

ADSORPTIVE REMOVAL OF 4 CARBOXY-BENZALDEHYDE

A DISSERTATION

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

MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(With specialization in Industrial Pollution Abatement)

By

MOHAMMAD NASIR



DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY, ROORKEE

ROORKEE -247667 (INDIA)

JUNE, 2013

INDIAN INSTITUTE OF TECHNOLOGY

Roorkee

CANDIDATE'S DECLARATION

I hereby declare that the work being presented in the dissertation report entitled “**Adsorptive Removal of 4 Carboxy-Benzaldehyde**” in partial fulfillment of the requirements for the award of the degree of M.Tech. (With Specialization in Industrial Pollution Abatement) and submitted in the department of Chemical Engineering of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during the period from June 2012 to June 2013 under the supervision of **Prof. I. D. Mall**, Department Of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India. The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute

Date: June, 2013
Place: Roorkee

(MOHAMMAD NASIR)

CERTIFICATE

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

(I. D. Mall)
Professor
Department of Chemical Engineering
Indian Institute of Technology
Roorkee -247667, India

ACKNOWLEDGEMENT

I owe a great many thanks to all those who were of immense help and supported me during writing of this dissertation report. I wish to express my sincere gratitude and appreciations to **Prof. I. D. Mall**, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee for providing me an opportunity to work under his guidance. His superb guidance with enriched knowledge, regular encouragement and invaluable suggestions at every stage of the present work has proved to be extremely beneficial to me. Also I would like to thank and express my gratitude to **Dr. Vimal Chandra Srivastava**, Assistant Professor, Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee for guiding and correcting various documents of mine with attention and care. He has taken pain to go through the project and make necessary correction as and when needed. I consider myself fortunate to have had the opportunity to work under their able guidance and enrich myself from their depths of knowledge.

Thanks are due to Mr. R. Bhatnagar, Senior Lab Assistant, IPA Lab, Department of Chemical Engineering, Indian Institute of Technology Roorkee, for his guidance in using sophisticated equipments in the lab. I extend my heartiest thanks to Mr. Chandrakant Thakur for his valuable suggestions during the work.

Mohammad Nasir
E.No. 11515008
M.Tech. 2nd year
IIT Roorkee

ABSTRACT

In this work, 4-carboxybenzaldehyde (4-CBA) removal from aqueous solution onto low cost adsorbent- bagasse fly ash (BFA) was carried out. A 4-factor 5-level Central composite design under response surface methodology was used to optimize the 4-CBA removal and adsorption uptake. Variable considered for the study were pH, adsorbent dose, initial concentration and time. The optimum value of these parameters were found as pH=4, adsorbent dose=9 g/l, initial concentration=100 mg/l and time 7.5 h. At optimized condition the removal efficiency and adsorption uptake of 4-CBA onto BFA were found to be 79% and 9.9 mg/g, respectively. Quadratic regression model was developed to evaluate impact of linear and quadratic interaction and R^2 (=0.873) value suggest that the model was significant. Adsorption capacity of BFA and GAC was compared. BET surface area of BFA and GAC was found to be 284 m²/g and 591 m²/g, respectively. Both the adsorbents were predominately mesoporous in nature. Kinetic study was carried out by employing pseudo first and pseudo second order model and possibility of intra particle diffusion controlling the adsorption mechanism was also investigated. Adsorption equilibrium data were fitted for Langmuir, Freundlich, Redlich- Peterson, Sips, Hills, Temkin model. Positive value of ΔH^0 suggest that the adsorption process was endothermic. Change in the entropy was found to be positive. Negative values of ΔG_{ads}^0 indicates that the adsorption process is feasible and spontaneous.

TABLE OF CONTENTS

CANDIDATE'S DECLARATION	i
CERTIFICATE	i
ACKNOWLEDGEMENT	ii
ABSTRACT.....	iii
TABLE OF CONTENTS.....	iv
LIST OF TABLES.....	vii
LIST OF FIGURES	viii
Chapter- 1.....	1
INTRODUCTION.....	1
1.1 GENERAL.....	1
1.2 STRUCTURE OF PETROCHEMICAL COMPLEXES.....	2
1.3 TEREPHTHALIC ACID PRODUCTION AND GENERATION OF 4-CARBOXYBENZALDEHYDE.....	3
1.3.1 Different side product obtain during terephthalic acid production.....	6
1.4.1 Physical properties	7
1.4.2 Chemical structure:	7
1.4.3 Effect of 4-carboxbenzaldehyde	7
1.5 DISCHARGE STANDARDS FOR INDUSTRIAL WASTEWATER.....	7
1.6 ADSORPTION AS WASTEWATER TREATMENT PROCESS.....	8
1.7 ADSORBENT USED FOR THE ADSORPTION PROCESS.....	9
1.7.1 Bagasse fly ash (BFA)	9
1.8 AIM AND OBJECTIVE OF PRESENT WORK.....	11
Chapter- 2.....	12
CENTRAL COMPOSITE DESIGN (CCD).....	12
2.1 RESPONSE SURFACE METHODOLOGY (RSM) AND CENTRAL COMPOSITE DESIGN (CCD).....	12

2.2 TERMINOLOGY USED IN CENTRAL COMPOSITE DESIGN.....	13
Chapter- 3.....	15
LITERATURE REVIEW	15
3.1 GENERAL.....	15
3.1.1 Synthesis of adsorbent and its application for removal of toxic compound from terephthalic acid waste water:	15
3.1.2 Treatment of petrochemical waste water by coagulation flocculation method	17
3.1.3 Biodegradation of petrochemical waste water in bioreactor reactor	19
3.1.4 Aerobic treatment of 4-carboxybenzaldehyde containing PTA wastewater.....	20
3.1.5 Detection of presence of 4-CBA in solution by studying fluorescence properties.....	23
Chapter- 4.....	30
EXPERIMENTAL PROGRAMME	30
4.1 GENERATION OF EXPERIMENTAL DATA FROM CCD	30
4.2 ADSORBENTS AND ADSORBATE.....	31
4.3 ANALYTICAL MEASUREMENT	31
4.4 BATCH EXPERIMENTAL PROGRAMME.....	32
4.5 ADSORBENTS CHARACTERIZATION.....	33
4.5.1 Bulk density and proximate analysis of adsorbents.....	33
4.5.2 Surface area and pore size distribution of adsorbents.....	33
4.5.3 X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis of adsorbent	34
4.5.4 FTIR analysis of adsorbents.....	34
4.5.5 TGA/DTG/DTA study of adsorbents.....	34
4.5.6 Point of zero charge determination of adsorbents.....	34
Chapter- 5.....	36
RESULT AND DISCUSSION	36
5.1 ADSORBENTS CHARACTERIZATION.....	36
5.1.1 Bulk density and proximate analysis of adsorbents.....	36

5.1.2 Surface area and pore size distribution of adsorbents.....	36
5.1.3 X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis of adsorbent.....	36
5.1.4 Point of zero charge determination of adsorbents.....	42
5.1.5 FTIR of adsorbents	42
5.1.6 Thermal analysis of GAC	44
5.2 CCD ANALYSIS.....	46
5.2.1 Fitting of second order polynomial equation and statistical analysis	48
5.3 EFFECT OF VARIOUS PARAMETERS ON 4-CBA REMOVAL EFFICIENCY	52
5.3.1 Effect of initial pH and adsorbent dose (m).....	52
5.3.2 Effect of initial 4-CBA concentration and contact time	53
5.3.3 Effect of pH, adsorbent dose, initial concentration and time on adsorption capacity .	55
5.4 KINETICS OF ADSORPTION FOR BFA AND GAC	57
5.4.1 Pseudo first order and Pseudo second order model.	57
5.4.2 Intra particle diffusion model/rate controlling step	61
5.5 ADSORPTION ISOTHERM STUDY	64
5.5.1 Effect of temperature	64
5.5.2 Isotherm modeling	64
5.6 ESTIMATION OF THERMODYNAMIC PARAMETERS.....	69
Chapter- 6.....	71
CONCLUSIONS AND RECOMMENDATIONS.....	71
6.1 CONCLUSION.....	71
6.2 RECOMMENDATIONS.....	72

LIST OF TABLES

Table No.	Title	Page No.
1.1	Physical properties of 4-CBA	7
1.2	Minimum National Standards (MINAS) for petrochemical industry effluents	8
3.1	Literature review for treatment of 4-CBA containing PTA waste water by adsorption	25
3.2	Literature review for treatment of terephthalic acid waste water by coagulation	27
3.3	Literature review for treatment 4-CBA containing PTA waste water	28
3.4	Literature review for treatment of 4-CBA containing PTA wastewater by oxidation process	28
3.5	Literature review for 4-CBA containing PTA wastewater acid waste water	29
4.1	Chosen process parameters and their levels for 4-CBA removal	30
5.1	Physicochemical characterization of BFA and GAC	38
5.2	Experimental and predicted values of % removal and q_e for 4-CBA adsorption onto BFA	47
5.3	Adequacy of model tested for 4-carboxybenzaldehyde removal on BFA and adsorption capacity of adsorbent	49
5.4	Different R^2 values for adsorption of 4-CBA on BFA and for adsorption capacity of adsorbent	50
5.5	ANOVA of the second-order polynomial equation for % removal and adsorption capacity	51
5.6	Kinetic parameters for the removal of 4-CBA by BFA ($t = 7.5$ h, $m = 9$ g/l, $T = 303$ K) and GAC ($t = 7.5$ h, $m = 20$ g/l)	63
5.7	Isotherm parameters for the removal of 4-CBA by BFA ($t = 7.5$ h, $m = 9$ g/l) and GAC ($t = 7.5$ h, $m = 20$ g/l)	67
5.8	Thermodynamic parameters for adsorption of 4-CBA by BFA ($t = 7.5$ h, $m = 9$ g/l) and GAC ($t = 7.5$ h, $m = 20$ g/l)	70

LIST OF FIGURES

Fig. No.	Title	Page No.
1.1	Process flow diagram for manufacture of terephthalic acid	5
1.2	Production of terephthalic acid and major side product obtain during process	6
1.3	4-carboxbenzaldehyde	7
4.1	Calibration curve of 4-CBA	32
5.1	X-ray diffraction pattern of BFA for before and after adsorption	37
5.2	Pore size distribution of GAC and BFA	39
5.3	Scanning electron micrograph of: (a) Virgin BFA (b) 4-CBA loaded BFA	40
5.4	Scanning electron micrograph of: (a) Virgin GAC (b) 4-CBA loaded GAC	41
5.5	Point of zero charge of GAC	42
5.6	FTIR spectroscopy of (a) BFA (b) GAC	43
5.7	Thermal analysis of (a) Blank BFA (b) 4-CBA loaded BFA	45
5.8	Effect of (a) adsorbent dose and initial pH on % 4-CBA removal (b) initial 4-CBA concentration and contact time on % 4-CBA removal	54
5.9	Effect of (a) pH and initial concentration (b) adsorbent dose and time on adsorption capacity	56
5.10	Effect of contact time on (a) adsorption of 4-CBA by BFA, $t = 7.5\text{h}$, $C_0 = 50-150\text{ mg/L}$; $m = 9\text{ g/L}$ (b) adsorption of 4-CBA by GAC, $t = 7.5\text{h}$, $C_0 = 50-150\text{ mg/L}$; $m = 20\text{ g/L}$. Experimental data points given by symbols and the lines predicted by Pseudo second order model.	59
5.11	Pseudo-second-order kinetic plot for removal of 4-CBA on (a) BFA ($C_0 = 50-150\text{ mg/L}$; $m = 9\text{ g/L}$, $t = 7.5\text{h}$) (b) GAC ($C_0 = 50-150\text{ mg/L}$; $m = 20\text{ g/L}$, $t = 7.5\text{h}$)	60
5.12	Webber-Morris plot for 4-CBA removal by (a) BFA ($C_0 = 50-150$, $t = 450\text{ min}$, mg/l , $w = 9\text{g/}$) (b) GAC ($C_0 = 50-150$, $t = 450\text{ min}$, 20 g/l).	62
5.13	Equilibrium adsorptions isotherms at different temperatures for (a) 4-CBA loaded BFA system, $t = 7.5\text{h}$, $C_0 = 20-200\text{ mg/l}$; $m = 9\text{ g/l}$. lines predicted by Sips model (b) 4-CBA loaded GAC system, $t = 7.5\text{h}$, $C_0 = 20-200\text{ mg/l}$; $m = 20\text{ g/l}$. The lines predicted by Redlich-Peterson. In both figures Experimental data points given by symbols.	66

Chapter- 1

INTRODUCTION

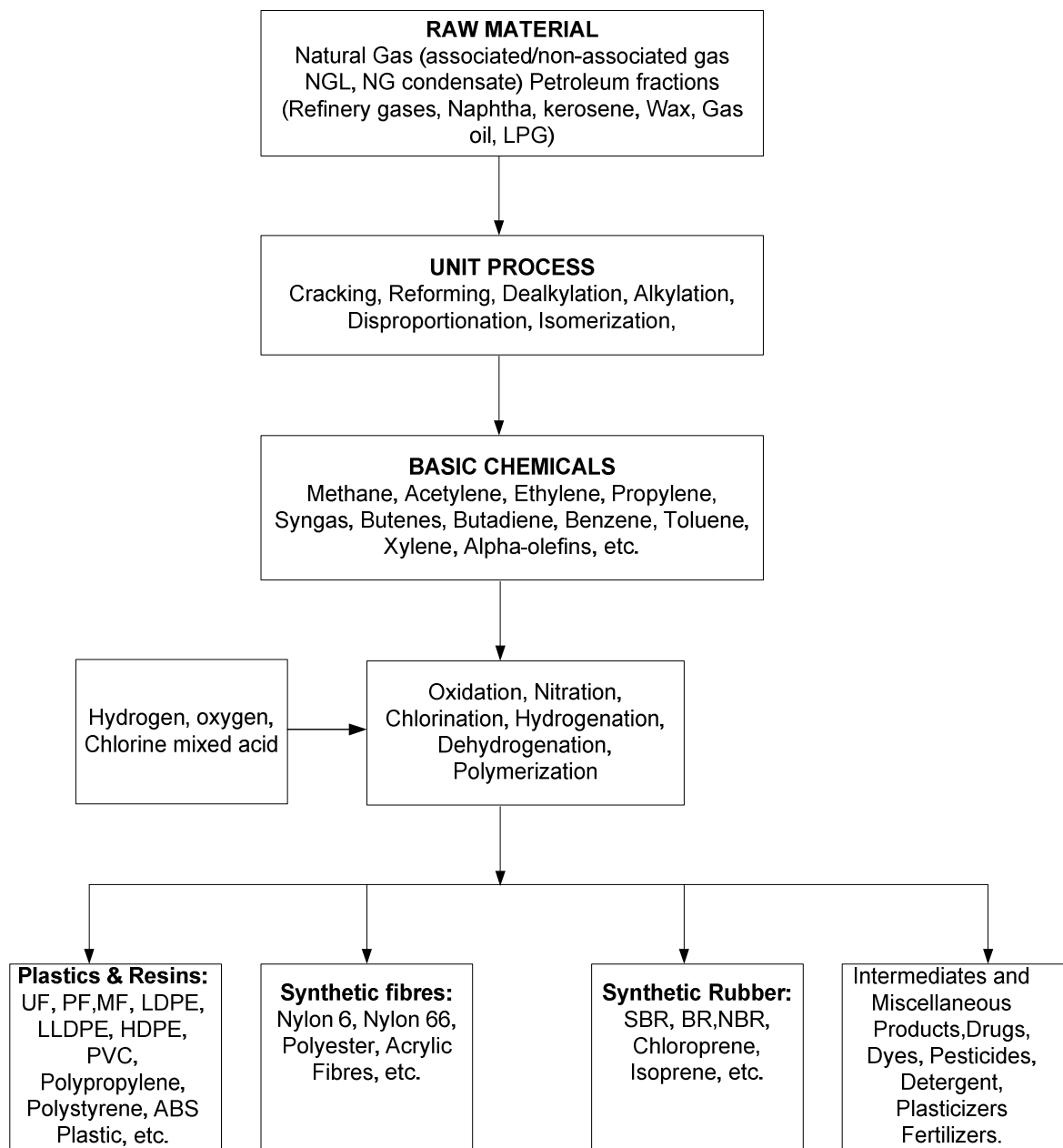
1.1 GENERAL

Petrochemical industry has registered tremendous growth in recent times due to high demand of value added petrochemicals and their vast applicability as well as ability to replace costly and heavy material. Reason behind this tremendous growth is the extraordinary simplification of various process used for synthesis of different compounds and the increase in demand of products over the last ten years. Simplicity of the process is attributed to the catalyst development and availability of new automatic control technology. The socioeconomic and cultural devolvement of a nation has been largely affected by petrochemical industry and now petrochemicals has become integral part of life. Petrochemical industry has fulfilled the some basic need of human such as food, shelter and clothing. Contribution of petrochemical industry to various area viz. automobile, packaging, construction, healthcare, home appliances, agriculture, telecommunication, personal care, chemicals, textile and tyre cords have been tremendous [Mall, 2007]. Terephthalic acid: a petrochemical product used for PET production, has witness increase in its production by 3.7% from 2009-10 2010-11 in India [Annual report, 2012-2013].

The growth of petrochemical industry is largely depends on cost and availability of feedstock. Petrochemicals are chemical products which are obtained from naturally occurring raw materials viz. petroleum, natural gas, coal. To produce petrochemical from raw materials various processes viz. fluid catalytic cracking of petroleum fraction, steam cracking of natural gas, catalytic reforming of naphtha are employed. Olefins and aromatic can be obtained from refinery by fluid catalytic cracking of petroleum fractions. Olefins and aromatics can also obtain from chemical plant by steam cracking of natural gas and catalytic reforming of naphtha, respectively. These olefins and aromatics are grouped together as basic petrochemicals and form the major building blocks. The classification of entire product spectrum is done into the following three classes: (a) Primary petrochemical products or building block, (b) Secondary petrochemical products or Intermediate products or (c) product obtain from building block product, final or end products coming from intermediate products.

Synthetic fibre industry is one of the major segments of petrochemical industry. Synthetic fibre production has witness rapid growth due to its cost effectiveness, turnkey technology and ease of processability and care. Polyester is one of the major synthetic fibre used in the woven and non woven industry. Dimethyle terephthalate (DMT) and terephthalic acid are the monomer for the production of polyester (PET). However polyester production is now mainly manufactured from terephthalic acid because of the several advantages of terephthalic acid over DMT.

1.2 STRUCTURE OF PETROCHEMICAL COMPLEXES [Mall, 2007]



1.3 TEREPHTHALIC ACID PRODUCTION AND GENERATION OF 4-CARBOXYBENZALDEHYDE

Terephthalic acid, a precursor for Poly Ethylene terephthalate (PET) production is commercially produced by The American Amoco process in two-stage. The first stage involve wet oxidation of p-xylene into acetic acid (solvent) by employing a catalyst consisting of cobalt, manganese and bromide ions [Landau and Staffer, 1968; Kloorbezem et al., 1997; Daniels et al., 1999]. The product from first-stage known as Crude Terephthalic Acid (CTA) is dissolve in water at 250 °C to purify it. In second stage the hydrogenation of CTA takes place, in this stage CTA and highly pressurized hydrogen are contacted in concurrent manner and they pass through a Pd/C embedded fixed bed. The product obtain from second stage is 99.95 % pure [Meyer, 1971; Azarpour and Zahedi, 2012]. 4-Carboxybenzaldehyde (4-CBA) is produced as a side product or intermediate product due to incomplete oxidation of p-xylene during the manufacturing of Purified Terephthalic acid (PTA) and it is considered as impurity. Other compounds produced during the process are benzoic acid, p-toluic acid and phthalic acid along with small concentration of p-xylene and methyl acetate. The amount of wastewater generated for each ton of PTA production is approximately 3-4 m³ [Jhung et al., 2001; Guyot et al., 1990; Macarie et al., 1992; Young et al., 2000; Noyola et al., 1990; Zhang et al., 2006]. 4-CBA causes problem during the production process due to the similarity in the structure with terephthalic acid. It cocrystallizes with terephthalic acid and get entrapped thus it becomes inaccessible for completion of the oxidation [Khachane et al., 2003].

The complete process is description below

Oxidation of p-xylene: This section is heart of the process and oxidation reaction takes place in the reactor. The raw materials used in this process are para-xylene, fresh acetic acid, air and manganese or cobalt as catalyst. The air used in this process was compressed at about 2000 kPa. The acetic acid recovered from recovery unit is mixed with fresh acetic acid and it is recycle back. The reactor was operated at a temperature of 150°C and the pressure inside the reactor was maintained in between 1500-3000 kPa. In order to minimize side reaction and avoid by product formation the amount of air supplied was more than calculated by stoichiometric ratio. The oxidation reaction is exothermic and heat generated due to reaction is exchanged in condenser by first condensing and then refluxing acetic acid. The liquid stream (mother liquor) emerging from centrifuge primarily consist of unreacted p-xylene, acetic acid, methyl acetate catalyst and water

and it is sent to dryer. Terephthalic acid obtain from oxidation process is crystallized in the series of three crystallizer under vacuum. The slurry obtain from last crystallization unit is filtered in rotary filter, washed and crude TPA is sent to dryer. The resident time inside the reactor was varied from 30 min to 3 hr and approximately 95% conversion was achieved.

Purification of crude TPA: In this process mainly catalytic hydrogenation and recyclization of crude TPA is carried out. Hydrogenation of TPA slurry is done in presence of palladium catalyst. During hydrogenation process 4-CBA is converted into p-toluic acid. With help of hydrogenation process coloring impurities are also converted into materials which can be easily removed. The high pressure outlet stream from the reactor is flashed into the crystallizers. Centrifuge is provided to remove water from the terephthalic acid formed in the reactor while as drier is used to remove the moisture predominately acetic acid with the help of preheated air. The outlet stream from the centrifuge is distributed into two portions; first stream is fed to crystallization unit while second stream which is in form of a wet cake is passed into rotary drier. Purity of terephthalic acid obtain from drier is about 99%.

