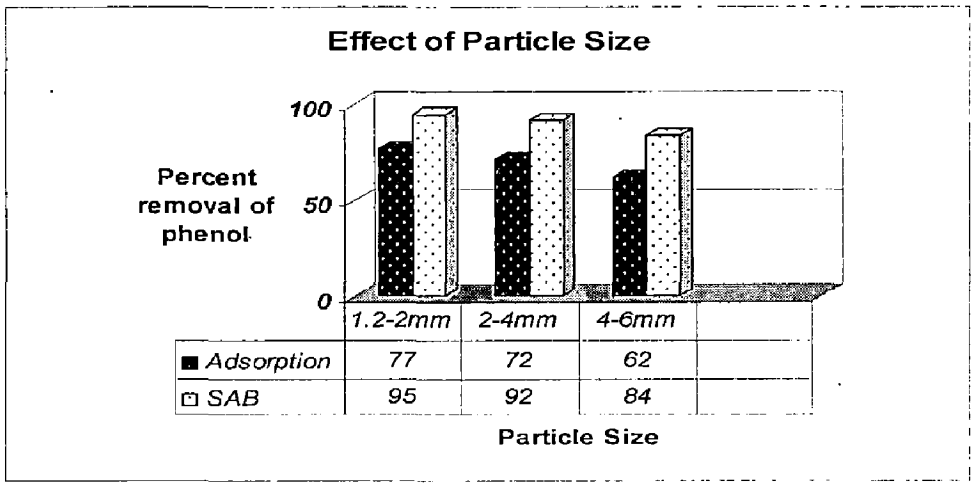


Fig.5.19: Effect of Particle Size of Adsorbent

5.5.3: Effect of pH

The bio adsorption nature of pseudomonas putida laid on bagasse pith bed material as activated carbon was studied at three different pH in flasks at batch level. The experiments were run for 300 mg/l phenol concentration and the optimum pH was found to be 7.The resultant graph fig. 5.20 is shown below showing the percent removal of phenol three different pH for three different processes i.e. adsorption ,biodegradation and biosorption(SAB).

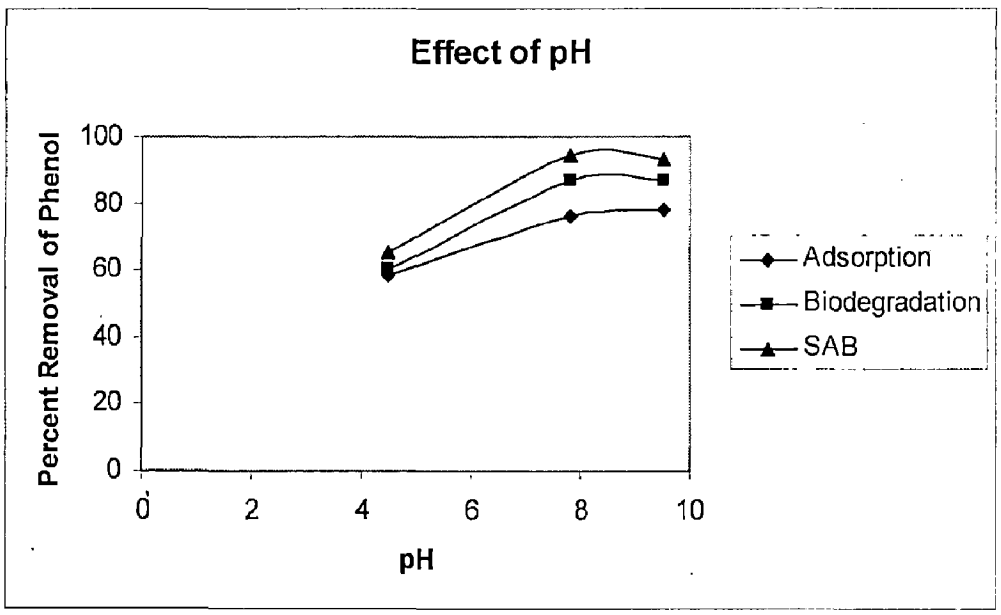


Fig.5.20: Effect of pH

5.6 Comparison of Adsorption , Biodegradation and SAB

Fig.5.21 below shows the comparison of the three processes viz. adsorption, biodegradation and simultaneous adsorption and biodegradation for 300 mg/l phenol concentration during batch experiments.

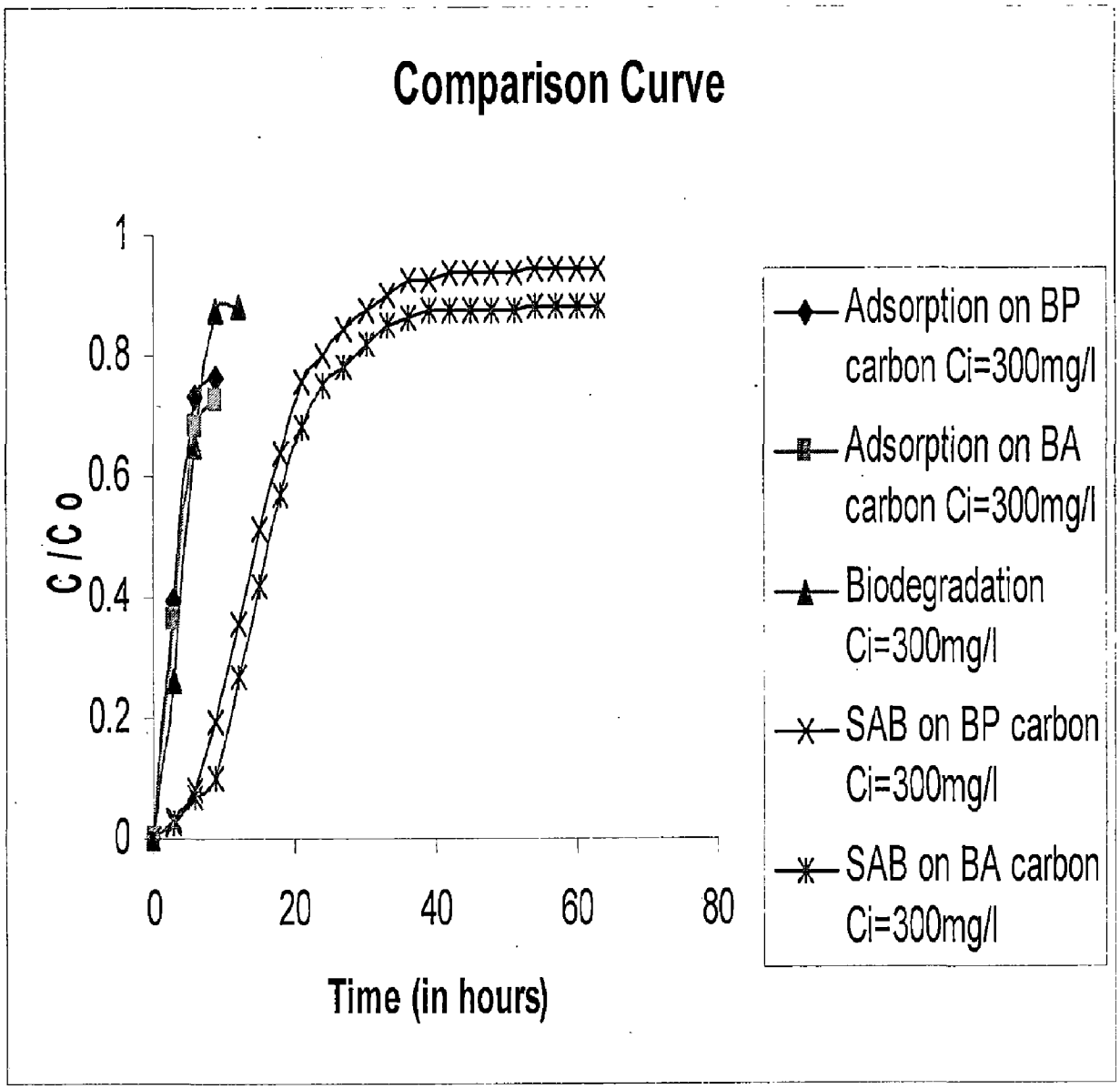


Fig. 5.21: Comparison of Adsorption , Biodegradation and SAB

5.7 COLUMN STUDY

The aim of the bio adsorption column study is to investigate the phenol degrading and phenol removal capacity during operation.

In the test phenol was used as the testing pollutant at different concentrations as it has good biodegradable and carbon absorbable properties.

5.7.1 Adsorption of phenol on bagasse pith carbon in biodegradation column

The graph 5.22 below shows the adsorption capacity of the activated carbon prepared from bagasse pith. The percent removal curve for phenol is shown in fig. 5.23 and from the graph it is clear that bagasse pith carbon removes around 78% of phenol when only adsorption process was removed through adsorption process.

