# Adsorptive removal of Bisphenol A by activated carbon and its regeneration study

SUBMITTED IN THE PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE AWARD OF THE DEGREE OF

**MASTERS OF SCIENCE**
**IN**
**BIOTECHNOLOGY**


SUBMITTED BY

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UNDER THE SUPERVISION OF


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July 2015

## Candidate's Declaration

I hereby certify that the work presented in the thesis entitled **"Adsorptive removal of Bisphenol A by activated carbon and its regeneration study "** in partial fulfillment of the requirement for the award of degree of **Masters in Biotechnology, Department of Biotechnology, Thapar University, Patiala**, is an authentic record of my own work during the period of six months from January 2015 to June 2015 under the supervision of **Dr. Moushumi Ghosh**, Professor, Department of Biotechnology and **Dr. Dipaloy Datta**, Assistant Professor, Department of Chemical Engineering, Thapar University, Patiala. The matter embodied in this report has not been submitted for the award of any other degree or certificate in this or any other university.

Place: Patiala

Date: 16/7/15

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(Shivani Jain)



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## Certificate

This is to certify that the thesis entitled "**Adsorptive removal of Bisphenol A by activated carbon and its regeneration study.**" submitted by **Ms. Shivani Jain** (301301013) in partial fulfillment of the requirements for the award of Degree of Masters of Science in Biotechnology to Thapar University, Patiala, Punjab is a record of student's own work carried out by her under my supervision and guidance. The report has not been submitted for the award of any other degree or certificate in this or any other University or Institute.

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# *Acknowledgement*

Apart from personal effort and steadfastness to work, this work would not have been accomplished without the help, support and guidance of large number of people that enabled me to submit my thesis in the present form.

First of all, I would like to express my sincere appreciation and deep gratitude to my supervisors, **Dr. Moushumi Ghosh,** Professor, Department of Biotechnology and **Dr. Dipaloy Datta,** Assistant Professor, Department of Chemical Engineering, for his enduring commitment to quality education and research. Their guidance, constant encouragement, constructive criticism and useful suggestions as a teacher and mentor were inspirational.

My sincere thanks to **Dr. Dinesh Goyal**, Head, Department of Biotechnolgy, and to Dr. Raj Kumar Gupta. Department of Chemical Engineering, Thapar University, Patiala, for allowing me to continue my dissertation work by providing necessary laboratory facilities to fulfill this work.

I am thankful for the help rendered by Mrs. Taranpreet Kaur, PhD Scholar, for her support, valuable suggestions, her guidance and input has been invaluable towards this thesis. I am also thankful to Mr. Pawandeep Singh, Research Scholar, for his timely help, support and valuable discussion throughout my project. Special thanks goes to my fellow member Ms. Kamalpreet Kaur and Ms. Gurjeet Kaur for her companionship and valuable suggestions. I am also thankful to Ms. Parul Gulati, Ms. Supriya Arora, Ms. Komal Sharma and Mr. Vivek Sharma who also helped throughout my project period.

Additionally, it would be failing my duty if I don’t acknowledge the kind cooperation of lab assistants, Mr. Babban, Mr. Chandan, Mr. Surinder for their assistance and provided regular technical support.

I owe thanks to my beloved parents for sending me to Thapar University, whose blessings and continuous encouragement have shown me tha path to achieve the goal. I pay my regards to almighty for his forever love and blessings. I am grateful for the knowledge learned

**Shivani Jain**

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# *List of Abbreviations*

| | |
|---|---|
| BHA | Butylated hydroxyanisole |
| BHC | Benzene hexa chloride |
| Bis-GMA | Bisphenol A diglycidylether methacrylate |
| BPA | Bis phenol A |
| CILE | Carbon Ionic Electrode |
| CTS | Chitosan |
| DES | Diethylstilbestrol |
| DDT | Dichloro diphenyl trichloroethane |
| EDC | Endocrine disrupting chemical |
| EPA | Environmental Protection Agency |
| g | Gram |
| GAC | Granular Activated Carbon |
| GR | Graphene |
| HCl | Hydrochloric Acid |
| HOMO | High Occupied Molecular Orbital |
| l | Liter |

| | |
|---|---|
| LUMO | Low Unoccupied Molecular Orbital |
| mg | Milli gram |
| ml | Milli liter |
| MPa | Mega Pascal |
| PAC | Powdered Activated Carbon |
| PVC | Polyvinyl chloride |
| SD | Standard Deviation |
| WWF | World Wide Fund for nature |

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## *Abstract*

Bisphenol A (BPA) is mostly manufactured for the plastics industry. It is an intermediate in the production of epoxy resins and polycarbonate plastics. The plastics are utilized in many food and drink packaging productions to line metal food cans, bottle tops and water supply pipes. BPA is an endocrine disruptor that has been shown to alter the structure or function(s) of the endocrine system and causes adverse effects in individuals, their offspring or populations. Effective technologies for BPA removal are limited; therefore the present study was aimed to study the adsorptive removal of bisphenol A (2-2-bis-4-hydroxypheniyl propane) from aqueous solution by using granular activated carbon. The contact time, adsorbent, BPA concentration, temperature and pH were optimized to obtain the maximum removal. A study of the adsorption kinetics, adsorption isotherm, effect of initial pH and effect of ionic strength were carried out. The adsorption capacity was determined by Langmuir, Freundlich and Temkin isotherms. The adsorption kinetics fit pseudo-second-order kinetic model well and the adsorption isotherms follow the Langmuir model. The maximum adsorption capacity (qe) of BPA by activated activated carbon obtained by Freundlich and Temkin isotherms was 241 mg/g and 257 mg/g . The adsorption kinetics and capacity of BPA over granular activated carbon generally depend on the average pore size and specific surface area (or pore volume) Finally, it can be suggested that granular activated carbon possessing high porosity and large pore size can be used as potential adsorbent to remove the harmful endocrine disrupting chemical BPA in contaminated water. Quantitative recovery of BPA was readily achieved by exploiting the reversibility of activated carbon sorption in BPA solutions. Thus, the study demonstrates the potential use of this inexpensive, easily accessible material as a superior sorbent medium for BPA in aqueous media

# 1. *Introduction*

Bisphenol A (BPA) is one of the highest volume chemicals produced worldwide because of its application and growing demand. It is an essential building block of polycarbonate plastics and epoxy resins and is used in the manufacture of a great variety of products including: consumer electronics, compact disks, food can linings, thermal paper, safety helmets, bullet resistant laminate, plastic windows, car parts, adhesives, protective coatings, powder paints, polycarbonate bottles and containers and the sheathing of electrical and electronic parts. BPA is also used in PVC production and processing, where it may be used as a reaction inhibitor, and as an anti-oxidant. Thus Bisphenol A has become ubiquitous in the environment because of its presence in a multitude of products.

It is estimated that the yearly release of BPA to the environment accounts for over six million tons globally (Lyons *et al*., 2000) Discharges to the environment occur not only from factories producing BPA, but also from numerous factories where BPA is incorporated into plastics or used in other products. Releases to the environment can also occur also from landfill sites. Reports have shown discharges to water are likely to be more persistent and more of a problem (Asakura *et al*., 2004). BPA has been shown to leach from food and beverage containers, and some dental sealants and composites under normal conditions of use. As BPA is widely used in both households and industry, it may present in raw sewage, waste water effluents and concentrated in sewage sludge. Studies have shown that BPA can leach from these and other products in contact with food and drink, and as a result, routine ingestion of BPA is presumed. This compound is also found in an enormous number of other products that we come into contact with daily.

BPA today is a global concern as from the recent studies it is been proven as an endocrine disrupting chemical (EDC) that when absorbed into the body either mimics or blocks hormones and disrupts the body's normal functions. Endocrine systems regulate a multitude of developmental, metabolic, and reproductive processes including embryonic development, gonad formation, sex differentiation, growth, and digestion. Endocrine-disrupting compounds may

affect these processes by either binding to or blocking hormone receptors, thereby triggering or preventing hormonal response (Akhtar *et al*., 1996)

Therefore, there is an urgent need to develop an effective technology to remove BPA. A potential way to mitigate the environmental risks of BPA is through implementing effective source control to reduce its entry into the environment. Various technologies, including biological (e.g., activated sludge process), chemical (e.g., advanced oxidation), and physical (e.g., adsorption and membrane filtration) processes, have been investigated to remove EDCs from contaminated drinking water, river water, and wastewater effluent. However, minimal research has been conducted to determine the ability of these processes to remove BPA, Adsorption has been applied for water and wastewater treatment as this process has a low initial cost, is easy to operate, is unlikely to produce secondary harmful substances. Studies on the removal of BPA from water and wastewater have been conducted using activated carbon (Xu *et al*., 2012) carbon nanotubes, grapheme (Xu *et al*., 2012), zeolites (Dong *et al*., 2010), membrane filtration and photo-catalytic degradation**.** Activated carbon is a common, well-established adsorbent The advantages of using activated carbon are its large porous surface area, controlled pore structure, thermo-stability, and low acid/base reaction, which improve the removal can therefore potentially be applied in the removal of BPA .

Thus the main objectives of this study are:-

1. Adsorptive removal of standard Bisphenol A from aqueous solution
2. Isotherm modeling of Bisphenol A adsorbent interaction
3. Detection and removal of Bisphenol A from waste water
4. Regeneration of adsorbent by extracting the BPA from the adsorbent

# 2. *Review of literature*

## 2.1 Background

BPA is a single hydrocarbon molecule that binds with other molecules to form polymers, such as polystyrene and polycarbonates (Le *et al*., 2008**).** BPA have been used for many applications, for example as a varnish on the inside of cans and as other packaging used for storage of food products, beverages, and pharmaceuticals (Staples *et al*., 1998). Polycarbonates have been commonly used for production of components of medical equipment (for dialysis and blood oxygenation), bottles for feeding infants, and kitchen dishes (Jobling *et al*., 1995).