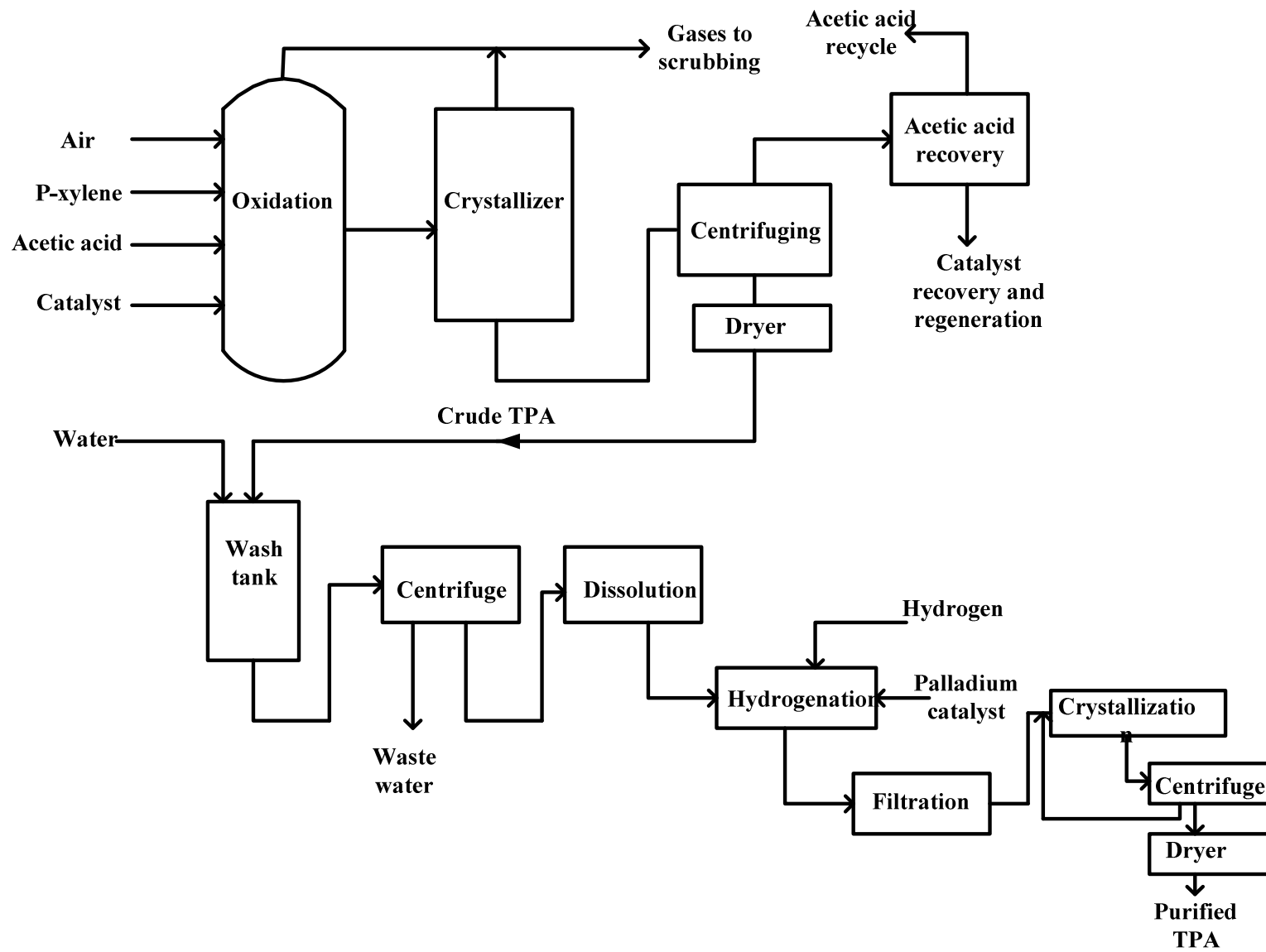


Fig.1.1. Process flow diagram for manufacture of terephthalic acid (AMCO PROCESS) [Mall, 2007]

1.3.1 Different side product obtain during terephthalic acid production

During the production of terephthalic acid some side reactions occurs causing the formation of byproducts. Most of these byproducts are aromatic compounds which enter the wastewater. Apart from terephthalic acid PTA wastewater also contain 4-CBA, p-toluic acid (p-Tol), benzoic acid (BA) and phthalic acid. All the aromatic compounds present in wastewater nearly makeup to 75% of the COD of the wastewater

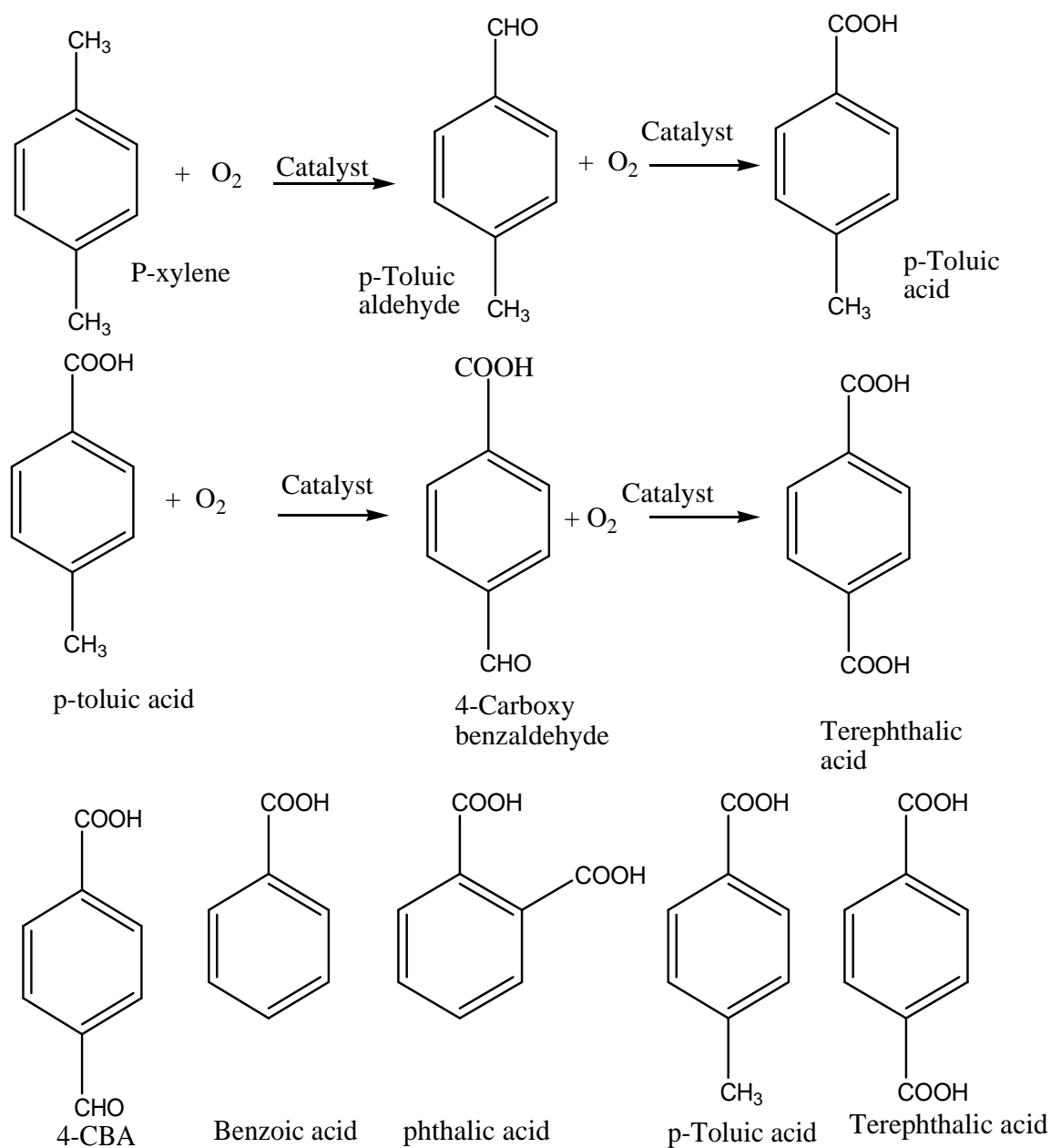


Fig. 1.2. Production of terephthalic acid and major side product obtain during process.

1.4 4-CARBOXYBENZALDEHYDE

Synonyms: Terephthalaldehydic acid; P-Carboxybenzaldehyde; P-Formylbenzoic acid; 4-Formylbenzoic acid. P-CBA or 4-CBA,

1.4.1 Physical properties

Table 1.1: Physical properties of 4-CBA

Physical property	Value
Molecular Formula	C ₈ H ₆ O ₃
Formula Weight	150.13 (g/mol)
λ _{max}	258 nm
Melting Point	256°C (492.8°F)
Boiling point	332.6°C at 760 mmHg
Flash Point	76°(168°F)
Specific Gravity	1.060
Moisture	0.5%(max)
Vapor Pressure	5.72E-05mmHg at 25°C
Physical state	White to yellow crystal powder

1.4.2 Chemical structure:

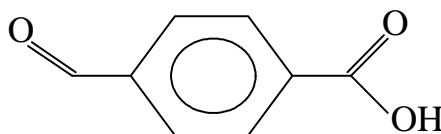


Fig. 1.3. 4-Carboxybenzaldehyde

1.4.3 Effect of 4-carboxybenzaldehyde

4-CBA causes irritation to skin, eyes, mucous membrane and respiratory tract; it may also cause chemical conjunctivitis. Laboratory experiment has been resulted in mutagenic effect.

1.5 DISCHARGE STANDARDS FOR INDUSTRIAL WASTEWATER

There are standards set by various regulatory authorities to monitor the water pollution caused by effluent from industries. The wastewater as well as emissions from any manufacturing complex must adhere to these standards. Almost all countries in the world have independent bodies which

take care of industrial pollution. In India, these standards are set by the Central Pollution Control Board (CPCB) under the guidance of Ministry of environment and forest (MOEF). These have been communicated in the form of MINAS (Minimum National Standards) for the discharge of pollutant from these industries. MINAS have been established by understanding of pollution control measures which are within the techno-economic capability of the industry and shouldn't be violated in any case. Various water treatment techniques focused on water treatment to match these standards have been developed. MINAS for petrochemical industry (basic and intermediate) is given in Table 1.2

Table 1.2: Minimum National Standards (MINAS) for petrochemical industry effluents [CPCB, 2012]

Parameter	Value (mg/l except pH)
pH	6.5 – 8.5
BOD (3 days 27 C)	50
COD	250
Sulphide as S	2
Phenol	5
Fluoride	15
Cyanide	2
Total Suspended Solids	100

1.6 ADSORPTION AS WASTEWATER TREATMENT PROCESS

The large amount of waste water produced due to rapid industrialization, formulation of strict law against the pollution and regulation of quality of effluent has made it mandatory to devolve a process or modify existing process so that the above requirements could be accomplished. Recent advancement in the adsorbent has developed adsorption process as a potential wastewater treatment process and this process has attracted considerable interest recently. Adsorption process largely depends upon the cost and availability of adsorbent along with type of pollutant to be removed. Simplicity of operation, complete removal of pollutant, sludge free operation, recovery of adsorbent, low power requirement, easy handling and promising technology is some silent features which give edge to adsorption over other treatment processes [Lakshmi et al.,

2007]. Product obtain after treating by adsorption process have very good quality also adsorption process have high economic feasibility [Choy et al., 1999].

Adsorption process has been successfully applied for the competitive removal of cadmium and nickel [Srivastava et al., 2009], Brilliant green dye (BG) [Mane et al., 2007], Petroleum hydrocarbons [Poliana et al., 2010], furfural [Singh et al., 2009]. Apart from its application in solid-liquid it is equally popular for treatment of solid-gas system. High treatment cost makes it very difficult to remove toxic pollutant from wastewater [Weng and Huang, 1994]. Adsorption process is now widely considered as feasible technique for the removal of pollutant from wastewater [McKay, 1995]. Due to its versatility and high and removal efficiency adsorption process has been extensively used for PTA wastewater treatment.

1.7 ADSORBENT USED FOR THE ADSORPTION PROCESS

Different adsorbent used for removal of toxic compounds from PTA wastewater includes activated carbon cloth [Ayranci et al., 2005; Ayranci and Duman, 2006], activated carbon [Chern and Chien, 2003], cationic MCM-41 [Huang et al., 2004], Mesoporous silica (FSM-16) [Tozuka et al., 2005], Modified bentonites [Yildiz et al., 2005]. However the high cost, long adsorption contact time and low adsorption equilibrium uptake of these adsorbent leads to search for suitable adsorbent that can fulfill above requirements. However, most of these adsorbents either do not have considerable adsorption capacities or need relatively long adsorption contact times. Therefore, it is of interest to develop effective adsorbents with short contact time for the removal of toxic species from aqueous solution.

1.7.1 Bagasse fly ash (BFA)

After juice extraction from the sugarcane the remaining waste is known as bagasse and it is burned in boiler to produce energy for sugar mills. The higher calorific value of BFA has prompted its industrial use as solid fuels for steam boilers. Combustion of sugarcane approximately generates 5.5 kg of bagasse fly ash (BFA) per metric ton of cane [PPAH, 1998]. Apart from direct recycling as low fertilizer in sugar cane plantation no significant utilization of BFA has been reported. High porosity of BFA makes it suitable adsorbent for wastewater treatment. The carbonaceous solid waste collected from the particulate separation equipment attached to the flue gas line of the sugarcane bagasse-fired boilers is known as Bagasse fly ash (BAF) [Srivastava et al., 2007]. BFA is a carbonaceous adsorbent and like all other carbonaceous it also contains amorphous form graphite carbon. It has various pore size including micropores

and macropores. The slit-like micropores are the driving force for high adsorption capacity [Mall et al., 2006]. Due to low cost (almost free of cost), short adsorption contact time, plentiful availability: India being second largest producer of sugarcane after Brazil, BFA has established itself as an extremely favorable adsorbent for various pollutant removal from waste water. However scarcity of significant work for 4-CBA removal from PTA wastewater using BFA as an adsorbent motivated us to use it as an adsorbent. Desorption process is not very suitable due to high affinity of sorbate on BFA but adsorbate can be chemically transformed into innocuous product as reported by Lataye et al. [2005] through dewatering, drying and refiring back the solute loaded sorbent into the boiler, this process also results in the recovery of significant amount of energy. From petrochemical wastewater to distillery wastewater BFA has enormous applicability for wastewater treatment.

The BFA has been used for the COD removal from sugar mill [Mall et al., 1994], dairy mill wastewater [Kushwaha et al., 2010], dyes [Mall et al., 2005a, b, 2006, Mane 2007] and paper mill effluents [Srivastava, 2003]. Various studies have carried out using BFA as an adsorbent for the adsorptive removal of phenolic compounds [Mall et al., 2003; Swamy et al., 1997, Srivastava et al., 2006, a,b,2008], metals [Gupta et al., 2003, Gupta and Ali, 2000a] pyridine [Lataye et al., 2006] and dyes [Gupta et al., 2000b].

1.8 AIM AND OBJECTIVE OF PRESENT WORK

4-carboxybenzaldehyde (4-CBA) has been subjected to a lot of research particularly because of its toxicity and importance in the petrochemical industry. Adsorption has already proved its worth as a wastewater treatment technology for a wide variety of pollutants. However, literature review are very scarce on removal of 4-CBA from aqueous solutions. Hence, keeping this in mind following objectives has been set forth for the present study:

1. To characterize the adsorbents (BFA and GAC) before and after treatment by various characterization techniques.
2. To investigate the feasibility of central composite design (CCD) method for optimizing the removal of 4-Carboxybenzaldehyde from aqueous solution using bagasse fly ash as an adsorbent.
3. Development of mathematical model, design of experiment as well as study of interactive effect of process parameter by using CCD under response surface methodology (RSM).
4. To optimize the following design parameters for the removal of 4-Carboxybenzaldehyde by using central composite design method. These design parameters include :
 - Initial pH of solution
 - Dose of BFA
 - Initial concentration of 4-CBA
 - Contact time
5. To compare the removal efficiency for different types of adsorbents: low cost adsorbent (Bagasse fly ash (BFA)), commercial adsorbent (activated carbon).
6. To carry out adsorption isotherm modeling, determining kinetics of reaction, accessing feasibility of adsorption process with the help of thermodynamic parameters.

Chapter- 2

CENTRAL COMPOSITE DESIGN (CCD)

2.1 RESPONSE SURFACE METHODOLOGY (RSM) AND CENTRAL COMPOSITE DESIGN (CCD)

Response surface methodology is a collection of statistical and mathematical technique which is used for designing experiments, building models, evaluating the effect of several factors, searching optimum conditions for desirable responses, and reducing the number of experiments. RSM mainly consist of three stages (i) selecting the parameters and designing the experiments, (ii) response surface modeling through regression and (iii) optimization of response [Kütahyalı et al., 2011; Jaouachi et al., 2007]. In order to optimize the considered parameter different techniques applied in RSM are Central Composite Design, Box Behnken statistical experimental design and two level full factorial design.

CCD was initially introduced by Box and Wilson [1951] and later it was modified by Wilson and Hunter [1961]. CCD is preferred over full factorial design because it gives comparable result while reducing the required number of experimental runs. Statistical model provided by CCD are helpful in understanding the interaction among optimized parameter. In CCD all effective factors are optimized simultaneously. The central point for each factor is assumed to be 0, and the design is considered to be symmetric around central point [Brereton, 2003].

For statistical calculation the following relationship between coded value (x_i) and real value (X_i) is established

$$\text{Coded value} = x_i = \frac{X_i - X_0}{\Delta X_i}, i = 1, 2, 3, \dots, n \quad (1)$$

Where; ΔX is step change and X_0 is real value at the centre point

Since the input parameter interact in linear to linear and linear to quadratic manner hence taking all interaction into the consideration the system behavior can be described as

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i < j}^n \sum_j \beta_{ij} X_i X_j + \epsilon \quad (2)$$

Where i and j are linear, quadratic coefficients; n is number of parameters (here $n=4$), β_0 constant coefficient, β_i slope or linear effect of input factor x_i , β_{ii} is quadratic effect on input factor x_i and β_{ij} is the linear interaction effect between input factors x_i and x_j , ϵ is the residual error [Benyounis et al., 2005].

In adsorption process various parameter such as pH of solution, dose of adsorbent (m), contact time (t), initial adsorbate concentration (C_0), agitation speed and temperature of operation, surface area of adsorbent plays an important role but out of these parameter pH(X_1), adsorbent dose (X_2), initial concentration (X_3) and time (X_4) primarily affect the adsorption process and in this study these factors are considered for design parameter [optimization] and CCD was applied to design the experiments using Design Expert software (Trial version 6.0.8).

2.2 TERMINOLOGY USED IN CENTRAL COMPOSITE DESIGN

Let df = Degree of freedom of variance source; SS =Sum of squares; MS = Mean of squares.

Then, mathematical relationship among SS , df and MS is defined as:

$$MS = \frac{SS}{DF} \quad (3)$$

F is the F - value of variance source it is defined as:

$$F = \frac{(MS)}{(MS_{res})} \quad (4)$$

The large value of fisher test value ‘ F ’ indicates that most of the variation in the response can be explained by the regression equation. The numerical value of probability factor ‘ p ’ gives the idea whether the obtain value of F is large enough to indicate statistical significance. If the value of probability factor ‘ p ’ is less than 0.05 then the model obtain will be statistically significant [Segurola et al., 1999]

Probably the most widely used summary statistic is the “ R^2 adjusted” that is also written R^2_{adj} or “adjusted R-square”. With addition of variable to the model the value of R^2 will increase while as “ R^2 adjusted” will compensate the values. Numerical value of R^2_{adj} will witness increase only when addition of new variable will make model more suitable. Value of “ R^2 adjusted” will always be lower or equal to R^2 . In order to determine the adjusted R-square, it is convenient to use a $n \times n$ matrix. Then, the adjusted R-square (R^2_{adj}) is given by

$$R^2_{adj} = [1 - \frac{(n-1)}{(n-p)}(1-R^2)] \quad (5)$$

It is common to interpret R^2_{adj} as the “fraction of the variation in the response data explain by the model. Where n is no. of experiments; p is no. of variables in the model; SSE is sum of squares estimated errors; SST is sum of squares total.

Also, coefficient correlation or coefficient of determination (R^2) is defined as:

$$R^2 = [1 - \frac{(SSE)}{(SST)}] \quad (6)$$

For a good experiment al fit the values of coefficient correlation and adjusted R^2 must be close to each other.

The “ R^2 prediction” or “ R -square prediction” is given as fallows

$$R^2_{prediction} = [1 - \frac{(n-1)}{(n-p)} \frac{(PRESS)}{(SST)}] \quad (7)$$

The significance of coefficient is checked by evaluating the probability factor ‘p’ while as the significance of model is checked by determining fisher test ‘F’ value under the ANOVA analysis section. Probability factor ‘p’ also used to indicate the interaction strength among independent parameters. The goodness of fit of the model could be confirmed by using the determination coefficient (R^2). The adjusted R^2 (x) values indicates that the model fails to explain only (1-x)% of the total variations. Moreover, the determination coefficient ($R^2=y$) value used to find the relationship between the experimental and predicted values of the response. The lack-of-fit measures the failure of the model to represent the data in the experimental domain at points which were not included in the regression. In significance of model develop can also be verified from the lack-of-fit value. If the value of lack of fit is greater than 0.05 the model will be statistically significant.

Chapter- 3

LITERATURE REVIEW

3.1 GENERAL

Terephthalic acid (PTA) is mainly produced by catalytic oxidation of p-xylene. During this process some side reactions occurs causing the formation of byproducts. Most of these byproducts are aromatic compounds which enter the wastewater. Apart from terephthalic acid PTA wastewater also contain 4-carboxybenzaldehyde (4-CBA), p-toluic acid (p-Tol), benzoic acid (BA) and phthalic acid. All the aromatic compounds present in wastewater nearly makeup to 75% of the COD of the wastewater. The pollution potential is generally estimated in terms of chemical oxygen demand (COD). 4-CBA causes irritation to skin, eyes, mucous membrane and respiratory tract; it may also cause chemical conjunctivitis. Laboratory experiment has been resulted in mutagenic effect [MSDS, 2012]. Presence of large amount of these organic compounds in wastewater increases the potential to cause harmful effect on environment and ecological system.

Treatment studies of 4-Carboxybenzaldehyde containing PTA wastewater has been carried out by numerous scholars and some successful method proposed are: Activated sludge process [Lau, 1978], biological degradation [Yan et al., 2004; Kleerebezem et al., 2005; Zhang et al., 2006] Coagulation and flocculation [Karthik et al., 2008; Wen et al., 2006; Verma et al., 2010], Photocatalytic degradation [Shafaei et al., 2009], advance Oxidation processes [Park et al., 2003; Thiruvengatachari et al., 2007; Andreozzi et al., 2009], solvent extraction, nanofiltration, electro dialysis, pervaporation [Anbia and Salehi, 2011], super critical water oxidation and adsorption.

Following literature review includes the popular method applied for treatment of PTA wastewater. Understanding these methods gives the idea to treat the aqueous solution of 4-acrboxybenzaldehyde

3.1.1 Synthesis of adsorbent and its application for removal of toxic compound from terephthalic acid waste water:

Anbia and Salehi [2011] synthesized polyelectrolyte (polydiallyldimethyl ammonium chloride) modified ordered mesoporous carbon (CMK-1/PDDA) employed for the removal of

main aromatic compounds present in PTA wastewater. The adsorbents were synthesized through a simple preparation procedure and they were applied for selective removal of p-Tol, BA, 4-CBA, PA and TA from aqueous solutions. Batch experiments were performed to study the adsorption behavior of these major aromatic compounds and UV- spectrophotometer was used to determine the concentration of each compound.

The adsorbent CMK-1 mesoporous carbon was modified by a cationic polyelectrolyte agent: PDDA. The modified adsorbent (CMK-1/PDDA) was used as a new nanosorbent for the adsorptive removal of acidic compounds from synthetic PTA wastewater. During modification process the surface characteristic of adsorbent improves due to impregnation of PDDA which results in higher sorption capacity of adsorbent for acidic compounds from aqueous solution. Various physicochemical characteristic of modified adsorbent as structural order and textural properties, functional groups of modified were studied by XRD analysis, nitrogen adsorption and FTIR analysis, respectively. Various operating parameters observed were effect of chemical modification, effect initial solution pH, adsorbent dose, initial concentration, contact time, agitation speed and reaction temperature.

Adsorption capacity of CMK-1 and CMK-1/PDDA was compared, from the experimental result it was concluded that the modified adsorbent (CMK-1/PDDA) has higher adsorption capacity as compared to CMK-1. The aqueous solution of acid compound contains the acidic ions while as the adsorbent was positively charged, due to opposite charge the electrostatic attraction becomes a dominant force which lead to a higher adsorption capacity of CMK-1/PDDA. The % removal of these acidic compound witness decrease with increase in temperature and initial pH of solution. The equilibrium adsorption isotherm was well explained by Langmuir model at all the temperature.

Different types of adsorbents were found to have different affinity towards the compound present in the PTA wastewater. Feasibility of adsorptive recovery of organic compounds present in PTA wastewater was performed by [Khachane et al. \[2007\]](#) using four different polymeric resins. Main purpose of this study was to remove the undesirable component from aqueous effluent emerging from crystallization section so that it can be recycle back to the reactor. This process will result in the saving of significant quantity of water.

