

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE**  
**ENGINEERING AND TECHNOLOGY**

**GRAFTING OF POLY(ACRYLAMIDE) ONTO CROSSLINKED  
POLY(HEMA-co-MMA) RESIN FOR REMOVAL OF PHENOL AND  
BISPHENOL A**

**M.Sc. THESIS**

**Handan USTA**

**Department :Polymer Science and Technology**

**Programme:Polymer Science and Technology**

**DECEMBER 2016**



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**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**POLİ(AKRİLAMİD)'İN ÇAPRAZ BAĞLI POLİ(HEMA-co-MMA) REÇİNEYE  
AŞILANMASI VE FENOL İLE BİSFENOL A 'NIN GİDERİLMESİNDE  
KULLANILMASI**

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*To My Family,*



## **FOREWORD**

I would like to thank all people who made this work possible. First of all, I would like to thank my thesis advisor, Prof. Dr. Bahire Filiz ŞENKAL, for leading me toward my work, and educating me on polymer chemistry and science.

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Handan USTA  
Chemist



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## **ABBREVIATIONS**

<b>EGDMA</b>	:Ethylene Glycole Dimethacrylate
<b>HEMA</b>	:Hydroxy ethyl methacrylate
<b>MMA</b>	:Methyl methacrylate
<b>PVA</b>	:Poly(vinyl alcohol)
<b>NMP</b>	:N-Methyl-2-Pyrrolidone
<b>DMF</b>	:Dimethylformamide
<b>AIBN</b>	:Azobisisobutyronitrile
<b>FTIR</b>	:Fourier Transform Infrared Spectroscopy
<b>UV-Vis</b>	:Ultraviolet-Visible
<b>BPA</b>	:Bisphenol A
<b>NaPh</b>	:Sodium phenolate





## **SYMBOLS**

<b>q<sub>t</sub></b>	: Teorical capacities
<b>q<sub>e</sub></b>	: Experimental capacities
<b>k</b>	: Equilibrium rate constant
<b>t</b>	: Time
<b>R</b>	: Coefficient factor



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# **GRAFTING OF POLY (ACRYLAMIDE) ONTO CROSSLINKED POLY(HEMA-co-MMA) RESIN FOR REMOVAL OF PHENOL AND BISPHENOL A**

## **SUMMARY**

Phenol and its substituted derivatives are widely found in the effluents from pesticides, synthetic rubber, plastic, pharmaceuticals, petrochemicals, and other industries.

It is also used in the production of caprolactam and bisphenol A. They are intermediates in the manufacture of nylon and epoxy resins, respectively.

It is primarily used in the production of phenolic resins, which are needed in the automotive plywood, construction and appliance industries. Other important uses of phenol are as a disinfectant and in medicinal products. Minor uses of phenol contain the manufacture of paint and varnish removers, lacquers, paints, rubber, ink, illuminating gases, tanning dyes, perfumes, soaps and toys

Phenol and phenolic compounds are generally considered as one of the important organic pollutants discharged into the environment causing unpleasant taste and odor of drinking water.

Even at very low concentrations in the presence of water, is undesirable and toxic to the aquatic beings including fish. Especially, chlorinated phenols are more toxic to aquatic life.

Phenols have great risk to the human health and cause negative effects on the brain, digestive system, heart, eye, liver, kidney, lung, peripheral nerve, skin and the unborn child.  $0.002 \text{ mg L}^{-1}$  is the permissible limit for phenol concentration in potable water according to the World Health Organization regulation.

Removal of phenolic pollutants in aqueous solutions can be divided into three main categories: chemical, physical and biological treatment.

Several wastewater treatment methods for removal of phenolic pollutants have been used including membrane filtration, advanced oxidation, biological degradation, photocatalytic degradation, electrochemical oxidation and adsorption.

Adsorption is very important method to remove organic and inorganic pollutants.

Different adsorbents such as zeolites, carbon nanotubes, polymeric sorbents and clay have been investigated for the removal of phenol and phenolic pollutants from wastewater.

Three mechanisms of phenolic compounds adsorption is postulated namely,  $\pi$ - $\pi$  dispersion interaction, electron-donor acceptor complex formation and hydrogen

bond formation. This methodology was used to prepare new polymeric sorbents for phenol removal.

In this thesis, two types of polymeric sorbents were prepared for removal of phenol and BPA from water.

The poly(HEMA-MMA-EGDMA) terpolymer were prepared by using suspension polymerization method starting from polymerization of hydroxyethyl methacrylate (HEMA) (50%), methyl methacrylate (MMA) (40%) and ethylene glycol dimethacrylate (EGDMA) (10%) as crosslinker in the presence of toluene as porogen and AIBN as an initiator (resin 1).

Other polymeric resin was prepared grafting polymerization of poly (acrylamide) onto resin 1 by redox polymerization method. Grafting reaction is carried out through the hydroxyl groups on HEMA units.

The resulting polymer resin2 , which had a total nitrogen content of about 7.0 mmol/g, was effective in extracting phenol from aqueous solutions. The phenol and BPA sorption capacities were found depending on concentration and pH.