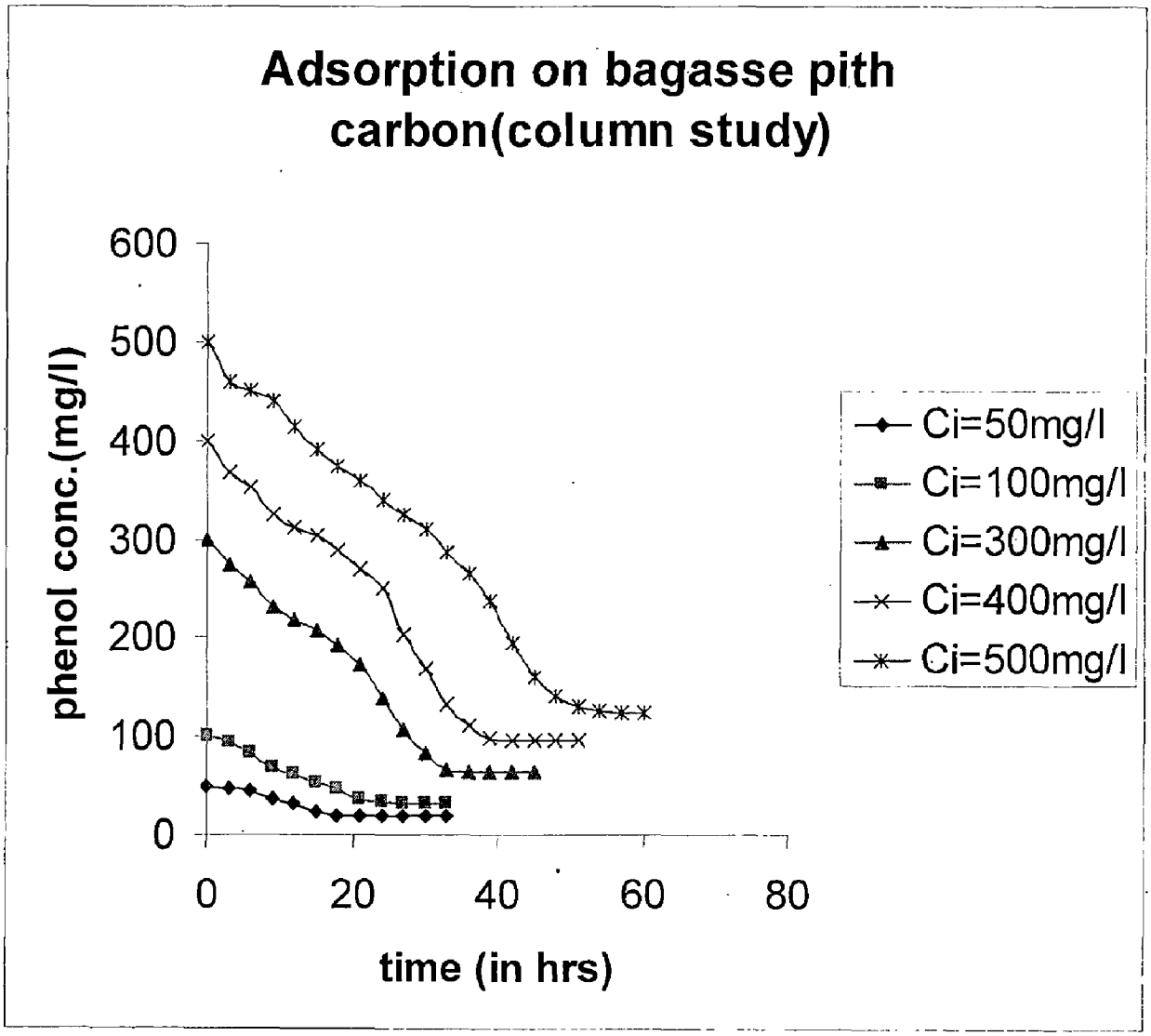


Fig. 5.22: Adsorption of phenol on bagasse pith carbon in biodegradation column

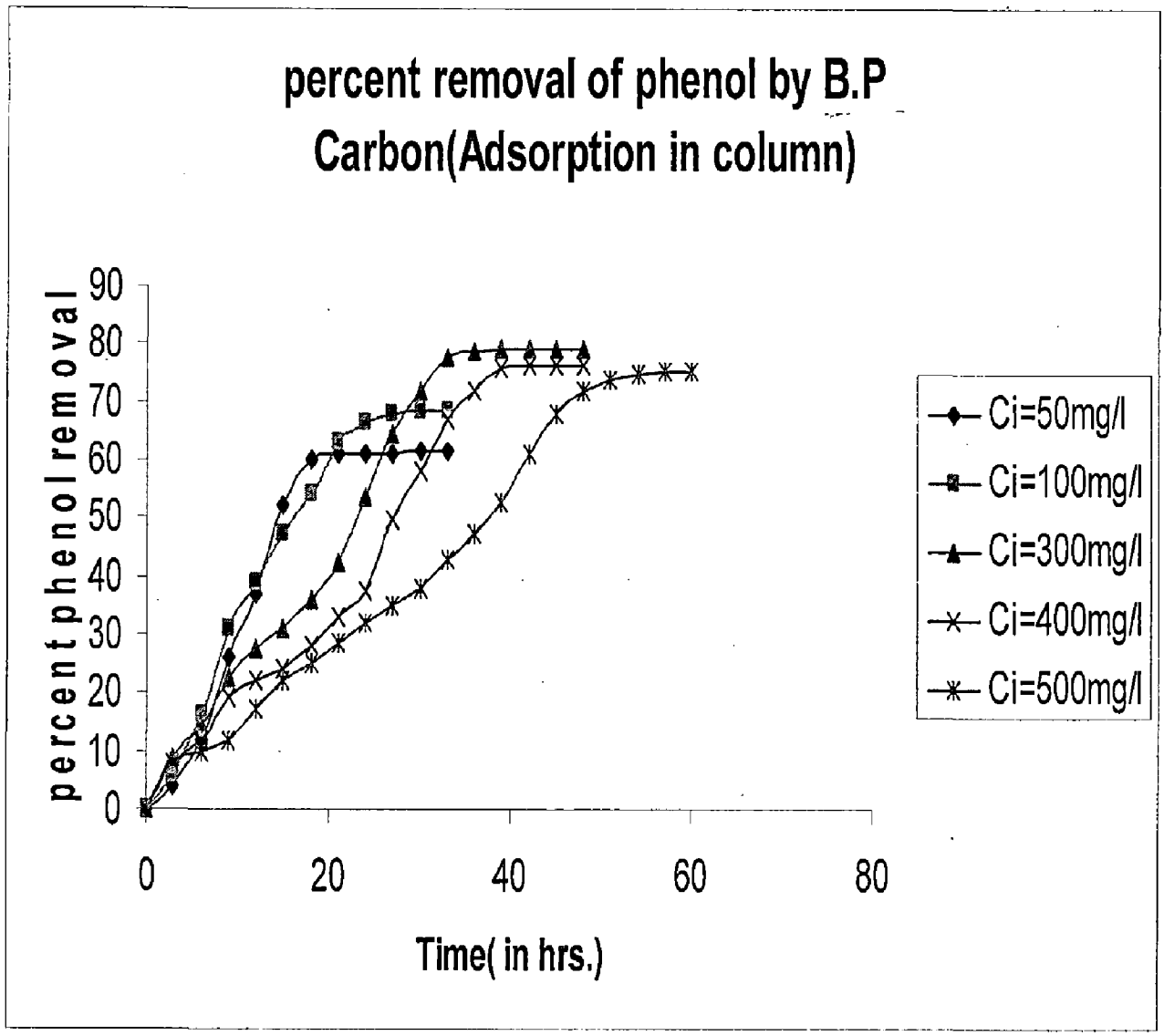


Fig. 5.23: Percent removal of phenol by Bagasse Pith Carbon

5.7.2 Adsorption of phenol on bottom ash carbon in biodegradation column

The graph 5.24 below shows the adsorption capacity of the activated carbon prepared from bottom ash. When activated carbon from bottom ash was used as a bed material in the column around 72% of phenol was removed through adsorption when phenol concentration was 300 mg/l. The percent removal curve for phenol is shown in fig. 5.25 and from the graph 5.24 it is clear that phenol concentration comes down to 89.4 mg/l in the effluent from 300 mg/l initial concentration. So it is clear from the above experiment that bagasse pith carbon is a better bed material for phenol biosorption