The adsorbent amberlite XAD-2, amberlite XAD-4, amberlite XAD-7 and INDION 1014 MN-2 were conditioned by methanol washing and then further dried by at 60°C. Aqueous solution of

single solute of 800 ppm concentration was prepared and adsorption study was carried out for 24 hours. The multisolute adsorption study was done by studying the PTA effluent from crystallization section. The adsorption study was done for variety of adsorbents. The single component sample were analyzed by spectrophotometer while as solution of multi-component was analyzed by HPLC having Novapack C-18 column. Operating parameters were loading vs. on various polymeric adsorbent for single and multi- solute adsorption, Bed volume vs. concentration for single and multi-solute adsorption at a fixed temperature.

For single solute system the highest adsorption capacity was found in case of INDION 1014 MN-2, this higher adsorption capacity can be attributed to the higher surface area of the adsorbent. The adsorption decreases in order to their surface area. In case of multisolute adsorption the study reveals that with increase in $-\text{COOH}$ group in the structure of solute its adsorption becomes difficult due to steric hindrance. From the results it was also concluded that percentage removal for a particular component in case of single solute adsorption is always higher than it adsorption in case of multisolute adsorption system. This pattern is result of competitive adsorption in multisolute and availability of less surface area for the component. Treatment of PTA wastewater was carried out in two columns, arranged in series. First column was operated at the breakthrough point and the effluent from the first column, which mainly contains trimellitic acid, was treated in second column. Acetic acid, used as solvent during oxidation of p-xylene was regenerated from PTA wastewater.

3.1.2 Treatment of petrochemical waste water by coagulation flocculation method

The applicability of coagulation–flocculation process to treat PTA wastewater contacting 4-carboxybenzaldehyde and other aromatic acid was investigated [Verma et al. \[2010\]](#). Percentage removal of these organic acids was determined interms of COD reduction. Analysis of component present in PTA waste water was done by GCMS. Coagulation study was done on numerous coagulant viz. FeCl_3 , FeSO_4 , PACl (Poly-aluminum chloride) and CMC (Carboxy methyl cellulose). Various physico-chemical characteristic of PTA wastewater was performed using appropriate instruments. Main parameter considered for study includes initial sample pH and dose of coagulant along with sludge settling characteristic as well as effluent filterability. Settling characteristic of sludge was quantified by determining sludge volume index (SVI). The study of pH that with increase in pH of solution the COD reduction decreases for each coagulant, however the rate of reduction and final COD is different for different coagulant. Precipitation on

each coagulant was observed in lower pH (2-4) range and optimum COD reduction varies for each coagulant. Optimum dose and COD removal efficiency for each dose was examined through experiments and results reveals that FeCl_3 has best removal efficiency among all the adsorbents. The optimum COD removal was 75.5%. Highest removal efficiency for ferric chloride has been reported due to increase surface area resulting from higher FeCl_3 precipitation. The increment in BOD_5/COD ration from 0.17 to 0.38 affirms the improve biodegradability of PTA wastewater. In order to improve the settling characteristic of sludge without affecting the COD removal C-PAA was added. Study of filtration characteristic was performed by gravimetric filter. Values of specific cake resistance and filter medium resistance was determined from the slope and intercept of plot between $\Delta t/\Delta V$ vs. V . After addition of C-PPA the values of specific cake resistance and filter medium resistance decreases. Thermal stability of sludge before and after the coagulation was performed Thermal analysis of the sludge showed that the weight loss of sludge occurs in three temperature region. Qualitative access of the addition of new functional group after treatment was done by FTIR analysis where as quantitative analysis of added compound after adsorption was done by EDX analysis.

[Karthik et al. \[2007\]](#) also studied coagulation–flocculation for the pretreatment of PTA waste water containing benzoic acid, p-toluic acid, 4-carboxybenzaldehyde, terephthalic acid and phthalic acid. The treatment was done by batch method in jar by varying the coagulant dose. The coagulants used for this study were aluminium sulphate, FeCl_3 , FeSO_4 , polyaluminium chloride (PAC), in combination with anionic polyelectrolyte. For most of the discharge effluent treatment by solely biodegradation process do not fulfill the discharge standard, keeping it as motivation the objective for applying coagulation-flocculation method was to enhance the biodegradability of PTA wastewater so that PTA wastewater can easily further treated by aerobic treatment. Many studies have suggested that the presence of terephthalic acid in wastewater is major source of hindrance in biodegradation process. Terephthalic acid removal by coagulation flocculation process was reported about 90%. The settling ability of PTA sludge was improved by adding significant amount of polyelectrolyte. The pretreated sludge results in the reduction of COD values from 35% to 41% for different coagulant having different dose. The pretreated sludge was further treated by aerobic treatment and the microorganism culture was collected from clarifier section of an activated sludge process.

The performance of coagulation and flocculation process is greatly affected by type concentration and degree of dispersion of colloidal particle along with composition of wastewater as well as mixing rate of coagulant and flocculants. Presence of electrolyte and charge on suspended particles affects the settling property. Selection of coagulant is done in such a way that it should have opposite charge to the colloidal particles. The coagulant and suspended particle thus neutralize each other charge and help destabilizing the suspension and provides driving force to floc each other.

The biodegradability of wastewater is represented by BOD₅/COD, higher the ratio greater will be the biodegradability of the sludge. The study shows increase in the ratio of BOD₅/COD from 0.45 to 0.67, hence significant increases in the biodegradation nature of sludge. The COD and BOD reduction of PTA wastewater by coagulation–flocculation process in combination with aerobic bio-oxidation was 97.4% and 99.4%, respectively.

3.1.3 Biodegradation of petrochemical waste water in bioreactor reactor

[Tsuno and Kawamura \[2008\]](#) studied the anaerobic treatment of 4-Carboxybenzaldehyde and terephthalic acid containing PTA wastewater by employing anaerobic reactor embedded with granular activated carbon. The operation of reactor was continuous, where organic loading was increased while as hydraulic retention time was decreased. In order to keep microorganism capable of removal at higher concentration of toxic compounds, the amount of nutrient supplied were increased. The reactor was design to perform two operations, first adsorption on the surface of GAC and further degradation with the help of microorganism. Presence of terephthalic acid in PTA wastewater in concentration range of 150 mg/l has been reported as main source of problem in biodegradation and methane production. The adsorption process will cause in the decrease in concentration of terephthalic acid in aqueous phase to make the solution easily biodegradable. At lower concentration of terephthalic acid the removal percentage was high but with increase in concentration have negative effect on the percentage removal. Adsorption experimental data were will explained by freundlich isotherm model. Maximum COD and terephthalic acid removal by combined adsorption and anaerobic treatment method was reported as 90% while as fermentation ratio of methane was also about 90%.

The suitability of anaerobic and aerobic process for PTA wastewater was thoroughly studied by [Pophali et al. \[2007\]](#). In recent years the treatment process has shifted from activated sludge process to aerobic fallowed to anaerobic process due to flexibility in energy consumption,

volume required to handle sludge, ease of process control along with better settling characteristic. The main objective of this study was to treat the PTA wastewater to a prescribed effluent limit, improve the settling ability of sludge and design an economically feasible process. To achieve the objective the PTA wastewater was treated by two stage activated sludge process followed by upflow anaerobic fixed film fixed bed reactor (AFFFBR). To assess the capability of activated sludge process firstly two stage ASP process was employed and the experiment was carried out for different retention rate. The experiments were conducted for BOD concentration vs HRT and concentration vs days of operations. During activated sludge process the seeding of reactor was done by providing some activated sludge from treatment plants. The level of dissolved oxygen was maintained between 2-3 by providing accurate flow rate of air and the microorganism were kept activate by providing a mixture of nutrient in exact composition. The result of two stage ASP indicates that after operation of 36 hr at 3000 MLSS the removal of BOD, COD and suspended solid was maximum. After operation of 36 hr the effluent COD was found to be within prescribed standards. Increase in the retention rate and MLSS causes the increase in COD and BOD values of treated effluent. The ASP treated effluent was fluffy in nature having higher values of sludge volume index, representing the poor settling rate of sludge. The sole application of two stage ASP process could not reduce the values of toxicants/pollutant to the prescribed limit. Treatment study by AFFFBR process was done at HRT 0.1-0.8 day for 60 days and the removal of COD and BOD was approx 25 and 26%, while as at increased HRT of 1-1.2 day and for 90 days of operation the COD was reduced by only 60%. Analyzing the result of ASP and AFFFBR process it was concluded that neither of these two processes can be employed for complete treatment. A combine process was suggested where effluent was pretreated by AFFFBR process to reduce the COD and later the AFFFBR effluent was treated by single stage ASP process. The effluent after combined treatment was found to contain all the pollutant within prescribed limit. The power required and generated during the process were also determined and calculations shows that about 257 kW/d energy can be saved by applying improved process or combine process for treatment.

3.1.4 Aerobic treatment of 4-carboxybenzaldehyde containing PTA wastewater

Presence of 4-carboxybenzaldehyde, terephthalic acid, benzoic acids and toluic acid has created a lot of environmental problem and they contribute about 70-80% of COD of PTA wastewater. [Zhang et al. \[2006\]](#) work on method to treat these compounds present in PTA

wastewater by degradation process with introduction of some innovation to the aerobic process. Chemical fibres were used as carrier. Metabolization of aromatic was successfully done by introducing a microbial fusant Fhhh, by metabolizing aromatics hydraulic retention time was decreased and removal efficiency was increased. The concentration measurement of individual component was done by gas chromatograph which have inbuilt mass selective detector device. The three microbes; Basidiomycetous fungus *Phanerochaete chrysosporium* and, yeast *Saccharomyces cerevisiae*, and bacterium *Bacillus* YZ1 were fused together to form Fhhh strain. In this study biodegradation was found to be affected by enzymes catalytic action. The biodegradability of all aromatic acid was accessed by determining the sludge loading rate and removal percentage. The results indicate that Increase in the specific activity of manganese peroxidase (MnP) have a positive effect on sludge loading rate and removal percentage. Linear regression analysis was performed by developing four linear regression equations. In the regression equation MnP-SA was taken as independent variable while as sludge loading rate of (a) COD (b) TOC (c) aromatic compound and (d) removal percentage was considered as dependent variable. Sludge retention rate by this method for Fhhh was found to be 6 fold in comparison to anaerobic treatment reported by [Cheng et al. \[1997\]](#) and comparably more than conventional aerobic and anaerobic treatment methods. The slope of regression equation between MnP Vs RPA indicates the ease with aromatic will be catalyzed; slope for 4-carboxybenzaldehyde was 0.017. Presence of Mn^{2+} is supposed be driving force for high degradation. From the data obtained it can be conclude that benzoic acid has highest degradation rate followed by phthalic acid, 4-CBA, terephthalic acid and p-toluic acid.

Feasibility and applicability of anaerobic treatment process for removal of aromatic acid from PTA wastewater was investigated for [Kleerebezem et al. \[2005\]](#) by employing two stage anaerobic sludge blanket reactor. Acetate and benzoate are readily anaerobically biodegradable while as presence of terephthalic acid, 4-carboxybenzaldehyde and p-toluic acid slows down the rate of degradation. Main advantage of this process was the production of biogas methane gas which can be utilized as source of power, this will cause decrease in operating cost of the process. . In first stage one reactor was employed and degradation of acetate and benzoate took place, in this stage the removal efficiency corresponding to these acids was about 90% at a HRT of 7 hr. The first stage operation was completed in three time periods (a) 1st period (day 25-150) (b) 2nd period (day 150-330) (c) 3rd period (day 303-398). For 1st period initial degradation of

acetate and benzoate was quite fast but for last days of this period degradation becomes slow. For 1st time period no change in concentration of terephthalic acid in influent and effluent was observed. 2nd time period of 1st stage also did not show any sign of terephthalic acid degradation despite of lower loading rate of acetate and benzoate. In 3rd time period of 1st stage enough terephthalic acid was present in the reactor, and terephthalic acid achieved stable removal capacity. Three reactors operating parallel to each other were employed for second stage treatment. For the second stage the terephthalic acid removal of 1st and 2nd reactor was much higher than 3rd reactor. Moderate to high removal of terephthalic acid was witnessed in three reactors of second stage in presence of methanogenic granular biomass.

Chidambara raj et al. [1997] studied the rates of biodegradation of all aromatic acid present in PTA wastewater including 4-carboxybenzaldehyde by employing continuous stirred tank reactor (CSTR). The mixed bacterial culture was provided to biodegrade the pollutant and the culture was enriched by adding baker yeast and bacillus pasteurri prior to its use. The mixing of synthetic wastewater and original wastewater was performed. The removal of aromatic acids present in PTA wastewater by biodegradation process was determine by evaluating COD values of untreated effluent and treated effluent. Initial COD value of two sets of synthetic wastewater was 600 mg/l and 3400 mg/l. The colour of wastewater changes from colorless to brown during the operation as COD reduces by 30-40%, change in composition and formation of metabolic products were the main reason cited for color change. The response of COD reduction with respect to time was damped oscillating in nature, major oscillation was observed for 1st ten days and in the last phase settling occurred. In between major oscillation and settling period minor oscillation a period of 4 days also occurred. It was observed that during complete course of biodegradation process the concentration of microorganism experience decrease and increase. Pattern of oxidation with time was studied and it was found that the degradation pattern closely fallows Monod kinetics, kinetics constants were determined by Lineweaver-Berk plot and values of constant suggest that degradation of benzoic acid is fast in comparison to terephthalic acid and p-toluic acid is least degradable.

The presence of aromatic acid was studied in detailed by employing three CSTR in series and effluent from each CSTR was investigated for COD value with the help of liquid chromatography. The effluent from 3rd CSTR has a very low COD and it meets the specification of discharge effluent set by monitoring organizations. During the operation from reactor 1 to

reactor 2 it was observed that the major aromatics did not undergo any significant change while as the COD value and pH of the effluent changes. The results from reactor 3rd imply that the concentration of aromatic acid experience large change. The result indicates that simpler compounds are attacked by microorganism easily and aromatics acids were consumed by bacteria as last entity.

[Kleerbezem et al. \[1997\]](#) investigated the PTA wastewater coming from PTA plant and the HPLC experiments reveals that the terephthalic acid, acetate along with benzoate was the leading pollutant present in the wastewater. In earlier studies the same author explored the degradability of various aromatic acids and concludes that the availability of terephthalic acid has negative effect on aerobic biodegradability of PTA wastewater stream. Anaerobic treatment process facilitates higher loading treatment in comparison to activated sludge process where low volume of wastewater waste treated. Anaerobic produces less surplus sludge however the driving force for anaerobic process is energy production via formation of methane production instead of energy consumption. Seeding of reactor was done by methanogenic granular sludge which was produced from wheat starch processing industry. A fixed percentage of each nutrient was supplied to the microorganism. In continuous mode operation three reactors were operated and the removal of acetate from reactor 1 and 3 was reported as high as 95% within a week whole as reactor 2 took 3 weeks for 95% removal of acetate. Data analysis of effluent from reactors1 for preliminary stage suggest that terephthalic acid was neither biodegrade nor it was adsorbed for complete experiment (120 days). For anaerobic treatment of terephthalic acid effluent from reactor 2 was used and results shows that after operation of 160 days about 85% terephthalic acid was removed. Specific activity of all components present in the sludge was studied in batch operation. From this study it can be concluded that terephthalic acid can be easily degraded by providing methanogenic granular sludge at a maximum rate of 3.9 g COD/ (l. day). For optimum condition SRT of 24 hr was provided and sludge loading rate was maintained at 4.4 g COD/ (l. day).

3.1.5 Detection of presence of 4-CBA in solution by studying fluorescence properties

[Daniels et al. \[1999\]](#) investigated how to detect the presence of 4-carboxybenzaldehyde in the effluent. Detection of 4-CBA is done by fluorescence method and fluorescence intensity indicates the extent of impurities present in the effluent. Polar and acidic characteristic of solvent will control the fluorescence properties of 4-CBA. Fluorescence spectra were recorded by using

an instrument named as Perkin Elmer luminescence spectrometer. Fluorescence of 4-CBA varies with the type of solvent; a more acid solution will provide fluorescence with greater intensity. Secondary alcohol is more acidic than primary alcohol, methanol and ethanol and this is the main reason for more availability of longer wavelength species. The fluorescence emission from crude terephthalic acid solution corresponds to the emission from 4-CBA and toluic acid. Fluorescence peak at lower wavelength is for toluic acid while as peak of higher wavelength represent 4-CBA. Increased emission in presence of strong acid like sulphuric acid can be attributed to generation of protonated carbonyl group. Dilution in sulphuric acid strength and solution concentration will cause a blue shift of spectra and decrease in fluorescence intensity however it will not affect the wavelength of radiation. Presence of terephthalic acid causes difficulty in direct determination of fluorescence, to avoid difficulty in direct determination of fluorescence characteristic, a condensation was carried out between 4-CBA was condensed with o-phenylenediamine which produces a very high fluorescent product. This condensation products helps in determining the fluorescence spectra at low concentration of 4-CBA as <5 ppm. The product resulting from condensation have $-\text{CH}=\text{N}-$ linkage which helps in achieving conjugation between two aromatic rings. Conjugation of aromatic rings helps in emission from $\pi-\pi^*$ state. The hydrogen bonding between $-\text{CH}=\text{N}-$ linkage and amine group imparts rigidity to fluorescence compounds.

Table 3.1: Literature review for treatment of 4-CBA containing PTA waste water by adsorption

Process: Adsorption											
Adsorbent	Petrochemical compound	Adsorption Isotherm	COD removal/Compound Adsorption (%)	Optimum condition/key parameter			Reference				
Modified mesoporous carbon	p-toluic acid benzoic acid 4carboxybenzaldehyde phthalic acid Terephthalic acid	Langmuir	p-toluic acid(53.18) benzoic acid(66.77) 4carboxybenzaldehyde(70.47) phthalic acid(74) Terephthalic acid(76.1)	Adsorbent dose:	Increase in adsorbent dose increases adsorption % but decreases adsorption capacity		Anbia and Salehi, 2011				
				pH:	3-5						
				Temperature	20 °C						
				Agitation Speed	150 rpm						
				Equilibrium time:	5 min						
Expanded bed GAC : adsorption takes place on GAC and further biodegradation of microorganism growing on GAC takes place	Terephthalate	Freundlich	90% Terephthalic acid removal	Treated waste water Terephthalic acid loading (kg/m ³ d)		Treated waste water COD loading (m ³ d)		Reactor Operating condition	Tsuno and Kawamura, 2008		
				Run1	Run2	Run1	Run1			T(°C)	days
				0.57	1	2.9	4.0			30	140

Polymeric adsorbent; AmberliteXAD-2 Amberlite XAD-4 Amberlite XAD-7 INDION 1014 MN-2	p-Toluic acid Benzoic acid Phthalic acid i-Phthalic acid t-Phthalic acid Trimelletic acid	Langmuir for INDION 1014 MN-2 andFreundlich for rest of the adsorbent	Capacity at break point for INDION 1014 MN-2 adsorbent			Khachane et al., 2007
			Solute	Capacity of adsorption moles/g resin of)*10 ⁴		
				Single solute	Double solute	
			p-toluic acid	4.04	0.38	
			Benzoic acid	1.63	-	
			Trimelletic acid	4.34	1.33	
Phthalic acid	1.23	0.008				

Table 3.2: Literature review for treatment of terephthalic acid waste water by coagulation

Process: Coagulation and flocculation										
Coagulant	Petrochemical compound		(%) Terephthalic acid removal/COD	Key parameter /parameter affecting removal/optimum condition for removal						
Ferric chloride	Terephthalic acid		90% Maximum removal 94.3%	pH	Coagulant dose	TPA concentration		Wen et al. 2006		
				Maximum removal at pH 11	Removal increases up to a maximum dose after that removal becomes constant	As TPA conc. Increases more coagulant needed for same % removal				
Coagulant: Ferric Chloride, Ferrous sulphate, Alum, polyaluminium chloride.	Terephthalic acid		75.5%	Ferric chloride		Ferrous sulphate		Alum	Verma et al.,2010	
				dose	pH	dose	pH	dose		pH
				3000	5.6	2000	8	3500		8

Table 3.3: Literature review for treatment 4-CBA containing PTA waste water [Pophali et al., 2007]

Process: Anaerobic- Aerobic Treatment	Reactor: Activated sludge process and upflow anaerobic fixed film fixed bed reactor (AFFFBR)	Influent Waste water properties				Operating condition of reactor			Removal At VLR 4-5 kg COD/m ³ d	
		BOD (mg/l)	COD (mg/l)	SS (mg/l)	TDS (mg/l)	Temp (T°C)	pH	alkalinity (mg/l)	COD removal (%)	BOD Removal (%)
		70-160	240-488	220- 470	3000- 4000	35-37	6.5-6.8	1800	63	62

Table 3.4: Literature review for treatment of 4-CBA containing PTA wastewater by oxidation process [Thiruvengkatachari et al., 2006]

28

Process: Advanced oxidation	Oxidant: UV-TiO ₂ , UV-H ₂ O ₂ , UV-H ₂ O ₂ -Fe O ₃ (Ozone oxidation) O ₃ -TiO ₂ /Fe (catalytic ozonation)	Complete destruction of TPA by various oxidant					
		UV-TiO ₂		O ₃ -TiO ₂ /Fe		UV-H ₂ O ₂ -Fe	
		Value of pH =8		Fe ₂ (SO ₄) ₃ conc=55mg/l		Fe ₂ (SO ₄) ₃ conc=90mg/l	
		TPA conc(mg/l)	Time(h)	TPA conc(mg/l)	Time(m)	TPA conc. (mg/l)	Time(m)
		10	4	50	10	50	45
30	7						
50	10						

Table 3.5: Literature review for 4-CBA containing PTA wastewater acid waste water [Kleerebezem, 2005]

Process: Anaerobic- Aerobic Treatment	Reactor: Activated sludge process and upflow anaerobic fixed film fixed bed reactor (AFFFBR)	Influent Waste water properties				Operating condition of reactor			Removal At VLR 4-5 kg COD/m ³ d	
		BOD (mg/l)	COD (mg/l)	SS (mg/l)	TDS (mg/l)	Temp (T°C)	pH	alkalinity (mg/l)	COD removal (%)	BOD Removal (%)
		70-160	240-488	220- 470	3000- 4000	35-37	6.5-6.8	1800	63	62

Chapter- 4

EXPERIMENTAL PROGRAMME

4.1 GENERATION OF EXPERIMENTAL DATA FROM CCD

A five level ($-\alpha, -1, 0, +1, +\alpha$) four parameter CCD was employed in this study to find the applicability of adsorption process as well as process parameters affecting the removal of 4-Carboxybenzaldehyde and adsorption capacity. The levels +1 and -1 are higher and lower level, respectively, 0 is center point while as $+\alpha$ and $-\alpha$ represent star points (α). Percentage 4-carboxybenzaldehyde removal and equilibrium adsorption uptake has been taken as a response of system. pH (pH: 2-10), adsorbent dose (w: 1-9 g/l), initial concentration (C_0 : 20-100 mg/l) and contact time (t: 0.5-7.5 h) are variable input parameters, while operating temperature at 30°C was kept as a constant input parameter. The variables and levels of the central composite design are given in Table 4.1. Total number of experiments to be conducted for optimization of parameters were determine by using the formula

$$N=2^n + 2 \times n + N_c \quad (8)$$

Where n are the numbers of parameters to be optimized and N_c are no of central points.

For four parameters total numbers of experimental runs (30) will consist of three parts

- (a) $2^4 = 16$ experimental runs corresponding to factorial points
- (b) $2 \times 4 = 8$ experimental runs corresponding to axial points, fixed according to rotatability condition at a distance α
- (c) $N_c = 6$ experimental runs replicating the center points used to determine the experimental error and the reproducibility of the data.