Also, phenol and BPA sorption kinetics of the resins were investigated. Kinetic models were applied for Resin 1 and Resin 2.



## **POLİ (AKRİLAMİD)'İN ÇAPRAZ BAĞLI POLİ(HEMA-co-MMA)'A AŞILANMASI İLE FENOL VE BİSFENOL A 'DAN GİDERİLMESİNDE KULLANILMASI**

### **ÖZET**

Fenollerin eldesi on dokuzuncu yüzyılın sonlarından itibaren kömür katranından sağlanmıştır. 1898 yılında Felix Hoffmann tarafından asetilsalisilik asitten fenol sentezi gerçekleştirilmiştir.

Fenol ve türevlerine pestisit, sentetik kauçuk, farmasötik ürünler, petrokimya yada diğer sanayilerden kaynaklı atık sularda yaygın olarak rastlanmaktadır.

Fenol kaprolaktam ve bisfenol A üretiminde de kullanılmaktadır. Bu ürünler naylon ve epoksi reçinelerinin üretiminde de o kullanılmaktadır.

Fenol aynı zamanda otomatik, inşaat ve alet endüstrisinde ihtiyaç duyulan fenolik reçinelerin başlangıç maddesi olarak kullanılmaktadır. Fenolün diğer önemli kullanım alanları dezenfektan ve tıbbi ürünlerdir. Boya ve vernik sökücüler, lake, kauçuk, mürekkep, aydınlatıcı gazlar, tabaklama boya, parfümler, sabunlar ve oyuncak gibi materyallerin üretiminde fenol kısmi olarak rol oynamaktadır.

Bu tezde bir fenol türevi olan bisfenol A için de incelemeler yapılmıştır. İlk bisfenol A sentezi Thomas Zincke tarafından gerçekleştirilmiştir. 1905 yılında fenol ve asetonun sentezi sonucunda bisfenol A elde edilmiştir.

1953 yılında yeni bir plastik olan polikarbonatın başlangıç materyali olarak bisfenol A kullanılmıştır. 1957 yılında Amerika Birleşik Devletlerinde ve 1958 yılında Avrupa da ticari olarak üretimi yapılmıştır. Aynı zamanda epoksi reçinelerinin üretiminde bisfenol A kullanılmaya başlanmıştır. Bunun yanı sıra bisfenol A doymamış polyester, polisülfon, polieterimid ve poliarilat reçineleri üretiminde başlangıç materyali olarak da kullanılmaktadır.

Fenol ve fenol türevleri çevreye zararlı en önemli organik bileşiklerdendir ve içme suyunda hoş olmayan tat ve kokuya sebep olurlar.

Fenol su varlığında çok düşük konsantrasyonlarda bile, balık dahil olmak üzere su içerisindeki canlılar için istenmeyen özelliklere sahiptir ve toksiktir. Özellikle, klorlanmış fenoller sudaki yaşam için daha da tehlikelidir.

Fenoller insan sağlığı üzerinde zararlı etkilere sahiptir. Özellikle beyin, sindirim sistemi, kalp, göz, karaciğer, böbrek, akciğer, periferik sinir, deri ve doğmamış çocuklar üzerinde olumsuz etkilere neden olurlar.  $0.002 \text{ mg L}^{-1}$ , Dünya Sağlık Örgütü tarafından yapılan düzenlemelere göre içme sularında fenol konsantrasyonunun izin verilen sınırıdır.

Sulu çözeltilerde fenol ve türevlerinin giderilmesinde kullanılan yöntemler üç ana kategoriye ayrılabilir. Bu yöntemler fiziksel, kimyasal ve biyolojik yöntemler olarak adlandırılabilir.

Atık sulardan fenolün kaldırılmasında çeşitli yöntemler kullanılmaktadır. Membran filtrasyon, oksidasyon, biyolojik yada fotokatalitik bozunma ve adsorpsiyon yöntemleri fenolün giderilmesinde kullanılan yöntemler arasında gösterilebilmektedir.

Adsorpsiyon organik ve inorganik kirleticileri gidermek için kullanılan önemli bir yöntemdir.

Atık sulardan fenol ve fenolik kirleticilerin giderilmesinde için zeolitler, karbon nanotüpleri, polimerik sorbentler ve kil gibi farklı adsorbanlar kullanılmaktadır.

Fenolik bileşiklerin adsorpsiyonunun üç mekanizması  $\pi$ - $\pi$  etkileşimleri, electron alışverişi ile kompleks oluşumu ve Hidrojen bağ oluşumudur. Bu deneyimler fenollerin giderimi için yeni polimerik sorbentlerin hazırlanmasında kullanılmıştır.

Bu tezde iki farklı sorbent hazırlanmış ve sulu çözeltilerden fenol ve Bisfenol A giderilmesi için kullanılmıştır.

