

**ADSORPTIVE REMOVAL OF BISPHENOL-A USING LOW COST  
ADSORBENT**

**A DISSERTATION**

*Submitted in the 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**

**BHOGADI BHASKARA RAO**



**DEPARTMENT OF CHEMICAL ENGINEERING  
INDAIN INSTITUTE OF TECHNOLOGY, ROORKEE  
ROORKEE-247667 (INDIA)  
JUNE-2013**



**INDIAN INSTITUTE OF TECHNOLOGY  
ROORKEE  
CANDIDATE'S DECLARATION**

---

I hereby declare that the work which is being presented by me in this dissertation report entitled “**Adsorptive Removal of Bisphenol-A Using Low Cost Adsorbent**”, submitted in partial fulfilment of the requirement for the award of the degree of, “**Master of Technology in Chemical Engineering**” with specialization in “**Industrial Pollution Abatement**”, and submitted to the Department of Chemical Engineering, Indian Institute of Technology, Roorkee, is an authentic record of the work carried out by me during the period June 2012 to June 2013, under the guidance of **Dr. I. D. Mall**, Professor, Chemical Engineering Department, Indian Institute of Technology, Roorkee.

Date:

Place: IIT Roorkee

**(BHOGADI BHASKARA RAO)**

---

**CERTIFICATE**

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

**Dr. I. D. MALL**

Professor

Department of Chemical Engineering

Indian Institute of Technology

Roorkee -247667, India

## ACKNOWLEDGEMENT

---

I am greatly indebted to my guide **Prof. I. D. Mall**, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee for his kind support and guidance during the entire course of this work. His cooperation and in depth knowledge have made my work possible.

I remain indebted to **Dr. V.C. Srivastava**, Assistant professor, Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee for enabling me to develop professionally and personally.

I am also thankful to **Dr. V.K. Agarwal, Prof. and Head**, Department of Chemical Engineering and other staff members for their instant help in all kinds of work.

My special thanks are due to Mr. Rajendra Bhatnagar for his kind help during experiments/analysis.

I would like to thank my friends for their continuous support and enthusiastic help.

Last but not least, it is owed to the blessings of my parents and God that I have come up with this work in due time.

**(BHO GADI BHASKARA RAO)**

## ABSTRACT

---

In the past few years, the research on the endocrine disrupting chemicals (EDCs) has been increased with great interest in the area of environmental science and technology owing to the reason that these chemicals (EDCs) have various properties such as estrogenic, antiestrogenic or antiandrogenic and hence their existence leads to the potential damage the endocrine systems of human beings and wildlife.

One of the ECDs such as Bisphenol A [2, 2-bis (4- hydroxyphenyl) propane] or BPA is of the important concern due its adverse potentiality to the human health and environment. BPA is mainly used in the manufacturing of resins and polycarbonate plastics. There is chance of entering the BPA into water bodies while manufacturing plastic products, leaching from plastic products, disposed at the landfill sites, and many routes. Thus it causes contaminating the various sources of water such as ground water, surface water, etc. and poses danger to fecundity and reproductive health of human beings and aquatic animals.

The present work deals with optimization of various process variables for the removal of BPA from aqueous solutions by cheaply available adsorbent such as Bagasse Fly Ash (BFA) using Response Surface Methodology based Central Composite Design (CCD). The process variables such as BFA dose (w), time of contact (t), initial pH of BPA solution, temperature (T) were varied at five levels to examine the effects on the adsorption of BPA onto BFA and the results were analyzed by Sequential model sum of squares and analysis of variance (ANOVA). The optimum conditions for the removal of BPA were found to be pH = 5.8, adsorbent dose = 17.5 g/l, contact time = 270 min, temperature = 40<sup>0</sup>C. The characterization was done to determine the physicochemical properties, textural properties of BFA. Equilibrium isotherms for BPA-BFA system were studied by Langmuir, Freundlich, Redlich-Peterson, Hill, Sips, Tempkin, Toth isotherm models using a non-linear regression method.

## TABLE OF CONTENTS

---

---

	<b>Page No.</b>
<b>CANDIDATE'S DECLARATION</b>	<b>i</b>
<b>CERTIFICATE</b>	<b>i</b>
<b>ACKNOWLEDGEMENT</b>	<b>ii</b>
<b>ABSTRACT</b>	<b>iii</b>
<b>TABLE OF CONTENTS</b>	<b>iv</b>
<b>LIST OF FIGURES</b>	<b>vi</b>
<b>LIST OF TABLES</b>	<b>vii</b>

	<b>Page No.</b>
<b>CHAPTER 1: INTRODUCTION</b>	<b>1</b>
1.1    Bisphenol-A	2
1.2    Sources and uses of Bisphenol-A	3
1.3    Major issues of Bisphenol-A on human health	3
1.4    Characteristics of Bisphenol-A	4
1.5    Permissible limits of Bisphenol A	5
1.6    Objectives	6
<b>CHAPTER 2: LITERATURE REVIEW</b>	<b>7</b>
<b>CHAPTER 3: MATERIALS AND METHODS</b>	<b>13</b>
3.1    Adsorbent and adsorbate	13
3.2    Characterization of adsorbent	13
3.3    Analytical measurement	14
3.4    Experimental programme	14
3.5    Central composite design	15
<b>CHAPTER 4: RESULTS AND DISCUSSIONS</b>	<b>17</b>
4.1    Characterization of adsorbent	17
4.2    Experimental design and development of regression model	21
4.3    Fitting of second-order polynomial equation and statistical analysis	23
4.4    Combined effect of process variables	27

4.4.1	Effect of contact time and adsorbent dose	27
4.4.2	Effect of time of contact time and pH	28
4.4.3	Effect of pH and temperature	28
4.5	Optimization and model validation	30
4.6	Adsorption isotherm modelling	30
4.7	Determination of pseudo first and second order reaction from the experimental values	34
<b>CHAPTER 5: CONCLUSIONS</b>		37
5.1	Conclusions	37
<b>REFERENCES</b>		38

## LIST OF FIGURES

---

---

Figure	Title	Page No.
1.1	Structure of Bisphenol A	2
1.2	Synthesis of Bisphenol A	2
1.3	Reaction of Biphenol-A with diphenyl carbonate	3
1.4	(a) Effects of BPA found; (b) Effects of BPA yet to found	4
3.1	Calibration curve between concentration of BPA and Absorbance	14
4.1	FE-SEM image of Bagasse Fly Ash	18
4.2	EDAX analysis	18
4.3	Differential thermal gravimetric and differential thermal analysis of blank BFA	19
4.4	FTIR spectrum of Bagasee Fly Ash	20
4.5	XRD Analysis of BFA before and after adsorption of BPA	20
4.6	Removal % of Experimental vs Predicted	27
4.7	The effect of t and w on BPA removal pH =6 and T =30 °C	28
4.8	The effect of t and pH on BPA removal at w = 12.5g/l and T =30 °C	29
4.9	The effect of T and w on removal of BPA at t= 270min and w = 12.5g/l	29
4.10	Redlich-Peterson isotherm at different temperatures for BPA-BFA system, t= 0.5h, Co= 100 mg/l, w= 17.5 g/l.	31
4.11	Equilibrium adsorption isotherm at T= 283 K for BPA-BFA system, t= 0.5h, Co= 100 mg/l, w= 17.5 g/l.	33
4.12	Effect of contact time for the removal efficiency of BPA on BFA.	35
4.13	Effect of contact time on the adsorption capacity of BFA.	35
4.14	Weber Morrison model on the adsorption capacity of BFA.	36

## LIST OF TABLES

---

<b>Table No.</b>	<b>Title</b>	<b>Page No.</b>
Table 1.1	Physicochemical properties Bisphenol-A	5
Table 3.1	Process parameters and levels	16
Table 4.1	EDX analysis of BFA	19
Table 4.2	Actual and predicted values of responses for BPA-BFA system	22
Table 4.3	Adequacy of the models tested for BPA removal	23
Table 4.4	ANOVA of the 2 <sup>nd</sup> order polynomial equation for percentage of removal	25
Table 4.5	ANOVA of the second-order polynomial equation for $q_e$	26
Table 4.6	Model validation	30
Table 4.7	Fitting of experimental data for various isotherm models	32
Table 4.8	Kinetic parameters for the removal of BPA by BFA (t = 0.5 h, C <sub>0</sub> = 100 mg/l, w = 17.5 g/l, pH= 5.8)	34



### INTROUDCTION

---

In the past few years, the research on the endocrine disrupting chemicals (EDCs) has been increased with great interest in the area of environmental science and technology owing to the reason that these chemicals (EDCs) have various properties such as estrogenic, antiestrogenic or antiandrogenic and hence their existence leads to the potential damage the endocrine systems of human beings and wildlife (Beverly s.Rubin, 2011).

One of the ECDs such as Bisphenol A [2, 2-bis(4- hydroxyphenyl)propane] or BPA is of the important concern due its adverse potentiality to the human health(European Food Safety Authority, 2006) and environment. BPA is mainly used in the manufacturing of resins and polycarbonate plastics. There is chance of entering the BPA into water bodies while manufacturing plastic products, leaching from plastic products, disposed at the landfill sites and many routes. Thus it causes contaminating the various sources of water such as ground water, surface water, etc. and poses danger to fecundity and reproductive health of human beings and aquatic animals (Zhou et al 2012).

In view of this, the new environmental technologies are to be explored in order to remove the harmful BPA and subsequently the EDCs to save the environment from being contaminated.

Various disposal methods of BPA were proposed for the removal of BPA such as photo catalytic oxidation, biodegradation, and membrane. Of the many techniques, adsorption was considered as one of the simple and effective methods. Moreover the sorption processes are most economical and promising (Nakanishi et al 2002, Megha Syam Rauthula, Vimal Chandra Srivastava 2011) when compared to other methods.

Many natural adsorbents were used for the removal of pollutants from the waste water like chitosan, bark, wood chips, sugarcane, peat, bagasse, rice husks, straw and activated bamboo, etc. (Zhou et al. 2012, Srivastava et al 2005).

The advantage of using the natural biosorbents being widely available and renewable, several materials are made use of to remove the pollutants in the aqueous solutions. Also, the organic pollutants are being removed by using these adsorbents with ease.

## 1.1 Bisphenol-A

Phenolic compounds are produced in the chemical and processing industries in a great extent and are profusely present in the environment. Their presence is determined in rivers, effluents and soils. Among the phenolic compounds, Bisphenol-A is has drawn attention to the researchers due to its adverse effect on human helath (DNP et al 2010).

BPA was first synthesized in 1905. It is manufactured by reaction of phenol with acetone using acid catalyst under specified conditions. Bisphenol-A is a fairly soluble in water and it dissociates in an alkaline environment. Figure 1.1 shows the structure of BPA and figure 1.2 shows the production of BPA (Prokop et al 2004).