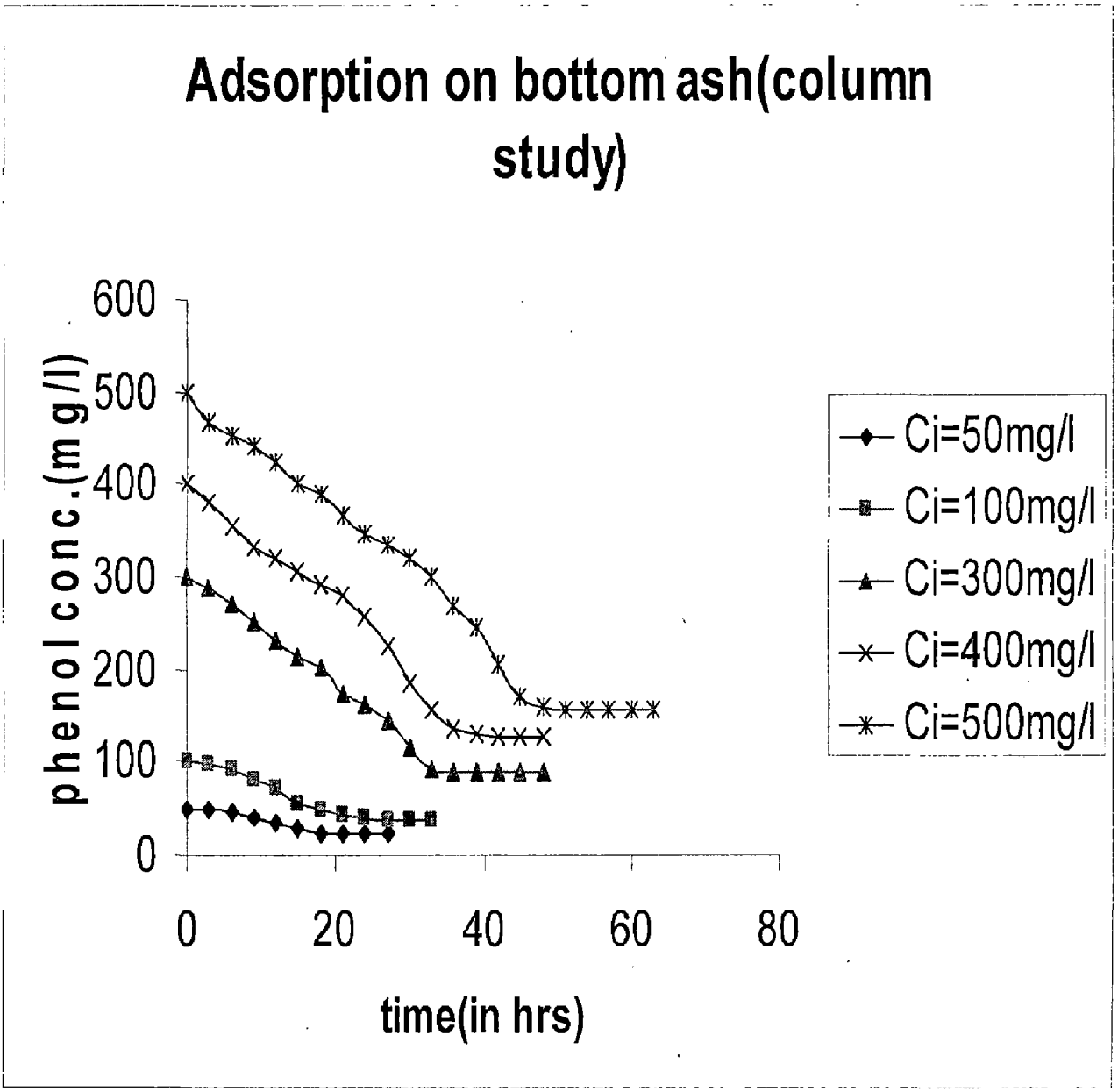


Fig. 5.24: Adsorption of phenol on bottom ash carbon

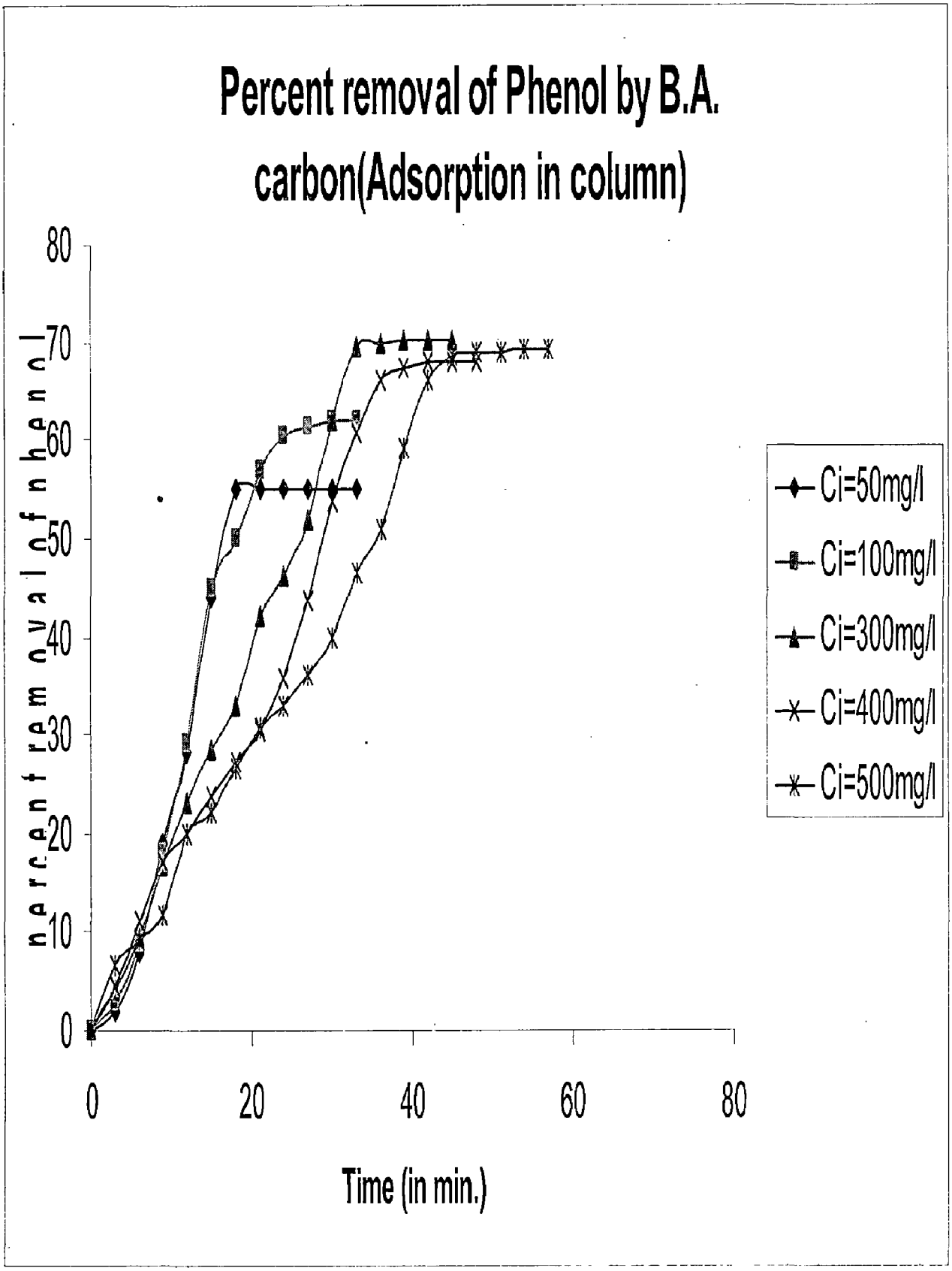


Fig. 5.25: Percent removal of phenol by Bottom ash Carbon

5.7.3 Simultaneous adsorption and biodegradation of phenol on bagasse pith carbon in biodegradation column:

Graph 5.26 and 5.27 below shows simultaneous adsorption and biodegradation of phenol when bagasse pith carbon was used as the bed material. The percent removal potential of phenol was improved to 99% for 300mg/l phenol concentration in the effluent .

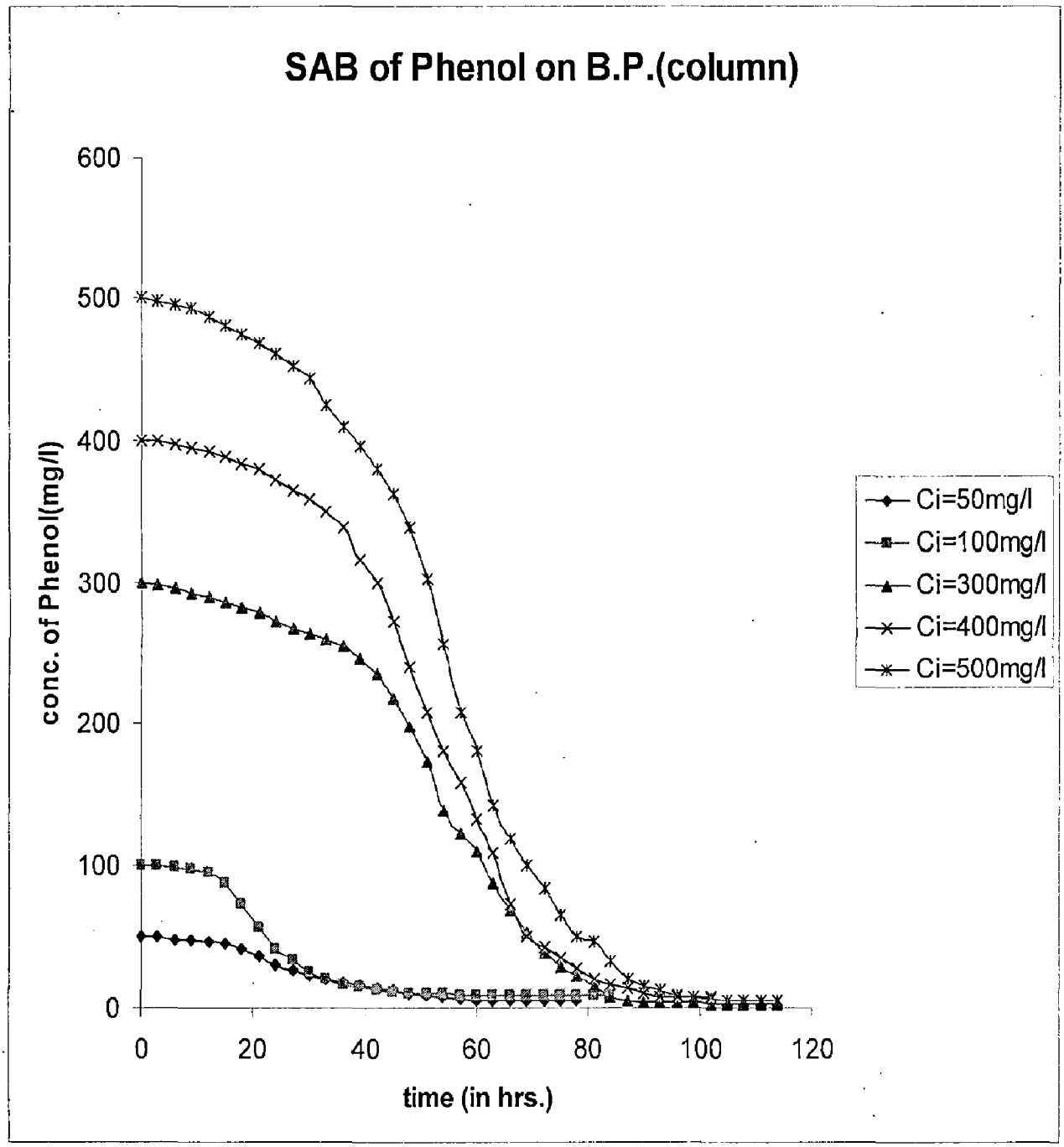


Fig. 5.26: Variation of conc. of phenol during Simultaneous adsorption and biodegradation of phenol on bagasse pith carbon in biodegradation column

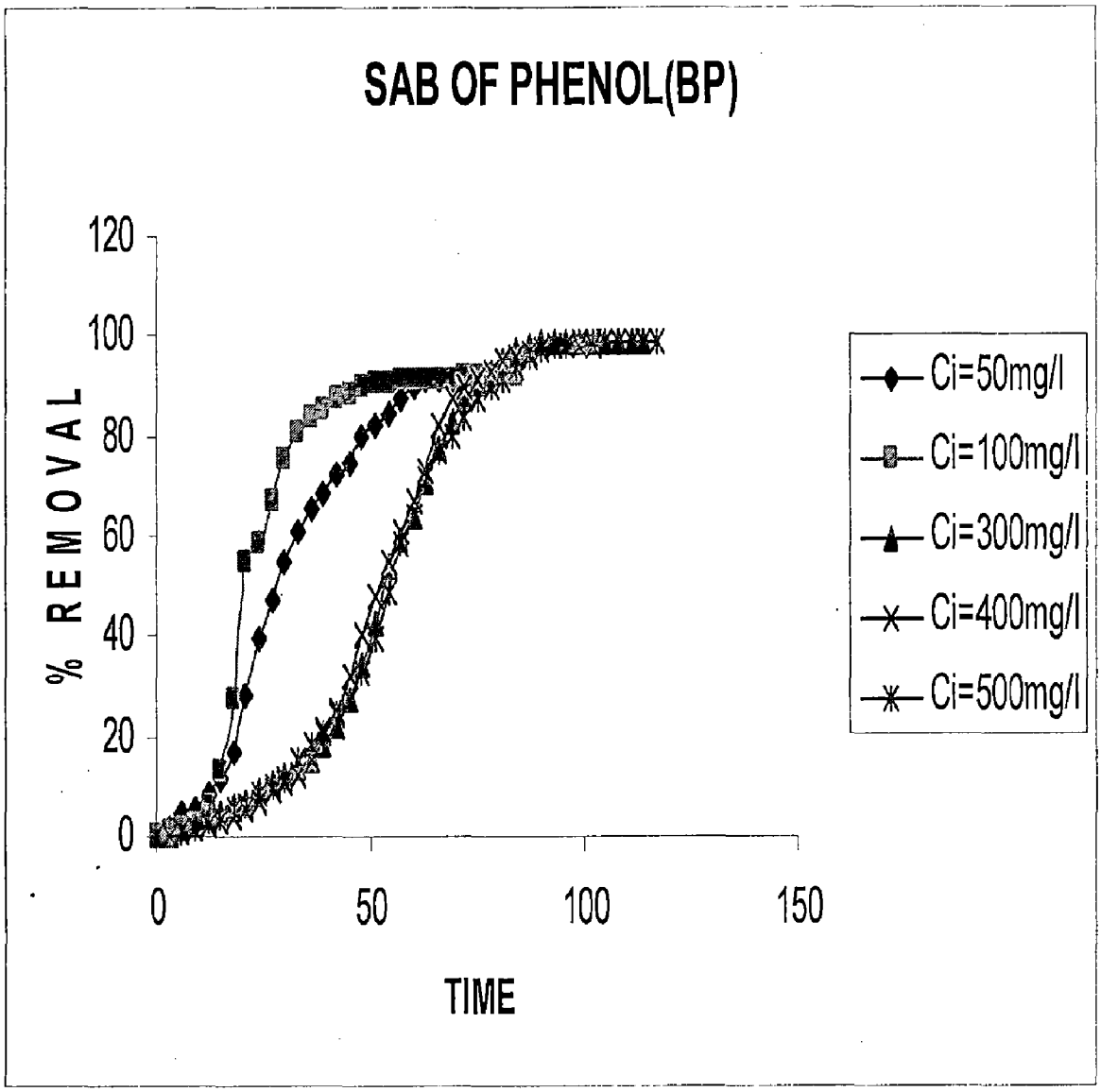


Fig. 5.27: Percent removal of phenol during Simultaneous adsorption and biodegradation of phenol on bagasse pith carbon in biodegradation column

5.7.4 Simultaneous adsorption and biodegradation of phenol on bottom ash carbon in biodegradation column

When bottom ash carbon was used as the bed material around 96% (from fig. 5.28) of phenol was removed from the effluent containing 300 mg/l phenol concentration. The concentration of phenol decreases from 300mg/l to around 12 mg/l (from fig. 5.29). So the best concentration of phenol for which maximum phenol bioadsorption was achieved is found to be 300mg/l.