Table 4.1: Chosen process parameters and their levels for 4-CBA removal

Variable	unit	Factors	Level				
			$-\alpha$	-1	0	1	α
			-2	-1	0	1	2
pH		X_1	2	4	6	8	10
Adsorbent Dose	g/l	X_2	1	3	5	7	9
Concentration	mg/l	X_3	20	40	60	80	100
Time	min	X_4	30	135	240	345	450

4.2 ADSORBENTS AND ADSORBATE

Low cost adsorbent BFA was obtained from Uttam Sugar Mills, Roorkee, U.K. (India) and it was sieved by using standard sieves (IS 437-1979) in order to remove fine particle. No further treatment was done and mass fraction between -1mm and +450 μm was used as an adsorbent for the removal of 4-CBA from aqueous solution. Laboratory grade GAC was supplied by GSE Chemical Testing Laboratory and Allied industry, New Delhi and it was used and adsorbent as procured. In order to access important property of adsorbents physico-chemical characterization was carried out using standard procedure.

4-Carboxybenzaldehyde a petrochemical compound was used as an adsorbate and it was supplied by HiMedia Laboratories Pvt. Ltd. Mumbai, India with minimum assay of 96%. 4-carboxybenzaldehyde is also known as P-carboxybenzaldehyde, 4-formylbenzoic acid, terephthalaldehydic acid. Due to low solubility at normal temperature, to prepare stock solution (200 mg/L) 4-CBA was dissolved in distilled water and was heated at appropriate temperature.

4.3 ANALYTICAL MEASUREMENT

The concentration of 4-CBA in the aqueous solution was determined by using UV-Spectrophotometer (Perkin Elmer Lambda 35, Shimadzu, Japan). A standard solution of 4-CBA was scanned and it was found that maximum absorbance occur at a wavelength of 257 nm. At this fixed wavelength absorbance corresponding to different concentration of 4-CBA solution was measured and a calibration curve was prepared between absorbance and 4-CBA concentration. The calibration curve between absorbance vs concentration was found to be linear for the 4-CBA concentration range of 1 to 20 mg/L with correlation coefficient (r) =0.998. Then calibration curves were plotted (Fig.3.1) between absorbance and concentration of standard 4-CBA solution for further use. During the experiment the sample was appropriately diluted to have 4-CBA absorbance in calibration range.

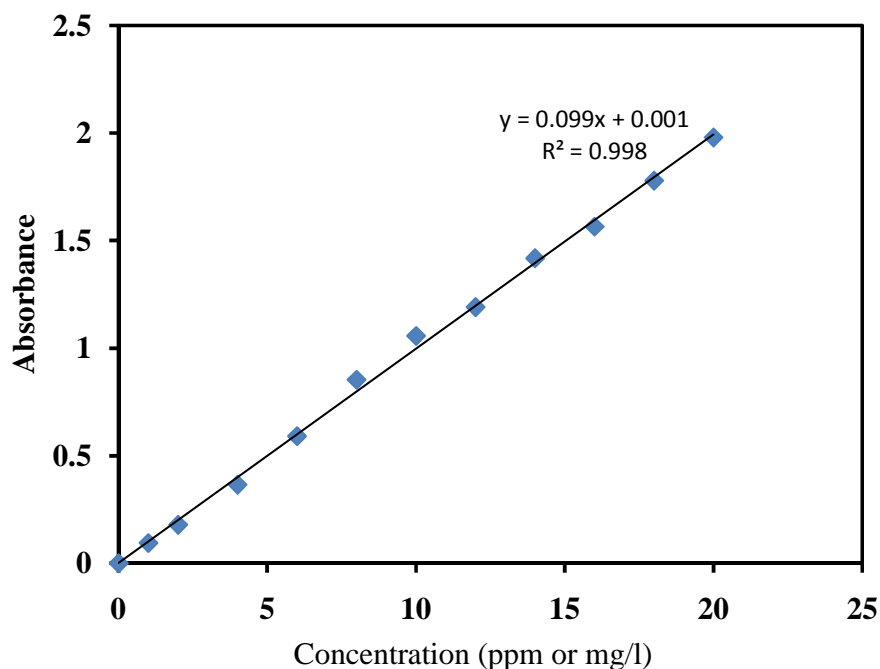


Fig. 4.1 Calibration curve of 4-CBA

4.4 BATCH EXPERIMENTAL PROGRAMME

Effect of pH, adsorbent dose, concentration and time on adsorptive removal of 4-CBA was studied by conducting batch experiments. Each experimental runs were performed according to Table 5.2 by taking 100 ml solution in 250 ml stoppered conical flask and agitating solution containing flasks into the incubator-shaker (Remi Instruments, Mumbai) at agitation speed of 150 rpm. Temperature of incubator shaker was maintained at 30 °C. In order to nullify the effect of adsorbent leaching into solution, blank experimental runs were carried out simultaneously at similar condition by adding 0.5 g of adsorbent in 100 ml distilled water. To check the stability of adsorbate, 100 ml of adsorbate solution was agitated without adding any adsorbent at similar condition and no difference in concentration was found before and after agitation which confirms adsorbate stability. pH of solution was adjusted by adding 1N HCl or 1N NaOH solution accordingly. After withdrawing samples from shaker it was found that some BFA particles were in suspended form so for complete settling all samples were centrifuged using Research centrifuged (Remi Scientific Works, Mumbai) at 5000 rpm for 5 min. The centrifuged samples were withdrawn, filtered and diluted if necessary and concentration was measured. . Kinetic study was performed by evaluating adsorption equilibrium uptake of 4-CBA at different time

interval from aqueous solution for a fixed initial adsorbate concentration. Study of adsorption isotherm was done by agitating initial aqueous solutions of different 4-CBA concentration with fixed amount of adsorbent till the equilibrium was reached. Calculation for % 4-CBA removal and adsorption equilibrium uptake was done as following

$$\text{Percentage 4-CBA removal at any time 't'} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (9)$$

And equilibrium adsorption uptake

$$q_t (\text{mg/g}) = \left(\frac{C_0 - C_t}{m} \right) \times V \quad (10)$$

Where, C_0 is initial 4-CBA concentration (mg/l), C_t is 4-CBA concentration at time t , m is mass of adsorbent g, q_t is adsorption uptake (mg/g) and V is volume of solution.

4.5 ADSORBENTS CHARACTERIZATION

4.5.1 Bulk density and proximate analysis of adsorbents

Bulk density determination of BFA and GAC was accomplished using bulk density meter supplied by Macro Scientific Works, Delhi. Percentage of fixed carbon, ash, volatile matter and moisture content of BFA and GAC was determined according to Bureau of Indian Standards (BIS) (IS 1984, 1985).

4.5.2 Surface area and pore size distribution of adsorbents

The textural properties of BFA and GAC were determined by employing automatic pulse chemisorption system (Micromeritics Chemisorb 2720) and applying N_2 adsorption isotherm at 77.15 K. During the experiment first degassing was done to avoid any error in the measurement of area. Surface area, micro-pore volume and micro-pore surface area of both adsorbent was determined by Emmett–Teller (BET) method [Brunauer et al., 1938]. Mesopore distribution for BFA and GAC was calculated by applying The Barrett–Joyner–Hanlenda (BJH) method [Barret et al., 1951].

Pore size distribution of BFA and GAC was carried out by BJH method. Classification of micropores, mesopore and macropores is done with accordance to international union of pure and applied science (IUPAC) [15]. Particles having pore diameter less than 20 Å are classified as micropores while as for 20 Å < d < 500 Å mesopores and for and for d > 500 Å, macropores.

4.5.3 X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis of adsorbent

In order to study structure of BFA, X-ray diffraction of these adsorbent was carried out using X-ray diffractometer (Bruker AXS, Diffractometer D8, Germany). To cover all the possible peaks the scanning angle (2θ) range was varied from 10° to 90° . Copper was used as a source to emit characteristic X-ray and only K- α ray were emitted from the shell to emit electron having sufficient energy. Nickel was used to filter the X-rays and allow only monochromatic X-rays to pass through it to fulfill necessary condition of diffraction. K radiation was maintained at 1.542 \AA whereas rotational speed of goniometer was fixed at $1^\circ/\text{min}$. When incident X-ray on sample satisfies the Bragg's equation ($n\lambda=2d\times\sin\theta$) constructive interference takes place and at this condition Intensity peaks occurs. Identification of compound was done by using international centre for diffraction data (ICDD) library.

4.5.4 FTIR analysis of adsorbents

Functional groups present in BFA before and after adsorption of 4-CBA were determined by using Fourier transform infrared spectroscopy (Thermo Nicolet, Magna 7600). The samples were prepared by pellet (pressed disk) method by mixing same amount of KBr in each sample. The selected spectral range was from $4000\text{-}400 \text{ cm}^{-1}$.

4.5.5 TGA/DTG/DTA study of adsorbents

In order to study the effect of temperature on the rate of mass change thermal analysis of GAC was carried out using Perkin Elmer (Pyris Diamond) thermogravimetric analyzer. Thermal degradation was studied in the temperature range of $25\text{-}1000^\circ\text{C}$ Heating rate was maintained at $10^\circ\text{C}/\text{min}$. The flow rate of air (moisture air) was maintained at $200 \text{ ml}/\text{min}$. the main application of these curve is to deduce drying and thermal degradation characteristic.

4.5.6 Point of zero charge determination of adsorbents

In order to determine point of zero of the GAC, solid addition method was applied [Balistrieri et al., 1981]. 45 ml KNO_3 solution of known strength was taken into a series of 100 ml conical flasks. The pH of solutions was maintained in the range of $3\text{-}11$, adjustment of pH was done by using either 0.1N HNO_3 or NaOH . Final volumes of solutions were made 50 ml by adding KNO_3 if required. Measurement of pH_0 of the solutions was done up to 1 point of decimal. After adding One gram of GAC into each flask, the flasks were securely capped. The resulting solutions were

shaken manually to provide good contact and sufficient time (48 hr) was provided to equilibrate with intermittent manual shaking. The solution was filtered and the final pH (pH_f) values of the supernatant liquid were noted. A curve was plotted taking the pH₀ as abscissa and the difference between the initial and final pH (pH_f) values ($\Delta\text{pH}=\text{pH}_0-\text{pH}_f$) as ordinate. The point of zero charge was found by locating the point of intersection of the curve pH₀ vs ΔpH . To make sure that result obtain are correct this experiment was performed at different concentration of KNO₃.

Chapter- 5

RESULT AND DISCUSSION

5.1 ADSORBENTS CHARACTERIZATION

5.1.1 Bulk density and proximate analysis of adsorbents

Bulk density of BFA and GAC was found to be 119.5 and 613 kg/m³, respectively. Result of proximate analysis is provided in Table 5.1, the result shows that BFA has higher fixed carbon than GAC.

5.1.2 Surface area and pore size distribution of adsorbents

The BJH adsorption shows that BFA have 27.3% and 35% micro-pore area, 72.7% and mesopores area there was absence of macropores area. According to desorption pore distribution the mesopores account for 67% and 63% of total pore area for BFA and GAC, respectively. Thus BFA was found to have larger mesopore area than GAC and both the adsorbents have larger contribution of mesopores and smaller contribution of micropores. From Fig. 5.2 it is clearly evident that pore size distribution of GAC is lower while as the BFA has much more wide average pore size distribution. Due to wide average pore size distribution BFA has wide distribution of surface area.

5.1.3 X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis of adsorbent

The x-ray of BFA is shown in Fig. 5.1. The big humps corresponds the presence of silica, absence of sharp peak confirms the amorphous nature of BFA.

Morphology study of BFA was done by scanning electron microscope (SEM) (QUANTA, Model 200 FEG, Netherland) and SEM micrographs of BFA and GAC for before and after adsorption are shown in Fig. 5.3 and Fig. 5.4 at different magnifications. In order to make samples conductive, sample were gold sputtered using a sputter coater, (Edwards S150), an energy dispersive X-ray (EDX) spectrometer was used for the elementary analysis of samples. From the Fig. 5.3 the porosity and surface texture of BFA can be analyzed. Lower magnifications (50×) do not show textural differences of blank and 4-CBA loaded BFA surfaces. The pores of various size and difference in surface texture in BFA can be envisaged at higher magnifications (500×). From the Fig. 5.3 it can be inferred that at higher magnifications some surface of BFA gets

covered due to adsorption and also the pores get filled after adsorption of 4-CBA. Elemental analysis of BFA was done by Energy dispersive X-ray spectroscopy (EDX) and it was found that blank BFA contains 74.37% carbon, 18.91% oxygen, 3.22% silicon and 1.74% potassium. After adsorption elemental percentage of carbon was increased by 5%.

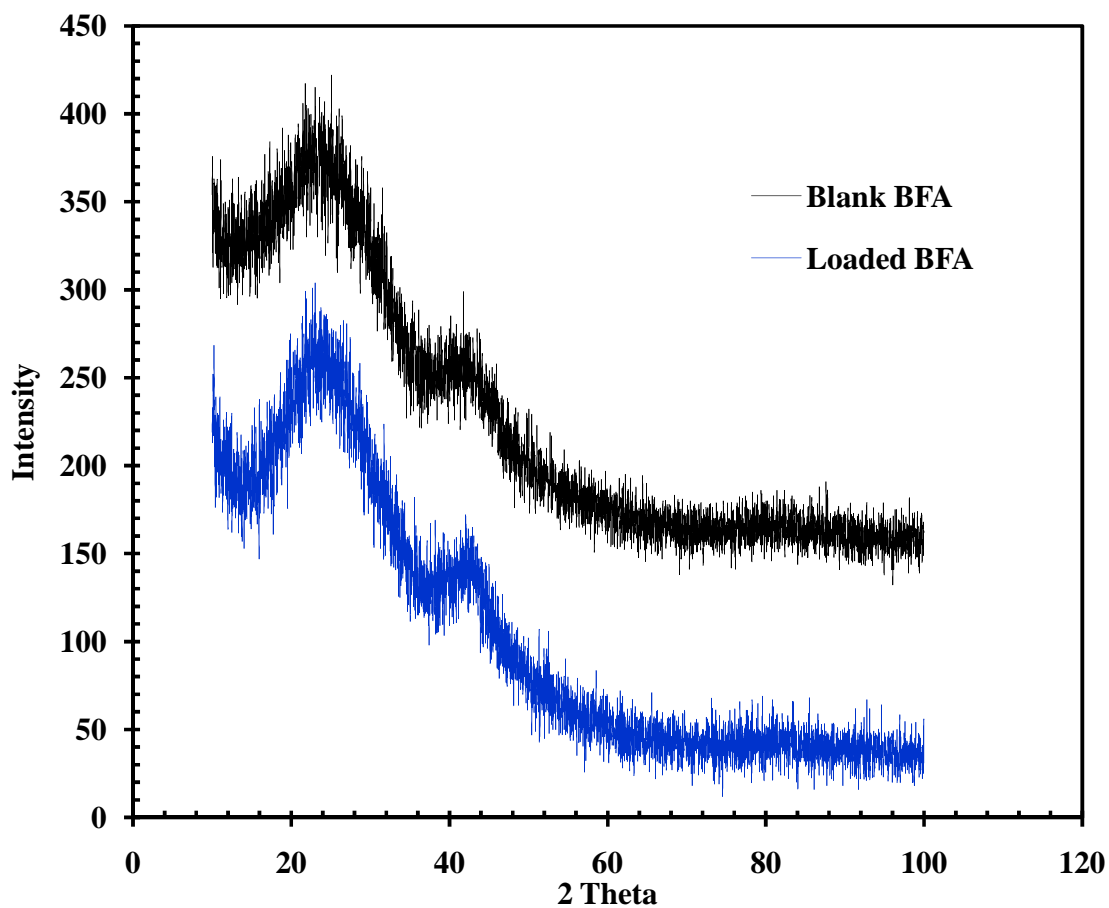


Fig. 5.1. X-ray diffraction pattern of BFA for before and after adsorption

Table 5.1: Physicochemical characterization of BFA and GAC

Characteristics	BFA	GAC
Proximate analysis		
Moisture (%)	6	10
Volatile matter (%)	7	9
Ash content (%)	21.3	30.2
Fixed carbon (%)	65.7	50.8
Bulk density (kg/m ³)	119.5	613
Surface area (m ² /g)		
(1) BET	284	591
(2) BJH		
(a) Adsorption cumulative	49.64	86.12
(b) Desorption cumulative	35.30	74.75
Pore volume(cm ³ /g)		
Single point total pore volume (d < 209.92 Å)	0.158	0.3124
BJH adsorption (between 17 Å and 3000 Å)	0.039	0.052
BJH desorption (between 17 Å and 3000 Å)	0.022	0.045
Average diameter (Å)		
BET	22.34	21.15
BJH adsorption	31.15	24.02

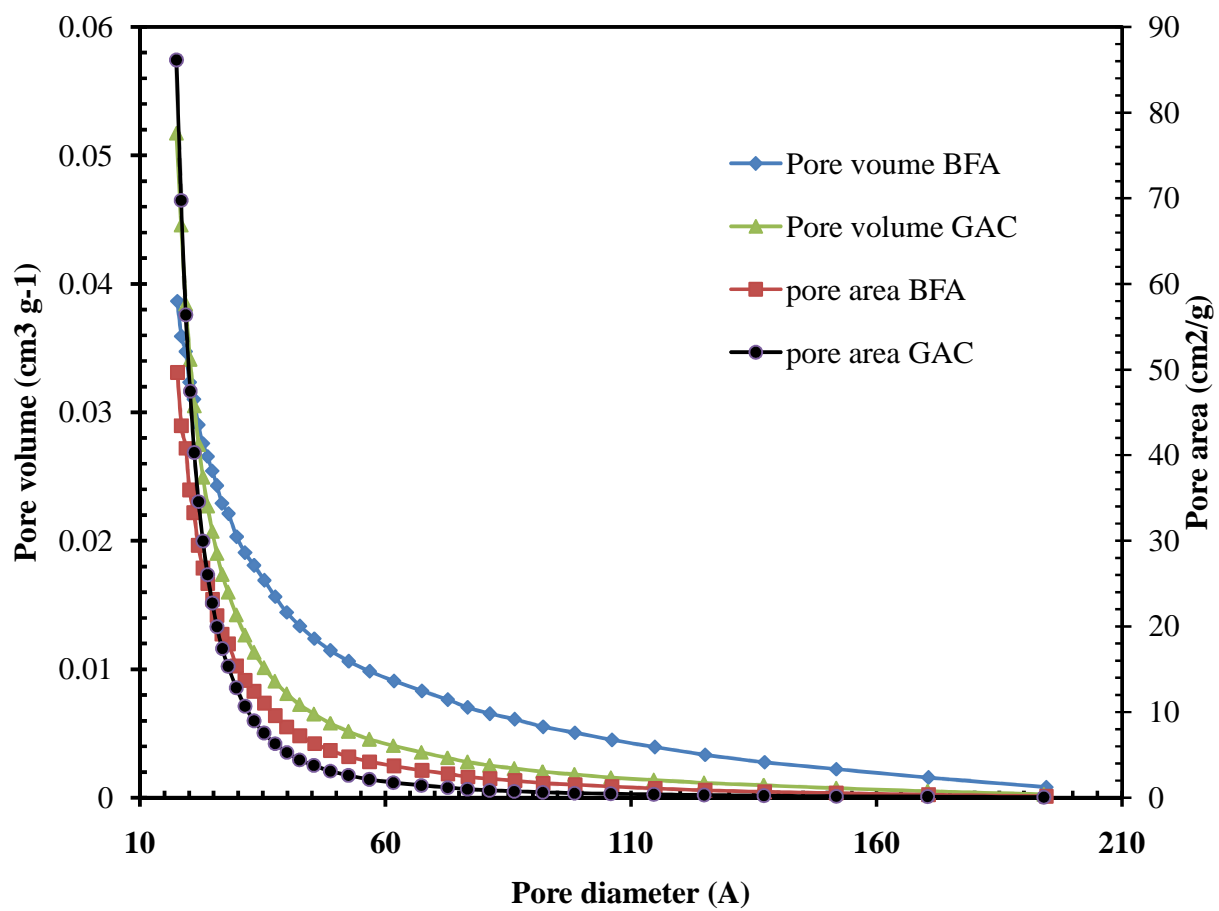
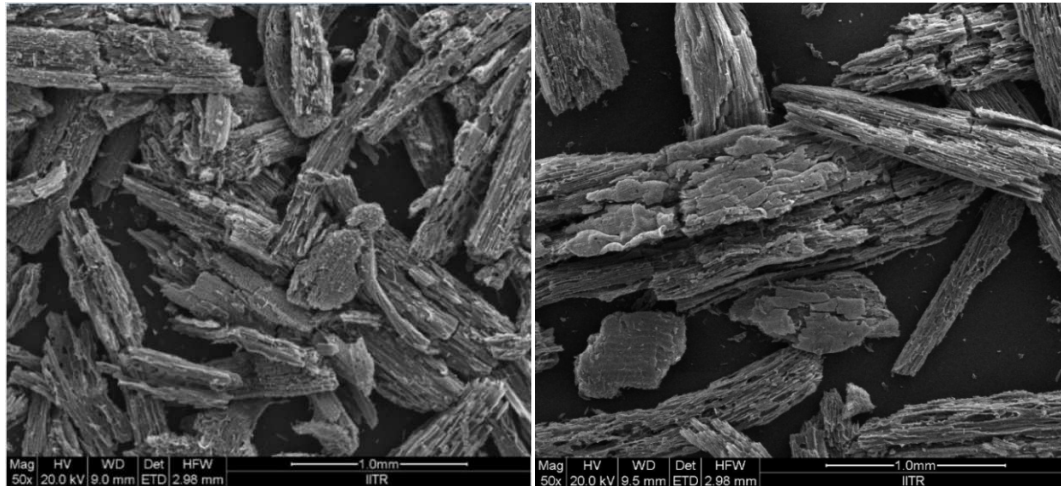
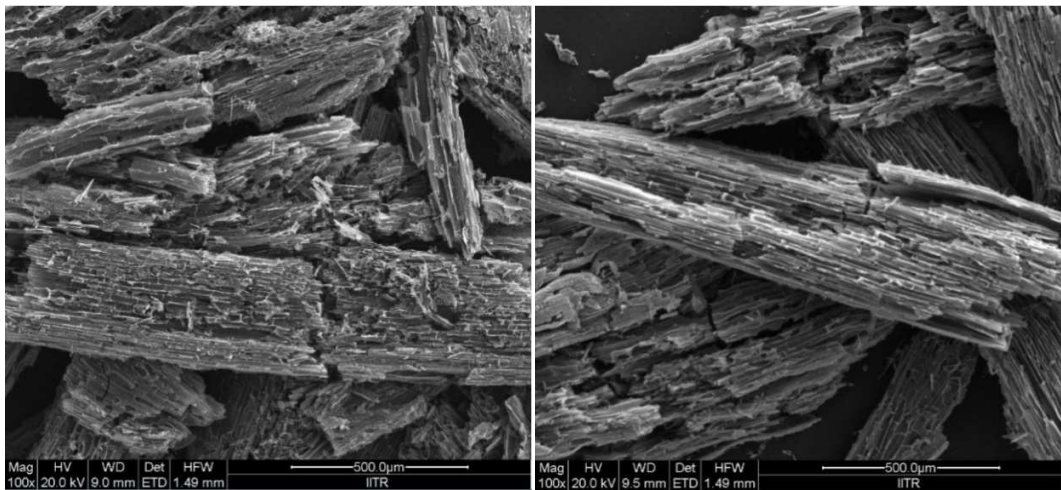