İlk olarak poli(HEMA-MMA-EGDMA) terpolimeri sentezi gerçekleştirilmiştir. Bu sentez işlemi için başlatıcı olarak AIBN, çapraz bağlayıcı olarak etilen glikol dimetakrilat (EGDMA) (%10), monomer olarak da hidroksietil metakrilat (HEMA) (%50) ile metil metakrilatın (%40) ve porojen olarak da toluen varlığında süspanسیون polimerizasyon yöntemi gerçekleştirilmiştir (reçine 1).

Elde edilen bileşiklerin spektroskopik karakterizasyonu için FT-IR kullanılmıştır. Reçine1'in FT-IR spektrumuna göre, 3300-3500  $\text{cm}^{-1}$  aralığındaki geniş aralık -OH gerilim titreşimleri ve 1722  $\text{cm}^{-1}$ 'deki keskin pik, terpolimer içindeki karbonil gruplarına karşılık gelmektedir.

Diğer polimerik reçine redoks polimerizasyonu metoduyla reçine 1 üzerine poli(akrilamid)'in aşılınmasıyla elde edilmiştir. Redoks polimerizasyonu sırasında başlatıcı olarak seryum amonyum nitrat kullanılmıştır. Aşı polimerizasyonu HEMA birimleri üzerindeki hidroksil grupları aracılığıyla gerçekleştirilmiştir.

Reçine 2 içerisinde bulunan toplam azot içeriğini belirlemek amacı ile Kjeldahl azot analizi yöntemi kullanılmıştır. Analiz sonucuna göre 7 mmol/g azot içeriği reçine 2 içerisinde saptanmıştır.

Reçine 2 nin amaçlanan bileşik olduğunu ispatlamak amacı ile tekrar reçine 2 için FT-IR analizi yapılmış ve istenilen sonucun elde edilmiş olduğu görülmüştür. Reçinenin FT-IR spekturumuna göre 3300-3500  $\text{cm}^{-1}$  arasında gözlemlenen -NH grubuna ait pikler ve 1655  $\text{cm}^{-1}$  deki pik, reçine'deki amid grubunun -C = O gerilme titreşimine karşılık gelmektedir

Poli (akrilamid) aşılınmış reçinenin (reçine2)'nin toplam azot içeriği 7,0 mmol/g olarak bulunmuştur. Fenol ve Bisfenol A reçine 1 ve reçine2 üzerinde ki tutma kapasiteleri pH ve konsantrasyona bağlı olarak bulunmuştur.

Aynı zamanda reçinelerin fenol ve Bisfenol A tutma kinetikleri incelenmiştir. Reçine 1 ve reçine 2 için kinetik modelleri uygulanmıştır.

Kinetik incelemeler için yalancı birinci dereceden kinetik denklem ve yalancı ikinci dereceden kinetik denklemler deneysel sonuçlara uygulanmıştır. Yapılan incelemeler

sonucunda fenol ve bisfenol A'nın adsorpsiyonunun yalancı ikinci dereceden kinetik modele uygun olduđu görülmüştür.

Bu sonuçların yanı sıra fenol ve bisfenol A'nın tutma kapasiteleri arasında ki farklar deneysel sonuçlar üzerinden de açıklanmıştır.



## 1. INTRODUCTION

Wastewater treatment is important environmental and public problem because of organic pollutants. Furthermore, faced with more and more stringent regulations, water pollution has also become a major source of concern and a priority for most industrial sectors. Aromatic compounds (including phenolic derivatives and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses [1].

Phenolic wastewater, is highly toxic and unhealthy; also occurred from chemicals, pharmaceuticals, petroleum, coal gasification, papermaking, wood, rubber, dye, and pesticide industries [2].

Some important effects from breathing phenol in air have been reported in humans. Short-term effects are caused respiratory irritation, headaches, or burning eyes. In addition, chronic effects of high exposures contain weakness, muscle pain, anorexia, weight loss, or fatigue. Effects of long-term low-level exposures include increases in respiratory cancer, heart disease, and effects on the immune system [3].

Many different methods are used for remove phenol from aqueous solution, such as, adsorption, microbial degradation, chemical oxidation, precipitation, ion exchange and solvent extractio. Adsorption is an effective separation process for treating industrial and domestic effluents [4,5,6].

Between them, physical adsorption method is usually considered to be best, effective, low cost, and most frequently used method for the removal of phenolic pollutants. It is now recognized as an effective, efficient, and economic method for water decontamination applications and for separation analytical purposes.

The mineral, organic, or biological origin: such as activated carbons, zeolites, clay, silica beads, etc are used as adsorbents. On the other hand the activated carbon is low

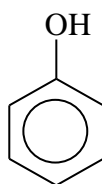
economically viable as excellent adsorbent because of high initial cost and the need for a costly regeneration system [7,8].

Consequently, the search for low cost and easily available adsorbents has led many researchers to search more economic and efficient techniques of using the natural and synthetic materials as adsorbents [9].