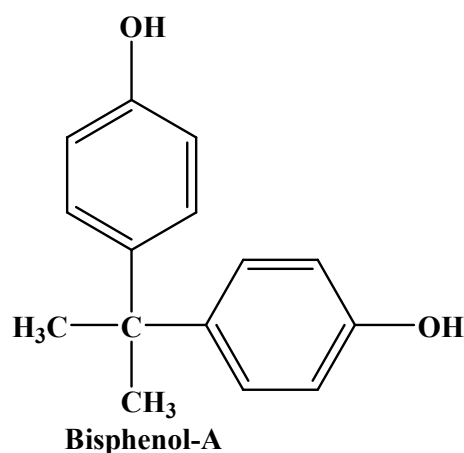


Figure 1.1: Structure of Bisphenol A

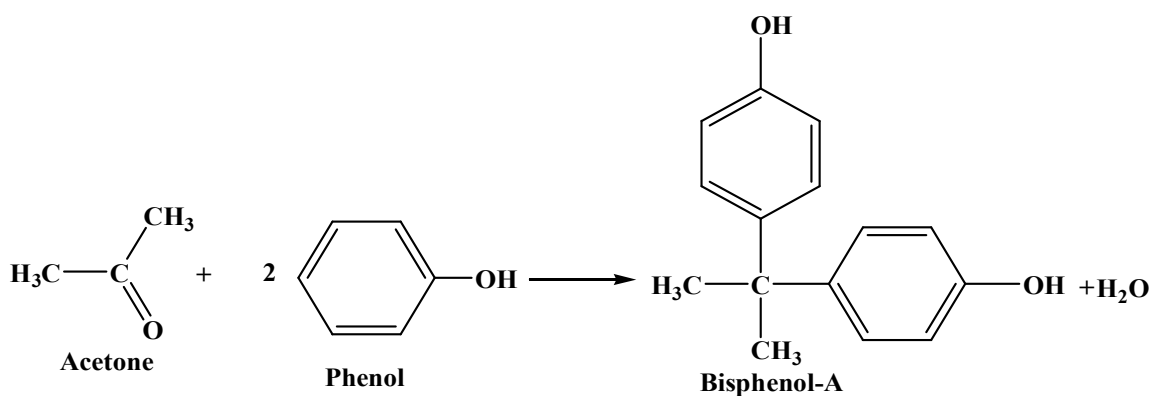
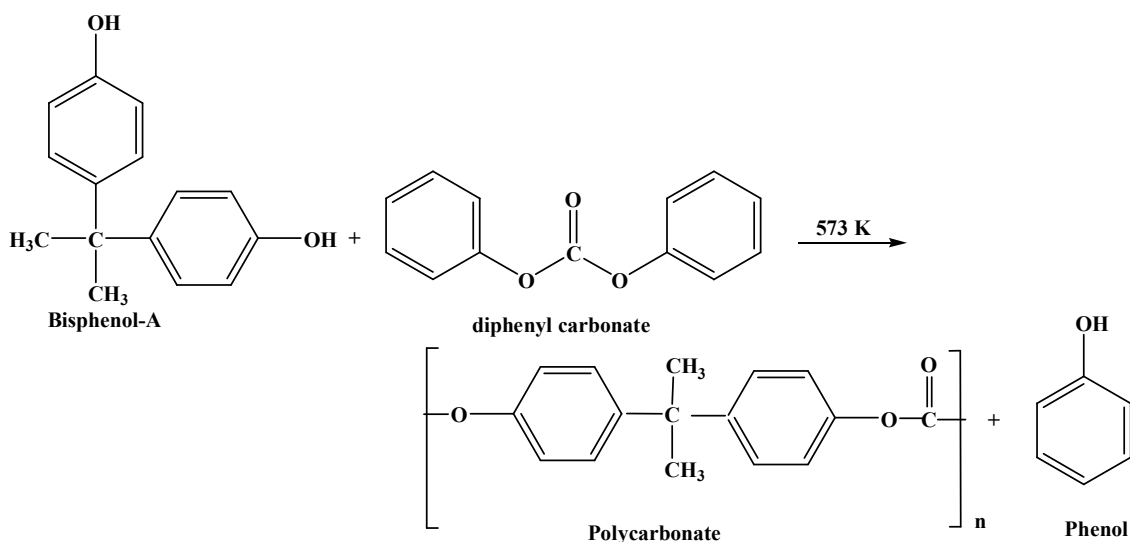


Figure 1.2: Synthesis of Bisphenol A

The scheme below shows the process of synthesis of polycarbonate resins. Figure 1.3 shows the process of synthesis of polycarbonate resins.



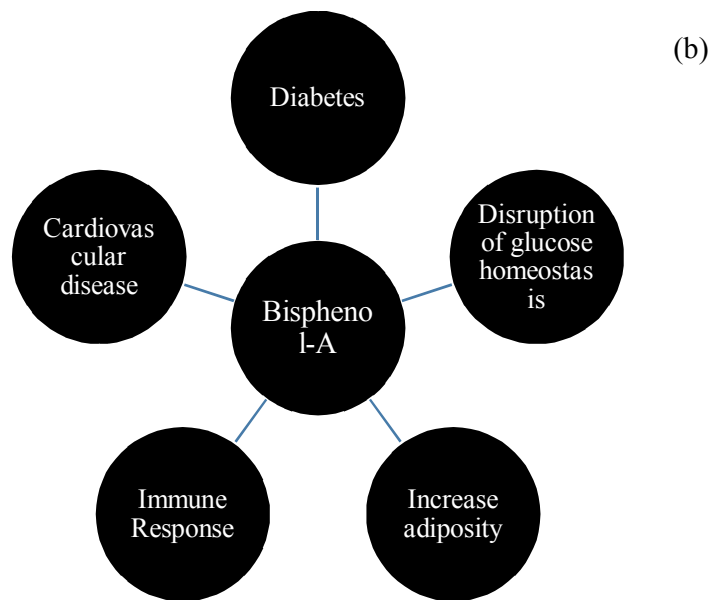
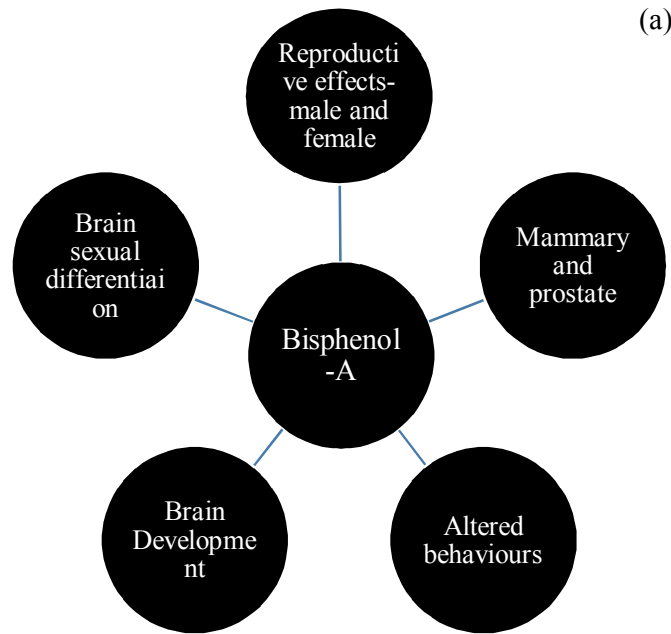
**Figure 1.3: Reaction of Bisphenol-A with diphenyl carbonate**

### 1.2 Sources and uses of Bisphenol-A

BPA is used in many applications such as antioxidant for glues, manufacturing of polycarbonate, epoxy, unsaturated polyester, and polysulfone resins. So the main sources of BPA are polymer industries. BPA entered into the surroundings due to the leaching of polycarbonate and epoxy resins (Tsai et al. 2006).

### 1.3 Major issues of Bisphenol-A on human health

EDCs have various properties such as estrogenic, antiestrogenic or antiandrogenic and hence their existence leads to the potential damage the endocrine systems of human beings and wildlife. In the figure 1.4 the issues of Bisphenol-A exposure on human beings and wild life and were given. The researches continue on the exposure of Bisphenol-A, and in the fig 1.5 the effects which are concerned are presented (Beverly S. Rubin 2011).



**Figure 1.4: (a) Effects of BPA found; (b) Effects of BPA yet to be found**

#### **1.4 Characteristics of Bisphenol-A**

For many years BPA was considered as neutral to human health. Since 1990 the researchers concentrated on the effects of BPA exposure after its detection in the natural environment, in potable water, and in food products. In 1996 the EU commission declared

BPA is a harmful to human health. Bisphenol A has been showed estrogenic activity even at concentrations below  $1 \text{ ngL}^{-1}$ .

**Table 1.1: Physicochemical Properties Bisphenol-A**

Molecular formula	$\text{C}_{15}\text{H}_{16}\text{O}_2$
Molar mass	$228.29 \text{ g mol}^{-1}$
Appearance	White solid
Melting point	$158\text{-}159^{\circ}\text{C}$
Boiling point	$220^{\circ}\text{C}$
Solubility in water	$300 \text{ mgL}^{-1}$
Acid dissociation constant	9.60 – 10.2
Dipole moment	0.71, 1.411

### **1.5 Permissible limits of Bisphenol A**

The central pollution control Board of India declared BPA as toxic compound. The Plastic Materials and Articles in Contact with Food (England) Regulations 2009 given permission to the manufacturing industries such that the migration of Bisphenol-A into food products should be less than  $0.6 \text{ mg/kg}$ . The European Commission and the Food Standard Agency of United Kingdom fixed NOAEL (no observed adverse effect level) is  $5 \text{ mg/kg bw/day}$ .

## 1.6 Objectives

1. To characterize the Bagasse Fly Ash (BFA) before and after adsorption of Bisphenol-A (BPA) by using FTIR, BET Surface Area, SEM, XRD and TGA and Proximate Analysis.
2. To optimize the process variables such as pH, adsorbent dose, concentration, contact time and temperature for the adsorption of BPA onto BFA using response surface methodology based central composite technique.
3. To study the equilibrium data for removal efficiency of the adsorbent using Freundlich adsorption isotherm, Langmuir adsorption, Redlich-Peterson, Hill, Sips, Tempkin, Toth isotherm models using a non linear regression method.
4. To study the adsorption kinetics of BPA-BFA system by using various models such as pseudo first order, pseudo second order and intra particle diffusion model.

## CHAPTER-2

### LITERATURE REVIEW

---

Many natural adsorbents and polymeric adsorbents were used for the removal of BPA from the waste water like chitosan, bark, wood chips, sugarcane, peat, bagasse, rice husks, straw and activated bamboo, polysulphone etc. in this chapter the adsorption studies of various researchers for the removal of BPA using different adsorbents were presented.

**Nakanishi et al. (2002)** presented an application for the removal of Bisphenol-A using carbonaceous adsorbents produced from woodchips an organic by-product. The carbonization of wood chips is done at temperatures ranging between 873K to 1073K. With the increase in carbonization temperature it has been found that there is an increase in iodine adsorption capacity of the carbonaceous materials. The carbonaceous material produced from carbonization of Sugi and Honoki at a temperature of 1073K shows higher adsorbing capacity when compared to that of activated carbon. The Freundlich constant,  $1/N$ , for the carbonaceous materials produced at 1073K from Sugi or Hinoki was similar to that of the activated carbon while the constant K follows in ascending order of activated carbon, Sugi sawdust, Sugi chips and Hinoki sawdust. This shows that carbonaceous materials can be used efficiently to remove Bisphenol-A.

**Yoon et al. (2003)** studied the adsorption of Bisphenol-A on six powdered activated carbons (PAC). The adsorption studies indicated that Bisphenol-A compound was adsorbed by PAC, but the amount removed ranges from 31% to >99% but it depended widely on dosage/type of PAC and absence /presence of naturally occurring organic matter. Studies showed that amount of Bisphenol-A removed increases with increase in PAC dose & time of contact. Freundlich isotherm parameters were fit to the experimental data. This study confirms that PAC can be used for >99% removal of treatment of water containing Bisphenol-A with concentration higher than 500 ng/l.

**Choi et al. (2005)** deals with the granular activated carbon (GAC) adsorption of Bisphenol-A. This study found that GAC adsorption was effective in removal of Bisphenol-A with high Kow value. Bisphenol-A was adsorbed on all the carbons, with

carbons based on coal being the most effective one on account of its larger pore volume. The year of operation of adsorbent effect the adsorption capacity and its reduction in adsorption depends on type of carbon and year of operation. With the increase in year of operation there is a decrease in pore volume which reduces adsorption capacity. Surface charge also plays a significant role due to electrical interaction between adsorbate and adsorbent.

**Tsai et al. (2006)** examined the removal of Bisphenol-A from aqueous solution onto 4 minerals & two activated carbons which are coal-based and coconut-based virgins. The results show that activated carbons on account of their low surface polarity and high surface area are better adsorbents when compared to mineral adsorbents. Even though the mineral adsorbents have distinct pore properties their adsorption capacities are almost same as a result of weak attraction between hydrophobic Bisphenol-A and negatively charged mineral surface. The adsorption of Bisphenol-A on activated carbon follows pseudo-2<sup>nd</sup> order reaction which shows that the reaction kinetics depends on initial concentration and pH of adsorbate. The reaction kinetics follows pseudo 2<sup>nd</sup> order model on the activated carbon adsorption and the kinetic parameters were effected by pH, initial concentration of adsorbate, dosage and particle size of adsorbent. Freundlich model was well fitted for the isotherm data when compared to Langmuir model.

**Tsai et al. (2006)** studied the adsorption of Bisphenol-A using a hydrophobic zeolite at 25 °C using batch adsorption process and using Langmuir, Freundlich and Redlich-Peterson isotherms. N<sub>2</sub> adsorption–desorption isotherms are used to determine properties of pores of adsorbent which reveals a super microporous structure with fewer mesopores. Due to high correlation coefficients this adsorption process could be well explained using kinetic model. The effect of size of the particle of adsorbent (< 0.3 mm) doesn't have considerable effect on adsorption process. The adsorption process varies with dosage of adsorbent as well as initial concentration of bisphenol-A. The affect of pH on adsorption capacity is pronounced only at basic pH values which may be due to electrostatic interactions arising out of deprotonisation of bisphenol. It is found that rate constant decreases with increase in initial concentration of adsorbent. This adsorption process can be best fitted using a three parameter based Redlich–Peterson model.



**Zeng et al. (2006)** deals with the adsorption of BPA on sediments collected from Xiangjiang River in south central china. The experiments reveal that rapid adsorption rather than slow adsorption plays a significant role in adsorption process. Owing to the complexities of sediment components Freundlich model best describes this adsorption process. The reason for nonlinear adsorption and desorption hysteresis was due to the presence of black carbon and organic matters present in the sediment. The process is an exothermic reaction propounded by the fact that the molar formation enthalpy is low and negative which shows that it is physical adsorption driven by enthalpy. The quantity of BPA adsorbed rose with increase in iron concentration and decreases with rise in sediment concentration and also with increase in pH value.