## 2.2 Polymerization using BPA

2.2.1 Bisphenol A

$C_{15}H_{16}O_2$ is obtained by condensation of acetone and phenol, as illustrated in *Figure 2.1*, and according to the equation: $(CH_3)_2CO + 2\ C_6H_5OH \rightarrow$ $(CH_3)_2C(C_6H_4OH)_2 + H_2O$

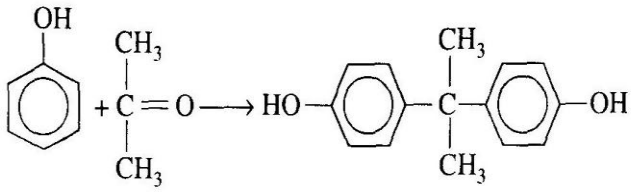


*Figure 2.1:-* Synthesis of BPA

The word "A" originates from "Acetone". One part of acetone reacts with two parts of phenol. Hence the name Bis-phenol A. The reaction is catalyzed by an acid such as HCl. Usually an excess of phenol is used in the condensation to assure complete reaction. The by-product of the condensation is water, and excess phenol that hasn't reacted (Wikipedia). The main polymers of Bisphenol A are epoxy resins and polycarbonates.

### 2.2.2 Epoxy resin

The raw materials for the epoxy resins are mostly epichlorohydrin ($C_3H_5ClO$) and Bisphenol A . Qualities of epoxy resins are: toughness, low shrinkage, high adhesion to many substrates and good alkali resistance. Epoxy resins may be prepared by reacting epichlorohydrin and a dihydric phenol. (Sinha, 26).

The general formula for epoxy resins is shown in *Figure 2.2*

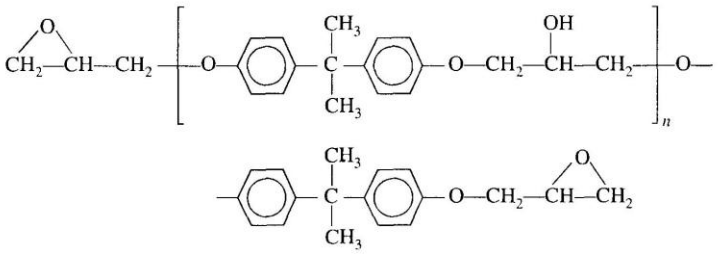

*Figure 2.2:* Synthesis of epoxy

Epoxy resins have a variety of uses such as surface coating (water tubes, canned food) adhesives, encapsulation, lamination and tooling. Non-Bisphenol A epoxies also exist, but these have the disadvantage of higher cost. (Sinha, 26).

### 2.2.3 Polycarbonate

Polycarbonates of Bisphenol A may be prepared by varying methods. The most common processes are phosgenation and ester-exchange. *Figure 2.3* depicts an ester-exchange process of making polycarbonate.

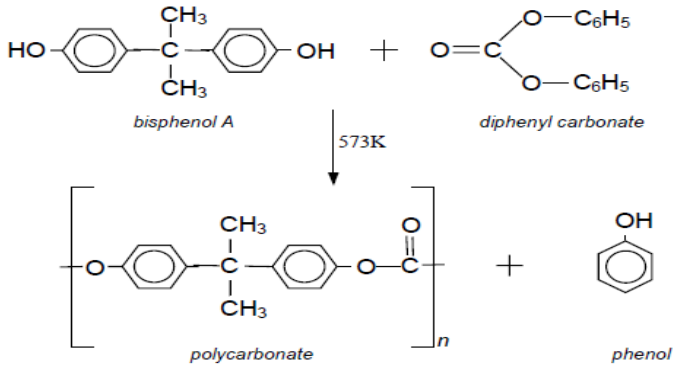


*Figure 2.3:-* Polymerization of polycarbonate

The ester-exchange process uses high temperature in which Bisphenol A is unstable. Thus an excess of diphenyl carbonate is used to assure a complete reaction of BPA. [Sinha, (26)]

### 2.2.4 Other sources of BPA

Thermal paper such as credit card receipts, etc. contain BPA which is used as a color developer molecule **(**Takashi *et al*., 19 They are thought to be the major contributor of BPA, contaminating recycled paper products. Up to 46 mg/kg (dry mass) of BPA has been found in recycled-paper-made toilet paper (Gehring *et al*., 20:25).


*Figure 2.4*:- Raw material symbol for recycle codes which confirms the presence of polycarbonate chemical (Erler *et al*., 2010).

## 2.3 Pollutant discharge

Heating polycarbonate flasks at 121$^{o}$ C for 25 minutes released 2-5μg/kg of Bisphenol A (Krishnan *et al.*, 1993). BPA is found in the wastewater from paper and plastic production plants and domestic sewage treatment plants. BPA also releases to the environment from sites where thermal fax paper is recycled. The concentrations of BPA contained in landfill leachates from solid waste disposal sites were measured. The concentrations of BPA contained in leachates from industrial waste sites were in the range below the detection limit to 2800 μg/l, and from municipal sites in the range 26–8400 μg/l (Urase *et al*., 2003).

## 2.4 Harmful effects of BPA

A large number of man-made chemicals have been released into the environment, as well as a few natural ones, have the potential to disrupt the endocrine system of animals and humans (Anderson *et al*., 1999). A workshop is organized to assess research needs for the assessment

of the effects of endocrine disruptors on wildlife and human populations.

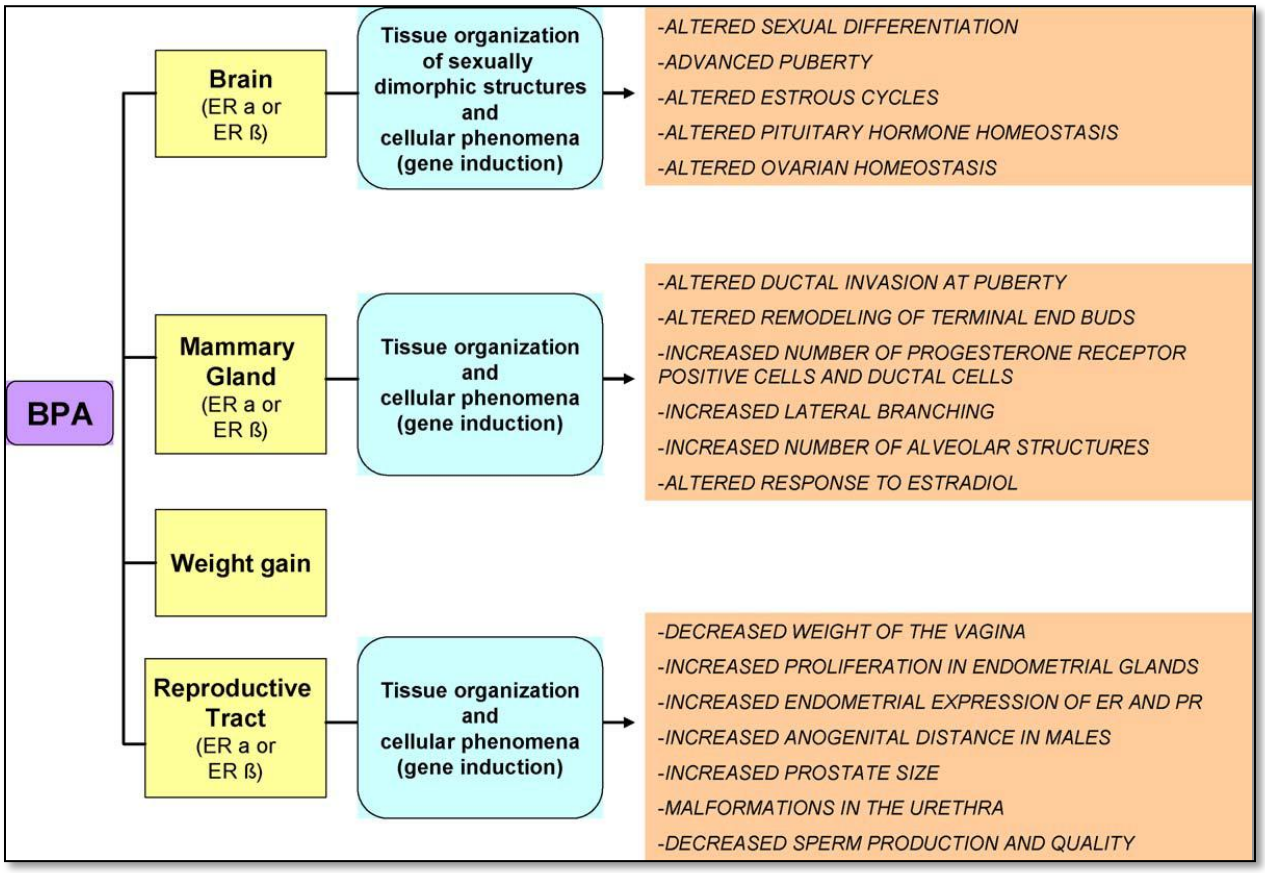


*Figure 2.5*:- Summary of the effects of perinatal exposure to BPA and their underlying mechanisms. It has been hypothesized that these effects may lead to altered fertility and fecundity, altered lactation and earlier onset/higher incidence of breast, testicular and prostate cancer (Maricel V. Maffini *et al.,* 2006)

BPA at levels down to 1µg/l, can cause effects in female freshwater ramshorn snails (Schlumpf *et al*.,2001). Toxicology studies have determined that the maximum tolerated dose for BPA is 1000 mg/kg body weight. BPA can cause effects at low doses (down to 2µg/kg bw/day) (Saal *et al*., 1997). In 1930, scientists discovered that BPA was an artificial estrogen, and its estrogen effect was used to enhance the rapid growth of cattle and poultry to promote industry profits (Breast Cancer Fund, 2008). In-utero exposure to a low dose of BPA can affect prostate size in male mice (Gupta *et al.*). The researchers found that higher urinary concentration of BPA were associated with increased incidence of diabetes, cardiovascular disease, and liver enzyme abnormalities (Lang *et al*., 2008). BPA has a wide range of effects

including structural and neurochemical changes in the brain associated with behavioral changes such as hyperactivity, increased aggression, and increased drug dependency; abnormalities in sperm production in males and oocytes in females; disruption of hormone production and fertility in both males and females; immune disorders, increased growth rate, and early secondary sexual maturation (Welshons *et al.,* 2006). BPA in mice and found that female mice exhibited structural changes in mammary duct glands after being exposed during gestation and lactational periods (Vandenberg *et al*., 2008). Determined if the maternal levels have an impact on the development of the newborn (Fisher *et al*., 2008). BPA in humans have examined urine concentrations, as BPA is excreted exclusively in the urine (Li *et al*., 2014). There are widespread pollutants which affects the hormonal system are listed below:-