## 2. THEORY

### 2.1 Phenol

Phenols are aromatic components, which include one or more hydroxyl groups, and these groups are added to an aromatic ring [10]. Phenol is a colourless, crystalline substance of characteristic odour. Also phenol is soluble in water and organic solvents. In The List of Priority Pollutants by the US Environmental Protection Agency (US EPA), phenol was one of the first compounds. The extraction of coaltar as it is formed by transformation of high quantities of cumene present in plants that were used for tar production is used for the synthesis of phenol on an industrial scale. Additionally phenol is occurred in a reaction between chlorobenzene and sodium hydroxide, toluene oxidation and synthesis from benzene and propylene [11]. Phenol is a benzene derivative; also, is the simplest member of the phenolic chemical. The formula of phenol is  $C_6H_5OH$ , and a hydroxyl group (-OH) bonded to a phenyl ring. Synonyms for phenol contain carbolic acid, benzophenol, and hydroxybenzene [12].



**Figure 2.1 :** Structure of the phenol

#### 2.1.1 History of phenol

Until the end of the nineteenth century, the coal tar was used synthesis of phenol. Nowadays, a small amount of phenol is still occurred from coal tar. Felix Hoffmann filed his patent in 1898 [14] for the synthesis of acetylsalicylic acid (Aspirin), which required phenol as starting material.

At the beginning of the twentieth century, the requirement for phenol grew significantly with the commercialization of the phenolic resins (Bakelite). In May 1910, first phenolic resins plant was released by Leo Baekeland in Germany since phenol was obtained coal tar. Much later, phenol became an important factor for

synthesis polycarbonates and epoxide resins Synthetic routes were improved at the end of the nineteenth century to meet the increasing request for phenol. The first synthetic method for occurred of phenol is sulfonation and later chlorination of benzene. Whereas, these methods are not longer used for the commercial production of phenol [15].

The cumene- to- phenol process (Hock-Process) developed and commercialized after the Second World War. It is currently the predominate route for the production of phenol. It is accompanied by acetone as a co-product.

In the 1960s, the first commercial plant using toluene as the feedstock was released. The method was developed at the same time by Dow [16] and the California Research Corp [17]. Nevertheless, all commercial plants were closed in 2006. Nowadays, commercial production of phenol is not obtained from toluene [18].

### **2.1.2 Synthesis of phenol**

The phenol is synthesised by different chemical ways. Some important chemical ways for producent of the phenol:

- By Displacement of other functional groups
- By Cycloaddition
- By Condensation
- By Oxidation
- By Rearrangement

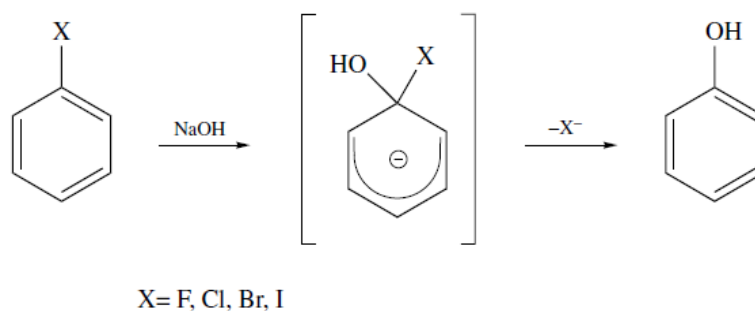
By displacement of other functional groups:

The aryl halides, sulphonic acids, and nitrogen derivatives are used for the synthesis of phenol.

- From aryl halides:

The an important industrial method of alkaline fusion is used for the production of phenol. For example, bromo benzene in dilute sodium hydroxide occure an 89% yield of phenol at 236 °C in 2.5 h. [19]

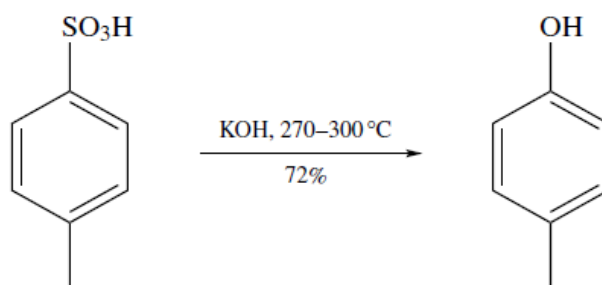




**Figure 2.2 :** Synthesis of phenol from aryl halides

➤ From sulphonic acids:

Aryl sulphonic acids can be changed to phenols by alkali fusion through their salts. The industrial production of phenol is obtained by this method. Although in extreme situations, the reaction gives fairly good yields, except when the substrate contains other groups that are attacked at the fusion temperatures by the alkali [20].



**Figure 2.3 :** Synthesis of phenol from sulphonic acids

➤ From nitrogen derivatives:

The synthesis of phenol from nitrogen derivatives are classified into three types:

- Hydrolysis
- Bunherer reaction
- Diazotation reaction

By oxidation :

The different ways are used to synthesis of phenol in the oxidation reactions:

- Hydroxylation
- Oxidation of organometallic derivatives
- Oxidation of nitrogen derivatives

- Oxidation of carbonyl groups

By condensation:

The cyclization, claisen and aldolic condensation, and radical cyclization are used for obtained of phenol. The aldolic condensation methods are classified two types: intramolecular reaction and intermolecular reaction. The intermolecular reaction is used for the obtained monophenols and resorcinols.