**Liu et al. (2009)** studied about the adsorption of Bisphenol-A on two carbons W20 and F20 which are modified with nitric acid and treated thermally under flow of nitrogen. The results indicate a pseudo 2<sup>nd</sup> order kinetic model and thermally modified sample of W20 tends to have more adsorption capacity (432.34 mg/g) than its non-thermally modified counterpart (382.12 mg/g). Adsorption of Bisphenol-A mainly depends on surface charge density of carbons and presence of acidic oxygen containing groups. Adsorption decreases with rise in temperature from 288K to 318K & changed nominally when pH varied in the range 5 to 9. At pH 11 due to the intense repulsive electrostatic interaction at a basic solution, the carbons show weakest adsorption capacity. The adsorption capacity of W20 and W20N initially decreases with increase in ionic strength as active sites were covered by these ions. But with the increase in ionic strength salting out effect and screening effect of surface charge takes place which enhances the adsorption capacity.

**Cao et al. (2009)** used Polyethersulfone (PES)–organophilic montmorillonite (OMMT) hybrid particles, made by using a liquid–liquid phase separation method for the adsorption of BPA from a solution. When the OMMT were embedded into particles, the increase in adsorbed amounts BPA on PES was observed. A Scanning electron microscope is used to determine its structure. The experimental data of BPA adsorption were decently fitted with Langmuir equations. The Kinetic studies provided that the kinetics agrees with the pseudo 2<sup>nd</sup> order model and the pore diffusion process is involved in adsorption of BPA on the PES–OMMT particles. The rate limiting step is thought to be intraparticle

mass transfer diffusion. The adsorbent can be reused as adsorbed BPA can be removed using Ethanol. These hybrid particles can be applied in various environmental projects as the size and chemical structure OMMT particles can be modified to remove molecules of various sizes.

**Dong et al. (2010)** studied the Bisphenol-A using Zeolite synthesized from coal fly ash (ZFA) was modified with surfactant hexadecyltrimethylammonium (HDTMA) were conducted. Characterization of adsorbents was done to obtain total and external cation exchange capacity, surface area and its chemical and mineralogical composition. It has been concluded from the results that SMZFA showed a significant increase in adsorption capacity when compared to ZFA which shows no affinity. The adsorption of BPA increased with increase in BET area, Amount of loaded HDTMA and also with increase of pH at alkaline pH levels. The adsorption also increased slightly at low temperature with introduction of ionic salt NaCl. With a simultaneous affinity towards inorganic cation and oxyanion and a higher adsorption capacity makes SMZFA a suitable adsorbent for water purification treatment.

**Hua et al. (2010)** investigated about the adsorption of bisphenol on polysulphone membrane. Adsorption ability of BPA on membranes is depending on the material, which has the best adsorption rate by polysulphone. The presence of calcium cation caused negligible shielding effect on negative charge of the membrane. The adsorption of BPA was influenced by pH and it declined sharply when the solution pKa value is exceeded by its pH value. Due to competitive adsorption which occurs due to the presence of natural organic matter there is decrease in retention of BPA on the membrane. Physical adsorption in the form of hydrophobic adsorption and chemical interaction in the form of Hydrogen bonding has been reported.

**Kim et al. (2011)** presented a work on the using organic-inorganic hybrid mesoporous material (Ph-MS) as adsorbent for selective adsorption of Bisphenol-A. Ph-MS, act as a good adsorbent for BPA removal on basis of its pore size and surface area and suitable textural properties. Using isotherm data and Langmuir model the adsorption capacities of adsorbents were calculated. The rate of adsorption of BPA on Ph-MS is swifter when compared to powdered activated carbon and the adsorption data fitted with the pseudo 2<sup>nd</sup> order kinetic model. Ph-MS shows high affinity towards BPA and less

affinity towards Phenol, where as other organic adsorbents like PAC shows higher adsorption capacity for both the compounds. To increase the adsorption affinity and selectivity of BPA phenyl groups are introduced into pores of mesoporous silica. The Adsorption selectivity of Ph-MS was at least 5 times larger than that of PAC was observed. Being a selective adsorbent, Ph-MS can be used as a substitute to PAC to remove EDC's such as BPA from aqueous solutions.

**Fan et al. (2011)** evaluated the removal of phenol, Bisphenol-A and nonylphenol ethoxylates from aqueous solutions using porous resins as adsorbents. The adsorption isotherms were fitted by the Langmuir equation, and the adsorption capacity was affected by the properties of adsorbent like functional group and matrix, surface area, pore size, and phenolics properties like dissociation constant pKa, water solubility  $S_w$ , distribution coefficient  $K_{OW}$  and adsorption coefficient  $K_d$ . The mechanism of the adsorption affinity of BPA was discussed on basis of following interactions namely, p-p bonds, electrostatic interaction, hydrogen bonding and hydrophobic effect. The adsorption capacity of BPA on polymeric adsorbents is hydrophobic effect and p-p bonds dependent. The adsorption process of BPA and NPEO10 by polymeric adsorbents was found to be endothermic whereas for phenol it was exothermic.

**Pan et al. (2011)** investigated the adsorption of BPA a micro emulsion CTS/ $\gamma$ - $Fe_2O_3$ /FACs magnetic composite was successfully prepared by emulsion process and used as an adsorbent. The characterisation done to the composites and the results indicated they exhibited spherical morphology, thermal stability and magnetic property. The Langmuir isotherm model gives a better fit to the equilibrium data than the Freundlich model, and the kinetics were well described by the pseudo 2<sup>nd</sup> order equation. Furthermore the adsorbent could be regenerated and reused.

**Sui et al. (2011)** studied BPA adsorption on a CMK-3 (mesoporous carbon), prepared from hexagonal SBA-15 mesoporous silica and is compared with PAC. The CMK complex so prepared has a mesoporous structure with high specific surface area (920m<sup>2</sup>/g) and a pore size of 4.9 nm. The adsorption followed a pseudo 2<sup>nd</sup> order kinetic model and the kinetic constant was much higher than the adsorption of BPA on PAC. The isotherm fitted better with the Freundlich model than the Langmuir model. The adsorption capacity declined with increase of temperature from 10 to 40 °C and adsorption capacity

decreased as temperature rose from 10 to 40. For pH ranging from 3 to 9 there is no significant impact on adsorption capacity but from pH 9 - 13 the adsorption capacity decreases.

**Xiao et al. (2012)** Studied adsorption of BPA using acetyl aniline modified hyper-cross-linked polymeric adsorbent GQ-02. Infrared spectroscopy and surface area analysis were used to determine chemical structure and pore structure of the adsorbent. Results showed that the NDA-150, H103, NDA-88, NDA-99, and XAD-4 due to the presence cross-linked bridge of acetyl aniline on GQ-02 adsorption capacity of BPA onto GQ-02 was larger than that of the commercial resins. The adsorption capacity wasn't effected by pH until it was greater than 6.39. The adsorption isotherms could be correlated to the Langmuir equation. The adsorbent can be regenerated using 80% ethanol and 0.5M NaOH and so can be a viable source to adsorb BPA from water.

**Zhou et al. (2012)** examined the performance of adsorption of BPA using biosorbents such as sawdust, peat, bagasse and rice husk, from aqueous solutions. The parameters effecting it includes competitive adsorption, ionic strength sorbent dose, temperature, and, solution pH. The results implied that the adsorption capacity of natural adsorbents was less when compared to that of activated carbon. Among the natural sorbents investigated peat shows maximum potential which can be augmented to the level greater than that of activated carbon by using quaternary ammonium surfactant. The sorption is conducted in presence of phenol as the rise in sorbent dosage and ionic strength increases the adsorption capacity so BPA itself was preferred over Phenol. The sorption process was best fitted by pseudo 2nd order model.

**MATERIALS AND METHODS**

---

**3.1 Adsorbent and Adsorbate**

The Bisphenol-A as adsorbate and bagasse fly ash (BFA) as adsorbent was used for the BFA-BPA adsorption studies. The chemicals used in the adsorption studies were analytical reagent grade. Bisphenol-A provided by S.D Fine chemicals Pvt. Ltd., Mumbai, India. Required amount of Bisphenol-A taken accurately and added to distilled water for the preparation of known concentration of synthetic solution.

**3.2 Characterization of adsorbent**

The adsorbent used for the adsorption studies was BFA took from Uttam Sugar Mills Ltd, U.K., India. It was used without any pretreatment. The physicochemical characteristics of BFA were determined using standard methods. FTIR analysis of the adsorbent was carried out to determine the basic functional groups using Fourier Transform Infra red (FTIR, Nicolet 6700, USA) spectroscopy by applying KBr pellet technique in the spectral range of 4000 to 400 $\text{cm}^{-1}$ . X-ray optical phenomenon analysis of blank BFA was administered with Phillips diffraction unit using Cu as target, Ni as filter media & K radiation maintained at 1.542 °A, goniometer speed was maintained at 1°/min. It gives crystallinity of the sample. By using MAC bulk density meter, bulk density of BFA was found. The thermo gravimetric analysis (TGA, Perkin Elmer, Japan) of blank and loaded BFA is done in the range of 25° C to 1000 °C. TGA measures the amount and rate of change in the mass of a adsorbent as a function of temperature or time in a controlled atmosphere. From these measurements we can know about thermal stabilities of materials. BFA was characterized for specific surface area and pore size distribution using an ASAP 2010 Micromeritics instrument. N<sub>2</sub> sorption isotherm was used to measure the specific surface area and pore diameter, the brunauer-To determine the surface morphology of BFA Scanning electron microscopic (SEM) and EDX analysis were done with help of Field Emission Scanning Electron Microscope (Model SEM-501 Phillips, Holland). pH adjustments was carried out by HI 2211 pH/ORP meter and purchased from Hanna Instruments. Shaking was done in Orbital Shaking Incubator and purchased from Remi Instruments and isotherms studies were done study at 10 °C, 20 °C, 30 °C.

### 3.3 Analytical measurement

A double beam UV spectrophotometer was utilised to find out the absorbance of BPA at its characteristic wave length. A standard solution of the BFA was taken and the absorbance was found at different wavelengths to get a diagram of absorbance against wavelength. The maximum absorbance was observed at 276 nm ( $\lambda_{\max}$ ). at this wavelength the calibration curve was prepared between the absorbance and concentration of BPA. The calibration curve is shown in figure 3.1.

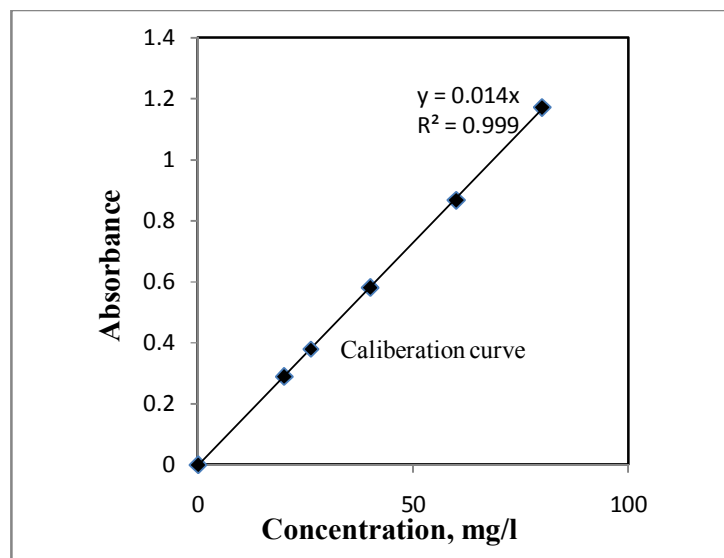


Figure 3.1: Calibration curve between concentration of BPA and Absorbance

### 3.4 Experimental programme

The experiments were conducted in batch mode in incubator-shaker to examine the effect of various process parameters on adsorption at different temperatures from 15 – 45<sup>0</sup>C with a fixed agitation speed of 150 rpm in 250 mL conical flask. The adsorption of BPA on BFA was executed for different intervals (60–480 min), initial solution pH (2–10), and BFA dose (2.5–22.5 g/L) in 100 mL BPA solution. H<sub>2</sub>SO<sub>4</sub> and NaOH are used for changing pH of BPA solution using pH meter. At the end of each batch study, samples were withdrawn, filtered and checked their absorbance.

The percentage removal of BPA was estimated by using relation:

$$\text{Percent removal} = \frac{(C_0 - C_e)100}{C_0} \quad (1)$$

Similarly for the equilibrium adsorption  $q_e$  (mg/g) was estimated as:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

Where,  $C_e$  is the equilibrium BPA concentration,  $V$  is the volume of the BPA solution (l) and  $w$  is the mass of BFA (g).

### 3.5 Central composite design

The statistical methods for optimizing process parameters are genetic algorithm, Taguchi, tabu search, simulated annealing heuristic search technique, iterative mathematical search technique and response surface methodology (RSM). RSM is a statistical tool, mainly used to obtain optimum conditions in minimum number of experiments. RSM includes Central Composite Design (CCD), Box–Behnken statistical experiment design (BBD), and two-level full factorial design (FFD) to predict the ultimate response.