**Metals**

***Table 2.1:- Number of metals which causes the adverse effects.***

| Compounds | Hormones affected | Mechanisms if known | References |
|---|---|---|---|
| Arsenic | Glucocorticoid | Selective inhibition of DNA transcription normally stimulated by the glucocorticoid-GR complex. | Kaltreider *et al.*, 2001 |
| Cadmium | Estrogenic | Activates estrogen receptor through an interaction with the hormone-binding domain of the receptor. | Johnson *et al.,* 2003 |

**Food antioxidants**

***Table 2.2:- Different food antioxidants which affects the hormonal system***

| Compounds | Hormone system affected | Mechanisms if known | References |
|---|---|---|---|

| | | | |
|---|---|---|---|
| BHA | Estrogen | Inhibits binding to the estrogen receptor. | Jobling *et al.*, 1995 |

## Organohalogens

| *Table 2.3:- Different organohalogens which affects the hormonal system* | | | |
|---|---|---|---|
| Compounds | Hormone system affected | Mechanisms if known | References |
| BHC | Thyroid | | Akhtar *et al.*, 1996 |
| Pentachlorophenol | Thyroid | Reduces thyroid hormone possibly through a direct effect on the thyroid gland | Bear *et al.*, 1999 |
| Chloroform | Reproductive | | Brittebo *et al.*, 1987 |

## Other compounds

| *Table 2.4:- Different compounds which affects the hormonal system* | | | |
|---|---|---|---|
| Compounds | Hormone system affected | Mechanisms if known | References |
| Bisphenol A | Estrogen | Estrogenic; binds to estrogen receptor | Anderson *et al.*, 1999 Fisher *et al.*, 1999 |
| Benzophenone | Estrogen | Binds weakly to estrogen receptors, roles of its metabolite remain to be clarified. | Schlumpf *et al.*, 2001 |
| Tyrene dimmers and trimers | Estrogen | Estrogen receptor agonists | Ohyama *et al.*, 2001 |

**Pesticide**

| *Table 2.5 :- Different pesticide which affects the hormonal system* | | | |
|---|---|---|---|
| Compounds | Hormone system affected | Mechanisms if known | References |
| DDT | Estrogen | disrupt endocrine function by binding with the estrogen receptor, including estrogen mimicry and antagonism, altering the pattern of synthesis or metabolism of hormones, and modifying hormone receptor levels | Lascombe *et al.*, 2000<br><br>Rajapakse *et al.*, 2001 |
| Dicofol (Kelthane) | Estrogen | | Vinggaard *et al.*, 1999 |
| Ziram | Thyroid | Inhibits the iodide peroxidase. | Marinovich *et al.*, 1997 |

## 2.5 Techniques to mitigate the BPA

BPA has been treated by chemically assisted-primary treatment, secondary treatment, and advanced treatment processes. Advanced oxidation processes can eliminate micropollutants from wastewater (Zhu *et al*., 2013).

## 2.6 Adsorbents

Quite a good number of adsorbents are discovered for the adsorption and removal of BPA from aqueous solution. Various carbonaceous and organoclays components are used to adsorb BPA. This is the inexpensive method for purifying water from these materials is through adsorption (Park *et al.*, 2010).

## 2.7 Types of adsorbent

### 2.7.1 Bentonite

An overview of the colloidal and rheological behavior of the bentonite for the interaction and adsorption of the non-ionic compounds (Luckham *et al*., 1999). The study examined the effectiveness of less expensive adsorbents such as peat, fly ash and bentonite in removing phenol from wastewater by adsorption (Viraraghavan, 1997). The removal of phenol from aqueous solutions by adsorption using surfactant-modified bentonite and kaolinite. The removal by modified clays seems to be more effective than unmodified samples (Alkaram et al., 2009). Characteristics of phenol and chlorinated phenols sorption onto surfactant-modified bentonite by using sorption isotherms (Rawajfih *et al.*, 2006). Study the effect of adsorption concentration on the adsorption of phenol by hexadecyl trimethyl ammonium-bentonite with the help of freundlich equation (Ozbudak *et al.,* 2005). Equilibrium, kinetic and thermodynamic study of removal of phenol from aqueous solutions by adsorption into organomodified bentonite (Senturk *et al*., 2009).

### 2.7.2 Chitosan

Use of chitin and chitosan derivatives for the treatment of wastewater for the removal of metal cations and metal anions, radionuclides, different classes of dyes, phenol and substituted phenols, different anions and other pollutants (Bhatnagar *et al*., 2009). Properties and applications of chitin and chitosan which is soluble in acidic aqueous media (Rinaudo, 2006). Cyclodextrin cavities present in the chitosan derivatives has been recognized as useful adsorbent matrices ( Prabaharan *et al.,* 2005). Determination of BPA on the application of chitosan-Fe3O4 nanocomposite modified glassy carbon electrodes (Yu *et al.,* 2011). Synthesis of chitosan for the removal of Bisphenol A from aqueous solution by microemulsion process (Pan *et al.,* 2011). Removal of Bisphenol A by use of chitosan through the tyrosinase-catalyzed quinine oxidation (Suzuki, 2009). Removal of Bisphenol A by use of chitosan through quinone oxidation by polyphenol oxidase (Kimura *et al.*, 2011). An acetylene black paste electrode modified with chitosan-graphene composite film had been developed for detection of Bisphenol A (Deng *et al.*, 2014).

### 2.7.3 Activated carbon

Two activated carbons coconut-based and coal-based are examined to adsorb the Bisphenol A and it is concluded that the adsorption capacities of activated carbons are larger than mineral adsorbents (Tsai *et al*., 2005). Two commercial carbons (W20 and F20) had been modified with nitric acid and thermal treatment under $N_2$ to study the adsorption of BPA from aqueous solution (Liu *et al.,* 2008). Producing carbonaceous material from wood chips to adsorb the Bisphenol A (Nakanishi *et al.,* 2002). 1-ethyl-3-methylimidazolium tetrafluoroborate based CILE was constructed and modified with CTS and GR composite film. The constructed CTS-GR/CILE was used for investigation of the electrochemical behavior of Bisphenol A by cyclic voltammetry and differential pulse voltammetry (Wang *et al.,* 2012). Two commercially activated carbon and one prepared from almond shell were used to remove Bisphenol A from water (Toledo *et al.*, 2005).

## 2.8 Classification of activated carbon

AC is classified into two groups: granular activated carbon (GAC) and powdered activated carbon (PAC). Size of GAC ranges from 40 mesh (0.425 mm) to 8 mesh (2.36 mm) and size of PAC is smaller than 325 mesh (0.025 mm) (Droste, 1997). GAC is characterized by small pore diameters and large internal surface areas. It can be prepared by crushing or pressing.

PAC is prepared by mixing sawdust with zinc chloride and subsequently grinding the product. On grinding, the shape of particles may differ which affects its absorptive properties. It is characterized by large pore diameters and small internal surface areas (Gloyna, 1992).

## 2.8 Adsorption by GAC

It is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. Decontamination of Bisphenol A from aqueous solution by graphene. The adsorption capacity was evaluated by Langmuir isotherm (Xu *et al.,*2012). Removal of phenolic compounds from commercial activated carbon but it is restricted due to high cost. It is proved that the low-cost adsorbents have high removal capabilities for certain phenolic compounds (Ahmaruzzaman, 2008). Study of adsorption of BPA from sewage water onto commercial

activated carbon because sewage contains additional amount of Bisphenol A (Bohdziewicz *et al*., 2013). Evaluation of adsorption of BPA on modified activated carbon. Modification had been done by nitric acid, sodium hydroxide and thermal treatment in an atmosphere of $N_2$ (Liu *et al.*, 2008).

## 2.10 Application of GAC

Granular activated carbons are used in tertiary treatment of waste water which remove the biologically nondegradable impurities (Nakanishi *et al*., 2002)

## 2.11 Regeneration of activated carbon

An important phase of carbon treatment is to permit reuse of carbon over many cycles. To improve the life of carbon treatment, it is necessary to find method for decreasing the physical loss of carbon and loss of adsorptive capacity (Krieger *et al*.).

1. Thermal regeneration

   It is the most widely used process, keep temperature at 800 $^0$C (Zhou *et al*., 2012). But the disadvantage is that it needs high energy requirement.

2. Wet air oxidation

   Regeneration of activated carbon would work under temperature of 130-250 $^0$C, high pressure and 0.1-1.0 MPa oxygen partial pressure (Zhou *et al*., 2012).

3. Chemical regeneration

   It is performed at room temperature and ambient conditions, the regeneration efficiency is not very high (Zhou *et al*., 2012).

4. Solvent regeneration

   It include the physical and chemical characteristics of the adsorbent, the pore size and energy of adsorption associated with the activated carbon; the degree of solubility of the adsorbate in the organic solvent; the miscibility of the organic solvent in water; and the temperature at which the generation is performed. (Cross *et al.*, 1982).

# 3. *Materials and Methods*

## 3.1 Materials

All the reagents used in study were of analytical grade. Before analysis with HPLC or FTIR, all samples were filtered with a 0.45 μm filter. An overall look of all specificities is seen in *Table 3.1*

| Name | Characteristic | Origin |
|---|---|---|
| Bisphenol A | Used in the production of polycarbonate and various consumer products. | Commercial sample. |
| Bentonite | Acts as emulsifier and adsorbent for proteins and virus particles. | Commercial sample. |
| Chitosan | It is an inelastic and enormous properties such as biodegradability, bio-compatability, non-toxicity and adsorption. | Industrially produced. |
| Activated carbon | Large surface area, large pore size, adsorbent for removing the impurities. | Commercial sample. |

*Table 3.1:-* Summary of all configurations

### 3.1.1 Bisphenol A

BPA was provided as solid granules of pure BPA of Lobachemie company which was white in colour and molecular weight is 228.29 and melt at temperature range of 154-156 $^{0}$C. BPA has low solubility in water and is more soluble in organic solvents. A method of dissolving

BPA is, in order to make 100 ppm, 10 mg of BPA dissolved in 100 ml of distilled water in a flask by using sonicator for atleast 45 mins. to obtain the BPA solution. This stock solution was stored at room temperature ($25^0$C). Organic solvents were not used to dissolve because in the presence of these would disturb the results obtained by UV spectrophotometer.