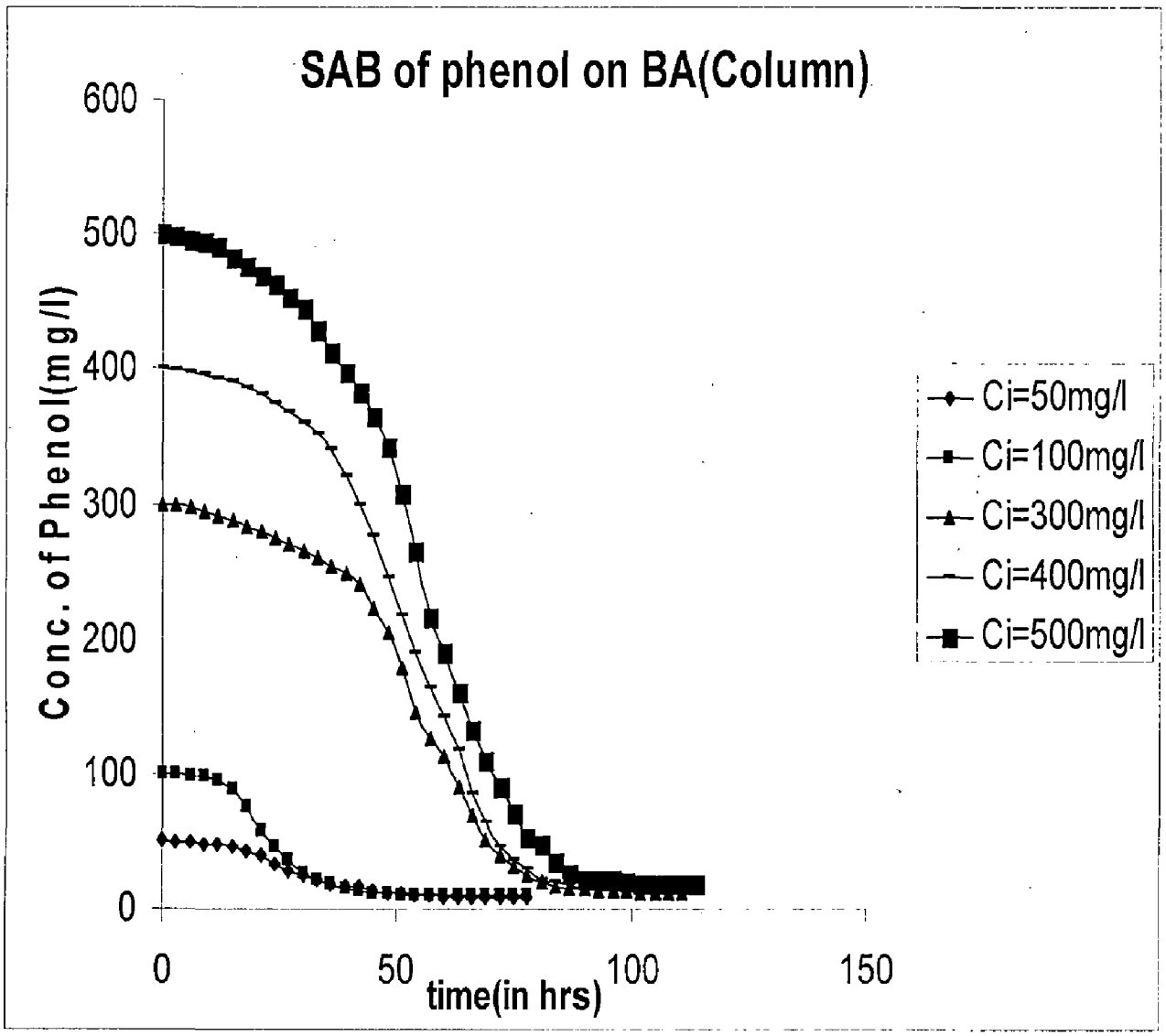


Fig. 5.28: Variation of conc. of phenol during Simultaneous adsorption and biodegradation of phenol on bottom ash carbon in biodegradation column

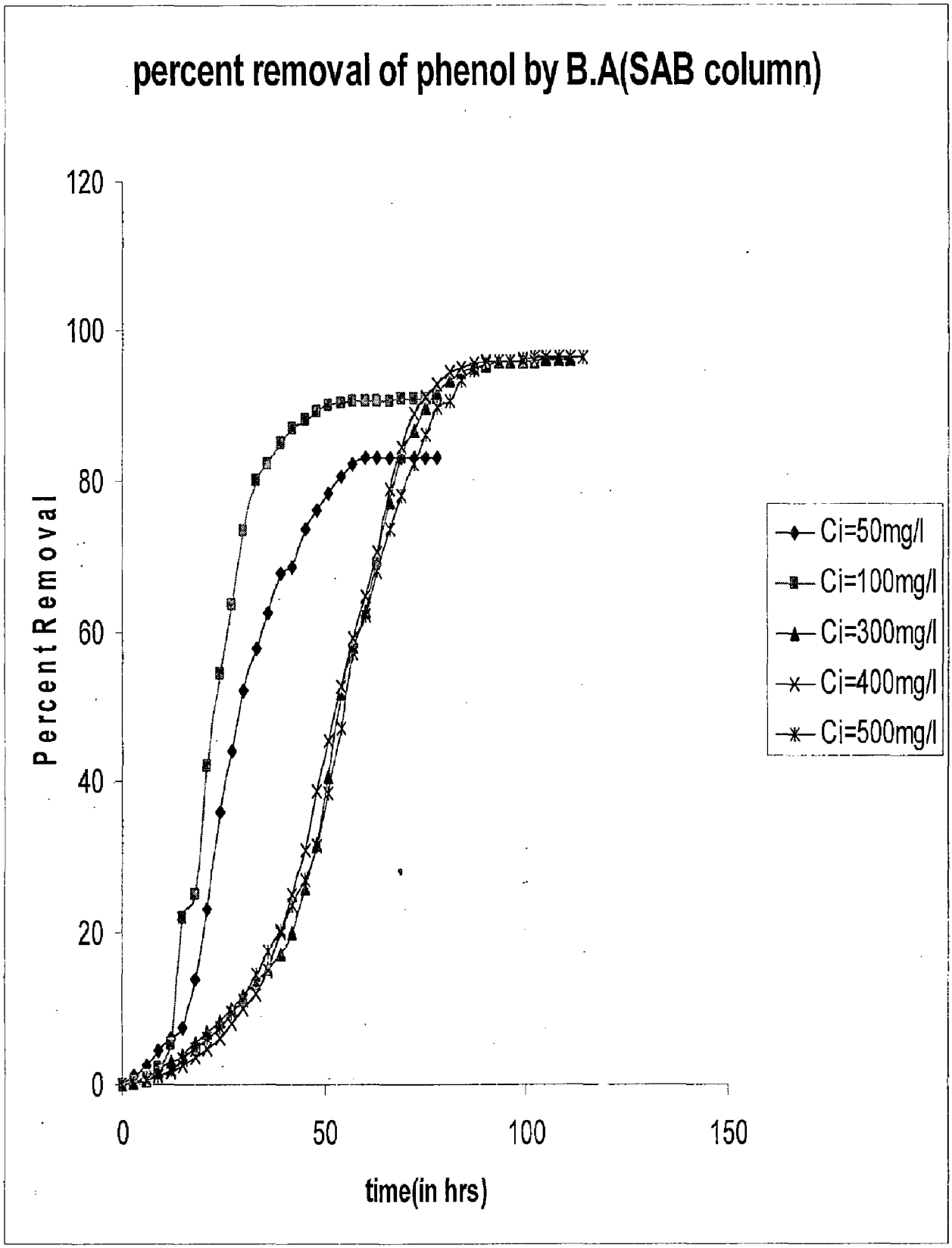


Fig. 5.29: Percent removal of phenol during Simultaneous adsorption and biodegradation of phenol on bagasse pith carbon in biodegradation column

5.7.5 Biomass curve of phenol at different concentration :

Biomass curve was plotted in between biomass concentration for simultaneous adsorption and biodegradation of phenol when bagasse pith was used as the bed material. From the fig,. 5.30 it is clear that the biomass concentration after reaching to a certain extent starts decreasing as the activity of the bacteria starts decreasing.

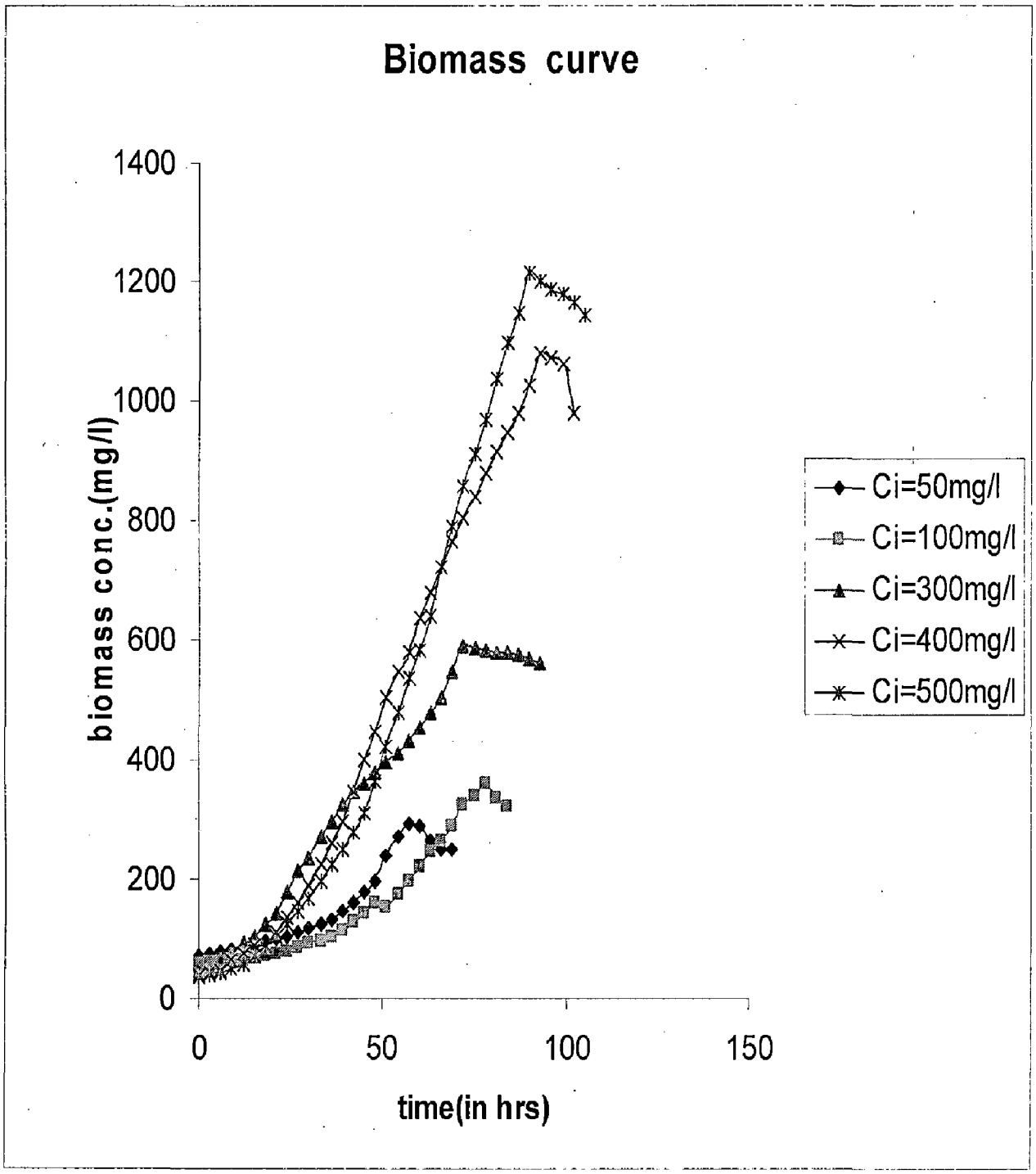


Fig. 5.30: Biomass curve for bagasse pith carbon

5.8 Comparitive study of Adsorption, and Simultaneous Adsorption and Biodegradation

A comparative study both the processes viz. adsorption, and simultaneous adsorption and biodegradation was done for 300 mg/l phenol concentration level as for this concentration the optimum removal was observed and the experiments were run on the activated carbon produced from bagasse pith. Column Experiments were conducted for studying the percent removal of phenol on variation of the amount of adsorbent dose, change in the particle size, and change in pH.