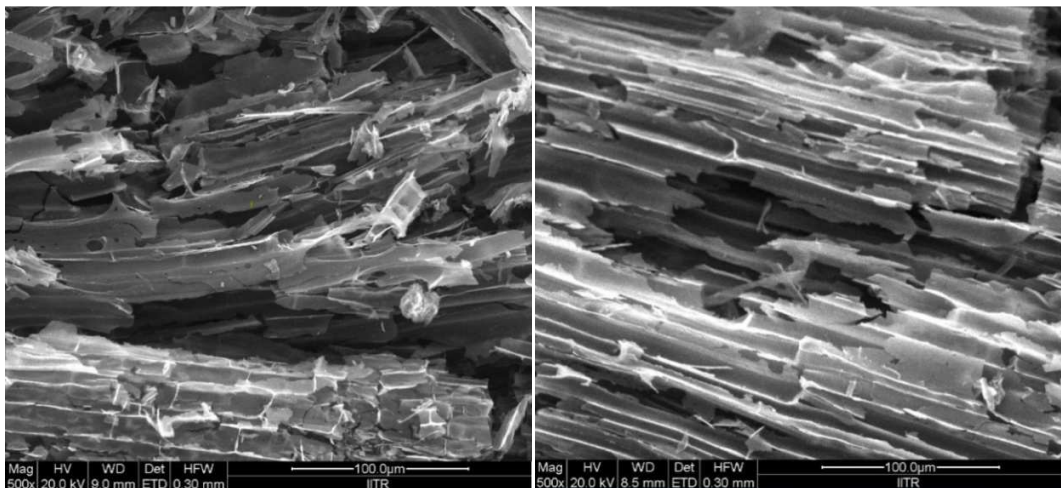
Fig 5.2. Pore size distribution of GAC and BFA



50 magnifications



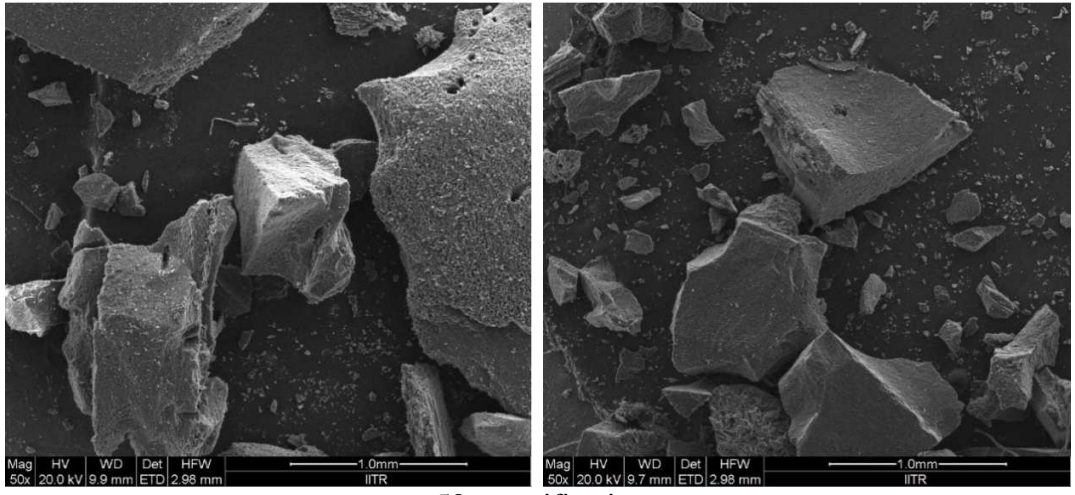
100 magnifications



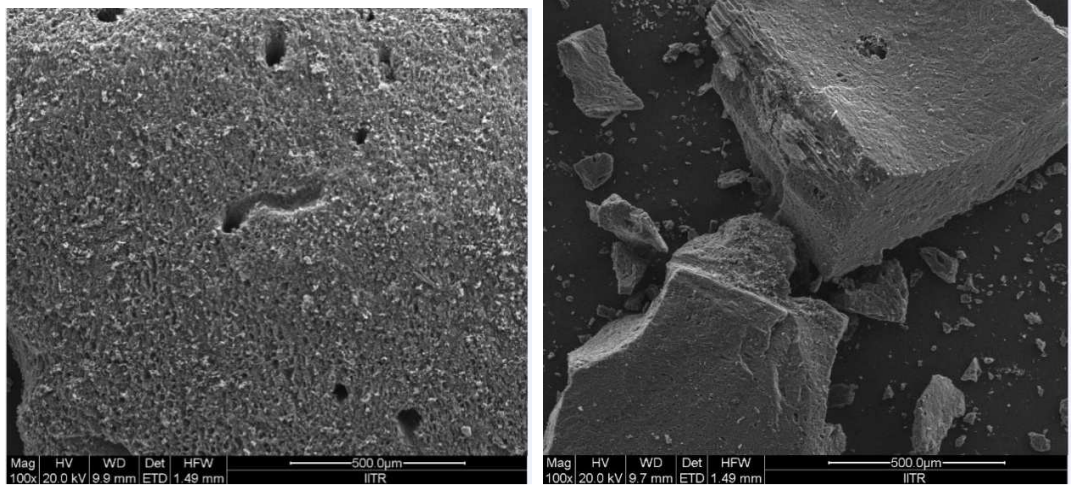
(a)

(b)

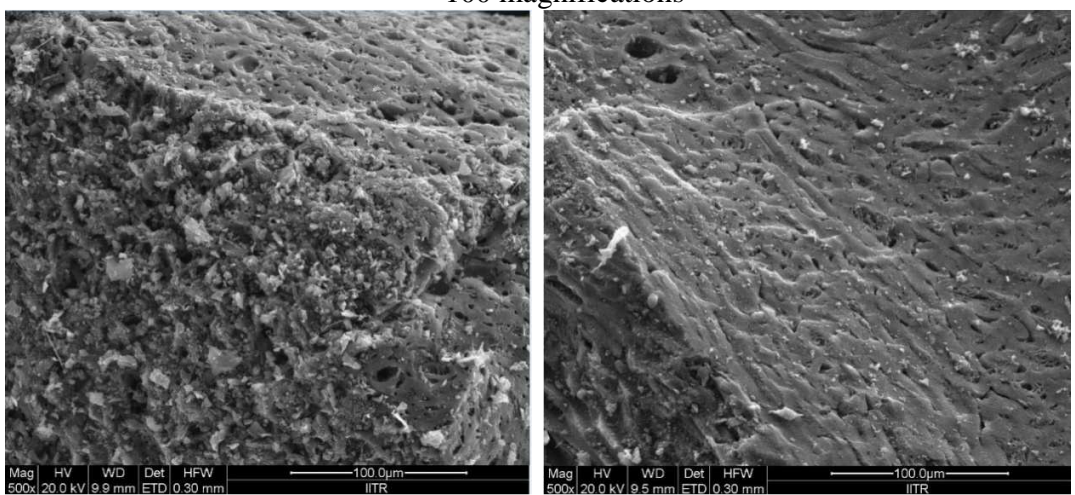
Fig. 5.3. Scanning electron micrograph of: (a) Virgin BFA (b) 4-CBA loaded BFA



50 magnifications



100 magnifications



1000 magnifications

(a) (b)

Fig. 5.4. Scanning electron micrograph of: (a) Virgin GAC (b) 4-CBA loaded GAC

5.1.4 Point of zero charge determination of adsorbents

Determination of point of zero charge (pH_{PZC}) of the adsorbent was carried out to understand the basic mechanism of adsorption. Adsorption of anions is favored at $\text{pH} < \text{pH}_{\text{PZC}}$, while the adsorption of cations is favored at $\text{pH} > \text{pH}_{\text{PZC}}$. As the pH decreases below the pH_{PZC} adsorption capability of adsorbent decreases for cations while as with increase in pH above pH_{PZC} the adsorption activity increases for anions. From Fig. 5.5 it is evident that for KNO_3 concentration of 0.01M and 0.001M, the zero value of pH lies at the initial pH value of 8.0, which is considered as the pH corresponding to point of zero charge of the adsorbent.

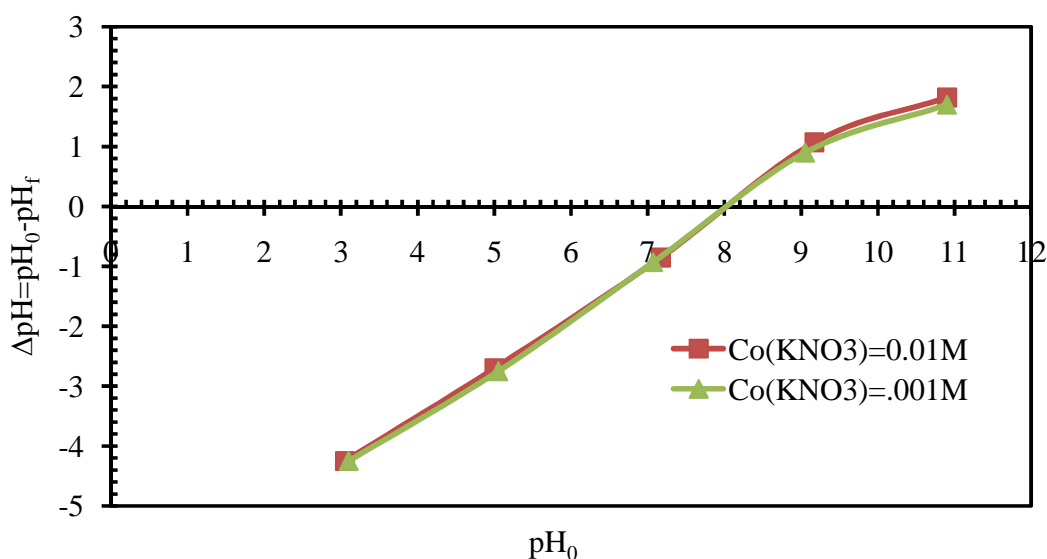
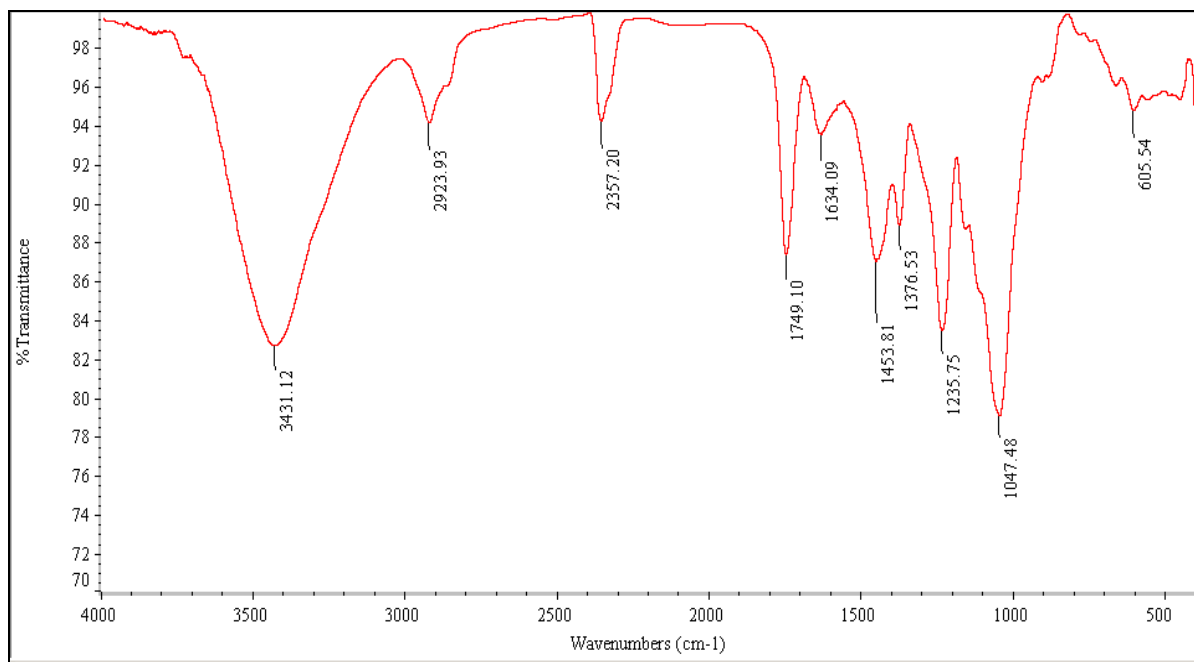


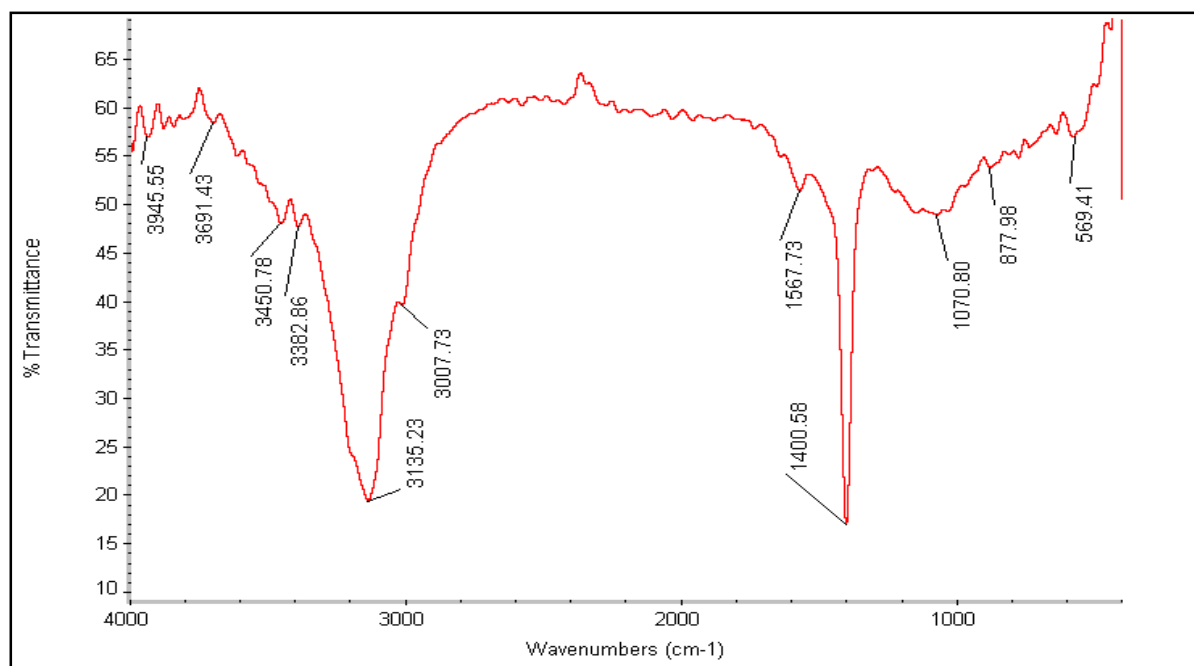
Fig 5.5. Point of zero charge of GAC

5.1.5 FTIR of adsorbents

The selected spectral selected for FTIR spectra was from $4000\text{-}400\text{ cm}^{-1}$ and the spectra are shown in Fig.5.6. From the figure a broadband can be seen in range of $3300\text{-}3600\text{ cm}^{-1}$, this broad band corresponds to the presence of both free and OH bonded functional group in BFA and GCA and stretching occurs due to presence of silanol (Si-OH) groups and adsorbed water [Abou-Mesalam, 2003]. A peak around 2924 and 2800 is attributed to stretching of OH groups bond to methyl radicals. The broad peak observed from FTIR spectrum in the region of $1748\text{-}1500\text{ cm}^{-1}$ indicates the presence of CO group stretching from aldehydes to ketones. The peak observed around 1450 cm^{-1} corresponds to $-\text{CH}_2$ and $-\text{CH}_3$ groups while as peak at 1376 cm^{-1} is attributed to the presence of $-\text{CH}_3$ groups. The transmittance for the region of $1234\text{-}1050\text{ cm}^{-1}$ indicates the vibration of CO groups in lactones [Ricordel et al., 2001]. The peaks at about 606 and 465 cm^{-1} could be identified as presence of Si-H.



(a)



(b)

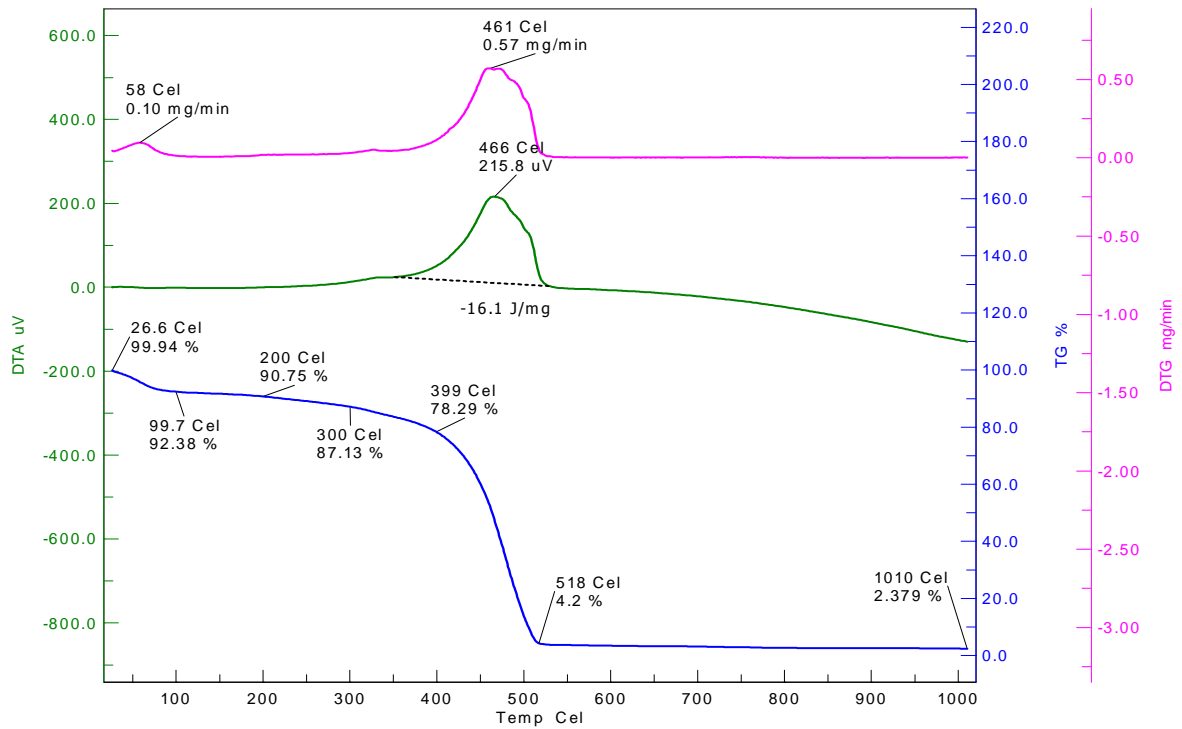
Fig. 5.6. FTIR spectroscopy of (a) BFA (b) GAC

5.1.6 Thermal analysis of GAC

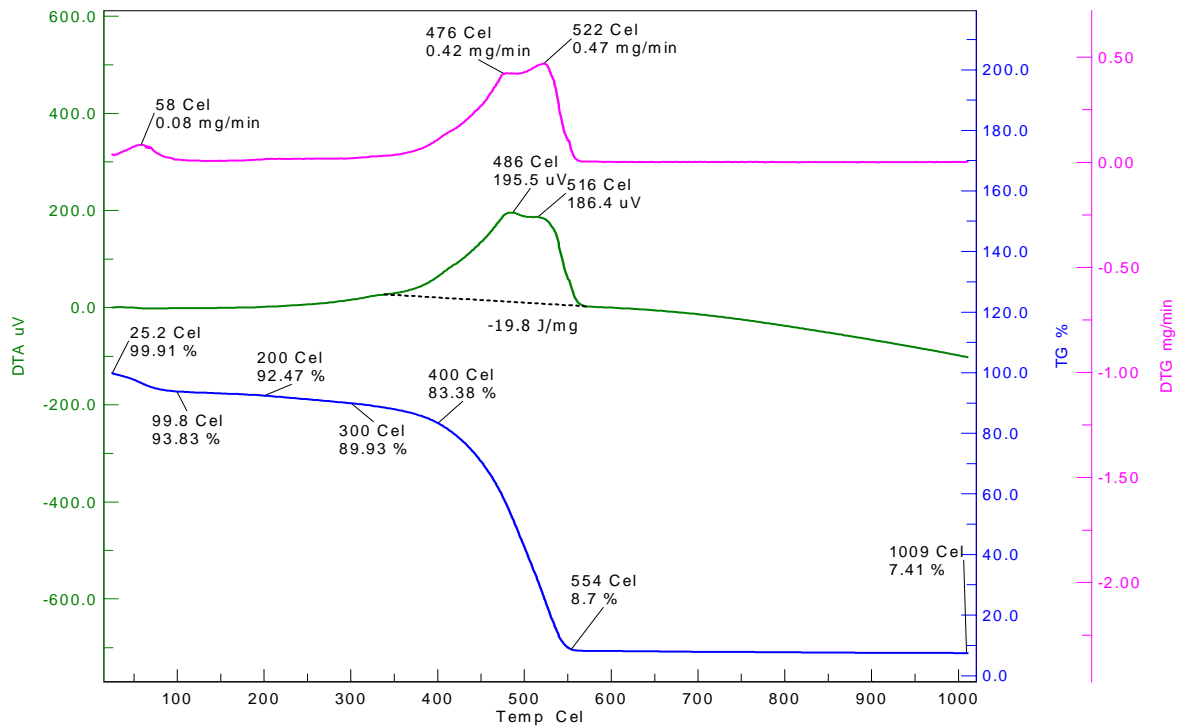
The thermo gravimetric analysis (TGA) for weight change, differential thermal analysis (DTA) for enthalpy change and differential thermal gravimetry (DTG) for rate of weight change, curves of blank GAC and surfactant loaded GAC for the heating rate of 10 °C/min are shown in Fig. 5.7. The Fig 5.7 indicates loss of moisture as well as removal of molecule having low weight was observed up to 400°C from the curve for TG analysis. The weight loss observed between 50 to 400 °C for Blank BFA and 4-CBA loaded BFA was 21.61% and 16.62%, respectively. When BFA is heated at higher temperature (> 100°C) then surface tension bound water evaporates and drying occurs. From initial heating temperature to 400°C no endothermic peak was observed from the Fig. 5.7 suggesting that no phase transition took place over this temperature range. For the increased temperature ranges of 400 °C to 547°C, oxidation of both the virgin and CBA-loaded BFA occurs and these materials lose their weight gradually, observed decreases in weight loss was 75.74% and 84.07% for Blank BFA and 4-CBA loaded BFA, respectively. In the temperature range 400–530°C a exothermic peak was observed and this peak suggest that oxidative degradation of sample takes place. The corresponding broad peak observed from DTG may be attributed to the combustion of carbon species. [Mall et al. \[2006\]](#) reported that higher temperature heating of carbonaceous produces CO, CO₂, free hydrogen and water vapor, these groups are obtained by virtue of surface group degradation. Gradual weight loss of samples has been observed for third zone (550-1000 °C) heating.

Following major difference in the thermal behavior of virgin and 4-CBA loaded BFA was observed from the TGA/DTA/DTG curve

- (a) For second degradation zone (400 °C to 547°C) weight loss of blank BFA was greater than 4-CBA adsorbed BFA.
- (b) Residue left after heating to 1000°C was higher for 4-CBA adsorbed BFA in comparison to the blank BFA



(a)



(b)

Fig 5.7. Thermal analysis of (a) Blank BFA (b) 4-CBA loaded BFA

5.2 CCD ANALYSIS

To evaluate the combine effect of pH, dose, concentration, time on removal and adsorption capacity, experiments have been conducted according to design matrix and results obtained are reported in Table 5.2.

System having many variables is mainly affected by some of the main effect and lower order interaction however higher order interaction can be neglected due to their small size in comparison to lower order interaction [Tripathi et al., 2009]. Regression equation was developed by fitting the experimental data to various models viz. linear, interactive, cubic, quadratic and cubic. To select the suitable model which will explain 4-CBA adsorption on BFA notable test applied are lack of fit, sequential model sum of square, model summary statistics [Kumar et al., 2008]. Sequential model sum of square and model summary statistics tests are sufficient to check the adequacy of the model and in this study only these methods are applied and result obtain are listed in Table 5.3 and Table 5.4. Cubic model was not selected because of being aliased.