### 3.1.2 Bentonite

Bentonite was purchased from Lobachemie company. It has been used as an emulsifier and adsorbent for BPA and for biological units such as proteins and virus particles. Bentonite was used in the concentration of 0.1 mg/ml of BPA solution. It is a swelling powder that swells at more than 24 ml. It loss on drying at 105 $^0$C (Xu *et al*.,2012).

### 3.1.3 Chitosan

1 g of chitosan flakes were added into 50 ml 2% (v/v) acetic acid in a beaker and the mixture was placed overnight. Then the chitosan solution was dropped through a syringe needle into 100 ml 3% (w/v) sodium hydroxide with 1.5 ethyl acetate solution to induce the formation of spherical gel beads, mechanically stirred for 3 h. After removing the sodium hydroxide solution, the beads were washed with DI water repeatedly until reaching neutrality and they were stored in DI water for further use. (Wang *et al.*, 2007)

### 3.1.4 Activated carbon

Activated carbon has been used in the adsorption of BPA. They were coal black in colour and used as flakes. The parameter of activated carbon vary along with temperature to obtain a maximum adsorption capacity of BPA.

## 3.2 Methods

### 3.2.1 Preliminary test

100 ppm stock solution of BPA was prepared and then find out at which BPA gives the maximum absorbance. Then the calibration curve was fitted at various concentration of BPA. After that regression value was determined.

### 3.2.2 Contact time and Adsorption

After the preliminary test to check out the BPA properties, next step is to adsorb the BPA from aqueous solution by different adsorbents and study with varying the parameters as mentioned below:-

1. Contact time
2. BPA concentration
3. Adsorbent concentration
4. pH
5. Temperature

Adsorbents:-

1. Bentonite

   The adsorption experiment was performed in the nine sealed 250 ml flask that contains 10 mg of bentonite powder and 10 ppm of 100 ml of BPA solution. The bottles were placed in shaking bath at a shaking speed of 200 rpm at the room temperature. Then to define the optimum parameters, the experiment was conducted as follows:-

   To evaluate the time of maximum adsorption, nine flask containing bentonite and BPA that has been placed in the shaking bath were taken out one by one at different interval of time, then centrifuged at 5000 rpm for 10 minutes to form the pellet of Bentonite + BPA complex and then check the absorbance of the supernatant by UV-Spectrophotometer to evaluate the adsorption.

2. Chitosan

   After the formation of the beads, they were transferred into the 10 ppm concentration of 100 ml BPA solution (adsorbate). Then these were placed on incubator shaker at room temperature and at a speed of 200 rpm to check the maximum adsorption.

3. Granular activated carbon

   1 g of activated carbon was put into the 10 ppm concentration of 100 ml of BPA solution and placed in the incubator shaker at 200 rpm at room temperature then check the absorbance at 277 nm.

**3.2.3 Isotherm tests**:- Performed the isotherm test to check the adsorption, four parameters were evaluated by adsorbent GAC.

1. Contact time

   Nine flask containing GAC and BPA, placed in the incubator shaker with 200 rpm speed and at room temperature and were taken out one by one at different interval of time, then filter out the GAC with the whatman filter paper then checked the absorbance of the clear solution by UV-Spectrophotometer to evaluate the adsorption.

2. BPA Concentration

   After concluded the optimum time for maximum adsorption, then optimum BPA concentration had to find by taking the different concentrations of BPA with added GAC onto the incubator shaker with 200 rpm speed, room temperature and for evaluated optimum time then after this checked the absorbance.

3. Adsorbent concentration

   Now, to find the optimum concentration of adsorbent at which the BPA is maximum adsorbed. Different concentration of adsorbent was taken with optimum BPA concentration and placed in incubator shaker under appropriate conditions and evaluated by UV- Spectrophotometer.

4. pH

   The pH has been vary among the optimum concentration of BPA and Activated carbon to find out the best ionic concentration at which it gives maximum adsorption.

5. Temperature

   Temperature plays an active role in the thermodynamic procedures. It affects the binding capacity of the ligand we place the solution at different temperature conditions to evaluate the temperature at which there is maximum adsorption.

### 3.3 Detection of BPA

To detect the BPA, collected waste water samples from dumped areas and solid waste leachates from sewage. The detection of BPA from was determined by HPLC treatment then the absorbance value was checked on the UV-Spectrophotmeter. Then the adsorption experiment was performed with activated carbon for the adsorption of BPA and absorbance was analyzed.

### 3.4 Regeneration procedure

BPA and Activated carbon complex was first air dried and weighed it. Then the granules were regenerated by positioned in the muffle furnace at 300 $^{0}$C for 30 minutes. Weighed it again to check the difference between adsorbed activated carbon and after thermal regeneration method. For the evaluation of the ability of the activated carbon to readsorb, we conducted same adsorption method of activated carbon again. These steps were repeated till it looses the capacity to regenerate.

### 3.5 Analytical method

#### 3.5.1 UV spectrophotometer

Ultraviolet-visible (UV-Vis) spectroscopy (Hitachi U/2900) is often used in the detection and quantification of organic compounds. A UV-Vis spectrometer emits monochromatic light in the range of 180-800 nm and in turn particular wavelength will be absorbed by the analyte molecule. The energy of the emitted light that is absorbed by the molecule will excite electrons from high occupied molecular orbital (HOMO) to the low unoccupied molecular orbital (LUMO) (Yadav *et al*, 2005).

#### 3.5.2 HPLC

High-performance liquid chromatography (Agilent compact 1120) is a technique used in analytical chemistry to separate the components in a mixture, to identify each component, and to quantify each component. HPLC Instrumentation Liquid chromatographic separation and detection of bisphenol were performed with HPLC instrument of Thermo fisher consisting of auto sampler and water pump.

### 3.5.3 FTIR

Fourier transform infrared spectroscopy (Agilent resolution pro, cary 660) is a technique which is used to obtain an infrared spectrum of adsorption, emission, photoconductivity or scattering of a solid, liquid or gas. A FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

### 3.5.4 Muffle furnace

A muffle furnace (Prefit India) is box type oven for high temperature applications. These are used in various research labs by chemists in order to determine the proportion of sample which is non-combustible and non-volatile. It is used to calcine the samples. Calcination is a thermal treatment process for the removal of volatile fraction. Muffle furnace consists of externally heated chamber, so that material being heated has no contact with the flame. This muffle furnace can achieve a maximum temperature of $600^{o}C$.

### 3.5.5 Sonicator

It is the instrument (Chromtech) of applying sound energy to agitate particles in a sample, for various purposes. Ultrasonic frequencies (>20 kHz) are usually used, leading to the process known as ultrasonication. It is applied using an ultrasonic bath or an ultrasonic probe, known as a sonicator.

# 4 Results and Discussion

Bisphenol A is one of the most ubiquitous endocrine-disrupting chemicals its occurrence stemming from the diverse sources comprising daily use materials.. The primary objective of this study was achieving a viable process for removing Bisphenol A from water. In order to quantify Bisphenol A, a simple and effective assay was optimized based on the fact that Bisphenol A absorbs at 277nm. Fig5.1 depicts a calibration curve generated using pure Bisphenol A standards, absorbance was recorded at 277 nm wavelength. The regression coefficient ($R^2$) indicated the validity of the process.

## 4.1 Standard curve of BPA

Different concentration of BPA gives distinct absorbance at 277 nm wavelength. The regression coefficient ($R^2$) value is 0.9991.

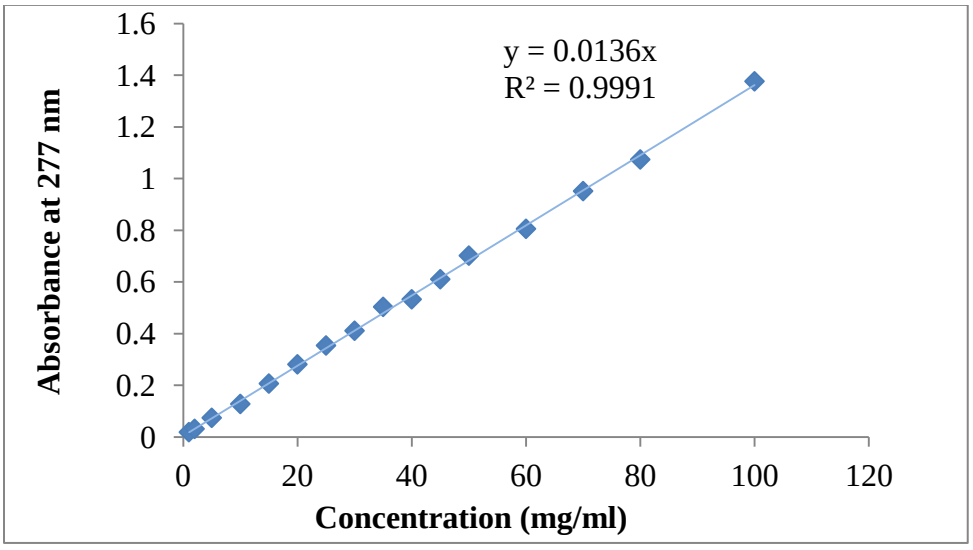


*Figure 4.1:-* Calibration curve of BPA standards

## 4.2 Adsorption studies for BPA removal

Adsorption processs have proved important in removal of several water borne contaminants; a principal advantage of such processes being their simplicity in operation and effectiveness. In this study, different adsorbents such as bentonite and chitosan were used to remove the BPA from aqueous solution. However, preliminary experiments indicated that activated

carbon was the most potent adsorbent over two other adsorbents bentonite and chitosan, therefore further studies were conducted with activated carbon.