By cycloaddition:

The cycloaromatization, diels-alder reaction and benzannulation methods are used for occurred of phenols.

By rearrangement:

This methods are included five types of synthesis of phenol:

- Alkyl and benzyl aryl ethers
- Allyl aryl ethers and aromatic claisen rearrangement
- Diaryl ethers and smiles rearrangement
- Dienones and dienone–phenol rearrangement
- Phenolic esters and fries rearrangement

### **2.1.3 Physical properties of phenol**

Phenol is a solid and appears as a white amorphous material at ambient temperatures. It possesses a melting point of 40.9 °C. In the molten state, pure phenol is a clear, colorless liquid and when exposed to air, phenol rapidly convert to a pink color in consequence of certain trace impurities for instance iron and copper that are present in its production process or during storage.

The melting and solidification temperature is lowered considerably by traces of water approximately 0.4°C per 0.1 wt% water. When around 6 wt% water is added and occurred liquid phenol at room temperature. Phenol is only partially miscible with water at temperatures below 68.4°C. Phenol is soluble in aromatic hydrocarbons, alcohols, ketones, ethers, acids, and halogenated hydrocarbons, but this material less soluble in aliphatic hydrocarbons. Phenol is occurred azeotropic mixtures with water, cumene, and a-methylstyrene (AMS) [21].

#### **2.1.4 Chemical properties of phenol**

The phenol has the unexampled chemical properties. Hydroxyl group and an aromatic ring is provided these unexampled chemical properties which are complementary to each other in facilitating both electrophilic and nucleophilic type of reactions. Phenol has a high reactivity of its ring toward electrophilic substitution and the reaction between phenol and formaldehyde with acid catalyzed is used for obtained phenolic resins. Also, phenol is a weak acid and readily forms sodium phenate (NaPh). When presence of NaPh, nucleophilic addition of the phenolic aromatic ring is occurred to the carbonyl group of formaldehyde. A base catalyzes the reaction is provide converting phenol into the more reactive (more nucleophilic) phenate or phenoxide ion for reaction with formaldehyde. In this way phenol's unique ability to react with formaldehyde under acidic or basic conditions provide either to novolaks resins (via acid conditions) or resole resins (basic conditions), were the resin reactions that fostered the commercialization of phenolic resins, Bakelite, by Baekeland. The unshared electron pair located on the hydroxyl group is delocalized over the aromatic ring leading to an electron excess at the ortho and para positions. The phenol is made classical electrophilic reactions with halogenation, sulfonation, and nitration. The reaction of bromine in aqueous solution provide in 2,4,6-tribromophenol in high yields. Under special conditions acid catalysts facilitate the conversion of phenol with formaldehyde to bisphenol-F or reaction of acetone to bisphenol-A. Phenol can be hydrogenated on palladium catalysts to cyclohexanone with high selectivities [22,23]. Cyclohexanone is the feedstock for the production of caprolactam monomer for Nylon 6.

#### **2.1.5 Usage areas of phenol**

Phenol is a important chemical with production exceeding 3-billion pounds annually in the United States and 6-billion pounds world wide. It ranks in the top 50 in production volumes for chemicals produced in the United States and is used housing and construction industries [24]. Produce of phenolic resins is the largest single use of phenol, reported to be 1.188 billion pounds in 1988 [25]. Phenol is usually sold commercially as a thick liquid.

The phenol is used for two major areas :

- Phenolic resins (human made polymers consisting of phenol) is used for plywood adhesive, construction, automotive, and appliance industries
- Caprolactam is made from phenol which is used in the manufacture of nylon 6 and other synthetic fibers

Phenol is also used as an antiseptic, a general disinfectant, and a slimicide (chemicals that kill bacteria and fungi in slimes), in medical preparations including lotions, ointments, mouthwashes, salves. Phenol is also the active ingredient in some over-the-counter oral anesthetics sprays used as a treatment for sore throats. Minor uses of phenol contain the manufacture of paint and varnish removers, lacquers, paints, rubber, ink, illuminating gases, tanning dyes, perfumes, soaps and toys [26,27].

### **2.1.6 Hazards of phenol**

Phenol also penetrates the environment through vehicle exhaust, and it is used as a disinfectant and reagent in chemical analysis. In the United States alone, are 580,000 people occupationally exposed to phenol influence [28]. Phenol is also formed as the result of chemical reactions that occurred in the atmosphere in condensed water vapour that forms clouds. Hydroxy benzene is also formed during natural processes like biosynthesis by plants or decomposition of organic matter [29]. This compound is also formed from aminoacids contained in plants' hemicelluloses under the influence of UV irradiation (sunlight) [30] and tyrosine transformation in mammalian (including human) digestive tract [31]. The concentrations of phenol in surface water are different. In natural waters its amounts are between 0.01 – 2.0 µg/L [32]. Relative fast degradation of phenol causes its concentration in waters exposed to strong anthropogenic pollution may be comparable.