From the table of sequential model sum of square comparing the values of probability factor 'p' for different model we get that the value of p is less than 0.01 for linear model in case of 4-CBA while p is less than 0.01 for quadratic model in case of adsorption capacity. In model summary statistics table the values the "adjusted R square" and "R square" were closer to unity for linear model incase of 4-CBA removal where as these values were near to unity for quadratic model in case of adsorption capacity. Taking consideration of p value, "adjusted R square" and "R square" values we can conclude that linear and quadratic model are best fit model for 4-CBA removal and adsorption capacity, respectively.

Table 5.2: Experimental and predicted values of % removal and q_e for 4-CBA adsorption onto BFA

Std	pH	Adsorbent dose(g/l)	Conc. (mg/l)	Time (min)	%Removal Actual	%Removal Predicted	q_e (mg/g) Actual	q_e (mg/g) Predicted
1	8	3	80	135	70.70	62.34	9.42	9.27
2	4	3	40	135	54.04	52.06	7.20	7.92
3	8	7	80	345	90.65	84.46	5.18	3.69
4	4	3	40	345	87.62	79.94	5.01	3.63
5	8	3	40	135	46.59	47.02	12.42	13.07
6	4	7	40	345	45.07	40.79	12.02	11.86
7	8	7	40	345	68.05	64.10	7.78	6.66
8	6	5	60	240	58.96	63.62	6.73	6.73
9	6	5	60	240	79.30	75.31	10.57	10.92
10	4	7	80	345	63.38	64.66	8.45	9.27
11	4	3	80	345	97.47	99.08	5.56	5.42
12	8	7	80	135	93.93	94.18	5.36	5.06
13	8	3	80	345	47.85	52.86	12.76	13.84
14	8	7	40	135	39.39	46.25	10.50	12.34
15	6	5	60	240	68.93	71.59	7.87	7.50
16	4	7	40	135	65.03	70.73	7.43	7.28
17	6	5	60	240	58.92	61.46	7.07	7.08
18	8	3	40	345	61.27	61.46	7.35	7.08
19	4	7	80	135	57.07	61.46	6.84	7.08
20	4	3	80	135	60.60	61.46	7.27	7.08
21	6	5	60	240	60.26	65.65	7.23	7.85
22	6	5	20	240	57.91	54.51	6.95	6.28
23	6	9	60	240	35.35	36.87	21.21	18.66
24	10	5	60	240	82.99	83.47	5.53	8.03
25	6	1	60	240	70.30	81.84	2.81	3.63
26	6	5	60	30	52.62	43.07	10.52	9.66
27	6	5	60	240	47.97	60.65	5.76	7.24
28	6	5	100	240	91.41	80.73	10.97	9.44
29	6	5	60	450	63.84	57.99	7.66	7.53
30	2	5	60	240	60.1	57.99	7.21	7.53

5.2.1 Fitting of second order polynomial equation and statistical analysis

Quadratic expressions obtained by fitting experimental result on basis of CCD experimental design and input variable for 4-CBA removal and for adsorption capacity interms of actual factor are given as

$$\begin{aligned} \% \text{ Removal} = & 59.72 - 2.78X_1 + 11.65X_2 - 9.69X_3 + 5.02X_4 + 0.52X_1^2 + 0.54X_2^2 + 1.12X_3^2 + 3.17X_4^2 \\ & + 1.44X_1X_2 + 1.01X_1X_3 - 1.26X_2X_3 - 1.78X_3X_4 \end{aligned} \quad (11)$$

$$\begin{aligned} q = & 7.31 - 0.39X_1 - 2.66X_2 + 1.51X_3 + 0.55X_4 - 0.12X_1^2 + 1.45X_2^2 - 0.22X_3^2 + 0.20X_4^2 + 0.32X_1X_2 \\ & + 0.035X_1X_3 - 0.074X_1X_4 - 0.21X_2X_3 + 0.019X_2X_4 - 0.22X_3X_4 \end{aligned} \quad (12)$$

The analysis of variance 'ANOVA' of data was carried out to check the significance of the model and results are listed in Table 5.5. Large fisher F-test value (9.24) and corresponding lower p value ($p < 0.0001$) suggest that the regression is statistically highly significant. Reliability and preciseness experiments conducted are checked by coefficient of variation (C.V.) value. Lower value C.V. = 12.05% indicates experiments conducted were precise and reliable. The correlation coefficient (R^2) and adjusted- R^2 values are used to check the fitness of model. Fairly moderate value of $R^2 = 0.8739$ and adjusted- $R^2 = 0.7794$ advocates the good correlation between observed and predicted value.

The significance of pH, adsorbent dose, concentration and time on adsorption process was determined by sum of square value, F- value and p value listed in Table 5.5. Model terms are significant for $p < 0.05$ while for $p > 0.1$ terms are considered as insignificant. From the regression equation (6) we can observe that adsorbent dose and time has positive coefficient which suggest that when these factors are changed from low to high removal of 4-CBA will increase while as negative coefficient of pH and concentration imply that with increase in the values of these factor 4-CBA removal will decrease. "Adeq Precision" is used to measure signal to noise ratio and the ratio greater than 4 is desirable. For our study the value is 11.608 and it suggest that the model can be used to navigate the design space.

Table 5.3: Adequacy of model tested for 4-CBA removal on BFA and adsorption capacity of adsorbent

Sequential model sum of square												
4-CBA removal							Adsorption capacity					
Source	Sum of squares	df	Mean Square	F value	Prob>F	Remark	Sum of squares	df	Mean Square	F value	Prob>F	Remark
Mean	125139.3	1	125139.25				2060.73	1	2060.73			
Linear	6302.082	4	1575.52	27.33	< 0.0001	Suggested	234.95	4	58.74	14.03	< 0.0001	
2FI	128.6188	6	21.43	0.307	0.9248		3.24	6	0.54	0.10	0.9954	
Quadratic	288.6327	4	72.15	1.045	0.4188		65.41	4	16.35	7.20	0.0023	Suggested
Cubic	878.0032	8	109.75	7.467	0.0123	Aliased	31.09	8	3.89	32.68	0.0002	Aliased
Residual	88.18353	6	14.69				0.71	6	0.12			
Total	132904.9	30	4430.16				2397.46	30	79.92			

Table 5.4: Different R^2 values for adsorption of 4-CBA on BFA and for adsorption capacity of adsorbent

Model summary statistics												
4-CBA removal							Adsorption capacity					
Source	Std deviation	Predicted R^2	Adjusted R^2	R^2	PRESS	Remark	Std deviation	Predicted R^2	Adjusted R^2	R^2	PRESS	Remark
Linear	7.59	0.6979	0.78	0.819	2321	Suggested	2.05	0.468	0.650	0.700	178	
2FI	8.34	0.5011	0.74	0.836	3834		2.32	0.315	0.549	0.710	230	
Quadratic	8.30	0.1185	0.748	0.874	6774		1.51	0.299	0.810	0.905	235	Suggested
Cubic	3.83	-3.1684	0.94	0.988	32036	Aliased	0.34	0.664	0.990	0.997	112	Aliased

Table 5.5: ANOVA of the second-order polynomial equation for % removal and adsorption capacity

Source	Coefficient Estimate	Sum of square	Df	Mean Square	F value	Prob>F	Remark	Coefficient Estimate	Sum of square	df	Mean Square	F value	Prob>F	Remark
	% 4-CBA removal							Adsorption Capacity						
Model		80.09	12	80.09	9.24	<0.0001	Si		303.61	14	21.69	9.55	<0.0001	Signi
Intercept	59.72		1	0.315				-0.39	1.32	1	1.32			
X ₁	-2.78	186.04	1	186	3.07	0.0998		-2.66	3.697	1	3.70	1.63	0.2228	
X ₂	-11.65	3257	1	3257	53.78	< 0.0001		1.51	169.49	1	169.50	74.62	< 0.0001	
X ₃	-9.69	2254	1	2254	37.22	< 0.0001		0.55	54.541	1	54.54	24.01	0.0002	
X ₄	5.02	605	1	605	9.99	0.0061		-0.12	7.216	1	7.22	3.18	0.0964	
X ₁ ²	0.52	7.49	1	7.49	0.12	0.7296		1.45	0.369	1	0.37	0.16	0.6929	
X ₂ ²	0.54	8.12	1	8.12	0.13	0.7191		-0.22	57.984	1	57.98	25.53	0.0002	
X ₃ ²	1.12	34.19	1	34.19	0.56	0.4634		0.20	1.355	1	1.36	0.60	0.4527	
X ₄ ²	3.17	276.32	1	276.3	4.56	0.0485		0.32	1.127	1	1.13	0.50	0.4927	
X ₁ X ₂	1.44	33.06	1	33.06	0.55	0.4707		0.04	1.651	1	1.65	0.73	0.4082	
X ₁ X ₃	1.01	16.36	1	16.36	0.27	0.6103		-0.07	0.020	1	0.02	0.01	0.9273	
X ₂ X ₃	-1.26	25.45	1	25.45	0.42	0.5260		0.02	0.706	1	0.71	0.31	0.5861	
X ₃ X ₄	-1.78	50.91	1	50.91	0.84	0.3728		-0.39	0.774	1	0.77	0.34	0.5686	
Residual		969	16	0.263					31.80	14	2.27			
Lack of Fit		951	12	0.361	18.05	0.0056	Signi		31.54	10	3.15	49.11	0.0010	Sign.
Pure Error		17.57	4	0.0182					0.257	4	0.06			
Cor Total		7766	29						336.73	29				Signi

5.3 EFFECT OF VARIOUS PARAMETERS ON 4-CBA REMOVAL EFFICIENCY

5.3.1 Effect of initial pH and adsorbent dose (m)

The initial pH of solution is an important parameter in adsorption process and it affects the surface charge of the adsorbent and as well as the degree of ionization speciation of different pollutants [Elliott and Huang, 1981]. Various functional group dissociate at different pH so the adsorption capability of adsorbent changes at different pH and this result in the shift in reaction kinetics and equilibrium characteristic of adsorption process. The cationic and anionic species adsorb on the surface of adsorbent depending on competitive adsorption of H^+ and OH^- ions with the adsorbates. It is general observation that anions favorably adsorb on adsorbent surface when $pH < pH_{pzc}$, whereas, the surface is active for the adsorption of cations at higher pH due to the availability of OH^- ions. Due to the presence of carboxylic and aldehydes groups in 4-CBA the aqueous solution of 4-CBA is acidic in nature hence pH values are less than pH_{pzc} (8.5, not shown here) i.e. the BFA surface in aqueous solution of 4-CBA is positively charged. So the type of interaction expected during adsorption of 4-CBA are electrostatic attraction and dispersion interactions. The dependence of 4-CBA removal on initial pH and adsorbent dose is shown in Fig. 5.8. From the Fig. 5.8 it is evident that the adsorption percentage increased with the decrease in initial pH and 4-CBA concentration. At lower pH (2-4) the surface of BFA is positively charged so in this pH range the electrostatic attraction between positively charged active groups of BFA and negatively charge molecules of 4-CBA will be maximum which will cause increased adsorption of 4-CBA. With further increase in the pH the adsorption on BFA decreases because with increase in pH the positive surface charge on BFA starts decreasing which lead to lesser electrostatic attraction between BFA and 4-CBA molecule. The natural pH value of 4-CBA solution without any pH adjustment by H_2SO_4 or NaOH was approximately 4 in this study. Therefore, $pH_0 = 4$ was selected as optimum pH for further experiments.

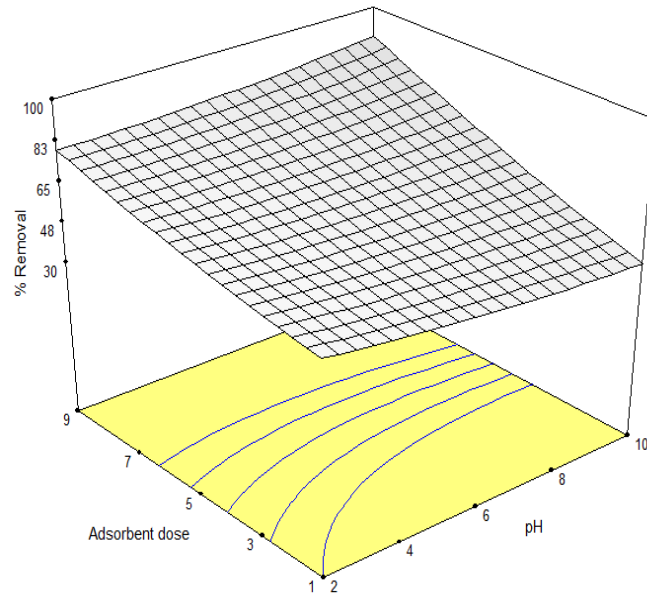
The cost of adsorption process is highly dependent on adsorbent so it is necessary to determine optimum adsorbent dose. The Fig. 5.8 clearly shows that at any fixed pH, with increase in adsorbent dose the 4-CBA removal increases initially but this increase in adsorbate removal becomes almost constant at a certain adsorbent dose. As adsorbent dose increases the total surface area available for adsorption as well as the availability of adsorption sites increases, these increase results in higher adsorption of 4-CBA. At adsorbent dose > 8.5 g/L, sufficient adsorption have occurred and at this condition the surface 4-CBA concentration and the solution 4-CBA

concentration come to equilibrium with each other so the incremental 4-CBA removal becomes very low, as. At about $m=9$ g/L, the removal efficiency becomes almost constant (84%).with further increase in adsorbent dose no significant enhancement in 4-CBA removal observed because the adsorbate has to travel more distance and due to equilibrium of adsorbate in both phase no driving force was available. Therefore, m value of 9 g/L for BFA was chosen as the m_{opt} value for further studies on adsorption of 4-CBA.

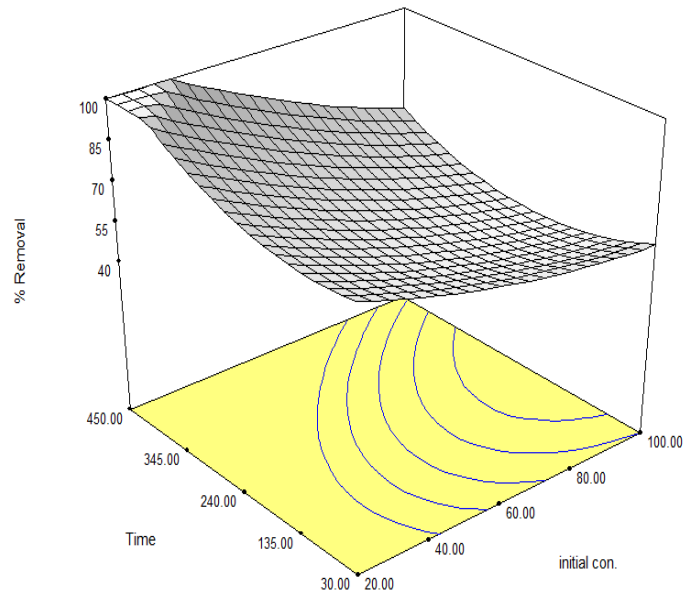
5.3.2 Effect of initial 4-CBA concentration and contact time

The effect of initial adsorbate concentration and contact time is shown in Fig. 5.8. From the figure it is clearly evident that at fixed time for 4-CBA adsorption, a significant decrease in % 4-CBA removal was observed as the 4-CBA concentration was increased from 20 to 90 ppm. At lower 4-CBA concentration, % removal is high because the number no adsorbate competing for the same no of adsorbent site are less in comparison to the higher 4-CBA concentration where large number of adsorbate are competing for same no of sites. So the residual concentration in case of higher initial concentration will be high that will lead to low removal at high concentration. With further increase in 4-CBA concentration from 90 to 100 ppm the adsorption of 4-CBA did not undergo any significant change.

The effect of contact time on 4-CBA removal by BFA under varying experimental condition of Table 5.2 is shown in Fig. 5.8. From the figure we can say that for a particular 4-CBA concentration, the % removal of adsorbate increases with increase in time. Due to longer contact time the adsorbate are able to diffuse longer distance and overcome to resistance until equilibrium is not achieved. Rate of adsorption is higher at initial stage of adsorption due to availability of larger vacant surface for adsorption. About 40% 4-CBA adsorption takes place with 30 minute. The initial high rate of removal indicates surface bound sorption and after some time low rate of removal can be attributed to long range diffusion of adsorbate on to the interior pores of the adsorbent [Chen and Wang, 2004]. After sufficient time the concentration of 4-CBA in aqueous phase and at adsorbent surface comes into equilibrium and after this time no adsorption can be observed.



(a)



(b)

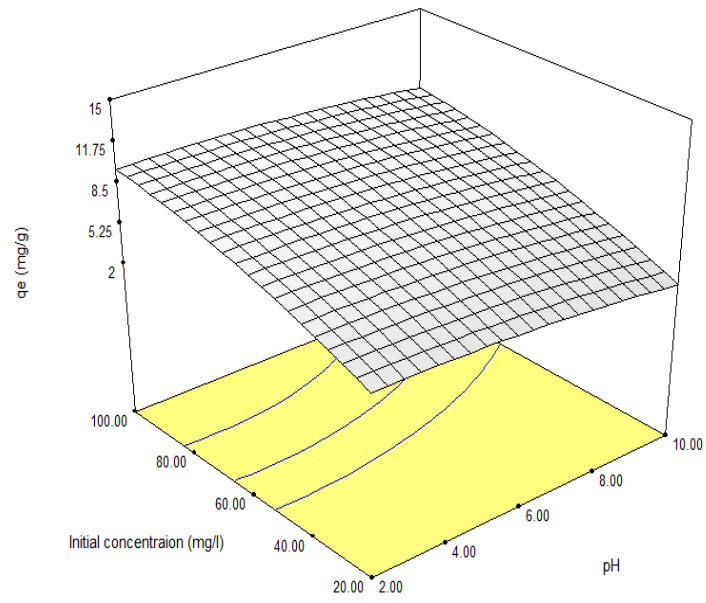
Fig. 5.8. Effect of (a) adsorbent dose and initial pH on % 4-CBA removal (b) initial 4-CBA concentration and contact time on % 4-CBA removal

5.3.3 Effect of pH, adsorbent dose, initial concentration and time on adsorption capacity

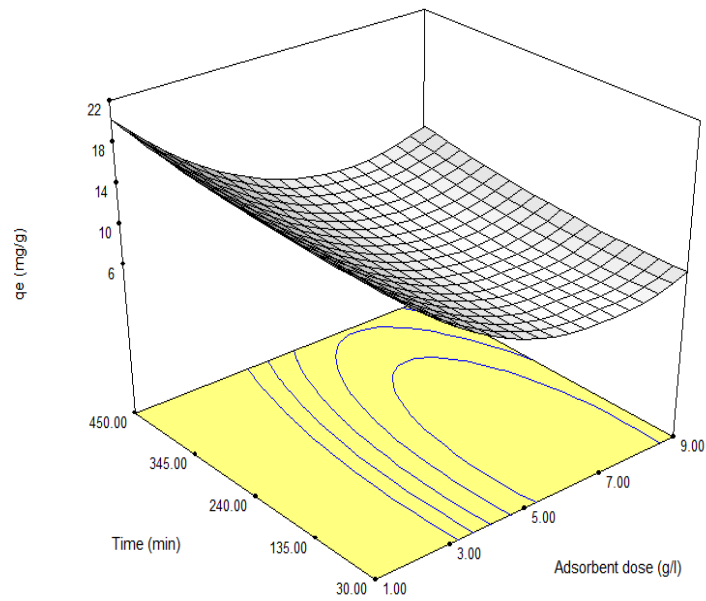
The effect pH, adsorbent dose, initial concentration and contact time is shown in Fig. 5.9. pH affect the adsorption capacity of adsorbent in the similar way as it effect the % removal of 4-CBA. The increase in the amount of 4-CBA adsorbed per unit mass of BFA with increase in initial concentration was observed from Fig. 5.9. Main driving force for adsorption capacity is the difference in concentration of 4-CBA between aqueous phase and solid phase, with increase in initial concentration the driving force increase it will be able to overcome the mass transfer resistance which will result in increase in adsorption capacity. Higher initial concentration also facilitates the higher interaction between 4-CBA and vacant BFA sites as well as functional groups.

As adsorbent dose increases the adsorption capacity of adsorbent decreases because with the availability of large no of adsorption sites the probability adsorbate to adsorb on a particular site decreases.

The effect of contact time on adsorption capacity can be explained from Fig. 5.9. To study the effect of contact time and to compare the equilibrium adsorption uptake of BFA to GAC separate experiment have been performed and the result is plotted in form of Fig. 5.10. The rate of adsorption was quite high at initial stage of adsorption (Within 3-4 hours) for both adsorbents due to availability of large no of vacant sites but with increase in time the rate of adsorption starts decreasing. The decrease in adsorption rate can be attributed to unavailability of outer surface for adsorption as well as the resistance caused by the adsorb molecule to the new molecules. From the Fig. 5.10 it can be seen after 7 hour no significant change in rate of adsorption occurs that's why $t = 7\text{h}$ was selected as equilibrium time. The initial rapid uptake indicates surface bound sorption and the slow second phase due to long range diffusion of adsorbate on to the interior pores of the adsorbent [[Chen and Wang, 2004](#)].



(a)



(b)

Fig. 5.9. Effect of (a) pH and initial concentration (b) adsorbent dose and time on adsorption capacity

5.4 KINETICS OF ADSORPTION FOR BFA AND GAC

The adsorption process of 4-CBA on BFA and GAC has been investigated by frequently used kinetic model viz. pseudo-first-order, pseudo-second-order and intra particle diffusion models.

5.4.1 Pseudo first order and Pseudo second order model.

Pseudo-first order-equation is represented in mathematical form as follow

$$\frac{dq_t}{dt} = k_f (q_e - q_t) \quad (13)$$

Where q_t is amount of adsorbate adsorb at time t (mg/g), q_e is adsorption capacity at equilibrium (mg/g), k_f is pseudo first order constant and t is contact time between adsorbate and adsorbent (min). Integrating and rearranging equation (9) with initial condition at $q_t=0$ at $t=0$, leads to [Lagergren, 1898]

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \quad (14)$$

A plot between $\log(q_e - q_t)$ vs t (not shown here) is used to determine the value of rate constant (k_f), the value of slope of the plot is equal to $-k_f/2.303$, while as intercept is $\log(q_e)$. The value of constant along best fit values, MPSD and coefficient correlation (R^2) values for both adsorbents are listed in Table 5.6.

Pseudo second order equation is represented in the following form [Ho and McKay, 1999]

$$\frac{dq_t}{dt} = k_s (q_e - q_t)^2 \quad (15)$$

Where k_s is pseudo-second-order rate constant (g/mg min), q_t and q_e are as defined before. Integrating and rearranging above equation at initial condition $q_t=0$ at $t=0$, we get

$$q_t = \frac{tk_s q_e^2}{1 + tk_s q_e} \quad (16)$$

Initial sorption rate, h (mg/g min) is defined as

$$h = k_s q_e^2 \quad (17)$$

Adequacy and accuracy of kinetic model fit with experimental data and best suitable model was determined by employing Marquardt's percent standard deviation (MPSD) error function

[Marquardt, 1963]. MPSD shows some similarity with geometric mean error distribution, but modified by including the number of degree of freedom. It is given as

$$\text{MPSD} = 100 \sqrt{\left(\frac{1}{n-p} \right) \sum_{i=1}^n \left(\frac{q_{i,\text{exp}} - q_{i,\text{pred}}}{q_{i,\text{mes}}} \right)^2} \quad (18)$$

In above equation subscript 'exp' represent the values obtain from experimental data while as 'pred' refers to the values obtain by fitting a particular model, n is number of measurement carried out and p is number of parameter in the model.