Graphical representation of the best adsorbent which shows maximum removal efficiency of BPA is shown in *Figure 4.2*

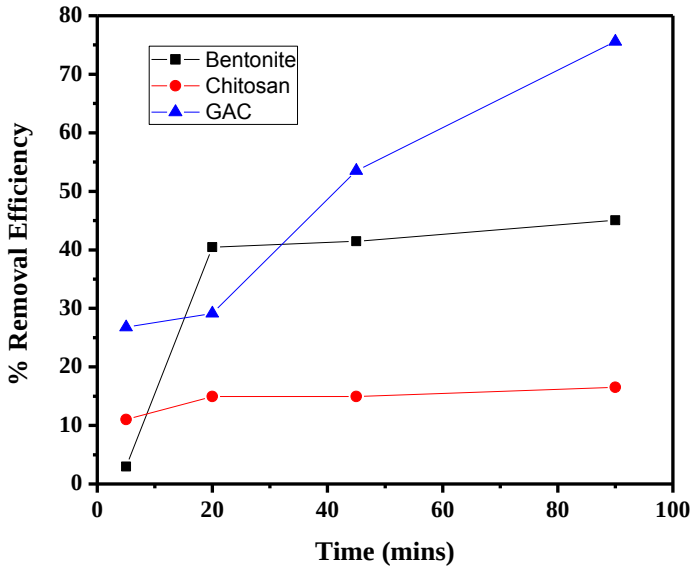


*Figure 4.2*:- It shows the percentage removal efficiency of different adsorbent with time

Among these, Activated Carbon was found to be the most potent with maximum efficiency of 75 % to adsorb BPA as compared to other adsorbents such as bentonite and chitosan used in similar studies and shows very less percentage removal as depicted from graph.

## 4.3 BPA Adsorption Parameters

The adsorption parameters are used to indicate the interaction between the adsorbent and the adsorbate when the adsorption process reach the equilibrium. Below figures depicts the effect of various parameters such as Contact time, BPA concentration, Adsorbent concentration, pH and Temperature on removal efficacy.

### 4.3.1 Effect of Contact Time on BPA Adsorption

The amount of adsorbed BPA at the equilibrium time denotes the maximum BPA adsorption under the experimental conditions (K.A. Guimaraes Gusmao *et al.*, 2012). The phenomenon can be explained by the fact that a large number of vacant surface sites are available for adsorption during the initial stages, and after a certain period of time, the remaining sites are occupied upto some extent and after that these are occupied with a lesser frequency due to repulsive forces between the solute molecules on the solid and liquid phases (Mall ID *et al.*2006). As observed from Figure 4.3, equilibrium time of adsorption of BPA was 15 hours, indicating that highest amount of BPA was adsorbed at 15 hours.

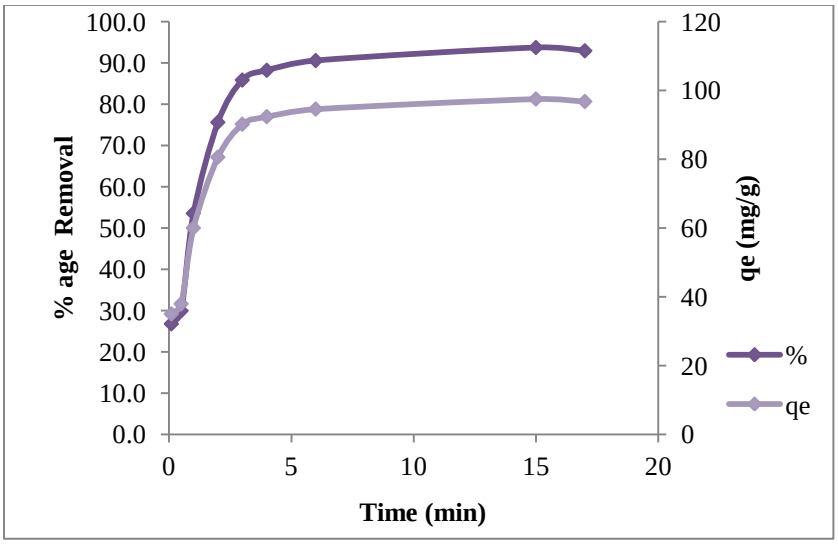


*Figure 4.3:-* Percentage removal and adsorption capacity of BPA with respect to time.

### 4.3.2 Effect of Initial Bisphenol A Concentration

A notable increase in the adsorption capacity of activated carbon was observed with the increasing concentration of BPA for reach equilibrium progressively. This could be due to increase in BPA concentration leading to an increase the diffusion of BPA molecules onto activated carbon granules subsequently increasing the driving force of the concentration gradient (Jing Xu *et al.*,2012). The range of Bisphenol A concentration for experimental study was 5, 10, 20, 30, 40, 50, 60 (ppm).

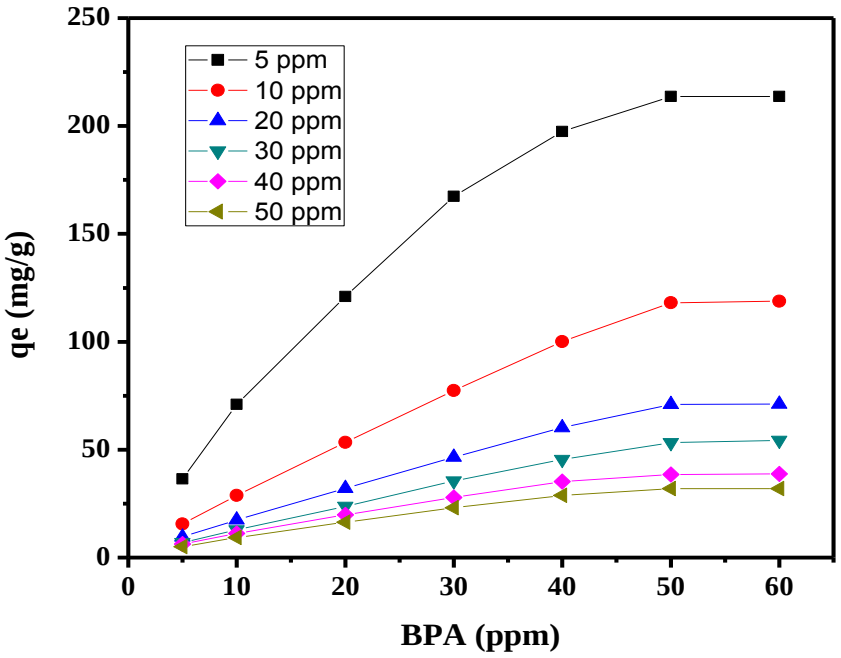


*Figure 4.4:-* Different concentration of BPA was examined for the maximum adsorption till the equilibrium point.

### 4.3.3 Effect of Adsorbent Dose

As observed from Figure 5.4, a dose dependent removal ensued. The adsorbent concentration in grams ranging from 0.1, 0.3, 0.5, 0.7, 0.8, 1 Lower removal was observed at higher initial doses, highest or near complete removal occurred at concentrations of 1mg/mL BPA.

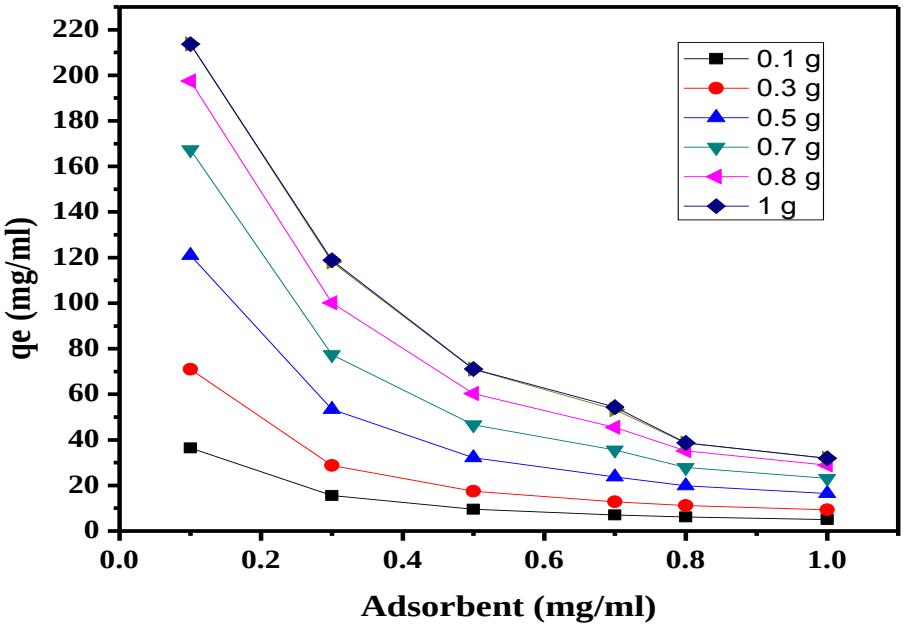


*Figure 4.5:-* Effect of adsorbent dose of BPA on its removal by activated carbon

### 4.3.4 Effect of Initial pH

It has been shown in several previous studies, that pH can change the net charge on the adsorbent and adsorbate. The effect of pH on BPA adsorption by activated carbon was investigated with the pH ranging from 2.0 to 10.0. The peak was higher at 6.0 pH. The maximum response to pH was lower than the pKa of Bisphenol A (pKa=9.73) (Sambe *et al*., 2006). This is due to the adsorption of non dissociated BPA on GAC (Sambe *et al*., 2006). The peak shifted towards lower potential with increasing pH value suggesting that at lower pH, excess of $H^+$ ions tend to compete with those of analyte showed little or insignificant changes (Ntsendwana *et al*., 2012). The result of this study was in congruence with observations from others where the amount of BPA adsorbed diminished with rising pH. The adsorption was maximal at acid or mildly basic pH values, with increasing pH values, adsorption was affected (Toledo *et al*, 2005).