5.8.1 Effect of pH (with bagasse pith carbon as bed material)

The bio adsorption nature of pseudomonas putida laid on bagasse pith bed material as activated carbon was studied at three different pH in column. The experiments were run for 300 mg/l phenol concentration and the optimum pH was found to be 7.8 as it is clear from fig. 5.31 which is in coincidence with the results obtained from the batch study.

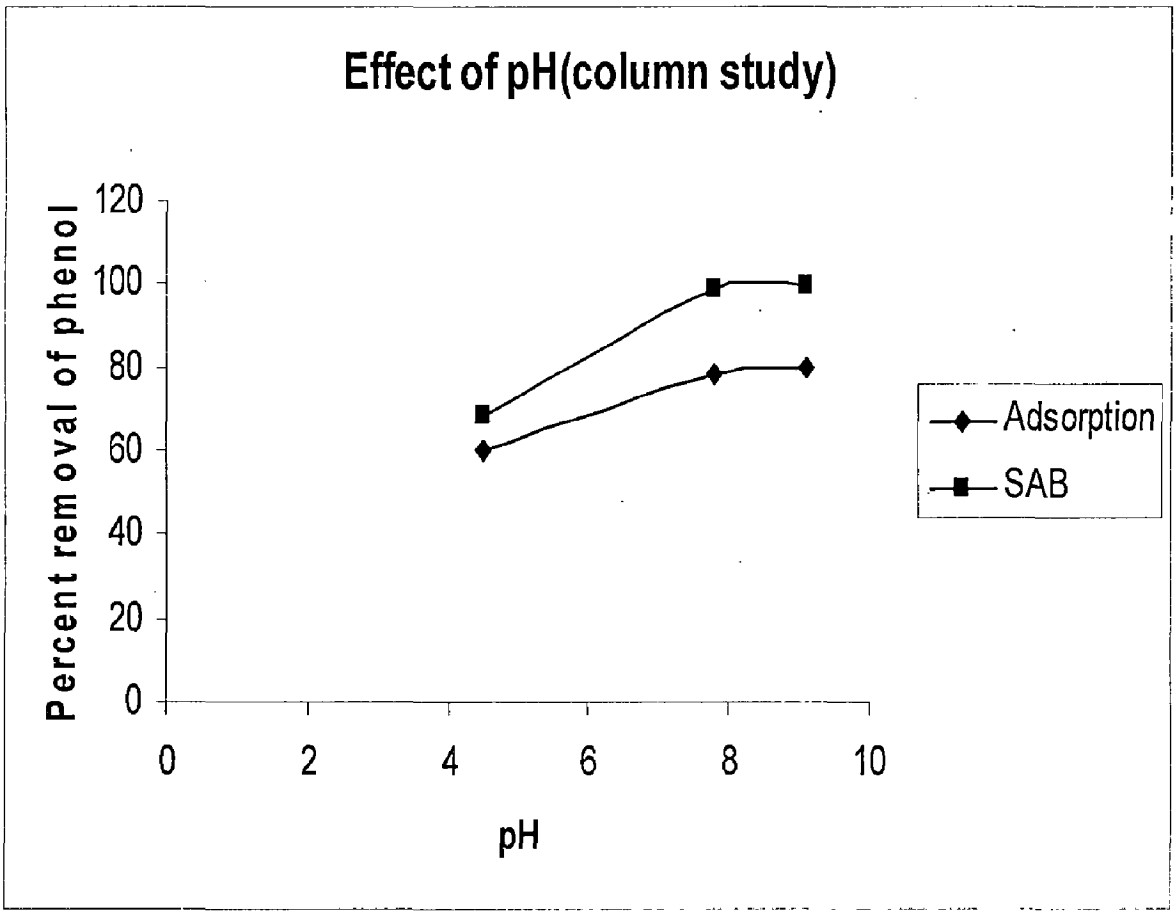


Fig. 5.31: Effect of pH for 300 mg/l phenol concentration

5.8.2 Effect of adsorbent dose for 300mg/l phenol concentration

The bio adsorption nature of pseudomonas putida laid on bagasse pith bed material as activated carbon was studied at three different doses of adsorbent in column. The experiments were run for 300 mg/l phenol concentration and the optimum dose of the adsorbent was found to be 6 mg which is in coincidence with the results obtained from the batch study. As the amount of adsorbent fed to the column increases the resultant cost of treatment of phenol also increases proportionally. As seen in the fig. 5.32 below as the amount of adsorbent increases beyond 6mg there is a very slight or marginal increase in the percent removal of phenol. So the optimum dose of phenol concentration for biosorption is 6 mg.

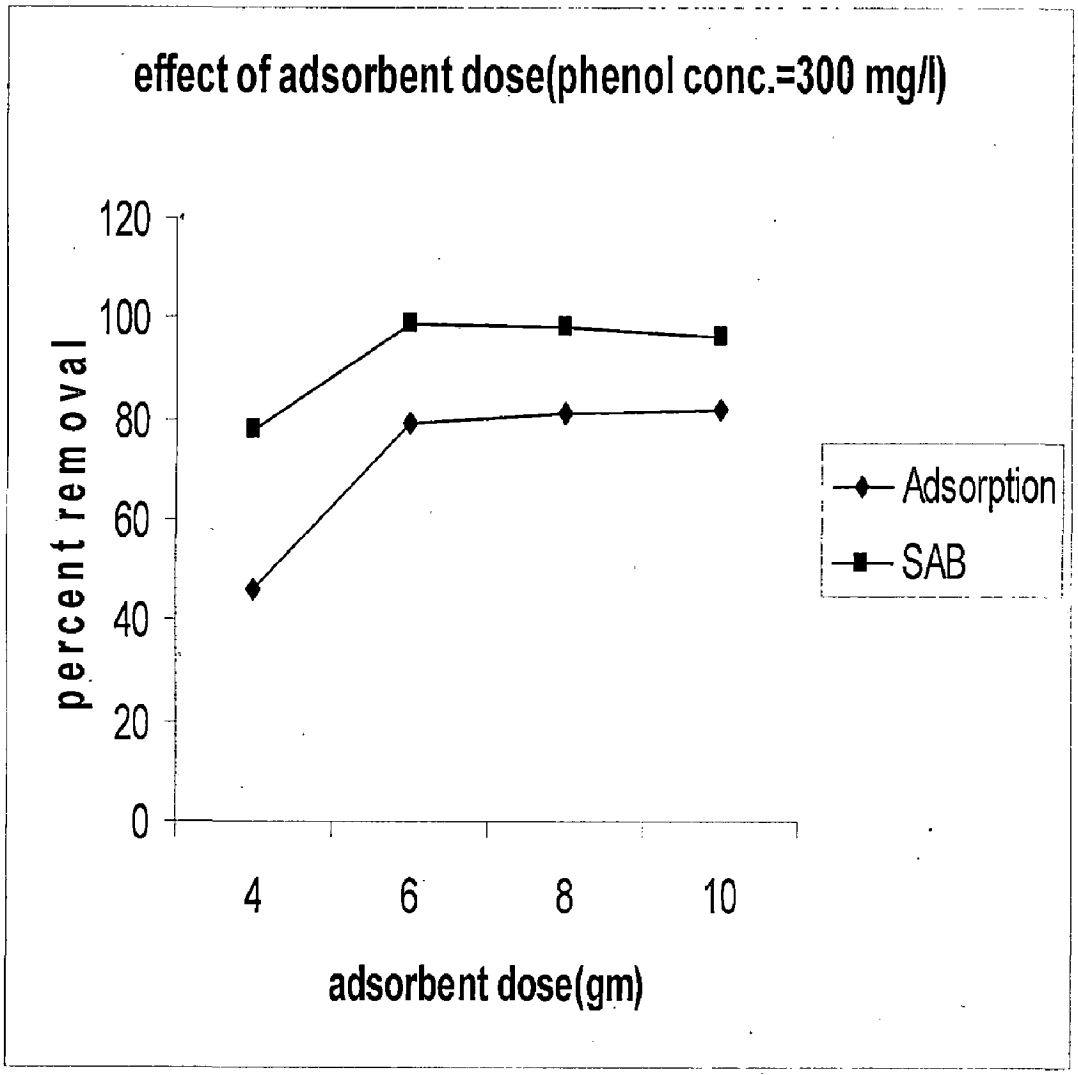


Fig. 5.32: Effect of adsorbent dose for 300mg/l phenol concentration

5.8.3 Effect of Flow Rate for 300mg/l phenol concentration (SAB)

The optimum flow rate was found to be 7.8 ml/ min in the column as observed from fig. 5.33. At this flow rate the maximum biodegradation was observed in the column.

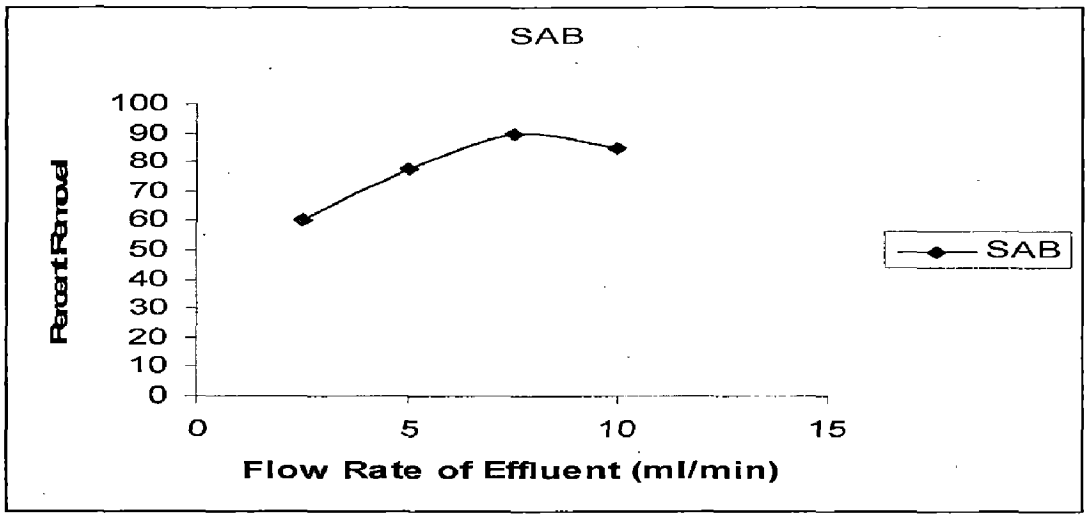


Fig. 5.33: Effect of Flow Rate for 300mg/l phenol concentration (SAB)

5.8 Breakthrough Curve for phenol in column study

Breakthrough curve for phenol in column study was drawn and through the curve in fig.5.34 it is clear that maximum phenol biodegradation is for 300mg/l phenol concentration in the optimum time period i.e. 65-70 hrs.