Box and Wilson are the first introducers of CCD in the year 1951 and is one of the most used of RSM. For optimization first the response of statistically designed combinations is studied, and then the experimental data is fitted to the response function, after that the response of fitted model is predicted and its adequacy is checked. . To analyze the response  $R$  which depends on the input variables  $I_1, I_2, \dots, I_n$  the functional response can be defined as

$$R = f(I_1, I_2, I_3, \dots, I_n) + \varepsilon \quad (3)$$

Where  $f$  represents the response function and  $\varepsilon$  is the residual error which may differentiation terms. The coded values are used instead of process variables in Central Composite Design. The coded form and actual value can be related as:

$$\text{Coded value } i_i = \frac{(I_i - I_{avg})}{\Delta I} \quad (4)$$

Where  $I_i$  is actual value of the  $i$ th factor in the actual units,  $I_{avg}$  is the mean of the low and high values of the  $i$ th factor &  $\Delta I$  represent the step change. The second order polynomial (Eq. (5)) is employed to get the relationship between response and independent variables. the effect of various parameters was described by polynomial equation in terms of quadratic, linear & cross product terms.

$$R = a_0 + \sum_{i=1}^n a_i i_i + \sum_{i=1}^n a_{ii} i_i^2 + \sum_{i < j}^n \sum_j^n a_{ij} i_i i_j + \varepsilon \quad (5)$$

Here  $i$  is linear coefficient and  $j$  is quadratic coefficient.  $a_0, a_i, a_{ii}, a_{ij}$  are constant coefficient, linear coefficient, interactive coefficient and quadratic coefficient. Each parameter is investigated for soul and combined affect on adsorption process. For the 4

independent variables, the Eq. (5) can be modified in the form shown below. Here R is ultimate response and variables are taken in form coded values.

$$R = a_0 + a_1i_1 + a_2i_2 + a_3i_3 + a_4i_4 + a_{12}i_1i_2 + a_{13}i_1i_3 + a_{14}i_1i_4 + a_{23}i_2i_3 + a_{24}i_2i_4 + a_{34}i_3i_4 + a_{11}i_1^2 + a_{22}i_2^2 + a_{33}i_3^2 + a_{44}i_4^2 \quad (6)$$

CCD takes minimal number of experiments as the standard  $2^n$  factorial with its origin at the center,  $2n$  points fixed axially at a distance, and replicate tests at the center. CCD design comprise of a  $2n$  factorial,  $2n$  axial points and  $nc$  center points.

The four independent parameters initial solution pH (A), adsorbent dose (B), contact time (C), temperature (D) were studied in the present study using CCD (with the aid of Design Expert software). The observational variables and their levels are shown in Table 3.1. The developed model should be checked to know the sufficiency of model. To know the significant parameters and their soul and combined effect on the BPA adsorption process, ANOVA technique was used. From the numerical value of p-value and F-value, the Significance of process parameters was assured.

**Table 3.1: Process parameters and levels**

Variables	Factors	Levels				
		-2	-1	0	1	2
pH	A	2	4	6	8	10
Adsorbent dose (g/l)	B	2.5	7.5	12.5	17.5	22.5
Time (min)	C	60	165	270	375	480
Temp (°C)	D	15	22.5	30	37.5	45



**RESULTS AND DISCUSSIONS**

---

**4.1 Characterization of Adsorbent**

The morphology and composition of BFA are quite variable and complex that depends upon the source. Since the adsorption is surface mechanism, therefore, knowledge of surface characteristics is important.

BFA obtained from Sugar industry was fine powdered material. SEM studies showed that BFA is usually spherical along with the presence of some pits and hollow particles known as cenospheres (Fig.5.1). Sphericity is generally due to surface tension and carbonaceous material form irregular surfaces. These unburned carbon particles contribute in adsorption process. Agglomerate particles and irregular amorphous particles may be accounted for rapid cooling or inter-particle contact. EDX was carried out to give the elemental composition of the samples. Results from FESEM EDX are shown in Fig. 5.2 showing the peaks mainly for elements Ca, K, C, Si, Mg. The elemental compositions in weight % obtained from EDX analysis are also tabulated in Table 5.1.

Proximate analysis showed that the moisture content of BFA to be 6% but the volatility of the sample is about 7% , Ash content and fixed carbon were 21.3 and 65.7 % respectively. The BET SA method showed the changes in surface area of BFA. It was found that surface area 332 m<sup>2</sup>/g in BFA. High surface area indicates the ability of BFA to be used as adsorbent. Thermo gravimetric analysis (DT/TGA) is used to determine the behavior of sample with the increasing temperature. The loss of weight percent as function of heating rate is measured which provide valuable information about phenomena like phase transition due to vaporization, adsorption, desorption, decomposition, oxidation or loss of volatiles. From Fig. 5.3, it can be noted that weight loss in BFA is quite smooth. The peak does not necessarily mean instability of sample with the change in temperature. Initially the weight loss is due to moisture further loss is due to decomposition of calcium hydroxide and calcium carbonate (CH and CO loss). The Highest mass loss occurred at temperature 400-514 °C. At this temperature almost complete combustion of BFA took place. FTIR spectrum presented in Fig. 5.4 helps to detect the functional group in compound corresponding to the molecular bond present. Peak at 3441 cm<sup>-1</sup> is related to T-O (T = Al, Si) and at 665 cm<sup>-1</sup> is associated to deformation vibrations of T-O bond

internal. Quartz and mullite showed the IR spectrum at 1589, 1031.5-665.31 (double bond), bands 3434 and 2922  $\text{cm}^{-1}$  is due to silicate and kaolin clay presence.

XRD (Fig. 5.5) analysis helps in elucidating the degree of crystallinity of the sample. It is based on Bragg's law. The crystalline component in the sample generate high intensity peak where as broader peaks occurs in amorphous compound. More the number of high intensity peak, greater is the crystallinity of the sample. From Fig. 6.3, it has been observed that BFA is amorphous in nature. Major components present in sample are crystalline quartz ( $\text{SiO}_2$ ) at  $26.5^\circ$ , mullite ( $\text{Al}_{2.3}\text{Si}_{0.7}\text{O}_{4.85}$ ,  $\text{Al}_2(\text{Al}_{2.8}\text{Si}_{1.2})\text{O}_{9.6}$ ) at  $13.6^\circ$ ,  $51.3^\circ$  and  $62.1^\circ$ , d-alanine ( $\text{C}_3\text{H}_7\text{NO}_2$ ) at  $22.4^\circ$ , sillimanite ( $\text{Al}_2\text{SiO}_5$ ) at  $41.2^\circ$  and muscovite ( $\text{KA}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ ) at  $60.8^\circ$ .

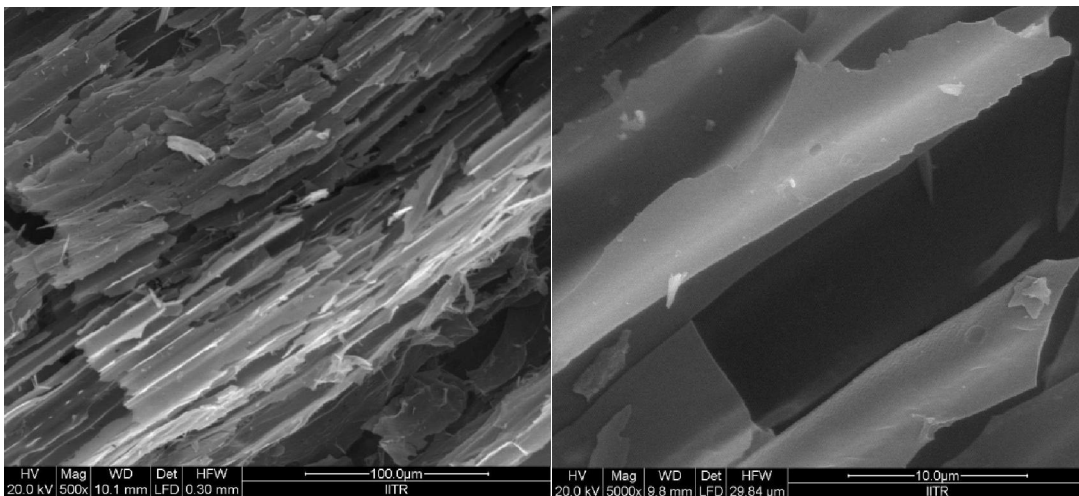


Figure 4.1: FE-SEM image of Bagasse Fly Ash

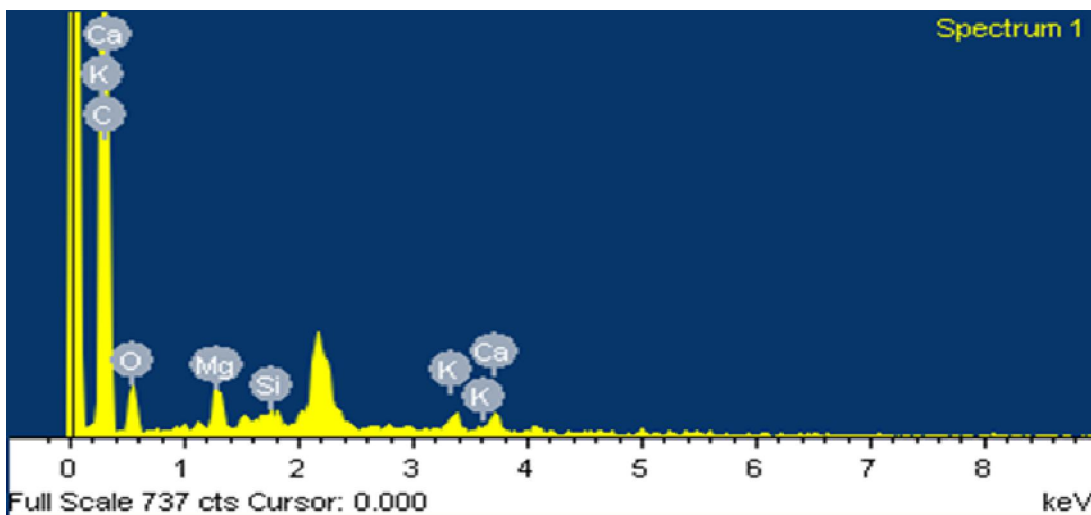
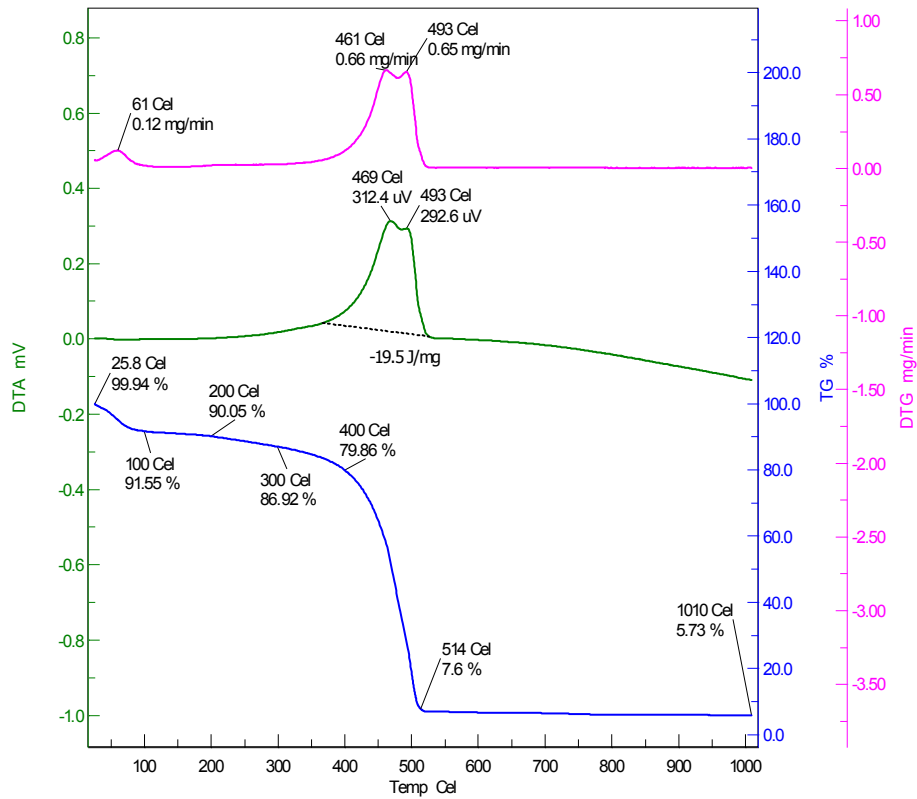