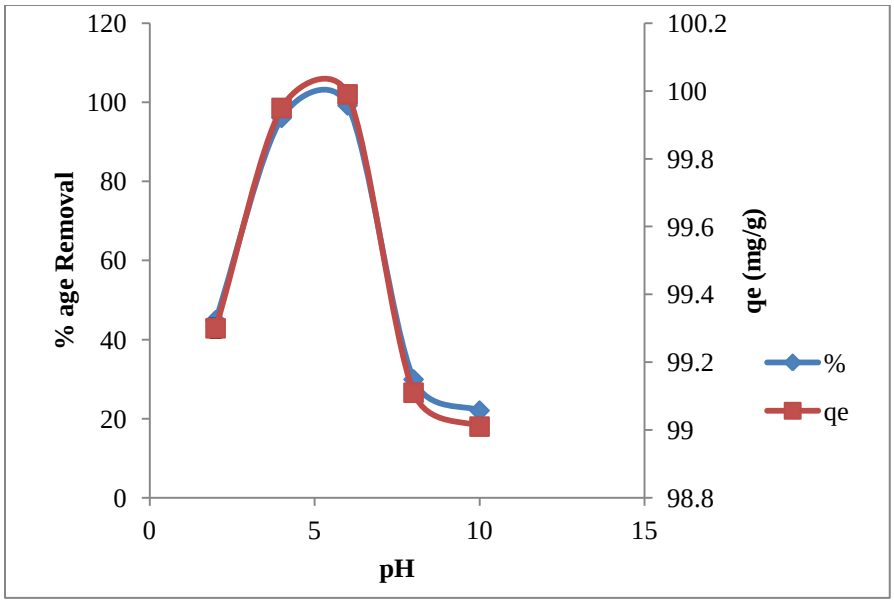


*Figure 4.6*:- Effect of pH

### 4.3.5 Effect of Temperature

Increasing of reaction temperature up to 40°C enhanced the removal percentage of Bisphenol A to 85%.

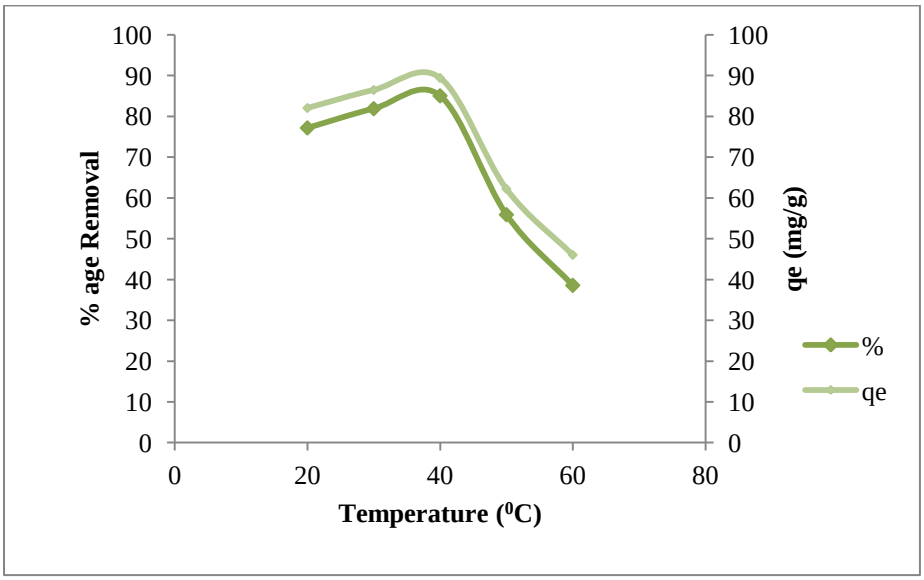


*Figure 4.7*:- Effect of temperature on the adsorption of BPA

## 4.5 Adsorption Isotherm

To understand and predict the adsorption capacity of the BPA by activated carbon, experimental data generated were applied to three models - Langmuir, Freundlich and Temkins; *Fig 5.6* depicts the curve fitting and validation of the experimental data. Similiar trends of the adsorption capacity of BPA using activated carbon has been reported in other studies ( Toledo *et al*., 2005).

### 4.5.1 Freundlich equation

Freundlich model assumes heterogeneous adsorption due to the diversity of sorption sites or the diverse nature of the adsorbate adsorbed, free or hydrolyzed species.

$$\ln q_e = \ln k_F + \left(\frac{1}{n}\right) \ln C_e$$

$K_F$ and n are the Freundlich constants (Wirasnita *et al*., 2014)

### 4.5 .2 Temkin equation

A is the Temkin equilibrium binding constant (L/g), and B is the Temkin constant related to heat of sorption (J mol−1) (Hameed and Rahman 2008).

$$q_e = B\ln A + B\ln Ce$$

B is the Temkin's constant (Wirasnita *et al*., 2014)

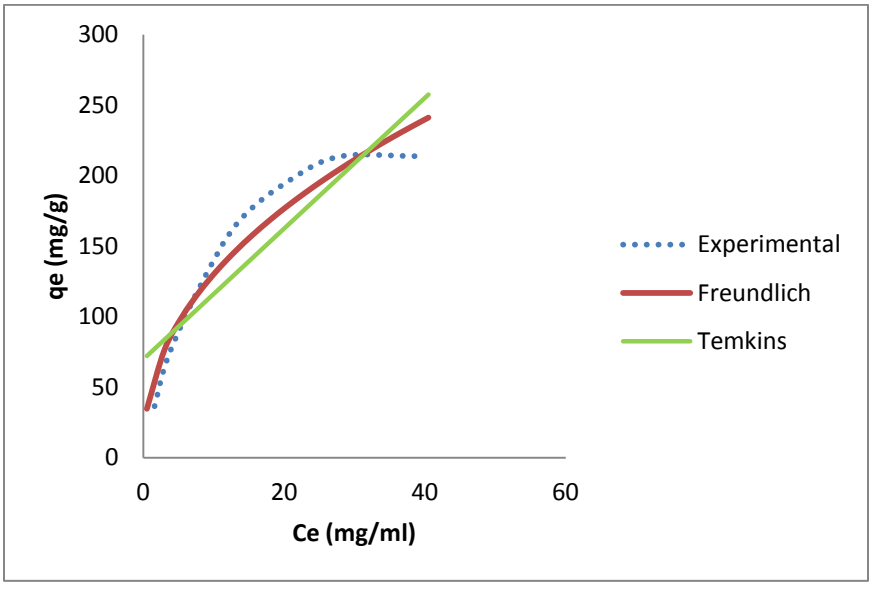


*Figure 4.8:-* Adsorption isotherm models

| Name | Equation | Constant | R-square | SSE |
|---|---|---|---|---|
| **Freundlich** | $\mathbf{lnq_e = lnk_F + (\frac{1}{n}) lnC_e}$ | $\mathbf{K_{F=}}$ **47.13**<br>**N= 0.44** | **0.9391** | **1858** |
| **Temkin** | $\mathbf{q_e = BlnA + BlnCe}$ | **a= 1.674**<br>**b= 15.04** | **0.8085** | **5843** |

*Table 4.1*:- Values of isotherm models

From this, we concluded that the best fitted model in the adsorption of BPA are Temkin and Freundlich isotherm model. The Langmuir model does not fit in this adsorption isotherm. The Freundlich and Temkin model generates a correlation factor $(R^2)$ of 0.9391 and 0.8085 respectively. By comparing the correlation factors of both these models, it is evident that the Freundlich model provides a better fit for explaining of BPA onto the activated carbon. The Freundlich model suggest that BPA-activated carbon heterogeneous adsorption due to the diversity of sorption sites or the diverse nature of the adsorbate adsorbed, free or hydrolyzed species. The Freundlich isotherm model can describes the capacity of BPA to be adsorbed by activated carbon that is 47.13 mg/g.

## 4.6 HPLC analysis of BPA adsorption by GAC

HPLC has lot of applications in biotechnology industries. The principle is based upon the separation of substances because of their different migration rates arising due to retention with the stationary and mobile phase.

Biphenol A samples were analysed by High performance liquid chromatography. This analysis is done at the wavelength of 275nm. The chromatographic separation was carried out using a Symmetry C18 column and the whole reaction is set at the temp of $35^0$C. The mobile phase, at a flow rate of 0.8 ml/min, consisted of a solution of 40% acetonitrile (solvent A) and 60% water (solvent B).

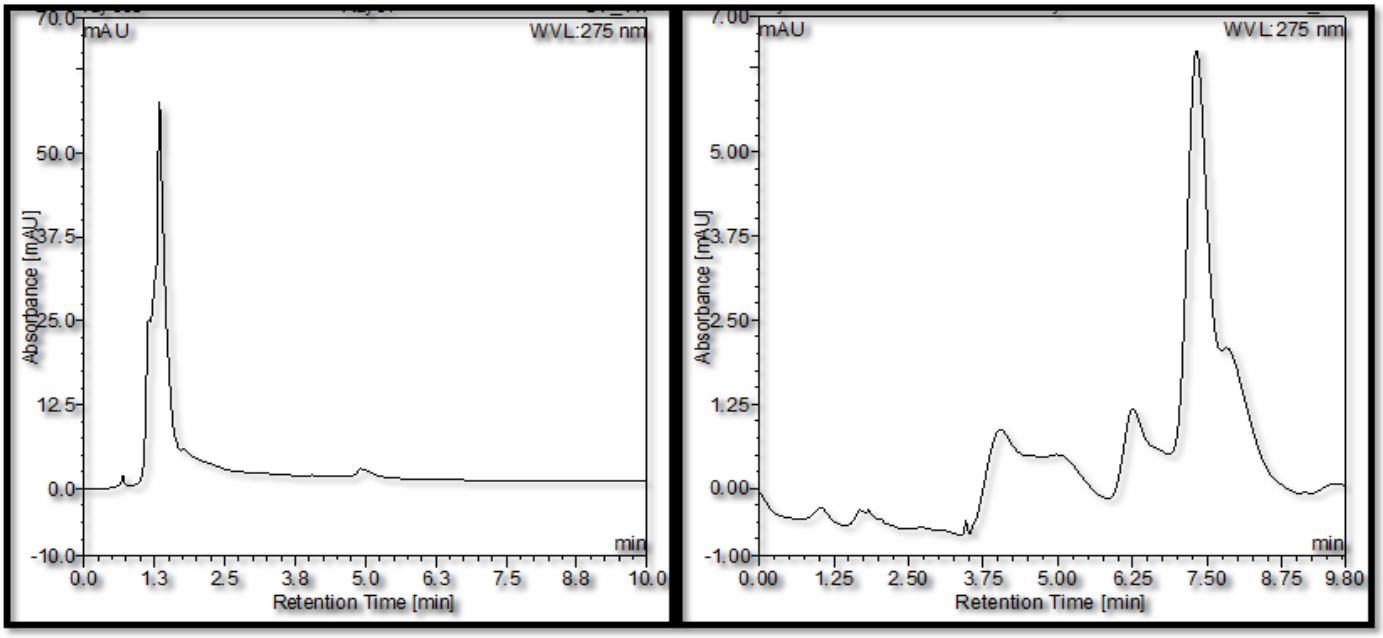


*Figure 4.9:-* The data clearly shows that after the adsorption of activated carbon the absorbance decreases with retention time. The peak shifted to 6mAU as compare to the standard peak which is at 60mAU which demonstrates the adsorption of bisphenol A.