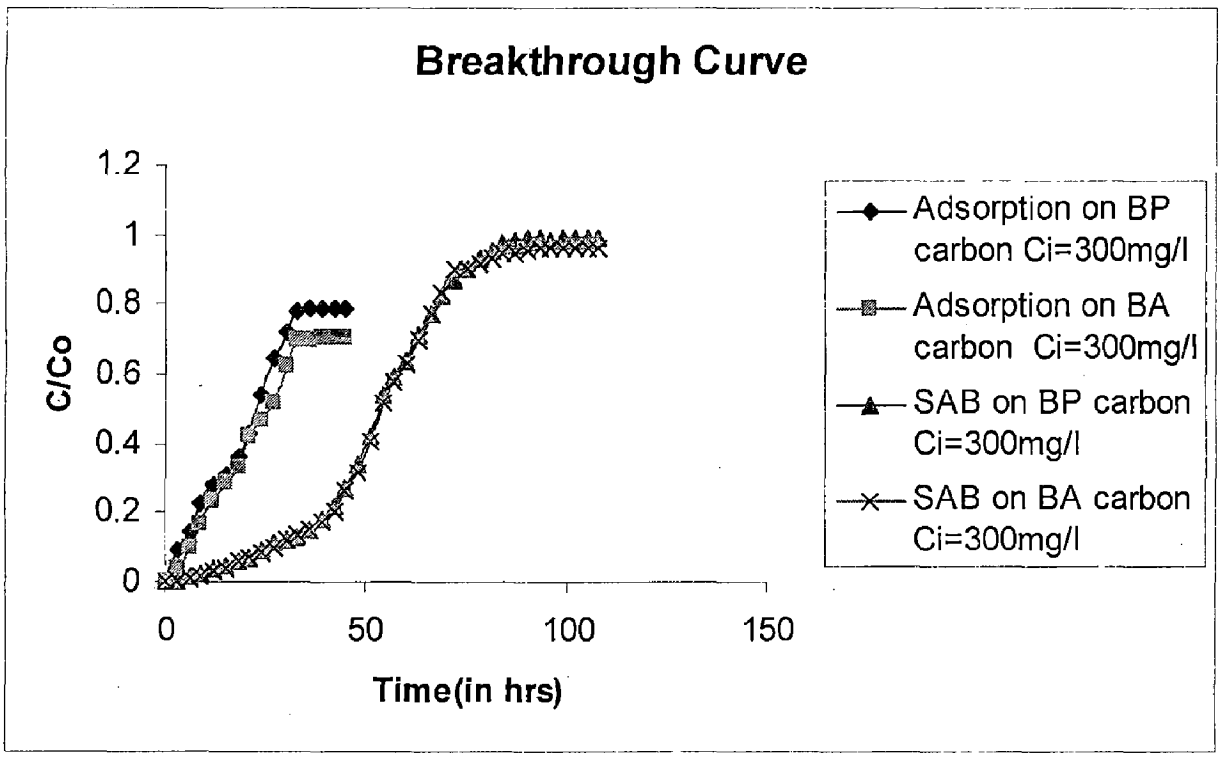


Fig. 5.34:Breakthrough curve for 300mg/l phenol(column)

CONCLUSION

On the basis of the work done following conclusions can be drawn

1) The nature of Pseudomonas putida (MTCC1194) and its ability to biodegrade the phenol present in effluent samples in different concentrations was studied and the results were found to be very satisfactory.

2) Phenol is inhibitory type compound and during the acclimatization of phenol to bacteria it was observed that biomass and pH increases with increase of phenol concentration.

3) It was found that pH increases with time as the biodegradation proceedes for free cell system.

4) Also the properties of two low cost adsorbents prepared from bagasse pith and bagasse pith were investigated and their elemental analysis was also carried out to find the best adsorbent properties of the two and after analysis it was found that activated carbon prepared from bagasse pith act as a better bed material.

5) Also the effect of change of particle size on the properties of the adsorbent material was examined and the results were up to expectation. Particles of smaller size had greater adsorption capacity as the surface area increases and hence proved to be a better bed material. But also for preparing fine activated carbon the cost of processing the activated carbon from agro waste increases proportionally. So it is better to have the particle size in the order of 2.38 - 4.75 mm.

6) Also work has been done to find the phenol removal capacity of these adsorbents. And activated carbons prepared from bagasse pith were found to be a better bed material for phenol removal in comparison to activated carbon from bottom ash.

7) In batch and column experiments it was found that percentage removal of phenol from effluent through simultaneous adsorption and biodegradation was more than when the same effluent was treated by adsorption or biodegradation alone.

8) The optimum concentration at which maximum removal of phenol from effluent was observed is found to be 300mg/l and the percentage removal was near to 99% when simultaneous adsorption and biodegradation treatment of effluent was done.

9) The main aim of present work is to find out the biodegradation capacity of removal of phenol from waste water and to compare the performance of adsorption , biodegradation

of phenol by pseudomonas putida, and bio sorption. 0f the three processes maximum phenol removal from phenol was observed when the treatment was carried out by simultaneous adsorption and biodegradation. Although the process takes a longer time to act on phenol as the bacteria takes a little time to get activated. So its a slower process but it is highly efficient.

10) Also break through curves were plotted for simultaneous adsorption and biodegradation (in column and batch study)

11) Further more the work has been extended to find out the optimum conc., pH and flow rate. Best phenol removal conditions were found to be:

Concentration: 300 mg/l

pH : 7.8

Flow rate : 7.5 ml/min

Adsorbent dose: 6 gm

Recommendations for future work: Phenol and its homologues are aromatic known since long for their toxic effects at higher concentrations in the environment. So in this report an effort was made to reduce the phenol concentration by using a combination of two processes i.e. adsorption and biodegradation. As the project was time bound so all the parameters could not be studied such as kinetic parameters were left untouched. So kinetic study of the growth of bacteria i.e pseudomonas putida on different bed material can also be done. Also different species of pseudomonas putida such as fluoroscenes or other microorganisms such as acinetobacter can also be tried.

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32 TECHNOLOGIES FOR WATER AND WASTE WATER TREATMENT

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APPENDIX A: TABLES FOR THE GRAPH

Table1: Calibration curve data for determination of phenol concentration

Phenol concentration (mg/l)	Absorbance (reading on spectrophotometer)
50	0.47
100	0.95
150	1.62
200	2.48
250	2.9
300	3.67
350	4.1
400	4.68
450	5.12
500	5.73
550	6.28

Table 2 : Removal of phenol by adsorption from bagasse pith and bottom ash

Time (in mins.)	Concentration (mg/l)		Percent Removal(%)	
	B.P.	B.A.	B.P.	B.A
0	20	20	0	0
45	18.8	19.2	6	4
90	17.2	17.6	14	12
135	15.5	16.2	22.5	19
180	11.8	12.3	41	38.5
225	8.6	10.4	57	48
270	8.51	9.7	57.45	51.5
315	8.48	9.2	57.6	54
360	8.47	9.18	57.65	54.1
405	8.47	9.1	57.65	54.5
450	8.47	9.1	57.65	54.5

Table 3: Removal of phenol (Ci=50mg/l) by adsorption from bagasse pith and bottom ash

Time (in mins.)	Concentration (mg/l)		Percent Removal(%)	
	B.P.	B.A.	B.P.	B.A
0	50	50	0	0
45	47.2	47.8	5.6	4.4
90	44	45.2	12	9.6
135	40.6	42	18.8	16
180	37	38.8	26	22.4
225	32	34.2	36	31.6
270	28.4	30.2	43.2	39.6
315	25.34	28	49.32	44
360	21.23	24.1	57.59	51.8
405	21.1	22.4	57.8	55.2
450	21.09	22.39	57.82	55.22

Table 4 : Removal of phenol (Ci=100mg/l) by adsorption from bagasse pith and bottom ash

Time (in mins.)	Concentration (mg/l)		Percent Removal(%)	
	B.P.	B.A.	B.P.	B.A
0	100	0	100	0
45	94	6	95	5
90	84.6	15.4	88.8	11.2
135	78	22	80	20
180	62	38	65	35
225	53.2	46.8	57.8	42.2
270	47.9	52.1	49.5	50.5
315	42.4	57.6	44.7	55.3
360	37.7	62.3	39.82	60.18
405	36.08	63.92	38.02	61.98
450	36	64	38	62

Table 5: Removal of phenol (Ci=300mg/l) by adsorption from bagasse pith and bottom ash

Time (in mins.)	Concentration (mg/l)		Percent Removal(%)	
	B.P.	B.A.	B.P.	B.A
0	300	0	300	0
45	164	12	272.4	9.2
90	246	18	253.8	15.4
135	206.4	31.2	216.54	27.82
180	181.8	39.4	191.25	36.5
225	156.6	47.8	167.4	44.2
270	132	56	143.1	52.3
315	105	65	121.5	59.5
360	80.4	73.2	96	68
405	72.6	75.8	84.6	71.8
450	72	76	83.4	72.2

Table 6: Removal of phenol (Ci=400mg/l) by adsorption from bagasse pith and bottom ash

Time (in mins.)	Concentration (mg/l)		Percent Removal(%)	
	B.P.	B.A.	B.P.	B.A
0	400	0	400	0
45	359.2	10.2	366	8.5
90	333.2	16.7	339.2	15.2
135	296	26	298.4	25.4
180	246.4	38.4	263.2	34.2
225	208.4	47.9	228	43
270	174.4	56.4	203.2	50.8
315	143.2	64.2	165.2	58.7
360	125.2	68.7	140	65
405	112.8	71.8	11.28	70.18
450	112	72.2	119.2	70.2

Table 7: Removal of phenol (Ci=500mg/l) by adsorption from bagasse pith and bottom ash

Time (in mins.)	Concentration (mg/l)		Percent Removal(%)	
	B.P.	B.A.	B.P.	B.A
0	500	0	500	0
45	434	13.2	447	10.6
90	412.5	17.5	419	16.2
135	390	22	405	19
180	379	24.2	381	23.8
225	316	36.8	330	34
270	262	47.6	269.5	46.1
315	229.4	54.12	230	54
360	168	66.4	171	65.8
405	145.5	70.9	151.5	69.7
450	145	71	151	69.8

Table 8: Effect of pH on phenol conc.