Organic compounds has toxic influence and this influence depends on many factors. Penetration of phenol to organisms is related with diffusion of the compound across a cell's membrane [33].

Phenol irritates skin and causes its necrosis, and same time it damages kidneys, liver, muscle and eyes. Damage to skin is caused by its coagulation related to reaction to phenol with aminoacids included in keratin of epidermis and collagen in inner skin [34]. In a dose of 1 g phenol maybe lethal for an adult man, but individual tolerance for this compound can be high. Some reports reveal that aman can survive even after

administration of 30 g of this compound (60 ml of 50% solution). In regard to fast absorption by skin (from 60%-90%) even contact of hand or fore hand with phenol solution may cause death [35].

Acute poison with phenol is caused by dryness in throat and mouth, dark-coloured urine and strong irritation of mucous membranes. The phenol vapours cause chronic exposure for workers and occurred anorexia, loss of body weight, weakness, headache, muscle pain and icterus on human [36].

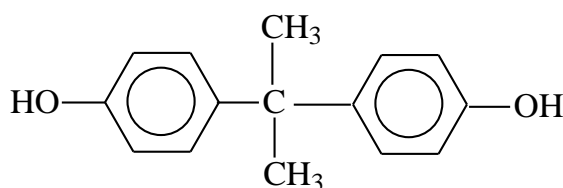


**Figure 2.4 :** Treatment of wastewater from phenol

## 2.2 Bisphenol A

Bisphenol A (BPA) is a chemical material and is used primarily in the production of polycarbonate plastics and epoxy resins [37].

Bisphenol-A (BPA) is one of the derivatives of phenol. BPA chemical name is 2, 2-(4,4-dihydroxy phenyl) propane and it occurs from one mol acetone and two mols phenol plus. The BPA is a solid material. It has a low volatility feature at normal environmental temperature and  $C_{15}H_{16}O_2$  formula. Its solubility in water is greater in an alkaline pH and ranges from 120 to 300 mg/L [38].



**Figure 2.5 :** Chemical structure of Bisphenol A

Polycarbonate is a light weight, high-performance plastic that possesses a unique balance of shatter-resistance and optical clarity as well as high heat and electrical resistance. A wide variety of polycarbonate products are made possible by these attributes. The polycarbonate products are used for eyeglass lenses, digital media (e.g., CDs, DVDs), electronic and electrical equipment housings (e.g., personal computers, appliances, power tools), automobile headlight lenses, sports safety equipment (e.g., helmets, goggles), components of medical devices (e.g., blood oxygenators, dialyzers, incubators) and reusable food and drink containers. Epoxy resins are most commonly used as protective coatings as a consequences of their exceptional combination of toughness, adhesion, formability and chemical resistance [39].

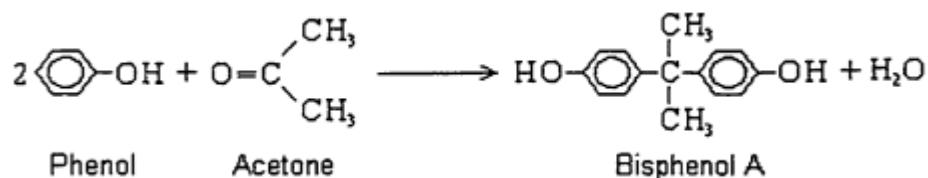
### **2.2.1 History of BPA**

The first reported synthesis of BPA was from Thomas Zincke of the University of Marburg, Germany. Zincke acknowledged in his paper that the obtained of BPA, from phenol and acetone, was based on chemical reactions previously reported by others as well as unpublished work (from thesis dissertations) conducted at the University of Marburg. His paper reporting the obtained of BPA and a number of related compounds was published in 1905.

In 1953, a new plastic material is independently obtained as known polycarbonate, form bisphenol A as the starting material by Dr. Hermann Schnell of Bayer in Germany and Dr. Dan Fox of General Electric in the United States. Polycarbonate plastic was accepted unique combination of very important properties, such as particular optical clarity, shatter-resistance and high heat-resistance, which have made polycarbonate an important part of everyday life in a wide variety of applications. In 1957 in the United States and in 1958 in Europe, commercial production was started. At the same time, epoxy resins were improved with the versatility to meet a wide range of industrial and consumer needs. Commercial production of BPA began in the 1950's when large-scale uses for polycarbonate plastic and epoxy resins were improved and has grown world wide along with the continued growth of the uses for these materials [40].

### 2.2.2 Synthesis of BPA

The acid catalyzed condensation of acetone with 2 moles of phenol is the earliest method for manufacturing bisphenol A.



**Figure 2.6 :** Synthesis of Bisphenol A

Serious conditions are not necessary; a 1:2 molar ratio mixture of acetone and phenol, in the presence of concentrated hydrochloric acid or sulfuric acid 70% at room temperature deposits a mass of crude BPA crystals [41].