### 4.7 Structural determination of activated carbon

To elucidate and ascribe identities of the adsorption process, FTIR spectra of activated carbon before and after adsorption were compared as shown in *Figure 4.10* and *Figure 4.11*. FTIR spectroscopy is a helpful tool for identifying the presence of certain functional groups on the surface of solid material (Jing Xu *et al*., 2012). The analyzed FTIR spectrum of activated carbon before adsorption shows a strong peak at 1090 $cm^{-1}$ indicate the C-N stretch bond and the presence of aliphatic amines. The other small and broad peak at 3413 $cm^{-1}$ suggested the appearance of O-H group and H-bond implying alcohols and phenols are present. The other peak at 794 $cm^{-1}$ associated with the C-Cl bond exhibited the alkyl halides group.

After adsorption of BPA, the complex was further analyzed by FTIR. A sharp peak was recognized at 1076 $cm^{-1}$ of C-O stretch which reveals the functional groups of alcohols, carboxylic acids, esters and ethers. Another medium peak at 775 $cm^{-1}$ with C-Cl stretch which carries the functional group of alkyl halides was also recognizable. These results suggested that BPA was adsorbed to activated carbon. FTIR spectrums of activated

carbon reveal the oxygen-containing groups had been removed after the adsorption of the activated carbon by BPA. The peak at 3413 $cm^{-1}$ corresponding to the O-H stretch and H-bond reduced significantly and the peak at 1090 $cm^{-1}$ attributed to C-N stretch also become relatively small. Upon comparison to activated carbon, many peaks appeared to be strong and sharp following BPA adsorption. The peaks at 1076 $cm^{-1}$ corresponds to C-O stretch, 775 $cm^{-1}$ corresponds to C-Cl stretch appeared at significant intensities.

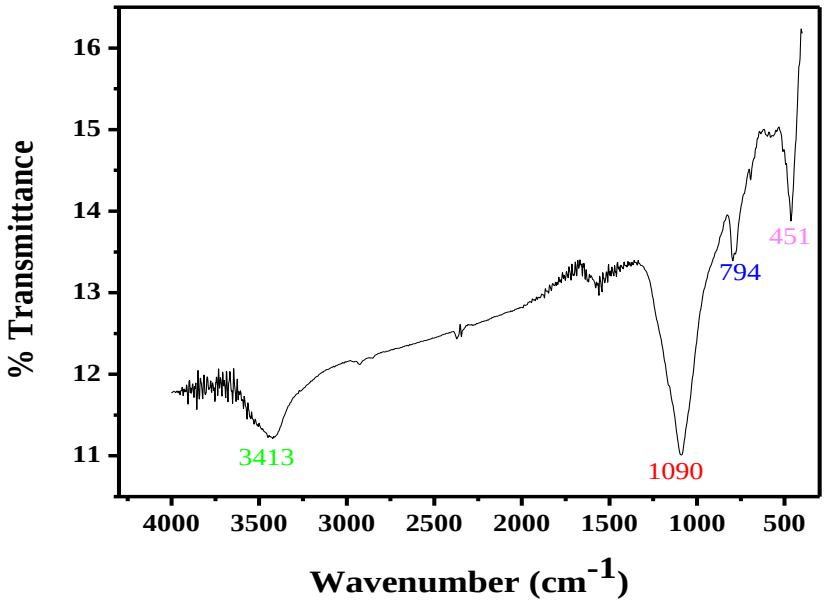


*Figure 4.10:-* FTIR spectrum of activated carbon before adsorption

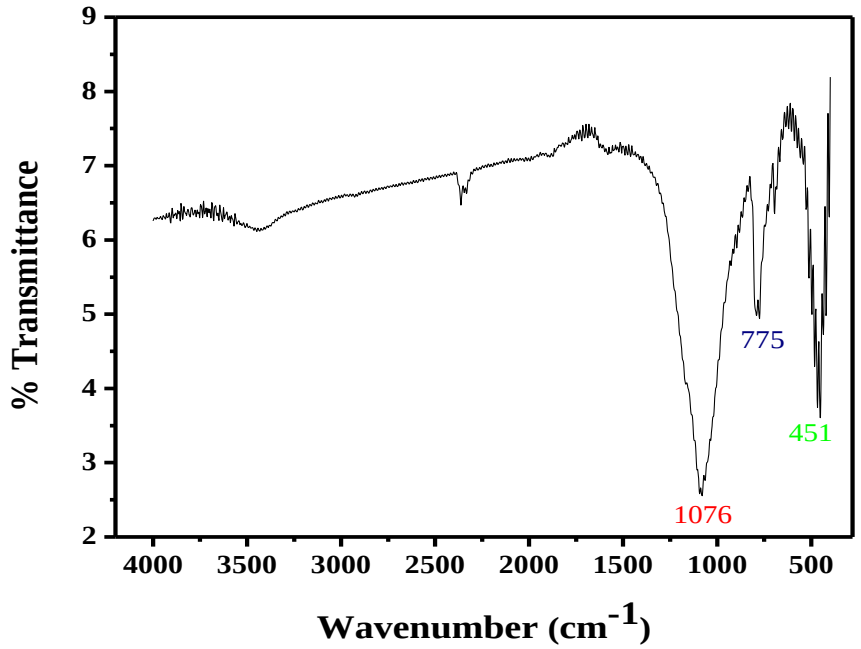


*Figure 4.11:–* FTIR spectrum of activated carbon after adsorption

**Adsorption Mechanism**

The π-π interactions may be resorted to for explaining the mechanism of adsorption of organic molecules C=C bonds or benzene rings adsorbed on the surface of activated carbon granules (Jing Xu *et al*., 2012). Organic molecules contain π electrons that interact with the π electrons of benzene ring of the activated carbon by means of π-π electron coupling because BPA also has benzene ring so it is reflected that the intermolecular force between BPA and activated carbon should be π-π interactions (Jing Xu *et al*., 2012). The oxygen containing groups such as hydroxyl groups present in the activated carbon which are reduced by adsorption of BPA. It may thus be postulated that the phenolic group of BPA binds with the hydroxyl group of activated carbon, enabling adsorption (Toledo *et al*., 2005). compared adsorption of BPA on different forms of activated carbon. The net positive charge on activated carbon and ionic strength of the solution played a predominant role in adsorption besides the presence of micro and macropores on carbon surface. A summation of these factors may be considered as governing factors for adsorption of BPA in this study.

### 4.7 Detection and removal of BPA from waste disposal

Biphenol A samples were analyzed by High performance liquid chromatography. The experiment was performed at $30^0$C and a UV-detector was applied at 275nm. For Bisphenol A, The chromatographic separation was carried out using a Symmetry C18 column and the whole reaction is set at the temp of $35^0$C. The mobile phase, at a flow rate of 0.8 ml/min, consisted of a solution of 40% acetonitrile (solvent A) and 60% water (solvent B) (Ng *et al.,)*

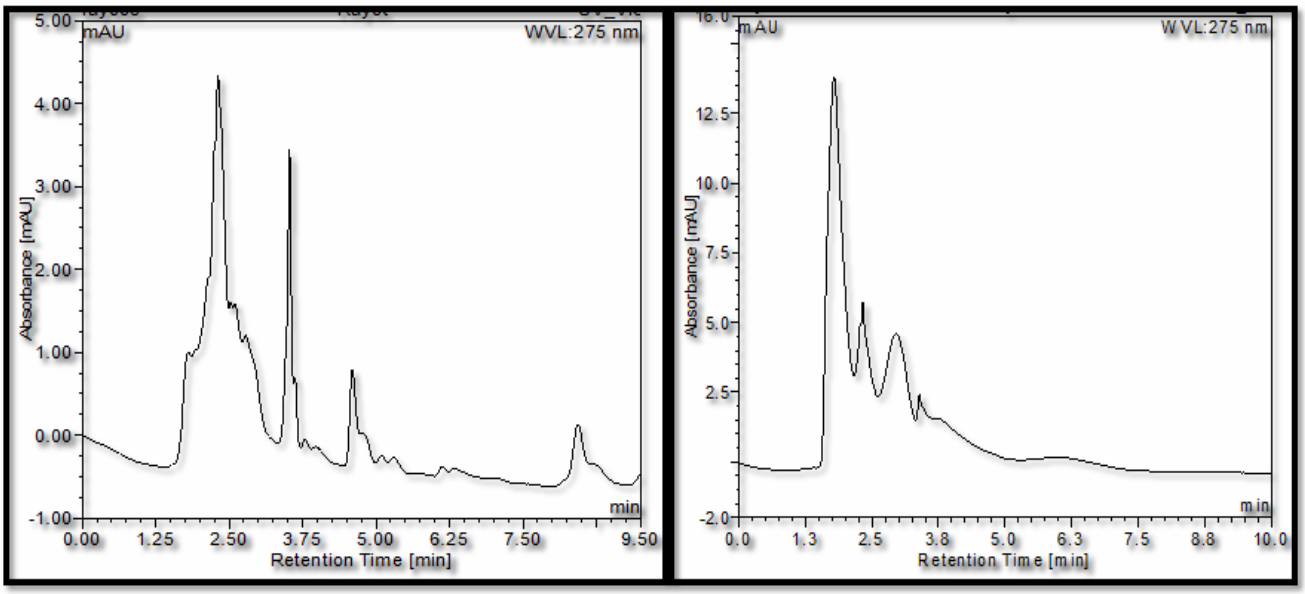


*Figure 4.12*:- Shows the difference of absorbance between waste water and solid waste Leachates. The absorbance of waste water is more as it contains more amount of bisphenol A than solid waste leachates.

#### 4.7.1 Waste water

The wastewater was collected from the domestic waste. It has been detected by HPLC and then treated with adsorbent to note the percent removal of the BPA from waste water by adsorbent. Before treatment, the BPA percent in the wastewater was 85% and after the removal by GAC it becomes 40%.