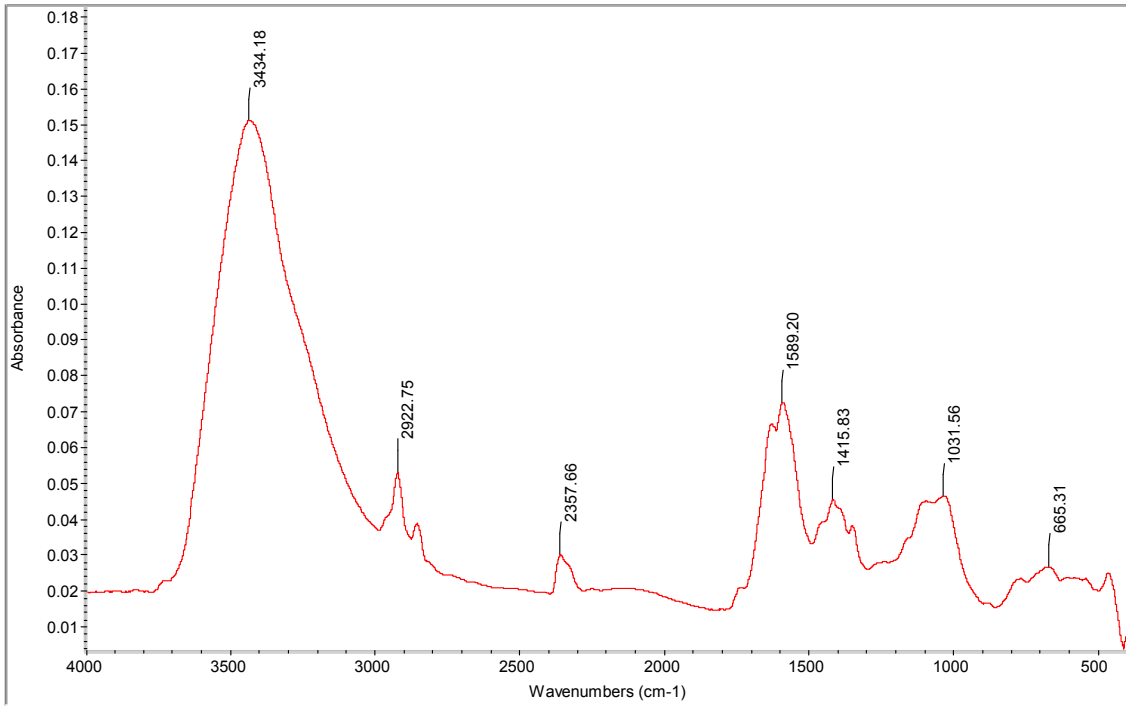
Figure 4.2: EDX analysis of Bagasse Fly Ash



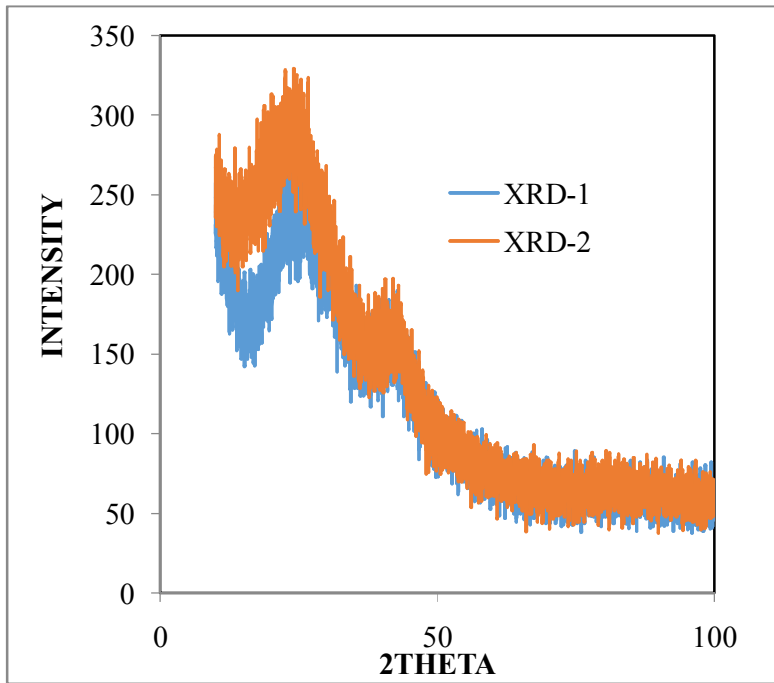
**Figure 4.3: Differential thermal gravimetric and differential thermal analysis of blank BFA**

**Table 4.1 EDX analysis of BFA**

Element	BFA
C K	77.12
O K	18.63
Mg K	1.76
Ca K	1.10
Si K	0.28
Totals	100.00



**Figure 4.4: FTIR spectrum of Bagasee Fly Ash**



**Figure 4.5: XRD Analysis of BFA before and after adsorption of BPA**

## 4.2 Experimental design and development of regression model

The process variables, which effect the removal percentage of Bisphenol-A by Bagasse Fly Ash are Time (t), Temperature (T), dose (w) & pH of BPA-BFA system. In the process of study the interactive effect of these parameters, experiments were conducted for various interactions of the physical variables using RSM based CCD. A  $2^4$  CCD model was produced. This model comprise of sixteen factorial points, eight axial points and six replicates at center. By using Design Expert software, experimental design was obtained which consists of 30 runs are presented in Table 4.2.

More or less of the main affects & low order interactions primarily affects a system with various independent parameters. In the present studies only two-way combinations were taken into account because it presumed that the lower order interactions greater when compared to higher order interactions. To get the regression equations several models (Interactive, quadratic, linear and cubic models) were fitted to the experimental data.

In the present study sequential model sum of squares and model summary statistics were done to verify the adequacy of models and the consequences are presented in Table 4.3. P value less than 0.01 was observed only for quadratic model in the Sequential model sum of squares (Table 4.3). Quadratic model was ideal for further analysis because Model summary statistics showed that the Adjusted  $R^2$  and the Predicted  $R^2$  values are highest for the quadratic model; here cubic model was not considered because it was aliased.

**Table 4.2: Actual and predicted values of responses for BPA-BFA system**

Run	pH	Adsorbent dose (g/l)	Time (min)	Temp (°C)	Removal (Y %)		q <sub>e</sub> (mg/g)	
	A	B	C	D	Experimental Y <sub>exp</sub>	Predicted Y <sub>pred</sub>	Experimental Y <sub>exp</sub>	Predicted Y <sub>pred</sub>
29	6	12.50	270	30.00	72.21	72.21	5.78	5.78
18	10	12.50	270	30.00	66.90	69.61	5.35	5.48
2	8	7.50	165	22.50	51.55	50.56	6.87	6.95
20	6	22.50	270	30.00	79.59	72.03	3.54	3.55
8	8	17.50	375	22.50	67.66	68.71	3.87	3.78
23	6	12.50	270	15.00	66.48	60.84	5.32	4.82
11	4	17.50	165	37.50	86.42	87.70	4.94	4.94
14	8	7.50	375	37.50	54.76	50.36	7.30	7.16
22	6	12.50	480	30.00	72.34	70.90	5.79	5.59
9	4	7.50	165	37.50	57.24	60.44	7.63	8.06
3	4	17.50	165	22.50	68.48	77.13	3.91	4.40
16	8	17.50	375	37.50	74.76	75.38	4.27	4.21
6	8	7.50	375	22.50	49.45	50.91	6.59	6.95
7	4	17.50	375	22.50	78.48	80.57	4.48	4.54
15	4	17.50	375	37.50	83.59	88.84	4.78	5.05
19	6	2.50	270	30.00	26.41	26.97	10.56	9.85
28	6	12.50	270	30.00	72.21	72.21	5.78	5.78
5	4	7.50	375	22.50	56.21	58.69	7.49	7.85
4	8	17.50	165	22.50	65.11	66.52	3.72	3.74
24	6	12.50	270	45.00	72.21	70.86	5.78	5.57
1	4	7.50	165	22.50	54.97	57.09	7.33	7.75
17	2	12.50	270	30.00	99.31	89.60	7.94	7.11
21	6	12.50	60	30.00	74.97	69.41	6.00	5.49
12	8	17.50	165	37.50	73.72	75.49	4.21	4.20
25	6	12.50	270	30.00	72.21	72.21	5.78	5.78
26	6	12.50	270	30.00	72.21	72.21	5.78	5.78
27	6	12.50	270	30.00	72.21	72.21	5.78	5.78
30	6	12.50	270	30.00	72.21	72.21	5.78	5.78
13	4	7.50	375	37.50	58.42	59.75	7.79	8.13
10	8	7.50	165	37.50	51.65	52.31	6.89	7.19

**Table 4.3: Adequacy of the models tested for BPA removal**

Source	Sum of squares	Df	Mean square	F value	Prob > F	Remark
Sequential model sum of squares						
Mean	1.365E+005	1	1.365E+005			
Linear	3798.50	4	949.63	14.98	< 0.0001	
2FI	81.44	6	13.57	0.17	.9814	
<u>Quadratic</u>	<u>1117.54</u>	<u>4</u>	<u>279.39</u>	<u>10.85</u>	<u>.00002</u>	<u>suggested</u>
Cubic	237.14	8	29.64	1.39	0.3381	Aliased
Residual	149.11	7	21.30			
Total	1.419E+005	30	4730.94			
Source	Std. Deviation	R <sup>2</sup>	Adjusted R <sup>2</sup>	Predicted R <sup>2</sup>	PRESS	remarks
Model summary statistics						
Linear	7.96	0.7056	0.6584	0.5523	2410.40	
2FI	8.90	0.7207	0.5737	0.3917	3274.74	
<u>Quadratic</u>	<u>5.07</u>	<u>0.9283</u>	<u>0.8613</u>	<u>0.5868</u>	<u>2224.79</u>	<u>Suggested</u>
Cubic	4.62	0.9723	0.8853	-2.9884	21472.23	Aliased

#### 4.3 Fitting of second-order polynomial equation and statistical analysis

The relationship conveyed by a 2<sup>nd</sup> order polynomial equation with combined terms was fitted between the actual results obtained on the basis of CCD model and the input variables. The net equation occurred in terms of actual (natural) factors are given below:

##### Removal Efficiency

$$\begin{aligned}
 &= 0.62046 - 5.57230 \cdot \text{pH} + 6.86150 \cdot w + 0.048565 \cdot t + 1.78644 \cdot T + 0.46232 \cdot \text{pH}^2 \\
 &- 0.22708 \cdot w^2 - 0.00004 \cdot 10^{-5} \cdot t^2 - 0.02828 \cdot T^2 - 0.10181 \cdot \text{pH} \cdot w - 0.00148 \cdot \text{pH} \cdot t \\
 &- 0.02670 \cdot \text{pH} \cdot T + 0.00087 \cdot w \cdot t + 0.04811 \cdot w \cdot T - 0.00072 \cdot t \cdot T
 \end{aligned}$$

(7)

$$\begin{aligned}
q_e = & 10.39594 - 0.56793 \cdot \text{pH} - 0.61544 \cdot w + 0.00394 \cdot t + 0.17154 \cdot T \\
& + 0.03241 \cdot \text{pH}^2 + 0.00920 \cdot w^2 - 0.000005 \cdot t^2 - 0.00258 \cdot T^2 + 0.00343 \cdot \text{pH} \cdot w \\
& - 0.00011 \cdot \text{pH} \cdot t - 0.00123 \cdot \text{pH} \cdot T + 0.00001 \cdot w \cdot t + 0.00149 \cdot w \cdot t \\
& + 0.00149 \cdot w \cdot T - 0.00001 \cdot t \cdot T
\end{aligned} \tag{8}$$

The net equations obtained in the form of coded factors is

$$\begin{aligned}
\text{Removal Efficiency} = & +72.21 - 5.00 \cdot A + 11.26 \cdot B + 0.37 \cdot C + 2.50 \cdot D \\
& + 1.85 \cdot A^2 - 5.68 \cdot B^2 - 0.51 \cdot C^2 - 1.59 \cdot D^2 - 1.02 \cdot A \cdot B \\
& - 0.31 \cdot A \cdot C - 0.40 \cdot A \cdot D + 0.46 \cdot B \cdot C + 1.80 \cdot B \cdot D \\
& - 0.57 \cdot C \cdot D
\end{aligned} \tag{9}$$

$$\begin{aligned}
q_e = & +5.78 - 0.41 \cdot A - 1.57 \cdot B + 0.027 \cdot C + 0.19 \cdot D \\
& + 0.13 \cdot A^2 + 0.23 \cdot B^2 - 0.059 \cdot C^2 - 0.15 \cdot D^2 \\
& + 0.034 \cdot A \cdot B - 0.025 \cdot A \cdot C - 0.018 \cdot A \cdot D \\
& + 0.009 \cdot B \cdot C + 0.056 \cdot B \cdot D - 0.008 \cdot C \cdot D
\end{aligned} \tag{10}$$

ANOVA is a statistical technique that divides the total variation in a set of data parts and used for testing the possibilities of variation of the data parts are related with particular sources. The implication of the ratio of mean square variation due to regression and mean square residual error was analyzed using ANOVA. The Analysis of Variance for the 2<sup>nd</sup> order equation is presented in Table 4.4 and Table 4.5. The ANOVA of the percentage removal of BPA implied that the equation well represented the actual relationship between the % removal of BPA and the significant variables. According to Analysis of variance (Table 4.4), the Fisher F values for all regressions were higher. The higher value of F indicates that maximum variation in the response can be explained by the regression equation. The associated p value is used to estimate whether F is large enough to indicate statistical significance. p values lower than 0.05 indicates that the model is statistically significant. The ANOVA solution for the BPA-BFA system shows F-value was 13.86, indicates the model is significant. The model gives coefficient of correlation  $R^2 = 0.9283$  and an adjusted- $R^2 = 0.8613$ , which is high and recommends a high correlation between the observed and the predicted values. The probability  $p(-0.0001)$  is less than 0.05 suggests that the model terms are significant at 95% of probability level. Any parameter or interaction of variables with  $p < 0.05$  are significant. The ANOVA table obtained from the response surface 2<sup>nd</sup> order model shows that pH, w, T,  $w^2$  lack of fit and the constant, whose value is +72.21 (in equation 9) are significant. The constant, which does not depend on any variables and interaction of variables



represent the mean removal of BPA from solution is 72.21%, and that this mean removal is does not depend on the variables set in the experiment.