Value of q_e and k_s is obtained from the plot of t/qt versus t , which is shown in Fig. 5.11. Slope of plot is $1/q_e$ whereas intercept is equal to $1/h$. values of different parameter along with MPSD and correlation coefficient are given in Table 5.6. $q_{e,\text{exp}}$ are values obtained from the experiment while as $q_{e,\text{pred}}$ values are predicted by curve fitting using the solver add-in function available in Microsoft Excel. From the Table 5.6, it can be seen that the value of adsorption capacity increases and rate constant decreases with increase in concentration for second order kinetics for both the adsorbents.

Comparing the value of R^2 and MPSD from Table 5.6, we get that the values of R^2 are near to unity for pseudo second order model and values of MPSD are minimum in case of pseudo second order model. From values of R^2 and MPSD it can be concluded that adsorption kinetics can be satisfactorily and adequately represented by pseudo second order model for adsorption of 4-CBA on BFA and GAC.

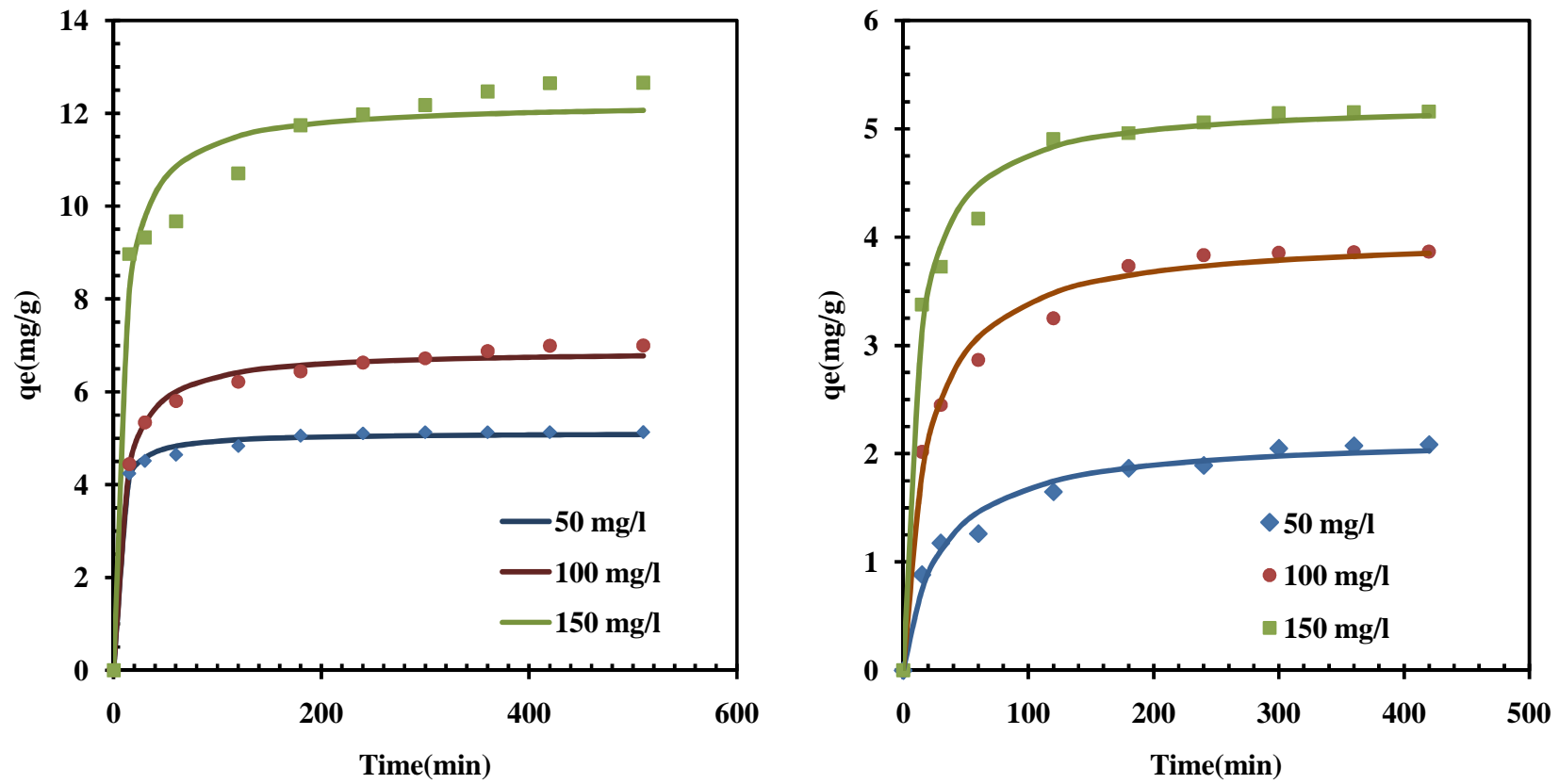


Fig. 5.10. Effect of contact time on (a) adsorption of 4-CBA by BFA, $t = 7.5$ h, $C_0 = 50-150$ mg/L; $m = 9$ g/L (b) adsorption of 4-CBA by GAC, $t = 7.5$ h, $C_0 = 50-150$ mg/L; $m = 20$ g/L. Experimental data points given by symbols and the lines predicted by Pseudo second order model.

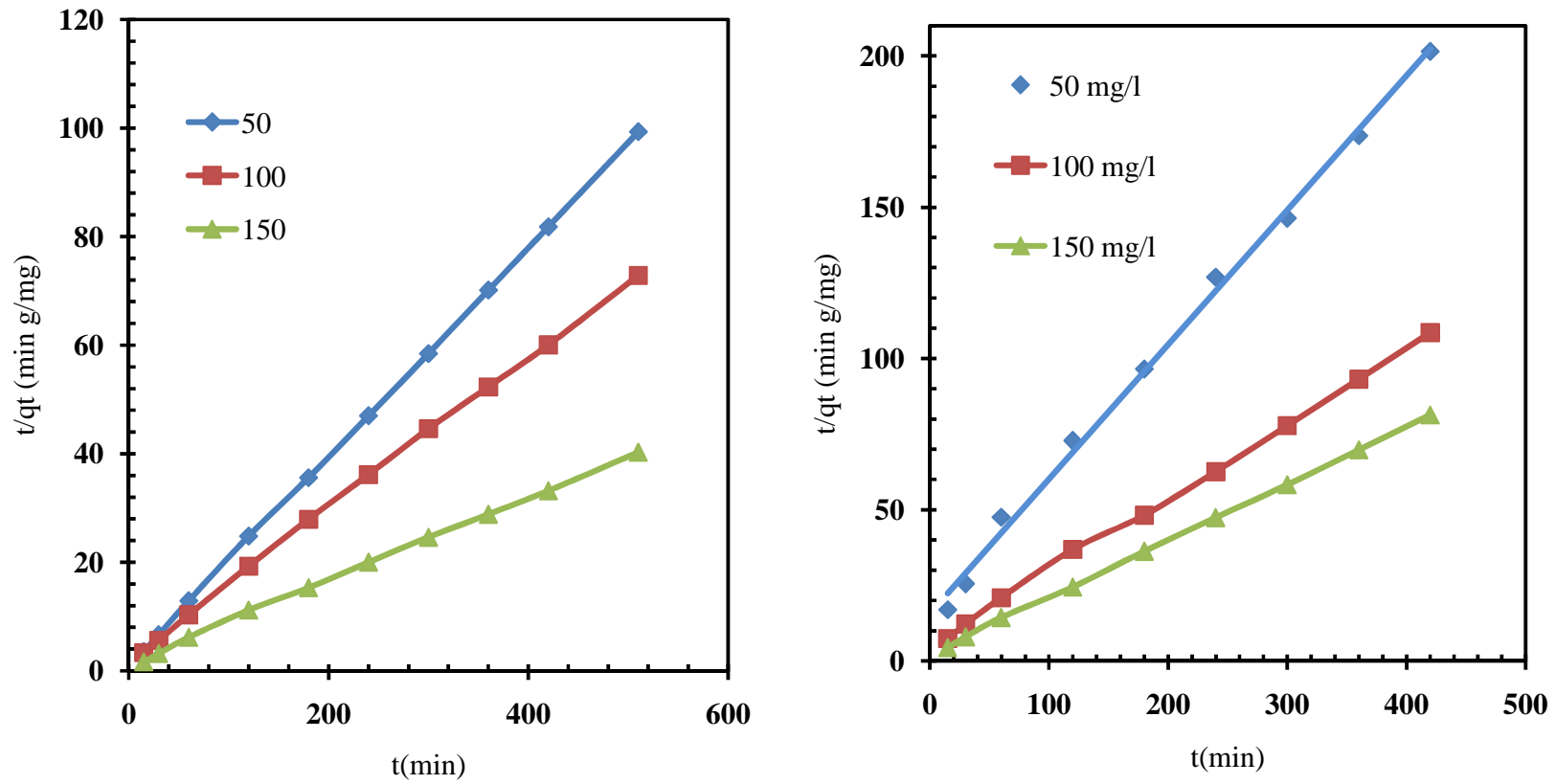


Fig.5.11. Pseudo-second-order kinetic plot for removal of 4-CBA on (a) BFA ($C_0= 50-150$ mg/L; $m=9$ g/L, $t= 7.5$ h) (b) GAC ($C_0= 50-150$ mg/L; $m=20$ g/L, $t= 7.5$ h)

5.4.2 Intra particle diffusion model/rate controlling step

The adsorption mechanism of 4-CBA on BFA and GAC was investigated by intra-particle diffusion mechanism [Webber and Morris, 1963] according to which uptake is directly proportional to $t^{1/2}$ as given below

$$q_t = K_{id}t^{1/2} + I \quad (19)$$

Where, K_{id} is defined as intra particle diffusion rate constant ($\text{mg/g min}^{1/2}$), while as I is a constant and obtain from the intercept of the plot q_e vs $t^{0.5}$ and it gives idea about the thickness of boundary layer i.e. the larger the intercept greater the boundary layer effect and slower will be corresponding step.

In adsorption process the transport of adsorbate from solution to the surface of adsorbent is considered to be complete in following steps (a) movement of adsorbate from solution to the surface of adsorbate. This step is also known as film or external diffusion. (b) mass transfer of adsorbate from boundary layer to surface of BFA (c) adsorption of adsorbate at a sites on the surface (internal or external) (d) diffusion of adsorbate molecule to the adsorption sites either by a pore diffusion process or by a solid surface diffusion mechanism [Cheung et al., 2006]. The slowest step among these steps will be rate limiting step and will control the sorption process. Film diffusion cannot be rate controlling step because sufficient agitation is provided during sorption process which reduces the resistance to the film diffusion and adsorption takes place by faster rate. Adsorption on sites is also considered to be taking place with extremely rapid speed, which prevents it to become slowest step.

Fig. 5.12 shows a plot between q_t and $t^{0.5}$ at different concentration of 4-CBA for both the adsorbent. The lines in the Fig. 5.12 do not pass through origin which leads to conclusion that there is difference in initial and final rate of adsorption. From the figure it is evident that the plot is multi-linear over the full $t^{0.5}$ range. The first sharper portion connecting origin to first point of each line (line not shown in Fig. 5.12 corresponds to boundary layer diffusion [Crank, 1965] and further two linear portion represent intra-particle diffusion. The first linear portion shown in figure where instantaneous adsorption takes place represents macro-pore diffusion or surface diffusion and it can be attributed to gradual equilibrium stage with intraparticle diffusion dominating. Second linear portion represents meso pore diffusion and in this portion intraparticle diffusion starts to slow down due to very low residual adsorbate concentration in solution

[Kumar and Sivanesan, 2005]. Multi-linear nature of curve suggests that mechanism is controlled by intra-particle pore diffusion along with surface diffusion.

Values of $K_{id,1}$, I_1 , $K_{id,2}$, and I_2 are shown in Table 5.6, From the table it is observe that the value of K_{id} for first linear portion is about 6 times than that of second portion which signifies higher initial rate of adsorption. Due to larger value of intercept for second line the resistance will be more causing slower rate of adsorption. From the Table 5.6, it is evident that with increase in concentration value of K_{id} increases so the rate of uptake.

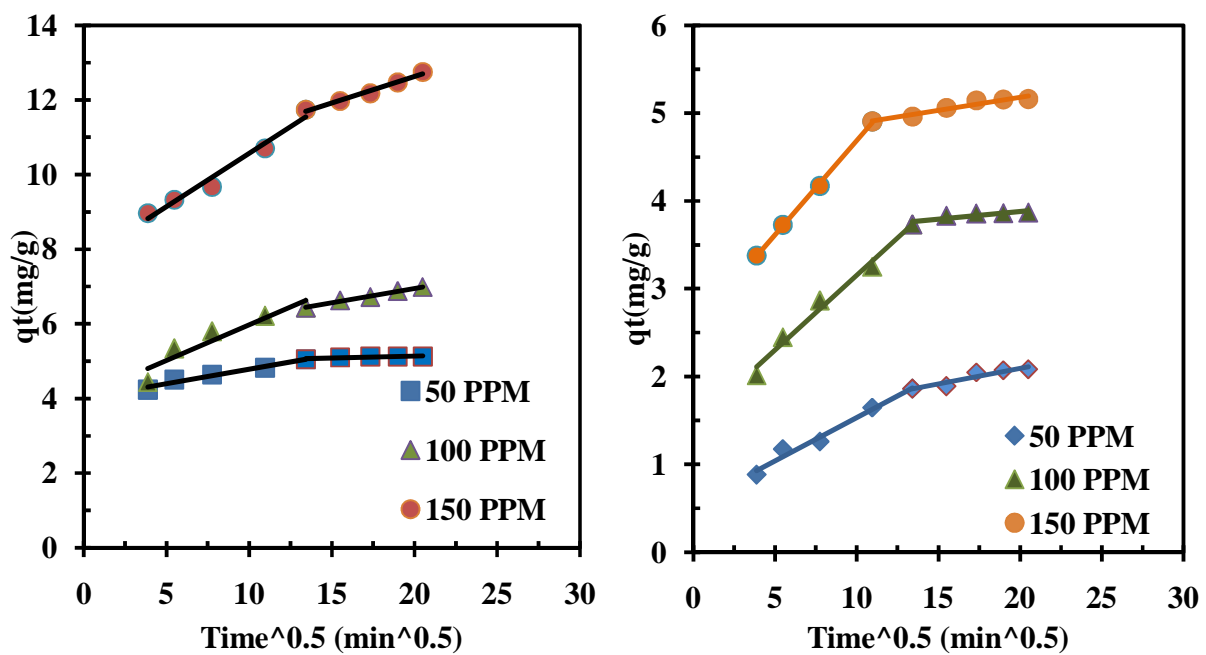


Fig. 5.12. Webber-Morris plot for 4-CBA removal by (a) BFA ($C_0= 50-150$, $t= 450$ min, mg/l, $m = 9$ g) (b) GAC ($C_0= 50-150$, $t= 450$ min, $m=20$ g/l).

Table 5.6: Kinetic parameters for the removal of 4-CBA by BFA (t = 7.5 h, m = 9 g/l, T= 303 K) and GAC (t=7.5 h, m=20 g/l)

4-CBA-BFA system						4-CBA-GAC system						
C ₀ (mg/l)	q _{e,exp}	q _{e,pred}	k _f (1/min)	R ²	MPSD	q _{e,exp}	q _{e,pred}	k _f (1/min)	R ²	MPSD		
Pseudo-first order												
50	5.13	4.97	0.0191	0.6160	4.48	2.08	1.85	0.0125	0.8143	14.52		
100	7.00	6.53	0.0108	0.7972	6.53	3.87	3.60	0.0177	0.8227	10.79		
150	12.66	11.48	0.0117	0.4764	10.63	5.16	4.88	0.0160	0.7567	8.97		
Pseudo-Second order												
C ₀ (mg/l)	q _{e,exp}	q _{e,pred}	k _f (g/mg.min)	R ²	MPSD	q _{e,exp}	q _{e,pred}	k _f (g/mg.min)	R ²	MPSD		
50	5.19	5.12	0.0356	0.9049	2.23	2.25	2.08	0.0125	0.9355	8.78		
100	7.15	6.91	0.0096	0.9613	2.73	4.08	3.94	0.0117	0.9540	5.49		
150	13.02	12.16	0.0045	0.7839	6.92	5.32	5.203	0.0155	0.9422	4.46		
Weber-Morris												
C ₀ (mg/l)	K _{id,1} (mg/g min ^{1/2})	I ₁ (mg/l)	R ₁ ²	K _{id,2} (mg/g min ^{1/2})	I ₂ (mg/l)	R ₂ ²	K _{id,1} (mg/g min ^{1/2})	I ₁ (mg/l)	R ₁ ²	K _{id,2} (mg/ g min ^{1/2})	I ₂ (mg/l)	R ₂ ²
50	0.0779	4.01	0.9663	0.0104	4.93	0.7878	0.0987	0.54	0.9791	0.0355	1.38	0.8794
100	0.1911	4.06	0.8858	0.0763	5.42	0.9927	0.1700	1.45	0.9849	0.0173	3.53	0.7554
150	0.2853	7.72	0.9719	0.1414	9.80	0.9841	0.2144	2.54	0.9989	0.0298	4.58	0.9349

5.5 ADSORPTION ISOTHERM STUDY

5.5.1 Effect of temperature

Operating temperature in adsorption process affects the adsorption equilibrium uptake in various capacities. A plot of q_e vs C_e for 4-CBA- BFA and 4-CBA- GAC system is shown in Fig. 5.13 at various temperatures (15, 30, 45 °C). Normally adsorption process is considered as exothermic and adsorption capacity should decrease with increase in temperature but in our study contrary to normal observation adsorption was found to be increasing with the increase in temperature for both adsorbents. Increase in adsorption capability can be attributed to activation of new sites due to increase in the temperature as well as increase in mobility of adsorbate ions at high temperature and decrease in retardation force. Diffusivity is positively affected by temperature and it contributes in the enhancement of adsorption capacity of adsorbate with increase in temperature provided that adsorption process is controlled by diffusion (intra-particle diffusion) process, which is, as we have established in kinetic section. Along with intra-particle diffusion adsorption is also controlled by surface diffusion and diffusion resistance can be neglected if process is continued for sufficient contact time. So increase in adsorption equilibrium uptake of 4-CBA on adsorbents can also may be due to chemisorption [[Srivastava et al., 2006](#)].

5.5.2 Isotherm modeling

The adsorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. In Langmuir isotherm monolayer adsorption takes place and it has homogeneous surface energy and there is no transmigration of solute. Value of constant 'b' is used to describe how strongly the adsorbate is adsorbed on adsorbent. Freundlich isotherm is applied in case of heterogeneous surface. Each site has different bond energy and sites having stronger bond energy are occupied first. Values of $1/n$ are used to measure adsorption intensity or surface heterogeneity. If $1/n$ is less than 1 then chemisorption takes place and if $1/n$ is greater than 1 then cooperative adsorption takes place [[Haghseresht and Lu, 1998](#)]. Redlich–Peterson (R-P) features both Langmuir and Freundlich isotherm. It approaches freundlich at high concentration (as g tends to zero) and Langmuir at low concentration (as g closes to 1). Temkin isotherm contains a factor that explicitly takes into account the interaction between adsorbate and adsorbent. In this model it is assume that the decrease in heat of adsorption of molecule is linear with coverage and adsorption is characterized by uniform distribution of binding energy [[Temkin and Pyzhev, 1940](#)]. Sips

isotherms represent combine from of Langmuir and Freundlich isotherm deduced for evaluating heterogeneous system and equation parameter are governed by operating conditions.

The values of parameter for different isotherm model viz. Langmuir, Freundlich, R-P, Hills, Sips, Toth and Temkin were evaluated along with sum of square error (SSE) and coefficient of correlation (R^2) at different temperature using MS Excel for Windows and tabulated in Table 5.7. For Langmuir isotherm the increase in the value of Q_0 and b with increase temperature confirms the endothermic nature of the process. From the Table 5.7, it can be observed that the values of $1/n$ for freundlich isotherm is less than 1 for all temperature as well as for both adsorbents hence adsorption of 4-CBA is favorable for both adsorbents. The data in Table 5.7 indicates the value of g in case of R-P isotherm lies between 0 to 1 (except for GAC at 318 K), so the adsorption is favorable at all temperatures.

The optimum adsorption capability of BFA was found to be greater than GAC. GAC have higher surface area than BFA yet higher adsorption capacity of BFA leads to the conclusion that available surface area BFA for adsorption is higher than that of GAC. It may also be due to greater affinity of 4-CBA to BFA. From the Fig. 5.13 it is also evident that the rate of adsorption at lower adsorbate concentrations is higher in comparison to the high adsorbate concentration.

In order to find best isotherm values of R^2 and SSE were compared for all isotherms. From the Table 5.7, it can be observed that the values R^2 is close to unity in case R-P and Sips isotherm for 4-CBA-BFA system while is it is near to unity in case of R-P for 4-CBA -BFA system. Values of SSE are lowest for R-P for both the system. Hence on the basis of R^2 and SSE it can be concluded that R-P isotherm best fit adsorption equilibrium data for both the system.

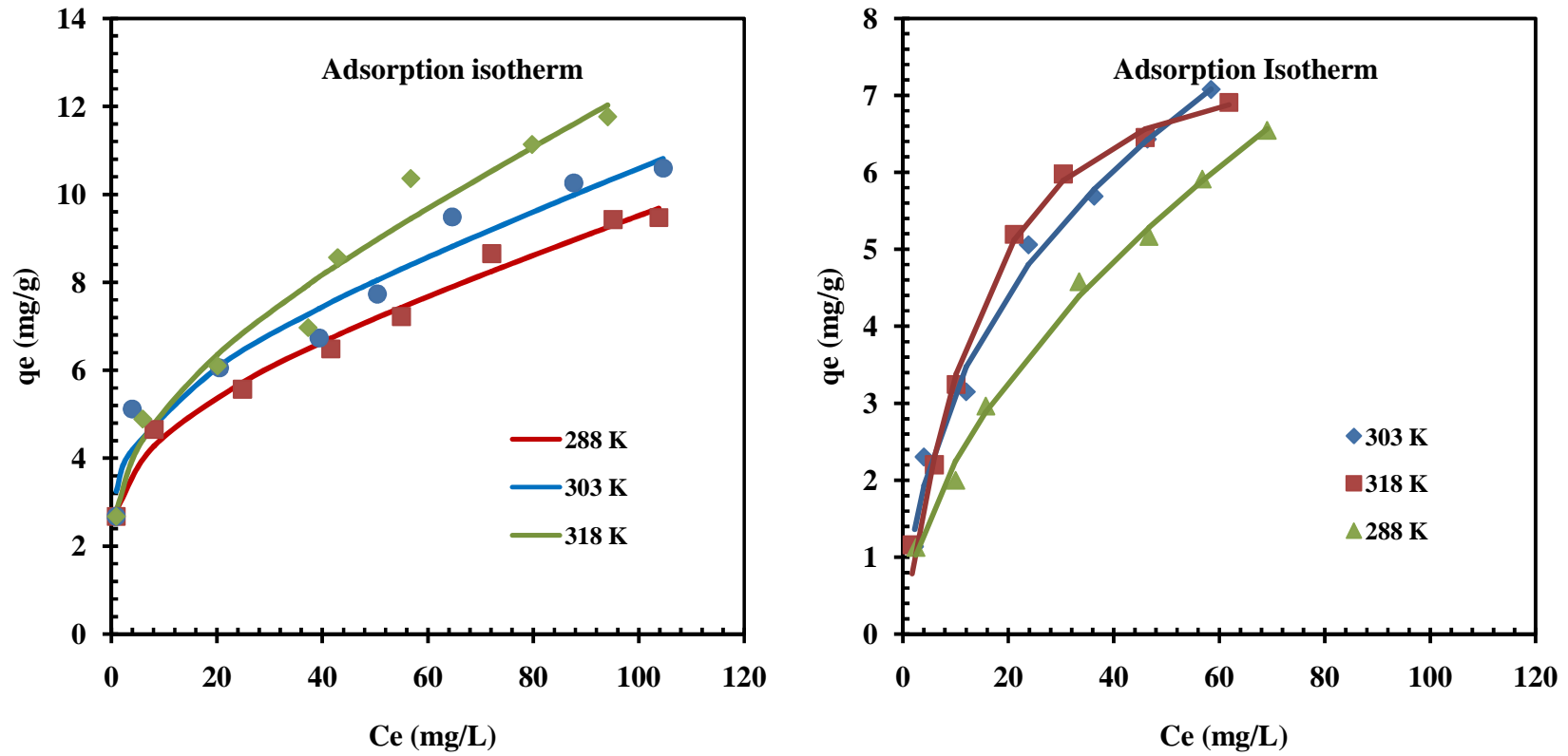


Fig. 5.13. Equilibrium adsorptions isotherms at different temperatures for (a) 4-CBA loaded BFA system, $t = 7.5\text{h}$, $C_o = 20\text{--}200\text{ mg/l}$; $m = 9\text{ g/l}$. lines predicted by Sips model (b) 4-CBA loaded GAC system, $t = 7.5\text{h}$, $C_o = 20\text{--}200\text{ mg/l}$; $m = 20\text{ g/l}$.