Time (in min)	Ads. of phenol for diff. pH(Ci=300mg/l)		
	pH=4.5	pH=7.8	pH=9.5
0	300	300	300
45	276	248.4	247.8
90	245.4	213.6	212.4
135	213.9	166.5	157.5
180	173.4	119.4	109.8
225	132	73.5	66.6
270	126	72	66
315	125.5	71.9	66

Table 9:Effect of pH on percent removal of phenol

Time(min)	Effect of pH on percent removal of phenol(Ci=300mg/l)		
	pH=4.5	pH=7.8	pH=9.5
0	0	0	0
45	8	17.2	17.4
90	18.2	28.8	29.2
135	28.7	44.5	47.5
180	42.2	60.2	63.4
225	56	75.5	77.8
270	58	76	78
315	58.27	76.2	78

Table10: Effect of particle size on phenol adsorption

Time(min)	Ads. of phenol for diff. particle size(Ci=300mg/l)		
	1-2mm	2-4mm	>4mm
0	300	300	300
45	250.8	243.6	258.6
90	210	201.6	224.4
135	171.6	159	204.9
180	130.8	113.4	172.8
225	102.9	81.6	139.8
270	66	80.4	132
315	65.4	79.5	126

Table 11:Effect of particle size on percent removal of phenol

Time(min)	Percent removal of phenol for diff. particle size(Ci=300mg/l)		
	1-2mm	2-4mm	>4mm
0	0	0	0
45	16.4	18.8	13.8
90	30	32.8	25.2
135	42.8	47	31.7
180	56.4	62.2	42.4
225	65.7	72.8	53.4
270	78	73.2	56
315	78.2	73.5	58

Table 12: Variation of conc. of phenol during bio degradation of phenol

Time(min)	Concentration of phenol				
	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	50	100	300	400	500
90	42	84	245.4	328	409
180	41	81	222	288	353
270	38.4	74.8	174	220	261
360	35.1	62.6	105	124	184
450	30.795	49.2	63	95.2	108
540	23	34	36.6	62	61
630	16.2	30.1	36	60	60
720	16	26	35.4	59.2	57
810	15.9	25.8	35.25	59.2	56

Table13: Percent removal of phenol during bio degradation of phenol

Time (in mins.)	Percent removal of phenol for varying concentration				
	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	0	0	0	0	0
90	16	16	18.2	18	18.2
180	18	19	26	28	29.4
270	23.2	25.2	42	45	47.8
360	29.8	37.4	65	69	63.2
450	38.4	50.8	79	76.2	78.4
540	54	66	87.8	84.5	87.8
630	67.6	69.9	88	85	88
720	68	74	88.2	85.2	88.6
810	68.2	74.2	88.25	85.2	88.6

Table14Variation of conc. of phenol during SAB of phenol for activated carbon from bagasse

Time(min)	Concentration of phenol				
	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	50	100	300	400	500
3	49	97.2	290.4	380	465
6	47	92.8	276	352	425
9	44.4	81.6	242.4	312	370
12	40.4	67.4	193.8	252	299
15	36.1	51.1	147	198	227
18	30.8	37.5	108	136	154
21	24	29	72.6	94.4	116
24	19.5	22	59.4	72	77
27	16.3	19.8	46.8	59.2	54
30	14	17.6	36.6	44.8	38
33	13	16.2	29.4	38.4	36
36	11.6	14.8	22.8	36.8	33
39	10.4	12.6	21.6	33.6	30
42	8.3	9.8	19.5	32.4	29
45	6.9	9.6	19.5	30.4	27.5
48	6.2	9.6	18.6	29.2	24
51	6	9.6	18	27.6	23.75
54	5.9	9.4	17.4	27.2	23.75
57	5.875	9.4	17.4	27	23.75
60	5.875	9.4	17.25	26	23.75
63	5.875	9.4	17.25	26	23.75

Table15 Percent removal of phenol during SAB of phenol for activated carbon from bagasse

Time (in mins.)	Percent removal of phenol for varying concentration				
	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	0	0	0	0	0
3	2	2.8	3.2	5	7
6	6	7.2	8	12	15
9	11.2	18.4	19.2	22	26
12	19.2	32.6	35.4	37	40.2
15	27.8	48.9	51	50.5	54.6
18	38.4	62.5	64	66	69.2
21	52	71	75.8	76.4	76.8
24	61	78	80.2	82	84.6
27	67.4	80.2	84.4	85.2	89.2
30	72	82.4	87.8	88.8	92.4
33	74	83.8	90.2	90.4	92.8
36	76.8	85.2	92.4	90.8	93.4
39	79.2	87.4	92.8	91.6	94
42	83.4	90.2	93.5	91.9	94.2
45	86.2	90.4	93.5	92.4	94.5
48	87.6	90.4	93.8	92.7	95.2
51	88	90.4	94	93.1	95.25
54	88.2	90.6	94.2	93.2	95.25
57	88.25	90.6	94.2	93.25	95.25
60	88.25	90.6	94.25	93.5	95.25
63	88.25	90.6	94.25	93.5	95.25

Table16Variation of conc. of phenol during SAB of phenol for activated carbon from bottom ash

Time(min)	Concentration of phenol				
	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	50	100	300	400	500
3	49.5	98	292.5	389.6	479
6	48	94.5	279.6	371.2	453
9	45.3	88	270	358.4	430
12	42.4	75	219	279.2	340
15	38.8	60	174	224	265
18	31.9	47.8	129	164	190
21	24.6	39.2	95.4	120	140
24	22.2	31	75.6	100	109
27	19.5	24.8	65.4	82.4	98
30	18	21.4	54	64.8	77
33	16.4	21.2	44.4	59.2	68
36	13.6	20.4	40.8	54.4	61
39	12.3	20	38.4	51.2	59.5
42	11.4	19.8	37.2	49.6	59
45	10.95	19.75	36.6	48.8	59
48	10	18.5	36.45	48.8	58.5
51	9.8	18.2	36.45	48.4	57.5
54	9.4	17.5	36	48.2	57
57	9.25	17.3	36	48.2	56
60	9.25	16.8	35.4	48.2	56
63	9.25	16.8	35.4	48.2	56

Table17: Percent removal of phenol during SAB of phenol for activated carbon from bottom ash

Time(min)	Percent removal of phenol for varying concentration				
	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	0	0	0	0	0
3	1	2	2.5	2.6	4.2
6	4	5.5	6.8	7.2	9.4
9	9.4	12	10	10.4	14
12	15.2	25	27	30.2	32
15	22.4	40	42	44	47
18	36.2	52.2	57	59	62
21	50.8	60.8	68.2	69	72
24	55.6	69	74.8	75	78.2
27	61	75.2	78.2	79.4	80.4
30	64	78.6	82	83.8	84.6
33	67.2	78.8	85.2	85.2	86.4
36	72.8	79.6	86.4	86.4	87.8
39	75.4	80	87.2	87.2	88.1
42	77.2	80.2	87.6	87.6	88.2
45	78.1	80.25	87.8	87.8	88.2
48	80	81.5	87.85	87.8	88.3
51	80.4	81.8	87.85	87.9	88.5
54	81.2	82.5	88	87.95	88.6
57	81.5	82.7	88	87.95	88.8
60	81.5	83.2	88.2	87.95	88.8
63	81.5	83.2	88.2	87.95	88.8

Table 18:Effect of Adsorbent dose

	Percent removal of phenol	
Adsorbent Dose	Adsorption	SAB
2	26	45
4	42	76
6	68	93
8	72	95
10	74	95

Table 19:Effect of particle size of adsorbent on phenol removal

	Percent removal of phenol	
Particle Size Range	Adsorption	SAB
1.2-2mm	77	95
2-4mm	72	92
4-6mm	62	84

Table 20:Effect of pH on phenol removal

	Percent removal of phenol		
	Adsorption	Biodegradation	SAB
4.5	58.27	60	65
7.8	76.2	86.5	94.5
9.5	78	87	93

COLUMN STUDY

Table 21: Variation of conc. of phenol during adsorption of phenol on bagasse pith carbon

Time (in hrs)	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	50	100	300	400	500
3	48	94	273	368	460
6	44	84	256.5	352	450
9	37	69	231.6	324	440
12	31.5	61	217.6	312	415
15	24	53	207.6	304	390.5
18	19.9	46	192	287.2	374.5
21	19.5	37	172.8	268.8	358
24	19.4	33.5	138.6	250.4	340
27	19.4	32	107.4	202	325
30	19.375	31.88	84	168	310
33	19.375	31.88	66.3	132	286
36			64.5	112	264
39			63	98	236.5
42			63	96	194
45			63	95.6	160
48				95.6	140
51				95.6	130
54					125
57					124.5
60					124.5

Table 22: Variation of conc. of phenol during adsorption of phenol on bottom ash carbon

Time (in hrs)	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	50	100	300	400	500
3	49	97	288	382	467.5
6	46	91	271.5	356	454
9	40.5	82	249.6	332	441
12	36	71	230.4	320	425
15	28	55	214.2	304.8	401
18	22.45	50	201	291.2	389
21	22.425	43	174	278.4	367
24	22.425	39.5	161.4	256.8	346
27	22.425	38.5	144.6	225.2	335
30		38	114	185.6	320
33		38	91.5	156.8	300
36			90	135.2	268
39			89.4	130.4	246
42			89.4	128	205
45			89.4	128	170
48			89.4	128	157.5
51					155
54					155
57					155
60					154.5
63					154.5

Table 23:Percent removal of phenol during adsorption of phenol on bagasse pith carbon

Time (in hrs)	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	0	0	0	0	0
3	4	6	9	8	8
6	12	16	14.5	12	10
9	26	31	22.8	19	12
12	37	39	27.4	22	17
15	52	47	30.8	24	21.9
18	60.2	54	36	28.2	25.1
21	61	63	42.4	32.8	28.4
24	61.2	66.5	53.8	37.4	32
27	61.2	68	64.2	49.5	35
30	61.25	68.12	72	58	38
33	61.25	68.12	77.9	67	42.8
36			78.5	72	47.2
39			79	75.5	52.7
42			79	76	61.2
45			79	76.1	68
48			79	76.1	72
51					74
54					75
57					75.1
60					75.1

Table 24:Percent removal of phenol during adsorption of phenol on bottom ash carbon

Time (in hrs)	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	0	0	0	0	0
3	2	3	4	4.5	6.5
6	8	9	9.5	11	9.2
9	19	18	16.8	17	11.815
12	28	29	23.2	20	19.8
15	44	45	28.6	23.8	22.2
18	55	50	33	27.2	26.6
21	55.1	57	42	30.4	30.8
24	55.15	60.5	46.2	35.8	33
27	55.15	61.5	51.8	43.7	36
30	55.15	62	62	53.6	40
33	55.15	62	69.5	60.8	46.4
36			70	66.2	50.8
39			70.2	67.4	59
42			70.2	68	66
45			70.2	68	68.5
48				68	69
51					69
54					69.1
57					69.1

Tables for Simultaneous Adsorption and Biodegradation

Table 25: Variation of conc. of phenol during SAB of phenol on bagasse pith carbon