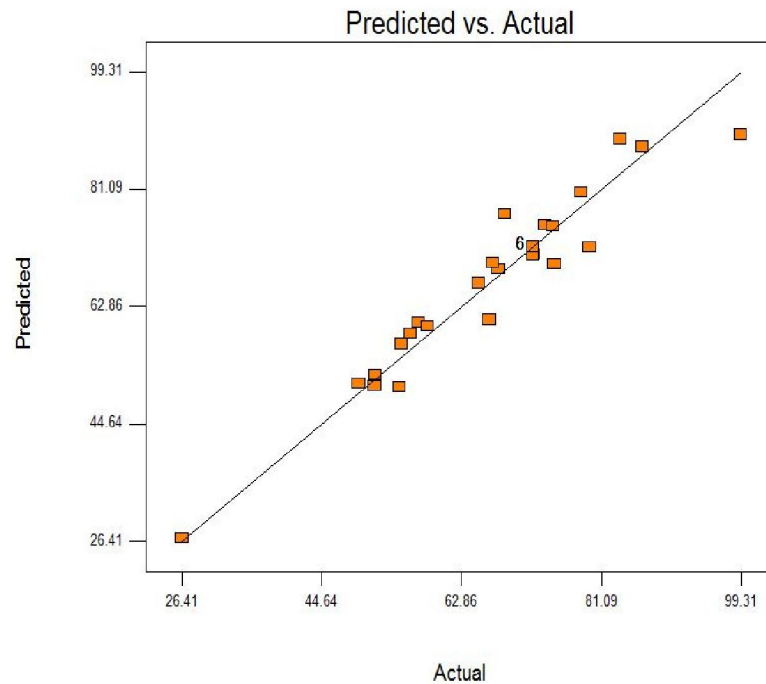
**Table 4.4: ANOVA of the 2<sup>nd</sup> order polynomial equation for percentage of removal**

Source	Coefficient Estimate	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Model		4997.49	14	356.96	13.86	< 0.0001	Highly significant
Intercept	72.21						
A	-5.00	599.70	1	599.70	23.29	0.0002	Significant
B	11.26	3044.93	1	3044.93	118.25	< 0.0001	Highly significant
C	0.37	3.32	1	3.32	0.13	0.7244	
D	2.50	150.55	1	150.55	5.85	0.0288	Low Significant
A2	1.85	93.80	1	93.80	3.64	0.0756	
B2	-4.68	883.97	1	883.97	34.33	< 0.0001	Highly significant
C2	-0.51	7.22	1	7.22	0.28	0.6041	
D2	-1.59	69.41	1	69.41	2.70	0.1214	
AB	-1.02	16.59	1	16.59	0.64	0.4348	
AC	-0.31	1.56	1	1.56	0.06	0.8091	
AD	-0.40	2.57	1	2.57	0.10	0.7565	
BC	0.46	3.36	1	3.36	0.13	0.7230	
BD	1.80	52.09	1	52.09	2.02	0.1754	
CD	-0.57	5.28	1	5.28	0.20	0.6572	
Residual		386.25	15	25.75			
Lack of Fit		386.25	10	38.62			
Pure Error		0.00	5	0.00			
Cor Total		5383.73	29				

**Table 4.5: ANOVA of the second-order polynomial equation for  $q_c$**

Source	Coefficient Estimate	Sum of Squares	DF	Mean square	F value	Prob > F	Remark
Model		67.330	14	4.810	24.090	< 0.0001	Highly significant
Intercept	5.78						
A	-0.41	4.020	1	4.020	20.120	0.0004	Significant
B	-1.57	59.44	1	59.44	297.780	< 0.0001	Highly Significant
C	0.027	0.018	1	0.018	0.089	0.7701	
D	0.19	0.830	1	0.830	4.130	0.0601	
A <sup>2</sup>	0.13	0.460	1	0.460	2.310	0.1494	
B <sup>2</sup>	0.23	1.450	1	1.450	7.280	0.0165	Low Significant
C <sup>2</sup>	-0.059	0.097	1	0.097	0.480	0.4972	
D <sup>2</sup>	-0.15	0.580	1	0.58	2.910	0.1086	
AB	0.034	0.019	1	0.019	0.095	0.7627	
AC	-0.025	0.009	1	0.009	0.048	0.8291	
AD	-0.018	0.005	1	0.005	0.027	0.8709	
BC	9.845E-003	0.001	1	0.001	0.007	0.9309	
BD	0.056	0.050	1	0.050	0.250	0.6233	
CD	-8.298E-003	0.001	1	0.001	0.005	0.9418	
Residual		2.990	15	0.200			
Lack of Fit		2.990	10	0.300			
Pure Error		0.000	5	0.000			
Cor Total		70.330	29				

Fig. 4.6 shows the relationship among the experimental and predicted values of BPA removal using BFA. The predicted values were obtained from the Eq. (7). Fairly moderate value of correlation coefficient R-squared (0.9283) was obtained among the experimental and predicted response due to coverage of broad range of process parameters in limited number of experiments and/or part of insignificant terms of Table 4.4.



**Figure 4.6: Removal % of Experimental vs Predicted**

#### 4.4 Combined effect of process variables

The affects of 4 process variables contact time, initial solution pH, adsorbent dose and temperature on BPA removal were studied with the help of 3-D response surface plots.

##### 4.4.1 Effect of contact time and adsorbent dose

The combined effect of BFA dose and time of contact on % removal of BPA using BFA is shown in Fig 4.7. From the plot it was noticed that %removal quickly with increasing time initially and reaches a constant value later. At the starting time of contact the % removal of BPA is fast and rapid due to the concentration variation of BPA is large in between surface of BFA and the solution. If the pores of BFA get saturated, the removal decreases slowly with time of contact and reached to constant value. The BFA dose has its effect on BPA removal, as dose of BFA increases the % removal of BPA was increased

due to the active sites, and overall surface area of BFA particles increased with increase in BFA dose.

#### 4.4.2 Effect of time of contact time and pH

The affect of time of contact and pH on removal of BPA by BFA by varying time from 1hr to 8hr and pH from 2 to 10 was shown in the Fig 4.8. With increase in initial solution pH the removal % was decreasing rapidly, with increasing contact time the BPA removal increases slowly. The highest %removal of BPA was observed at pH=2 is 90 at BFA dose 12.5g/l and temperature 30 °C.

#### 4.4.3 Effect of pH and temperature

The affect pH and temperature were studied in the range of temperature from 15-45 °C and pH from 2-10. The response surface plots were shown in Fig 4.9. The removal of BPA increases gradually with increasing in temperature whereas, the removal decreases with increase in pH. Generally adsorption is an exothermic process, so that one would be expected that % removal decreases with increasing in temperature of the system. But the present case contrasting to the general view because the diffusion controls the adsorption process. With raise in T the BPA ions mobility increases, slowing forces acting on ions decreases.

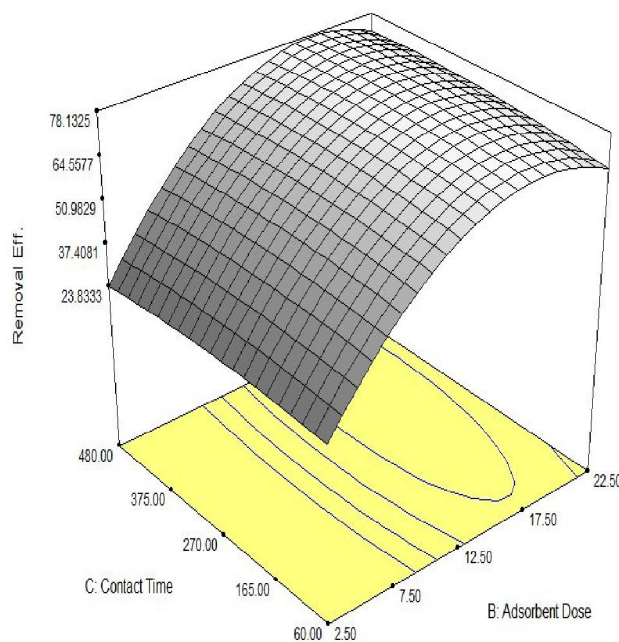
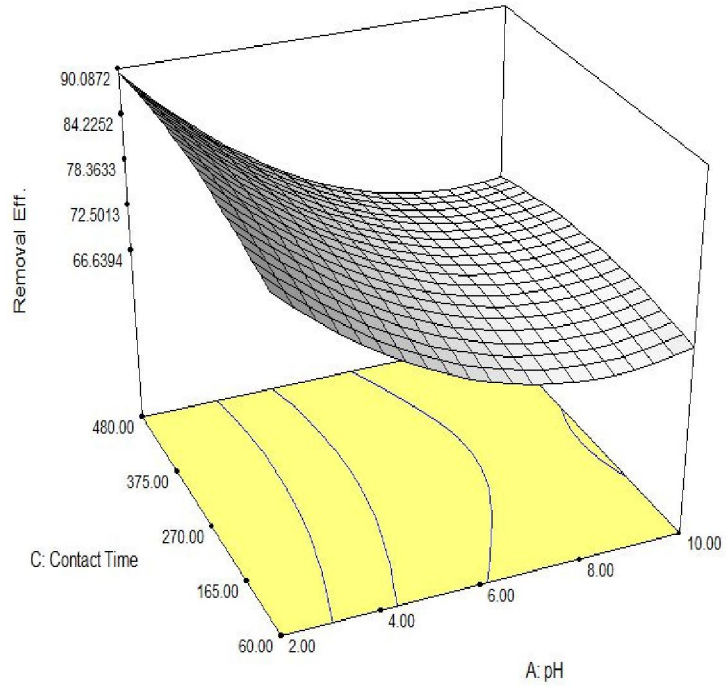
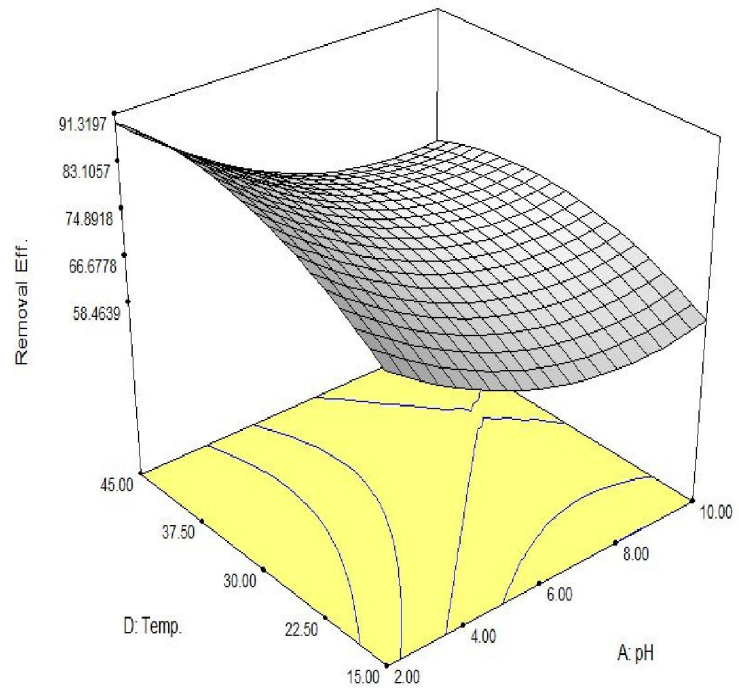


Figure 4.7: The effect of t and w on BPA removal pH =6 and T =30 °C



**Figure 4.8:** The effect of  $t$  and  $pH$  on BPA removal at  $w = 12.5\text{g/l}$  and  $T = 30^\circ\text{C}$



**Figure 4.9:** The effect of  $T$  and  $pH$  on removal of BPA at  $t = 270\text{min}$  and  $w = 12.5\text{g/l}$

#### 4.5 Optimization and model validation

It is important to determine the optimal condition to maximize Bisphenol-A removal using acquired mathematical model. The objective of the work is to adsorb maximum amount of Bisphenol-A with lowest amount of BFA. Table 4.6 summarizes the optimal level of different parameters found, after examining the response curves and Table 5.4. Table 4.6 indicates that at pH=5.8, w= 17.5 g/l, t= 270 min, T=40<sup>0</sup>C the predicted removal % was 82.32 for 100mg/l of BPA solution. This result was validated experimentally (85.30% BPA removal), which is close to the predicted value as shown in Table 4.6.