The lines predicted by Redlich-Peterson. In both figures Experimental data points given by symbols.

Table 5.7: Isotherm parameters for the removal of 4-CBA by BFA (t=7.5 h, m=9 g/l) and GAC (t=7.5 h, m=20 g/l)

Isotherms	Parameters	BFA			GAC			
		Temperature			Temperature			
		288	303	318	288	303	318	
Langmuir	Q_o (mg/g)	9.8042	9.4209	13.238	9.7269	8.8622	21.9026	
	$q_e = \frac{Q_o b C_e}{1 + b C_e}$	b (l/mg)	0.0795	0.2278	0.0518	0.0271	0.0563	0.0023
		R ²	0.8683	0.7702	0.8926	0.9888	0.9767	0.8683
		K _F	2.2937	2.7678	2.2427	0.6237	1.0310	0.0998
Freundlich	$(\text{mg/g})/(\text{mg/l})^{1/n}$							
	$q_e = K_F C_e^{1/n}$	1/n	0.3013	0.2822	0.3609	0.5558	0.4772	0.8075
		R ²	0.9680	0.9357	0.9559	0.9949	0.9853	0.8898
Redlich-Peterson	a _R (l/g)	1203.9	910.34	1777.3	19.612	0.7869	0.0270	
	$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	K _R (l/mg) ^{1/g}	2984.5	2574.2	4364.2	12.628	1.4044	0.4655
		g	0.7170	0.7229	0.6613	0.4500	0.6391	1.1561
		R ²	0.9651	0.9350	0.9528	0.9949	0.9876	0.9948
Hill	Q_{sH}	57.236	1318532	48.138	4312.4	527.29	4000.92	
	$q_e = \frac{Q_{sH} C_e^{nH}}{k_D + C_e^{nH}}$	k _D	1.4490	218100	2.2272	4410.8	618.02	4455.72
		n	39.363	0.5841	33.0454	1.0089	1.0664	1.02955

	R^2	0.4691	0.9501	0.4165	0.9704	0.9373	0.8390
	$K_s (l/g)^{1/\beta_s}$	1.1364	0.9318	1.7888	0.5947	0.9035	0.0208
Sips	$a_s (l/mg)^{1/\beta_s}$	-0.5900	-0.7105	-0.3608	0.0083	0.0472	0.0016
$q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	β_s	0.0743	0.0488	0.1479	0.5891	0.6184	1.2469
	R^2	0.9871	0.9559	0.9693	0.9950	0.9874	0.8309
	K_T	2.713	3.557	2.582	0.5922	1.3653	0.2941
Toth	$1/t$	1.36	1.291	1.492	0.4320	0.5908	0.3731
$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	$a_T (mg/l)$	1	1	1	-0.4554	1.7500	85.6340
	R^2	0.9949	0.9979	0.8873	0.9950	0.9877	0.8765
Temkin	B_1	1.4183	1.5374	1.9026	1.6615	1.7500	2.9125
$q_e = \frac{RT}{b} \ln(K_T C_e)$	$K_T (l/mg)$	4.3545	5.0570	2.6494	0.5209	0.7812	0.0493
where, $\frac{RT}{b} = B_1$	R^2	0.8879	0.8824	0.8648	0.9280	0.9694	0.9676

5.6 ESTIMATION OF THERMODYNAMIC PARAMETERS

Van't Hoff equation is used to relate the Gibbs free energy change for adsorption process to the equilibrium constant in the following manner [Smith and Ness, 1987]

$$\Delta G_{\text{ads}}^0 = RT \ln K_{\text{ads}} \quad (20)$$

According to thermodynamic changes in Gibbs free energy and entropy can also be related with heat of adsorption at constant temperature by following equation

$$\Delta G_{\text{ads}}^0 = \Delta H^0 - T \Delta S^0 \quad (21)$$

Combining and rearranging equation (1) and (2) we get

$$\ln K_{\text{ads}} = \frac{\Delta G_{\text{ads}}^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T} \quad (22)$$

Where ΔG_{ads}^0 is free energy change (kJ/mol), R is universal gas constant (8.314 J/mol K), T is absolute temperature (K), K_{ads} is the equilibrium constant of interaction between the adsorbate and adsorbent surface, ΔH^0 is change in enthalpy (kJ/mol) and ΔS^0 is change in entropy (kJ/mol K). From equation (3) it is clear that ΔH^0 can be calculated from the slope of the plot between $\ln K_{\text{ads}}$ and (1/T) according to following equation

$$\Delta H^0 = \left[R \frac{d \ln K}{d(1/T)} \right] \quad (23)$$

K_{ads} is evaluated from the intercept of $\ln(q_e/C_e)$ vs q_e [Srivastava et al., 2007]. Values of all parameters are listed in Table 5.8. Positive value of ΔH^0 is confirmation of overall endothermic nature of the adsorption process for both the adsorbents. Solid/liquid adsorption process complete in two steps: first step involves desorption of previously adsorbed water molecule (solvent) and in second step adsorbate species adsorb on adsorbent. The complete process requires displacement of water molecule by 4-CBA molecules. Energy is required for completion of process due to which this process becomes endothermic. With increase in temperature randomness increases at solid/solution interface causing some structural changes in adsorbate and adsorption system for the adsorption process. Increase randomness signifies the increase in the entropy of the system. Negative values of ΔG_{ads}^0 indicates that the adsorption process is feasible and spontaneous.

Table 5.8: Thermodynamic parameters for adsorption of 4-CBA by BFA (t=7.5 h, m=9 g/l) and GAC (t=7.5 h, m=20 g/l)

Temperature (K)	K_d	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)	K_d	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
4-CBA-BFA system				4-CBA-GAC system				
288	8.51	-5.12	1.03	0.02138	6.08	-4.32	4.25	0.029773
303	8.69	-5.44			6.64	-4.77		
318	8.93	-5.76			6.67	-5.21		

Chapter- 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSION

The present study involves the removal of 4-carboxybenzaldehyde (4-CBA) from aqueous solution by adsorption process using bagasse fly ash (BFA) as an adsorbent. In the present study important process parameters affecting adsorption process were optimized using central composite design under response surface methodology. Following conclusions can be drawn from the experimental studies:

- The optimized condition for the experiment was found as pH=4, adsorbent dose=9 g/l, initial concentration=100 mg/l and time 7.5 h.
- At optimized condition, the removal efficiency and adsorption uptake of 4-CBA onto BFA was found to be 79% and 9.9 mg/g, respectively.
- Adsorbent dose and contact time have synergistic effect while pH and initial sorbate concentration have antagonistic effect on percent removal of 4-CBA.
- Fairly good value of R^2 (0.87 for %4-CAB removal and 0.90 for adsorption uptake) obtained from ANOVA analysis ensured a satisfactory fit of regression model with data.
- Suitable kinetic model was determined on the basis of coefficient correlation and MPSD values, these values suggest that pseudo-second-order model best fitted the adsorption kinetic data for 4-CAB removal onto BFA and GAC.
- Adsorption capacity of BFA was compared with GAC and results shows that BFA has better adsorption capacity for 4-CBA removal.
- Various isotherm models were investigated for equilibrium isotherm, value of SSE and R^2 indicate Sips and Redlich-Peterson model were best fitted for BFA and GAC, respectively.
- Effect of temperature and feasibility of the process was accessed by evaluating thermodynamic parameters. Positive values of ΔH^0 suggest that the adsorption process was endothermic in nature.

- Increase randomness signifies the increase in the entropy of the system. Negative values of ΔG_{ads}^0 indicates that the adsorption process is feasible and spontaneous.

6.2 RECOMMENDATIONS

Based on the present experiments and results, following recommendations can be made:

- Further studies are required for treatment of other compounds present in the wastewater.
- Further pilot scale studies are required to evaluate the suitability of BFA for the adsorptive removal on plant scale.

REFERENCES

- Abou-Mesalam M.M., Sorption kinetics of copper, zinc, cadmium and nickel ions on synthesized silico-antimonate ion exchanger, *Colloids Surface A: Physicochemical and Engineering Aspects* 225 (2003) 85–94.
- Anbia M., Salehi S., Synthesis of polyelectrolyte-modified ordered nanoporous carbon for removal of aromatic organic acids from purified terephthalic acid wastewater, *Chemical Engineering Research and Design* 90 (2012) 975–983
- Andreozzi R., Caprio V., Insola A., Marotta R., Advance oxidation processes (AOP) for water purification and recovery, *Catalysis Today* 53 (1999) 51–59.
- Annual Report 2012-2013, Ministry of Chemical and Petrochemical ([http://chemicals.nic.in/AR_2012-2013_\(1-94\).pdf](http://chemicals.nic.in/AR_2012-2013_(1-94).pdf) as accessed on 7.05.2013)
- Ayranci E., Duman O., Adsorption of aromatic organic acids onto high area activated carbon cloth in relation to wastewater purification, *Journal of Hazardous Materials B* 136 (2006) 542–552.
- Ayranci E., Hoda N., Bayram E., Adsorption of benzoic acid onto high specific area activated carbon cloth, *Journal of Colloid Interface Science* 284 (2005) 83–88.
- Azarpour A., Zahedi G., Hybrid dynamic modeling of 4-CBA hydrogenation fixed-bed catalytic reactor of PTA production plant, 11 International Symposium on Process Systems Engineering, July 2012
- Balistrieri L.S., Murray J.W., The surface chemistry of goethite (α -FeOOH) in major ion seawater, *Am. J. Sci.* 281 (6) (1981) 788–806
- Barret E.P., Joyer L.G., Halenda P.P., The determination of pore volume and area distributions in porous substances: 1. Computations from nitrogen isotherms, *Journal of the American Chemical Society* 73 (1951) 373–380
- Benyounis K.Y., Olabi A.G., Hashmi M.S.J., Effect of laser welding parameters on the heat input and weld-bead profile, *Journal of Materials Processing Technology* 164/165 (2005) 978–985
- Box G.E.P., Hunter W.G., The 2^{k-p} fractional factorial design, *Technometrics* 3 (1961) 311–458.
- Box G.E.P., Wilson K.B., On the experimental attainment of optimum conditions, *Journal of Royal Statistical Society Series B Stat. Methodological* 13 (1951) 1–45

- Brereton R.G., *Chemometrics: Data Analysis for the Laboratory and Chemical Plant*, John Wiley (2003) 76–84.
- Brunauer S., Emmet P.H., Teller F., Adsorption of gases in multi-molecular layers, *J. Am. Chem. Soc.* 60 (2) (1938) 309–319
- Chen J.P., Wang L., Characterization of metal adsorption kinetic properties in batch and fixed-bed reactors, *Chemosphere* 54 (2004) 397–404
- Chern J., Chien Y., Competitive adsorption of benzoic acid and p-nitrophenol onto activated carbon: isotherm and breakthrough curves, *Water Research* 37(2003) 2347– 2356.
- Cheung W.H., Szeto Y.S., McKay G., Intraparticle diffusion processes during acid dye adsorption onto chitosan, *Bioresource Technology* 98 (2007) 2897–2904
- Chidambara raj C. B., Ramkumar N., Siraj A.H.J., Chidambaram S. P., Biodegradation of acetic, benzoic, isophthalic, toluic and terephthalic acids using a mixed culture: Effluents of PTA Production., *Trans. IChemE.* 75B (1997) 245–256
- Choy K.K.H., McKay G., Porter J.F., Sorption of acid dyes from effluents using activated carbon, *resource Conservation and Recycling* 27 (1999) 57-71
- Crank J., *The mathematics of diffusion*, Oxford Clarendon Press, London, (1965).
- Daniels J., Allen N. S., Edge M., Coote S., Fluorescence characterization and analysis of 4-carboxybenzaldehyde, a colour precursor to the manufacture of terephthalic acid, *Polymer Degradation and Stability* 65 (1999) 347–353
- Elliott H.A., Huang C.P., Adsorption characteristics of some Cu (II) complexes on aluminosilicates, *Water Research* 15 (1981) 849–854.
- Gupta V.K, Ali I., Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater, *Separation and Purification Technology* 18 (2000) 131-140
- Gupta V.K., Jain C.K, Ali I., Sharma M., Saini V.K, Removal of cadmium and nickel from wastewater using bagasse fly ash e a sugar industry waste, *Water Research* 37 (2003) 4038-4044
- Gupta V.K., Mohan D., Sharma S., Sharma M., Removal of basic dyes (Rhodamine B and Methylene blue) from aqueous solutions by bagasse fly ash, *Separation Science and Technology* 35(13) (2000) 2097-2113

- Guyot J.P., Macarie H., Noyola A., Anaerobic digestion of petrochemical wastewater using UASB process, *Applied Biochemistry and Biotechnology* 24/25 (1990) 579–589
- Haghseresht F., Lu G., Adsorption characteristic of phenolic compounds onto coal-reject-derived adsorbents, *Energy Fuels* 12 (1998) 1100–1107
- Ho Y.S., McKay G., Pseudo-second order model for adsorption processes, *Process Biochemistry* 34 (1999) 451–465.
- http://www.chemicaldictionary.org/dic/4/4-Formylbenzoic-acid_685.html as accessed on 29.05.2013)
- Huang L., Xiao H., Ni Y., Cationic MCM-41: synthesis, characterization and sorption behavior towards aromatic compounds, *Colloids Surf. A* 247 (2004) 129–136.
- IUPAC Manual of Symbols and Terminology of Colloid Surface, Butterworths, London, 1982
- Jaouachi B., Hassen M.B., Sakli F., Strength of wet spliced denim yarns after sizing using a central composite design, *Autex Research Journal* 7, 3. (2007)
- Jhung S.H., Romanenko A.V., Lee K.H., Park Y.S., Moroz E.M., Likholoboy V.A., Carbon-suspended palladium-ruthenium for hydropurification of terephthalic acid, *Applied Catalyst A: General* 225 (2002) 131–139
- Karthik M., Dafale N., Pathe P., Nandy T., Biodegradability enhancement of purified terephthalic acid wastewater by coagulation-flocculation process as pretreatment, *Journal of Hazardous Materials* 154 (2008) 721–730.
- Khachane P.K., Heesink A.B.M., Versteeg G.F., Pangarkar V.G., Adsorptive Separation and Recovery of Organic Compounds from Purified Terephthalic Acid Plant Effluent, *Separation Science and Technology* Vol. 38, no. 1 (2003) 93–111
- Kleerbezem R., Mortier J., Hulshoff Pol L.W., Lettinga G., Anaerobic pre-treatment of petrochemical effluents: terephthalic acid wastewater, *Water Science and Technology* 36 (2–3) (1997) 237–248
- Kleerbezem R., Becker J., Hulshoff Pol L.W., Lettinga G., High rate treatment of terephthalic acid production wastewater in a two-stage anaerobic bioreactor, *Biotechnology Bioengineering* 91 (2005) 169-179
- Kumar A., Prasad B., Mishra I.M, Optimization of process parameters for Acrylonitrile removal by low cost- adsorbent using Box-Behnken design, *Journal of Hazardous Materials* 150 (2008) 174-182

- Kumar K.V., Sivanesan S., Comparison of linear and non-linear method in estimating the sorption isotherm parameters for safranin onto activated carbon, *Journal of Hazardous Materials B* 123 (2005) 288–292.
- Kushwaha J.P., Srivastava V.C., Mall I.D., Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash: parametric, kinetic and equilibrium modeling, disposal studies, *Bioresource Technology* 101 (10) (2010) 3474–3483
- Kütahyalı C., Çetinkaya B., Acar M. B., Işık N. O., Cireli I., Investigation of strontium sorption onto Kula volcanics using Central Composite Design, *Journal of Hazardous Materials* 201/202 (2012) 115–124
- Lagergren S., About the theory of so-called adsorption of soluble substances, *Kungliga Svenska Vetenskapsakademiens Handlingar* 24 (1898) 1–6
- Lakshmi U.R., Srivastava V.C., Mall I.D., Lataye H.D., Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye. *Journal of Environmental Management* 90 (2009) 710-720
- Landau R., Staffer A.. *Chem Eng Prog* 1968;64:20
- Lataye D.H., Mishra I. M., Mall I. D., Adsorption of 2-picoline onto bagasse fly ash from aqueous solution, *Chemical Engineering Journal* 138 (2008) 35–46
- Lataye D.H., Mishra I.M., Mall I.D., Removal of pyridine from aqueous solution by adsorption on bagasse fly ash, *Ind. Eng. Chem. Res.* 45 (11) (2006) 3934–3943.
- Lau C.M., Staging aeration for high efficiency treatment of aromatic acid plant wastewater, *Proceedings of 32nd Independent Wastewater Conference Purdue University* 32 (1978) 63–74
- Macarie H., Guyot J.P., Inhibition of methanogenic fermentation of p-toluic acid (4-methylbenzoic acid) by acetate, *Applied Biochemistry and Biotechnology* 38 (1992) 398–402
- Mall I.D, Mishra N., Mishra I.M., Removal of organic matter from sugar mill effluent using bagasse fly ash activated carbon, *Res Indus* 1994;39 (6):115-9
- Mall I.D., *Petrochemical Process Technology*, 1st ed., Macmillan, 2007.
- Mall I.D., Tewari S., Singh N., Mishra I.M., Utilization of bagasse fly ash and carbon waste from fertilizer plant for treatment of pyridine and 3-picoline bearing wastewater. *Proceeding of*

- the eighteenth international conference on ‘‘solid waste technology and management’’, held at Philadelphia, PA, USA; March 23-26, 2003
- Marquardt D.W., An algorithm for least-squares estimation of nonlinear parameters, *Journal of the Society for Industrial and Applied Mathematics* 11 (1963) 431–441.
- Material safety data sheet (<http://fscimage.fishersci.com/msds/76480.htm> as accessed on 08.05.2013)
- McKay G., *Use of Adsorbents for the Removal of Pollutants from Wastewaters*, CRC Press, Boca Raton, New York, London and Tokyo, 1995
- Meyer, D.H. (Standard oil) US Pat. 2,584,039, 1971
- Noyola A., Macarie H., Guyot J.P., Treatment of terephthalic acid plant wastewater with an anaerobic fixed film reactor, *Environmental Technology* 11(1990) 239–248
- Park T.J., Lima J.S., Lee Y.W., Kim S.H., Catalytic supercritical water oxidation of wastewater from terephthalic acid manufacturing process, *Journal of Supercritical Fluids* 26 (2003) 201–203
- Pophali G. R., Khan R., Dhodapkar R. S., Nandy T., Devotta S., Anaerobic -aerobic treatment of purified terephthalic acid (PTA) effluent: a techno-economic alternative to two-stage aerobic process, *J. Environ. Manage* 85 (2007) 1024–1033.
- Ricordel S., Taha S., Cisse I., Dorange G., Heavy metals removal by adsorption onto peanut husks carbon: characterization, kinetic study and modeling, *Separation and Purification Technology* 24 (2001) 389–401
- Shafaei A., Nikazar M., Arami M., Photocatalytic degradation of terephthalic acid using titania and zinc oxide photocatalysts: Comparative study, *Desalination* 252 (2010) 8–16
- Smith J.M., Ness H.C.V., *Introduction to Chemical Engineering Thermodynamics*, 4th ed., McGraw-Hill, Singapore, 1987
- Srivastava V.C., Mall I.D., Mishra I.M., Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA), *Chemical Engineering Journal* 132 (1–3) (2007) 267–278
- Srivastava V.C., Mall I.D., Mishra I.M., Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA, *Journal of Hazardous Materials* B134 (2006) 257–267.

- Srivastava V.C., Prasad B., Mishra I.M., Mall I.D., Swamy M.M., Prediction of breakthrough curves for sorptive removal of phenol by bagasse fly ash packed bed, *Ind. Eng. Chem. Res.* 47 (2008) 1603–1613
- Srivastava V.C., Treatment of pulp and paper mill effluent. M Tech dissertation, Indian Institute of Technology Roorkee, Roorkee, India; 2003
- Swamy M.M., Mall I.D., Prasad B., Resorcinol removal aqueous solution by bagasse fly ash and activated carbon. *Inst Eng (India) J Environ* 77(2) (1997) 49-54
- Temkin M.I., Pyzhev V., Kinetics of ammonia synthesis on promoted iron catalysts, *Acta Physicochimica URSS* 12 (1940) 327–356
- The World Bank Group, Pollution Prevention and Abatement Handbook 1998: Toward Cleaner Production, World Bank Inc., Washington, D.C., 1999.
- Thiruvengkatahari R., T.O. Kwon, J.C. Jun, S. Balaji, M. Matheswaran, I.S. Moon, Application of several advanced oxidation processes for the destruction of terephthalic acid (TPA), *Journal of Hazardous Materials* 142 (2007) 308–314.
- Tozuka Y., Sasaoka S., Nagae A., Moribe K., Oguchi T., Yamamoto K., Rapid adsorption and entrapment of benzoic acid molecules onto mesoporous silica (FSM-16), *Journal of Colloid Interface Science* 291(2005) 471–476
- Tripathi P., Srivastava V.C., Kumar A., Optimization of an azo dye batch adsorption parameters using Box-Behnken, *Desalination* 249 (2009) 1273–1279
- Tsuno H., Kawamura M., Development of an expanded-bed GAC reactor for anaerobic treatment of terephthalate-containing wastewater, *Water Research* 43 (2009) 417–422
- Verma S., Prasad B., Mishra I.M., Pretreatment of petrochemical wastewater by coagulation and flocculation and the sludge characteristics, *Journal of Hazardous materials* 178 (2010) 1055–1064
- Weber W.J. Jr., Morris J.C., Kinetics of adsorption on carbon from solution, *J. Sanit. Engng. Divn, American Society of Civil Engineers.* 89 (1963) 31–59
- Wen Y.Z., Tong S.P., Zheng K.F., Wang L.W., Lv J.Z., Lin J., Removal of terephthalic acid in alkalized wastewater by ferric chloride, *Journal of Hazardous Materials* 138 (1–2) (2006) 169–172

- Yan J., Cheng S.P., Zhang X.X., Shi L., Zhu C.J., Effects of four metals on the degradation of purified terephthalic acid wastewater by phanerochaete chrysosporium and strain Fhhh, *Bulletin of Environmental Contamination and Toxicology* 72 (2004) 387–393
- Yıldız N., Gonulsen R., Koyuncu H., Calımlı A., Adsorption of benzoic acid and hydroquinone by organically modified bentonites, *Colloids Surf. A* 260 (2005) 87–94.
- Young J.C., Kim I.S., Page I.C., Wilson D.R., Brown G.J., Cocci A.A., Two stage anaerobic treatment of purified terephthalic acid production wastewaters, *Water Science and Technology* 42 (5-6) (2000) 277–282
- Zhang X.X., Cheng S.P., Wan Y.Q., Sun S.L., Jhu C.J., Zhao D.Y., Pan W.Y., Degradation of five aromatic compounds in a pilot wastewater treatment system, *International Biodeterioration Biodegradation* 58 (2006) 94–98