Time (in hrs)	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	50	100	300	400	500
3	49.2	99.6	299	399	498
6	47.8	98.8	296	397.5	496
9	47.3	97.6	293	394	492.5
12	46	94.2	289.5	392	486.5
15	44.2	86.8	286	388.5	481
18	41.7	72.6	282	384	474
21	36	55.4	279	380	468.5
24	30.4	41.6	273	372	460
27	26.5	33	268	365	452
30	22.8	24.8	264	358	443
33	19.6	19.4	260	350	425
36	17.5	16.4	255.5	338	410
39	15.8	14.8	246	316	396
42	14	13	235	300	380
45	12.6	11.8	218	272	362
48	10.2	10.5	198	240	338
51	8.9	9.8	173	208	302
54	7.8	9.4	138	180	256
57	6.5	9.2	122	158	208
60	5.3	9	109	132	180
63	4.6	8.7	87	108	142
66	4.4	8.6	68	72	118
69	4.4	8.5	52	50	100
72	4.4	8.45	38	42	83
75	4.4	8.2	29	35	65
78	4.4	8.2	22	28	50
81		8.2	15	20	46
84		8.2	8	16	32
87			5.5	13.2	20
90			4	10	15.4
93			3.7	7.8	12
96			3.5	7.2	8.8
99			3.25	7.2	7.2
102			3.1	7.2	6.2
105			2.9		5.5
108			2.9		5.3
111			2.9		5.2
114			2.9		5.2
117					5.2

Table 26: Variation of conc. of phenol during SAB of phenol on bottom ash carbon

Time (in hrs)	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	50	100	300	400	500
3	49.4	99.6	299	399	498
6	48.8	98.8	298	397.5	496
9	47.8	97.8	295	396	494
12	47	94.8	291	393	490
15	46.2	88	288	390	483
18	43	75	283	386	476
21	38.5	58	279	381	470
24	32	45.8	275	375	462
27	28	36.4	270	368	453
30	24	26.8	265	360	445
33	21.2	21.2	260	352	428
36	18.8	17.8	254	340	412
39	16.2	15	248	320	398
42	15.8	13.2	240	300	382
45	13.2	12	222	276	365
48	12	10.8	205	245	342
51	10.9	10	178	218	308
54	9.8	9.8	145	190	265
57	9	9.6	126	164	215
60	8.5	9.45	112	142	190
63	8.5	9.4	90	118	160
66	8.45	9.4	69	85	132
69	8.45	9.35	50	63	110
72	8.45	9.3	40	45	90
75	8.45	9.3	31	36	70
78	8.45	9.3	25	29	52
81			20	22	47
84			17	20	34
87			15.5	18.5	26
90			14	17	22
93			13	16.5	21
96			12.8	16.4	20.5
99			12.8	16.4	20
102			12.2	16.4	18.5
105			12		18.5
108			12		18.5
111			12		18.5
114					18.5

Table 27:Percent removal of phenol during SAB of phenol on bagasse pith carbon

Time (in hrs)	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	0	0	0	0	0
3	1.6	0.4	0.33	0.25	0.4
6	4.4	1.2	1.33	0.625	0.8
9	5.4	2.4	2.33	1.5	1.5
12	8	5.8	3.5	2	2.7
15	11.6	13.2	4.66	2.88	3.8
18	16.6	27.4	6	4	5.2
21	28	54.6	7	5	6.3
24	39.2	58.4	9	7	8
27	47	67	10.67	8.75	9.6
30	54.4	75.2	12	10.5	11.4
33	60.8	80.6	13.33	12.5	15
36	65	83.6	14.83	15.5	18
39	68.4	85.2	18	21	20.8
42	72	87	21.67	25	24
45	74.8	88.2	27.33	32	27.6
48	79.6	89.5	34	40	32.4
51	82.2	90.2	42.3	48	39.6
54	84.4	90.6	54	55	48.8
57	87	90.8	59.33	60.5	58.4
60	89.4	91	63.67	67	64
63	90.8	91.3	71	73	71.6
66	91.2	91.4	77.33	82	76.4
69	91.2	91.5	82.67	87.5	80
72	91.2	91.55	87.3	89.5	83.4
75	91.2	91.8	90.3	91.25	87
78	91.2	91.8	92.67	93	90
81		91.8	95	95	90.8
84		91.8	97.3	96	93.6
87			98.17	96.7	96
90			98.67	97.5	96.92
93			98.77	98.05	97.6
96			98.83	98.2	98.24
99			98.92	98.2	98.56
102			98.97	98.2	98.76
105			99.03		98.9
108			99.03		98.94
111			99.03		98.96
114			99.03		98.96
117					98.96

Table 28:Percent removal of phenol during SAB of phenol on bottom ash carbon

Time (in hrs)	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	0	0	0	0	0
3	1.2	0.4	0.33	0.25	0.4
6	2.4	1.2	0.67	0.625	0.8
9	4.4	2.2	1.67	1	1.2
12	6	5.2	3	1.75	2
15	7.6	22	4	2.5	3.4
18	14	25	5.67	3.5	4.8
21	23	42	7	4.75	6
24	36	54.2	8.3	6.25	7.6
27	44	63.6	10	8	9.4
30	52	73.2	11.67	10	11
33	57.6	79.8	13.3	12	14.4
36	62.4	82.2	15.3	15	17.6
39	67.6	85	17.3	20	20.4
42	68.4	86.8	20	25	23.6
45	73.6	88	26	31	27
48	76	89.2	31.67	38.75	31.6
51	78.2	90	40.67	45.5	38.4
54	80.4	90.2	51.67	52.5	47
57	82	90.4	58	59	57
60	83	90.55	62.67	64.5	62
63	83	90.6	70	70.5	68
66	83.1	90.6	77	78.75	73.6
69	83.1	90.7	83.33	84.25	78
72	83.1	90.7	86.67	88.75	82
75	83.1	90.7	89.67	91	86
78	83.1	90.7	91.67	92.75	89.6
81			93.33	94.5	90.6
84			94.33	95	93.2
87			94.83	95.375	94.8
90			95.3	95.75	95.6
93			95.67	95.875	95.8
96			95.73	95.9	95.9
99			95.73	95.9	96
102			95.73	95.9	96.3
105			96		96.3
108			96		96.3
111			96		96.3
114					96.3

Table 29: Biomass concentration

Time (in hrs)	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	72	56	46	38	35
3	75	59	49	42	39
6	78	61	63	48	42
9	82	63	75	65	49
12	86	65	92	75	58
15	91	68	102	88	72
18	97	70	124	90	88
21	101	74	142	112	105
24	105	78	178	135	124
27	112	87	216	160	145
30	118	93	235	188	167
33	125	98	272	224	198
36	132	104	296	260	224
39	145	115	325	298	249
42	160	130	346	345	278
45	178	143	362	400	312
48	198	160	378	448	365
51	240	155	395	505	420
54	270	175	412	545	478
57	292	198	432	580	535
60	288	220	454	635	582
63	264	248	478	680	640
66	250	265	502	720	720
69	250	290	546	765	788
72		325	590	805	856
75		340	585	840	912
78		360	583	880	968
81		335	580	915	1034
84		320	578	948	1095
87			575	980	1145
90			568	1026	1216
93			560	1080	1200
96				1072	1185
99				1060	1180
102				980	1165
105					1142

Table 30: Percent phenol removal at different pH after 66 hrs
(Phenol conc. =300mg/l)

pH	Adsorption	SAB
4.5	60	68
7.8	78	99.1
9.1	80	99.2

Table 31: biomass data for SAB(bagasse pith carbon batch study)

	Ci=50mg/l	Ci=100mg/l	Ci=300mg/l	Ci=400mg/l	Ci=500mg/l
0	58	46	42	35	32
3	59	47	43	41	42
6	61	49	44	50	58
9	65	51	48	64	78
12	68	54	65	78	95
15	71	57	78	95	125
18	78	61	98	108	160
21	87	74	124	122	220
24	102	98	145	140	265
27	114	127	180	178	306
30	122	145	232	204	372
33	132	178	260	238	456
36	142	196	298	282	502
39	158	223	336	340	546
42	178	247	378	395	610
45	204	258	398	448	665
48	222	272	445	530	685
51	240	302	495	640	710
54	270	320	492	635	765
57	260	318	485	628	810
60	258	310	478	610	802
63	250	302	460	602	780

Table 32: Adsorbent dose of bagasse pith carbon v/s percent phenol removal(phenol conc. = 300 mg/l)

Adsorbent dose (gm)	Adsorption	SAB
4	46	78
6	79	99
8	81	98
10	82	96

Table 33: Data for breakthrough curve of phenol during batch study

Time(in hrs.)	Adsorption on BP carbon	Adsorption on BA carbon	Biodegradation	SAB on BP carbon	SAB on BA carbon
	Ci=300mg/l	Ci=300mg/l	Ci=300mg/l	Ci=300mg/l	Ci=300mg/l
0	0	0	0	0	0
3	0.394	0.3625	0.26	0.032	0.025
6	0.732	0.68	0.65	0.08	0.068
9	0.76	0.722	0.878	0.192	0.1
12			0.882	0.354	0.27
15				0.51	0.42
18				0.64	0.57
21				0.758	0.682
24				0.802	0.748
27				0.844	0.782
30				0.878	0.82
33				0.902	0.852
36				0.924	0.864
39				0.928	0.872
42				0.935	0.876
45				0.938	0.878
48				0.938	0.878
51				0.94	0.878
54				0.942	0.88
57				0.942	0.88
60				0.9425	0.882
63				0.9425	0.882

Table 34: Data for breakthrough curve of phenol during column study

Time(in hrs.)	Adsorption on BP carbon	Adsorption on BA carbon	SAB on BP carbon	SAB on BA carbon
	Ci=300mg/l	Ci=300mg/l	Ci=300mg/l	Ci=300mg/l
0	0	0	0	0
3	0.09	0.04	0.0033	0.0033
6	0.145	0.095	0.0133	0.0067
9	0.228	0.168	0.0233	0.0167
12	0.274	0.232	0.035	0.03
15	0.308	0.286	0.047	0.04
18	0.36	0.33	0.06	0.0567
21	0.424	0.42	0.07	0.07
24	0.538	0.462	0.09	0.083
27	0.642	0.518	0.11	0.1
30	0.72	0.62	0.12	0.1167
33	0.779	0.695	0.13	0.133
36	0.785	0.7	0.1483	0.153
39	0.79	0.702	0.18	0.173
42	0.79	0.702	0.2167	0.2
45	0.79	0.702	0.2733	0.26
48			0.34	0.3167
51			0.423	0.4067
54			0.54	0.5167
57			0.5933	0.58
60			0.6367	0.6267
63			0.71	0.7
66			0.7733	0.77
69			0.8267	0.833
72			0.873	0.8967
75			0.903	0.8967
78			0.9267	0.9167
81			0.95	0.9333
84			0.973	0.9433
87			0.9817	0.9483
90			0.9867	0.953
93			0.9877	0.9567
96			0.9833	0.9573
99			0.9892	0.9573
102			0.9897	0.9573
105			0.9903	0.96
108			0.9903	0.96

Table 35: Data for effect of flow rate

Flow Rate of Effluent	2.5	5	7.5	10
Percent Removal	60	78	90	85