**Table 4.6: Model Validation**

Optimum level of process parameters	Predicted optimal value of removal %	Experimental value of removal %
pH = 5.8 adsorbent dose = 17.5 g/l contact time = 270 min temperature = 40 <sup>0</sup> C	81.32	85.30

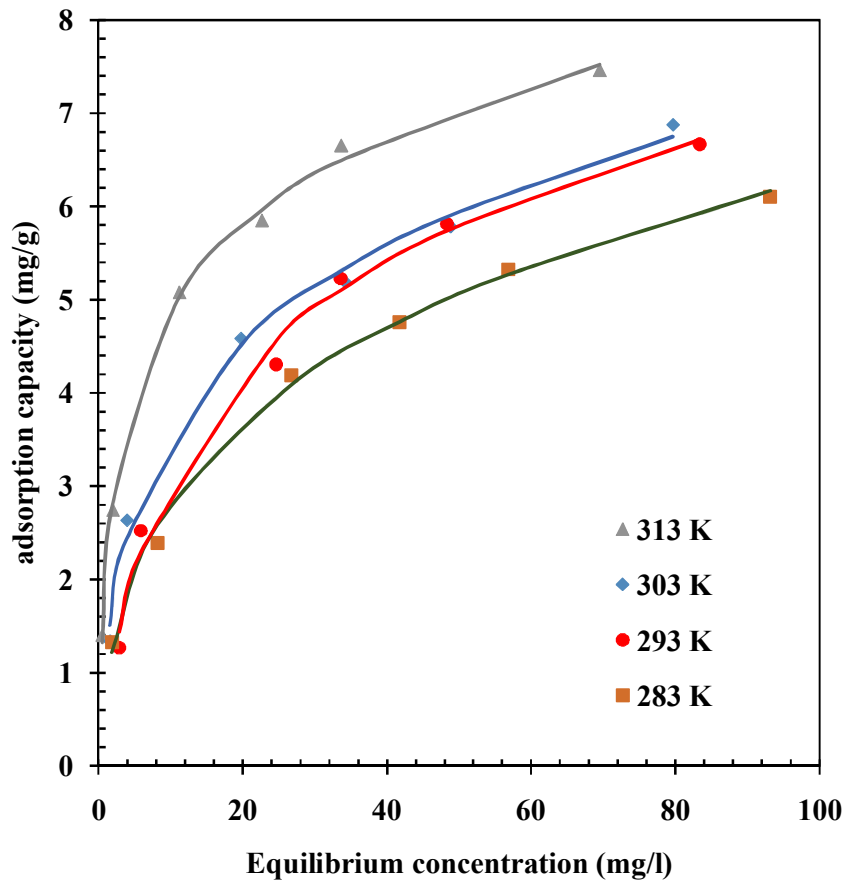
#### 4.6 Adsorption isotherm modelling

The adsorption isotherm studies were conducted at temperatures 10, 20, 30, 40<sup>0</sup>C. The equilibrium adsorption time was found to be 30 min. after the 30min the % removal of BPA fluctuating in the range 85 to 90. Adsorption capacity of BFA for BPA was increased with increase in temperature shows adsorption of BPA onto BFA is endothermic in nature and it also represents the diffusion controls the adsorption process. The increased in adsorption capacity was due to activation of pore sites of BFA at higher temperature and With raise in T the BPA ions mobility increases, slowing forces acting on ions decreases (Srivastava et al 2007). To optimize the design of BPA-BFA system, it is required to found the most proper correlation for the equilibrium curves. The adsorption isotherm draws the relationship among the quantity of adsorbate adsorbed on the adsorbent and the concentration of adsorbate in the liquid at equilibrium. Equilibrium isotherms for BPA-BFA system were studied by Langmuir, Freundlich, Redlich-Peterson, Hill, Sips, Tempkin, Toth isotherm models using a non linear regression method.

Fitting of experimental data for various isotherm models were presented in table 4.7. The R<sup>2</sup> values showed in table for the respective isotherms. Fig 4.11 shows adsorption isotherm of all studied models at 283K. By comparing the R<sup>2</sup> values the Hill isotherms showed lower values at all temperatures. For the Langmuir model the R<sup>2</sup> values increased with rise in temperature. The Redlich-Peterson, Sips isotherms are fitted for the isotherm

data at all temperatures. Langmuir isotherm was not fitted at any temperature. Freundlich isotherm was best fitted at only 293K. Toth isotherm was not fitted at 303K, Temkin isotherm not fitted at 293K.

The fig 5.10 shows the adsorption isotherms at various temperatures predicted by Redlich-Peterson model. From the fig it was observed that adsorption capacity increases with rise in temperature from 283K to 313K.



**Figure 4.10: Equilibrium adsorption isotherms at different temperatures for BPA-BFA system,  $t = 0.5\text{h}$ ,  $C_0 = 100\text{ mg/l}$ ,  $w = 17.5\text{ g/l}$ . Experimental data given by symbols and the line predicted by the Redlich-Peterson isotherm**

**Table 4.7: Fitting of experimental data for various isotherm models**

Isotherms	Parameters	BFA-Bisphenol- A system			
		Temperature (K)			
		283	293	303	313
<b>Langmuir</b> $q_e = \frac{Q_o b C_e}{1 + b C_e}$	$Q_o$	6.8529	6.7527	7.3133	7.6129
	b	0.1307	0.0677	0.2683	0.0668
	$R^2$	0.9629	0.9804	0.9724	0.9836
<b>Freundlich</b> $q_e = K_F C_e^{1/n}$	$K_F$	1.5227	1.1636	2.3254	1.1702
	1/n	0.3469	0.3724	0.2874	0.4046
	$R^2$	0.9850	0.9915	0.9759	0.9734
<b>Redlich-Peterson</b> $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	$a_R$	0.8677	0.8776	1.2223	0.2380
	$K_R$	2.1574	1.5711	4.4749	0.7841
	g	0.7629	0.7178	0.8245	0.8145
	$R^2$	0.9942	0.9960	0.9979	0.9921
<b>Hill</b> $q_e = \frac{Q_{sH} C_e^{nH}}{k_D + C_e^{nH}}$	$Q_{sH}$	150226	1000000	4000000	424.25
	$k_D$	78159	473358	884535	647.9
	N	0.8415	0.79	0.6182	1.144
	$R^2$	0.8971	0.9202	0.8765	0.8496
<b>Sips</b> $q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	$K_s$	1.436	0.9914	2.4885	0.7878
	$a_s$	0.1131	0.0808	0.2448	0.0802
	$\beta_s$	0.5262	0.5548	0.5702	0.7409
	$R^2$	0.9909	0.9978	0.9984	0.9914
<b>Toth</b> $q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	$K_T ()$	2.1891	1.4719	1.8939	2.5516
	1/t	0.7395	0.681	0.6743	0.7704
	$a_T$	1.4861	1.3104	-0.689	5.4681
	$R^2$	0.9951	0.9979	0.9230	0.9922
<b>Temkin</b> $q_e = \frac{RT}{b} \ln(K_T C_e)$ where, $\frac{RT}{b} = B_1$	$B_1$	1.3285	1.2332	1.2516	1.5794
	$K_T$	1.734	1.231	5.3092	0.7744
	$R^2$	0.9907	0.9748	0.9953	0.9924



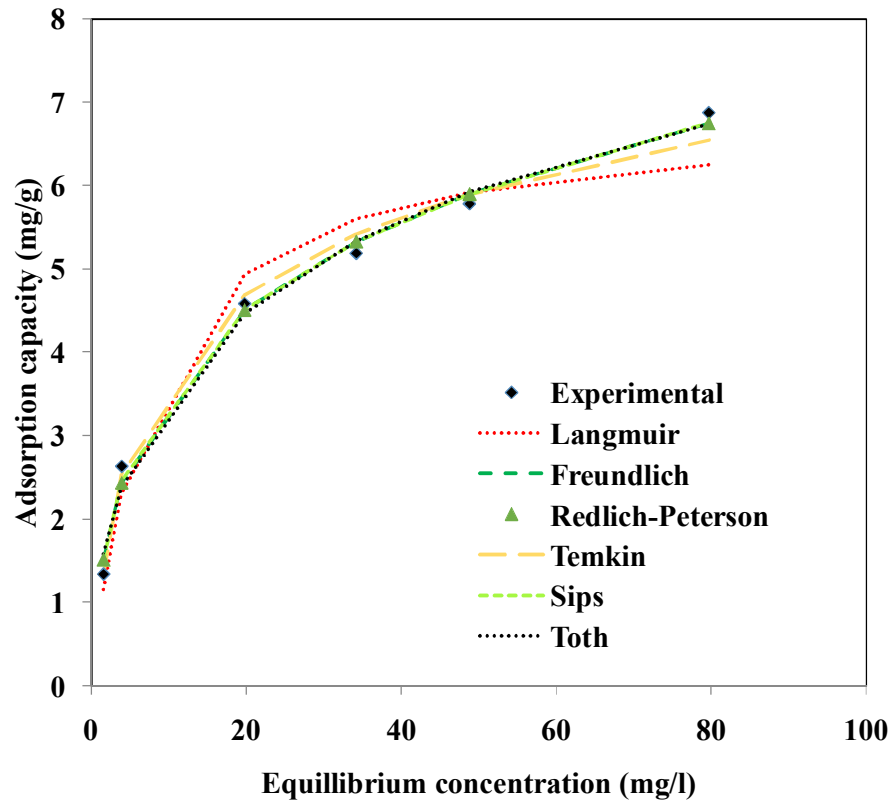


Figure 4.11: Equilibrium adsorption isotherm at  $T=283\text{K}$  for BPA-BFA system,  $t=0.5\text{h}$ ,  $C_0 = 100\text{ mg/l}$ ,  $w = 17.5\text{ g/l}$ . Experimental data given by symbols and the line predicted by the various models

#### 4.7 Determination of pseudo first and second order reaction from the experimental values

The kinetic parameters such as kinetic rate constants for pseudo first order, pseudo second order and Weber Morris model are determined by the kinetic studies at pH=5.8,  $C_0 = 100\text{mg/l}$ ,  $T= 40\text{ }^\circ\text{C}$  were presented in table 4.8. From the  $R^2$  values, pseudo first order kinetics is best fitted for the experimental data of BPA-BFA system and plot of pseudo first order model was shown in fig 4.13. The Weber Morris model was shown in fig 4.14 and the corresponding kinetic parameters are presented in the table 5.8. from the correlations coefficients it can be stated that intraparticle diffusion also plays vital role in adsorption BPA onto BFA.

**Table 4.8 Kinetic parameters for the removal of BPA by BFA ( $t = 0.5\text{ h}$ ,  $C_0 = 100\text{ mg/l}$ ,  $w = 17.5\text{ g/l}$ ,  $\text{pH} = 5.8$ )**

BPA-BFA							
Initial concentration = 100 mg/l							
Pseudo 1 <sup>st</sup> order				Pseudo 2 <sup>nd</sup> order			
$k_f$ (1/min)	$q_e$ (mg/g)	SSE	$R^2$ (non-linear)	$k_s$ (g/mg min)	$q_e$ (mg/g)	SSE	$R^2$ (non-linear)
0.2024	5.0731	0.1623	0.9930	0.0797	5.2692	0.7260	0.7824
Intra Particle Diffusion							
$k_{d1}$ (mg/g.min <sup>-0.5</sup> )	$I_1$ (mg/g)	SSE	$R^2$ (non-linear)	$k_{d2}$ (mg/g.min <sup>-0.5</sup> )	$I_2$ (mg/g)	SSE	$R^2$ (non-linear)
1.1958	0.5071	0.0040	0.9978	-0.0179	5.2068	0.0533	0.1815

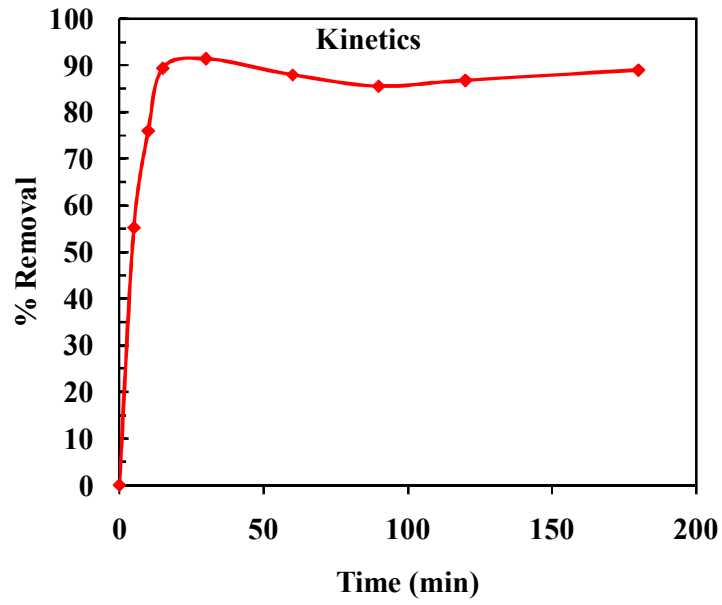


Figure 4.12: Effect of contact time on the removal efficiency of BPA on BFA.