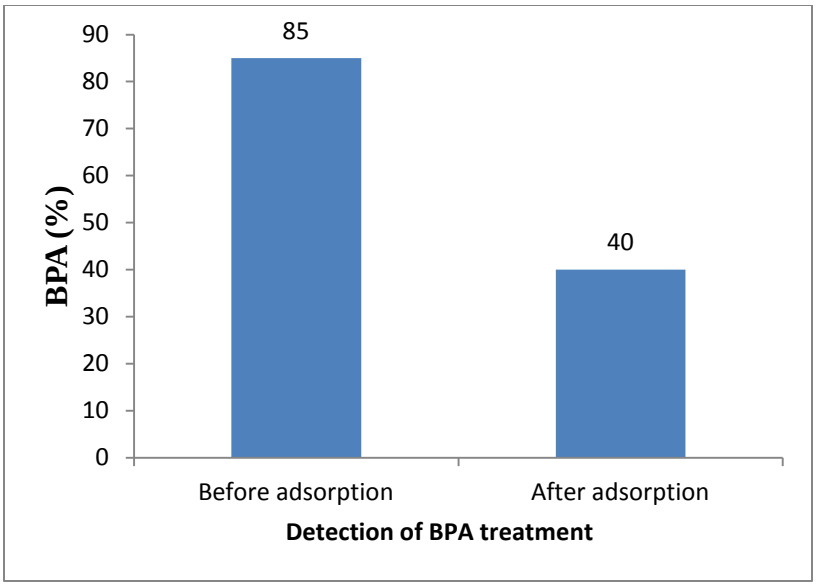


*Figure 4.13*:- Detection and removal of BPA

### 4.7.2 Solid waste leachates

The solid waste leachates was collected from the domestic waste. It has been detected by HPLC and then treated with adsorbent to note the percent removal of the BPA from waste water by adsorbent. Before treatment, the BPA percent in the wastewater was 60% and after the removal by GAC it becomes 25%.

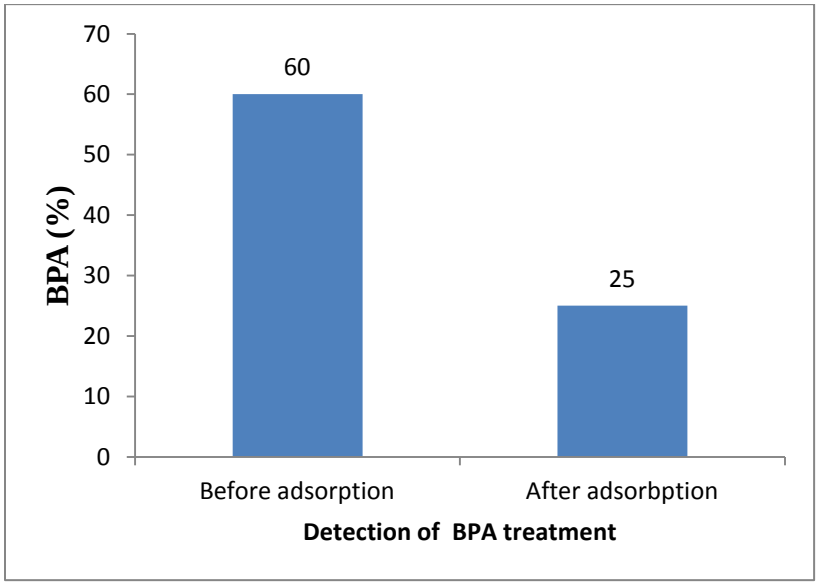


*Figure 4.14*:- Detection and removal of BPA

## 4.8 Regeneration of Activated carbon

Regeneration of bound BPA was attempted over a period of 6 days. Highest recovery was observed in day 1, whereas significantly low levels could be recovered after 6 days. Explicitly demonstrated the desorption kinetics of BPA from activated carbon (Zhou *et al.*, 2014). They proposed a pseudo second order kinetic model to explain the process. Desorption was greatly favoured by a combinatorial treatment of acquopistics and solvent extraction. The results obtained in this study are concur with those observed (Zhou *et al.*, 2014). A sound desorption process may be regarded crucial in reusing the adsorbents, thereby ensuring process viability in commercial runs.

| Days | Efficiency (%) |
|---|---|
| 1 | 94 |
| 2 | 81 |
| 3 | 66 |
| 4 | 42 |
| 5 | 24 |
| 6 | 12 |

*Table 4.2:-* Regeneration efficiency of BPA from activated carbon.

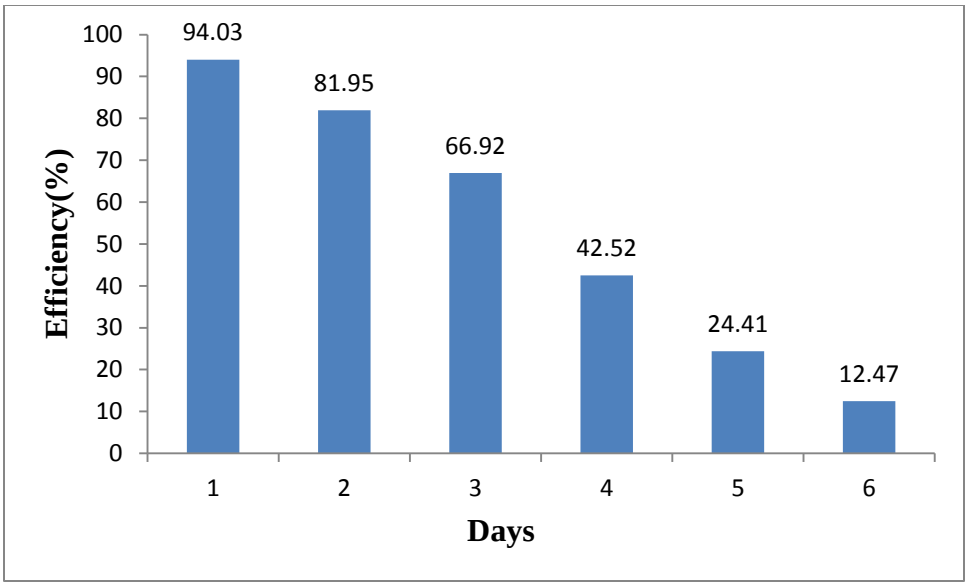


*Figure 4.15*:- Regeneration capacity to bind BPA

**Loss of activated carbon**

Due to heating of the activated carbon in the muffle furnace at 300 $^{0}$C to break the binding interactions between BPA and activated carbon, there is also some loss of activated carbon. Loss of activated carbon is shown below in graphical form.

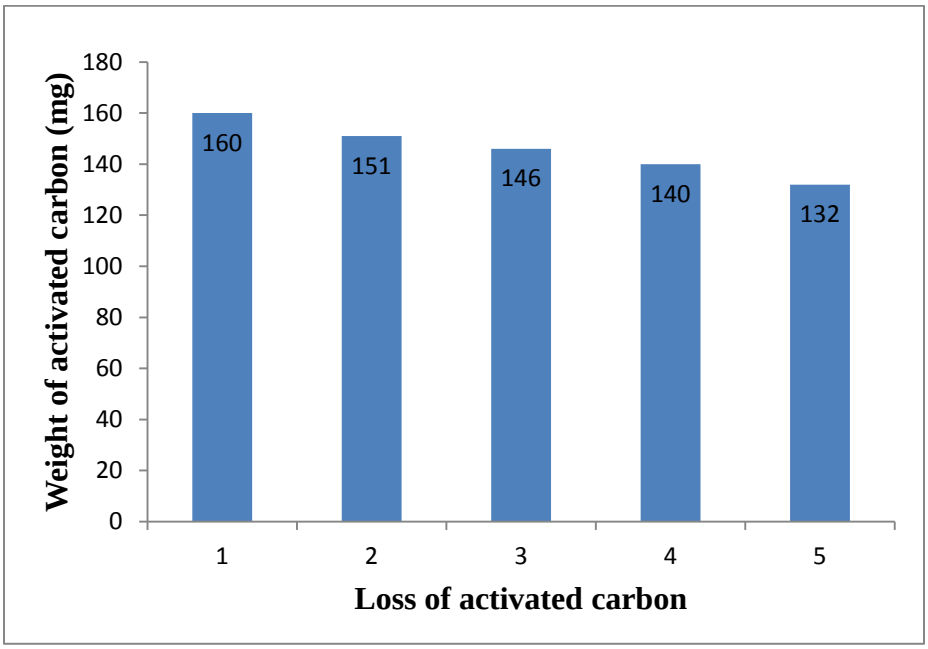


*Figure 4.16*:- Loss of activated carbon when treated with muffle furnace.

## *Conclusion*

Bisphenol A is a chemical produced in large quantities for use primarily in the production of polycarbonate plastics and epoxy resins. Polycarbonate have many applications including use in some food and drink packaging e.g., water and infant bottles, compact discs and medical devices. Low levels of BPA have also been found to cause biological effects and its mode of action appears to mimic the endocrine system. Therefore BPA belongs to the group of "endocrine disruptors".

So to mitigate its effect, the present study aimed to removal of BPA by adsorbent technique. Our main objectives are to remove the BPA from aqueous solution, regeneration of adsorbent material to reuse it again and to analyze the detection of BPA from wastewater and solid waste leachates.

To achieve our first objective, 10 ppm solution of BPA was adsorbed onto the activated carbon and the removal efficiency came to be 94%. So, by this result we conclude that due to the highly porous activated carbon, removes the BPA efficiently.

To achieve our second objective, we placed the granules of adsorbed activated carbon in the muffle furnace at 300 $^{0}$C. Then readsorbed again to check the capacity of the activated carbon to bind. The weight of GAC on the first day was 160 and after six days it become 132, so there is some loss of activated carbon due to some loss. So, regeneration efficiency revealed not only the rate of recovery of BPA was high but also the adsorbent could be to reused for multiple times.

To achieve the third objective, HPLC plays a significant role. It detects the presence of BPA in the waste water at intensity peak of waste water at 4.5 mAU and of solid waste leachates at 14 mAU. Therefore, biochemical characterization of BPA and presence of various functional groups on adsorbent helped to elucidate the adsorption mechanism.

We concluded that by optimization, regeneration and real time studies, treatment with the activated carbon has proven to be a feasible, economic and a promising technology for removal of BPA from the environment.

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