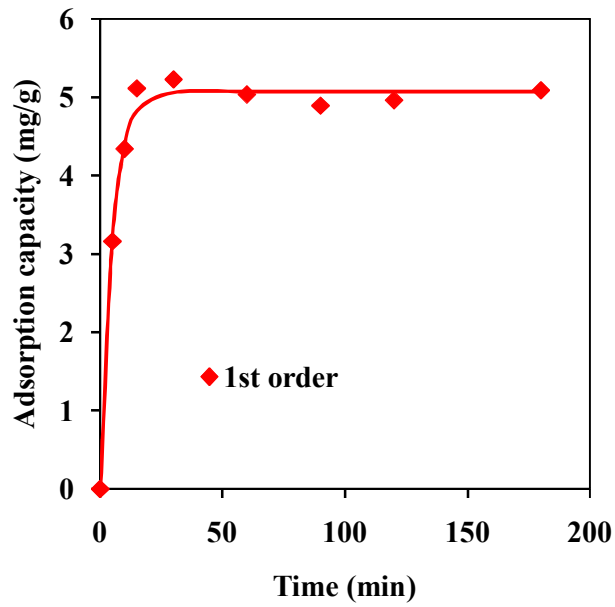
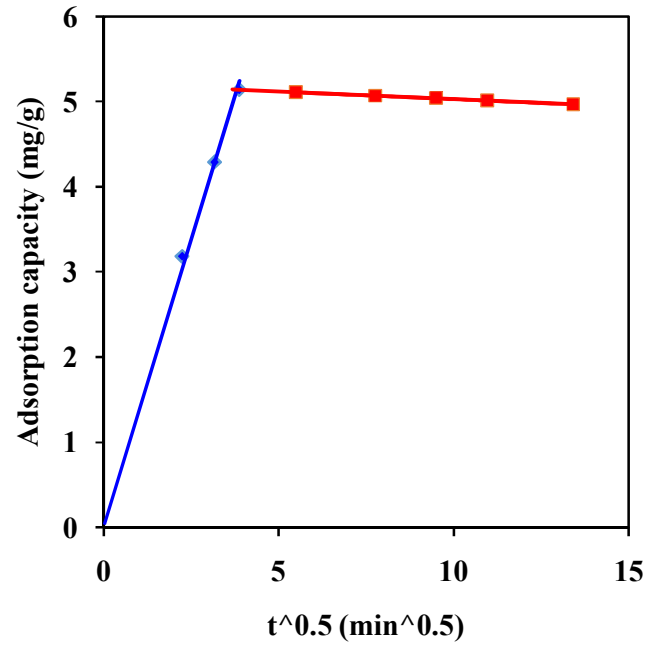


Figure 4.13 Effect of contact time on the adsorption capacity of BFA



**Figure 4.14: Weber Morrison model on the adsorption capacity of BFA**

### CONCLUSIONS

---

#### 5.1 Conclusions

The process variables such as BFA dose ( $w$ ), time of contact ( $t$ ), initial pH of BPA solution, temperature ( $T$ ) were varied at five levels to examine the effects on the adsorption of BPA onto BFA and the results were analyzed by Sequential model sum of squares and analysis of variance (ANOVA).

- The physicochemical properties and textural properties of BFA as follows:
  - BET surface area of BFA is  $332 \text{ m}^2/\text{g}$ .
  - XRD analysis showed that BFA is amorphous in nature.
  - Morphology of BFA exhibited fiber type pore structure.
  - FTIR of spectra of BFA reveal the presence of various types of function groups such as Si-OH, CO group, OH group etc.
  - TGA analysis revealed that BFA is an exothermic nature.
- More than 85 % removal of BPA was achieved at optimum conditions such as  $\text{pH} = 5.8$ ,  $w = 17.5 \text{ g/l}$ ,  $t = 270 \text{ min}$  and  $T = 40 \text{ }^\circ\text{C}$ .
- CCD technique is promising technique for the removal of BPA from aqueous solutions.
- The Redlich-Peterson, sips isotherm models were well fitted to BPA-BFA system.
- Kinetics studies showed that BPA-BFA system follows pseudo first order reaction.
- Intra particle diffusion model represents for this system and found to be endothermic nature.

**REFERENCES**

---

- Akio Nakanishi, Motoharu Tamai, Naohito Kawasaki, Takeo Nakamura and Seiki Tanada. (2002). “Adsorption Characteristics of Bisphenol A onto Carbonaceous Materials Produced from Wood Chips as Organic Waste”. *Journal of Colloid and Interface Science* 252, 393–396.
- Beverly S. Rubin (2011). “Bisphenol A: An endocrine disruptor with widespread exposure and multiple effects” *Journal of Steroid Biochemistry & Molecular Biology* 127, 27– 34.
- Cheryl Erler DNP, RN, Julie Novak DNSc, RN, CPNP, FAANP (2010). “Bisphenol A Exposure: Human Risk and Health Policy” *Journal of Pediatric Nursing* 25, 400–407.
- EU, Commission of the European Communities 90/128/EU, Off. J. Eur. Community, L75, 19 (1990).
- European Union commission 2006.
- Food standard agency United Kingdom 2011.
- Fuming Cao, Pengli Bai, Haocheng Li, Yunli Ma, Xiaopei Deng and Changsheng Zhao (2009). “Preparation of polyethersulfone–organophilic montmorillonite hybrid particles for the removal of bisphenol A”. *Journal of Hazardous Materials* 162, 791–798.
- Guangming Zeng, Chang Zhang, Guohe Huang, Jian Yu, Qin Wang, Jianbing Li, Beidou Xi and Hongliang Liu. (2006). “Adsorption behaviour of bisphenol A on sediments in Xiangjiang River, Central-south China”. *Chemosphere* 65, 1490–1499.
- Guifang Liu, Jun Ma, Xuchun Li and Qingdong Qin. (2009). “Adsorption of bisphenol A from aqueous solution onto activated carbons with different modification treatments”.
- Guqing Xiao, Lichun Fu and Aimin Li. (2012). “Enhanced adsorption of bisphenol A from water by acetylaniline modified hyper-cross-linked polymeric adsorbent: Effect of the cross-linked bridge”. *Chemical Engineering Journal* 191, 171– 176.
- Hongxiang Ou and Yongsheng Yan. (2011). “Synthesis of chitosan/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/fly-ash cenospheres composites for the fast removal of bisphenol A and 2, 4, 6-

trichlorophenol from aqueous solutions”. *Journal of Hazardous Materials* 190, 276–284.

<http://en.wikipedia.org/wiki/Bisphenol-A>

- I. Rykowska and W. Wasiak. (2006). “properties, threats, and methods of analysis of bisphenol A and its derivatives”. *Acta Chromatographica*, no. 16.
- I.B. Toledo, M.A. Ferro-Garcia, J. Rivera-Utrilla, C. Moreno-Castilla, F.J.V. Fernandez, *Environ. Sci. Technol.* 39 (2005) 6246
- Indra Deo Mall, Vimal Chandra Srivastava, Nitin Kumar Agarwal, Indra Mani Mishra (2005). “Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses”. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 264, 17–28.
- Jun Fan, Weiben Yang and Aimin Li. (2011). “Adsorption of phenol, bisphenol A and nonylphenol ethoxylates onto hypercrosslinked and aminated adsorbents”. *Reactive & Functional Polymers* 71, 994–1000.
- K.Y. Foo, B.H. Hameed (2010). “Insights into the modeling of adsorption isotherm systems” *Chemical Engineering Journal* 156, 2–10.
- Keun J. Choi, Sang G. Kim, Chang W. Kim and Seung H. Kim. (2005). “Effects of activated carbon types and service life on removal of endocrine disrupting chemicals: amitrol, nonylphenol, and bisphenol-A”. *Chemosphere* 58, 1535–1545.
- Manfred Clara, Birgit Strenn, Ernis Saracevic, Norbert Kreuzinger, (2004). “Adsorption of bisphenol-A, 17 $\beta$ -estradiol and 17 $\alpha$ -ethinylestradiol to sewage sludge”. *Chemosphere* 56, 843–851.
- Marcos Almeida Bezerra, Ricardo Erthal Santelli, Eliane Padua Oliveira, Leonardo Silveira Villar, Luciane Amelia Escalera (2008). “Response surface methodology (RSM) as a tool for optimization in analytical chemistry” *Talanta* 76, 965–977.
- Megha Syam Rauthula, Vimal Chandra Srivastava (2011). “Studies on adsorption/desorption of nitrobenzene and humic acid onto/from activated carbon” *Chemical Engineering Journal* 168, 35–43.
- Qian Sui, Jun Huang, Yousong Liu, Xiaofeng Chang, Guangbin Ji, Shubo Deng, Tao Xie and Gang Yu. (2011). “Rapid removal of bisphenol A on highly ordered mesoporous carbon”. *Journal of Environmental Sciences* 23(2), 177–182.

- Shailendra Bajpaia, S.K. Gupta, Apurba Dey, M.K. Jha, Vidushi Bajpai, Saurabh Joshi, Arvind Gupta (2012). "Application of Central Composite Design approach for removal of chromium (VI) from aqueous solution using weakly anionic resin: Modeling, optimization, and study of interactive variables" *Journal of Hazardous Materials* 227– 228, 436– 444.
- Venkat S. Mane, Indra Deo Mall, Vimal Chandra Srivastava (2007). "Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash" *Journal of Environmental Management* 84, 390–400.
- Vimal Chandra Srivastava, Indra Deo Mall, Indra Mani Mishra (2005). "Treatment of pulp and paper mill wastewaters with poly aluminium chloride and bagasse fly ash" *Colloids and Surfaces A: Physicochem. Eng. Aspects* 260, 17–28.
- Vimal Chandra Srivastava, Indra Deo Mall, Indra Mani Mishra (2007). "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, 267–278.
- Wen-Tien Tsai, Chi-Wei Lai and Ting-Yi Su. (2006). "Adsorption of bisphenol-A from aqueous solution onto minerals and carbon adsorbents". *Journal of Hazardous Materials* B134, 169–175.
- Wen-Tien Tsai, Hsin-Chieh Hsu, Ting-Yi Su, Keng-Yu Lin and Chien-Ming Lin.(2006). "Adsorption characteristics of Bisphenol-A in aqueous solutions onto hydrophobic zeolite". *Journal of Colloid and Interface Science* 299, 513–519.
- Wu Su-Hua, Dong Bing-zhi and Huang Yu. (2010). "Adsorption of bisphenol A by polysulphone membrane". *Desalination* 253, 22–29.
- Yanbo Zhou, Ping Lu, Jun Lu (2012). "Application of natural biosorbent and modified peat for bisphenol a removal from aqueous solutions" *Carbohydrate Polymers* 88, 502– 508.
- Yanbo Zhou, Ping Lu and Jun Lu. (2012). "Application of natural biosorbent and modified peat for bisphenol a removal from aqueous solutions". *Carbohydrate Polymers* 88, 502– 508.
- Yeomin Yoon, Paul Westerhoff, Shane A. Snyder and Mario Esparza. (2003). "HPLC-fluorescence detection and adsorption of bisphenol A, 17 $\beta$ -estradiol, and 17 $\alpha$ -ethynyl estradiol on powdered activated carbon". *Water Research* 37, 3530– 3537.



- Yi Dong, Deyi Wu, Xuechu Chen and Yan Lin. (2010). “Adsorption of bisphenol A from water by surfactant-modified zeolite”. *Journal of Colloid and Interface Science* 348, 585–590.
- Yong-Ho Kim, Byunghwan Lee, Kwang-Ho Choo and Sang-June Choi. (2011). “Selective adsorption of bisphenol A by organic–inorganic hybrid mesoporous silicas”. *Microporous and Mesoporous Materials* 138, 184–190.
- Zdenek Prokop, LibuseHankova and Karel Jerabek. (2004). “Bisphenol A synthesis – modeling of industrial reactor and catalyst deactivation”. *Reactive & Functional Polymers* 60, 77–83.