The most industrially used processes for making BPA in the ‘United States and Western Europe’ are the acetone-phenol ones, in homogenous as well as heterogeneous catalysis; also if considered the costs involved and the net advantages the heterogeneous catalysis offers, the resin-catalyzed process is preferred and it has been developed continuously.

A process which considers reacting acetone with very little excess phenol (1:4 to 1:12 molar ratio acetone:phenol in the initial reaction mixture) was reported [42]. The reaction of this process is separated two stage. In the first stage the acetone is reacted with very little excess phenol in the presence of a sulfonated cation exchange resin catalyst modified with a mercapto group including compound to convert 20 to 60% of acetone. Then the reaction mixture from the first stage is reacted in the presence of hydrochloric acid as catalyst in the second stage [41].

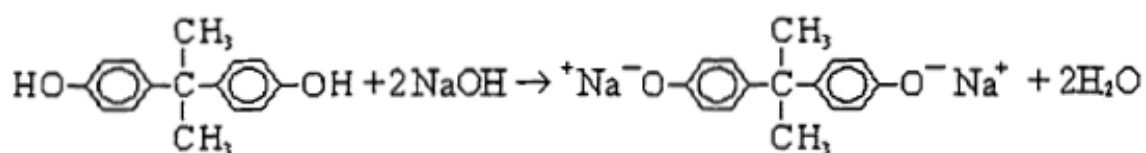
### 2.2.3 Physical properties of BPA

BPA is a solid and is sold as crystal, prills or flakes at ambient conditions. While BPA is molten at elevated temperatures during manufacturing (melting point=150-155°C), releases to the environment are generally dissolved in

water or are in the form of particulates. BPA has a reported water solubility of 120-300 mg/L [43,44]. The U.S. Environmental Protection Agency (EPA) cites an unlisted reference that states that BPA has greater solubility at alkaline pH values due to its dissociation constants, pKa 9.6 to 10.2 [45].

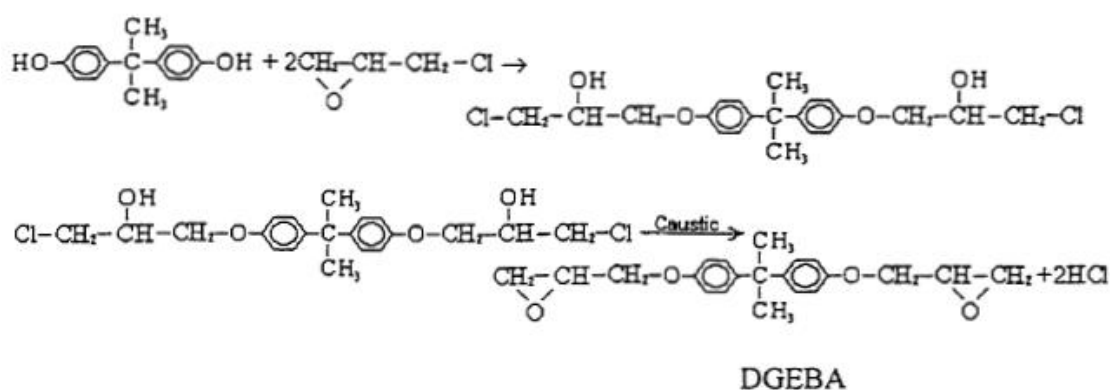
## 2.2.4 Chemical properties of BPA

Bisphenol A reacts as a typical para-substituted phenol. One or both hydroxyl groups, one or both rings can experience modifications. Transformations involving the aliphatic methyl groups of the bonding group can also take place.



**Figure 2.7 :** BPA is converted by caustic alkalis into its soluble alkali salts

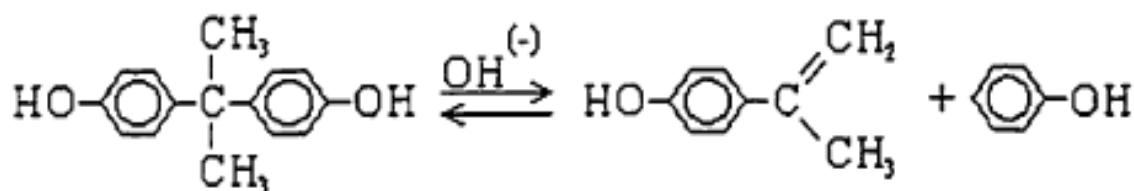
Bisphenol A is reacted with epichlorohydrin to form a bis(chlorohydroxypropyl) ether which yields the diglycidyl ether (DGEBA), the monomer for most epoxy resins, in a caustic medium [41]:



**Figure 2.8 :** Synthesis of DGEBA

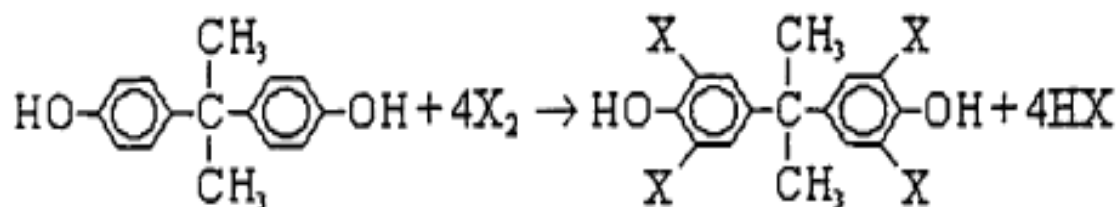


One of the side reactions that can obtain in the melt polycondensation, one of the processes used for producing polycarbonate resins, is generated by the instability caused by the hydroxyl groups. At temperatures exceeding 150°C more reactive isopropenyl phenol is produced:



**Figure 2.9 :** Side reaction of the polycarbonate resins

The aromatic protons contiguous to the hydroxyl groups in BPA are easily substituted. The halogenation of the aromatic rings in the ortho positions relative to the hydroxyl groups is useful for making flame retardants [46]:



**Figure 2.10 :** The halogenation of the aromatic rings

The electrolysis of a concentrated aqueous solution of BPA conducted on a platinum mesh obtain with total degradation of the aromatic rings, leading in the end to simple short chain aliphatic acids. This procedure is preferred for BPA removal from wastewaters. BPA forms solid bring closer with phenol and cresols. The formation of these products is not well understood. They are used in the procedure of BPA purification [41].

### 2.2.5 Usage areas of BPA

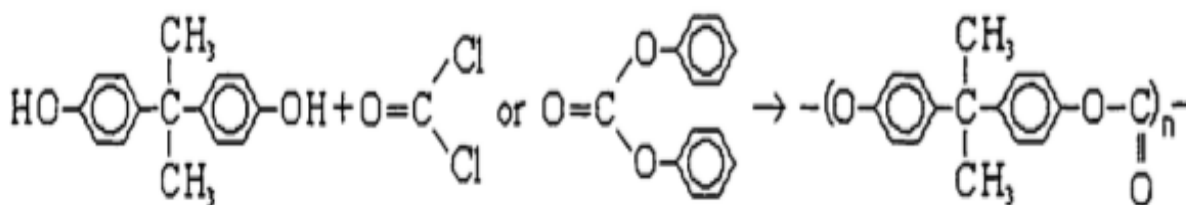
BPA is used generally as an intermediate for the production of other products. The important uses of BPA are binding, plasticizing, or hardening functions in plastic products, paints/lacquers, binding materials and filling-in materials. The material is used for different areas such as the chemical industry, the iron/metal industry, the building and construction industry, the plastics industry and the service industry.

BPA is usually used for the manufacture of polycarbonate resins (71%); epoxy resins (27%); unsaturated polyester, polysulfone, polyetherimide and polyarylate resins (25%). Non polymer BPA is preferred as additive because of many different properties such as flame-retardants, brake fluids and thermal papers [47].

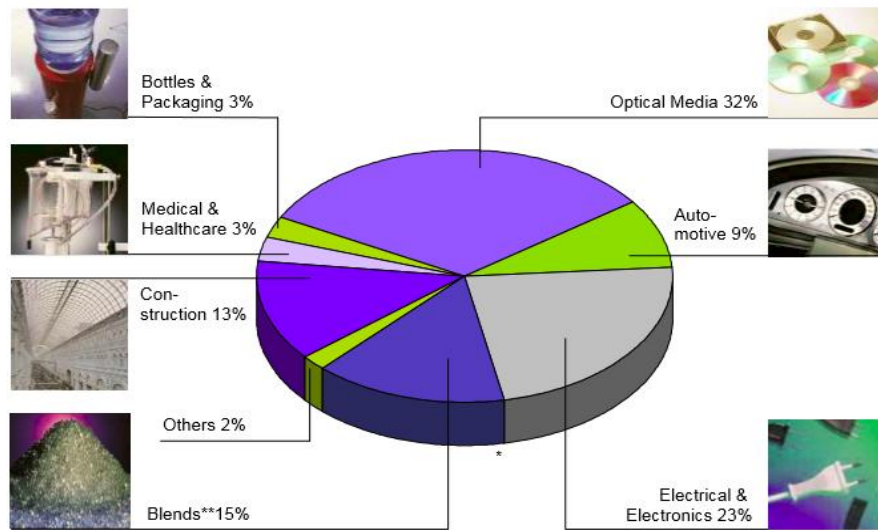
In 1953, Dr. Hermann Schnell of Bayer in Germany and Dr. Dan Fox of General Electric in the United States independently developed manufacturing processes for a new plastic material, polycarbonate, using BPA as the starting material [40].

Polycarbonates are obtained by esterification of BPA with phosgene or its dibenzoate ester [41]. Other diacid chlorides have been also reacted with BPA to obtain polycarbonates [48].

Polycarbonate plastic is used for structural parts, impact-resistant glazing such as safety helmets and bullet resistant laminate, street-light globes, household appliance parts, sheet and glazing applications, components of electrical/electronic devices, compact discs, automotive applications, reusable polycarbonate bottles, food and drink containers, powder paints protective coatings and many other products [49].

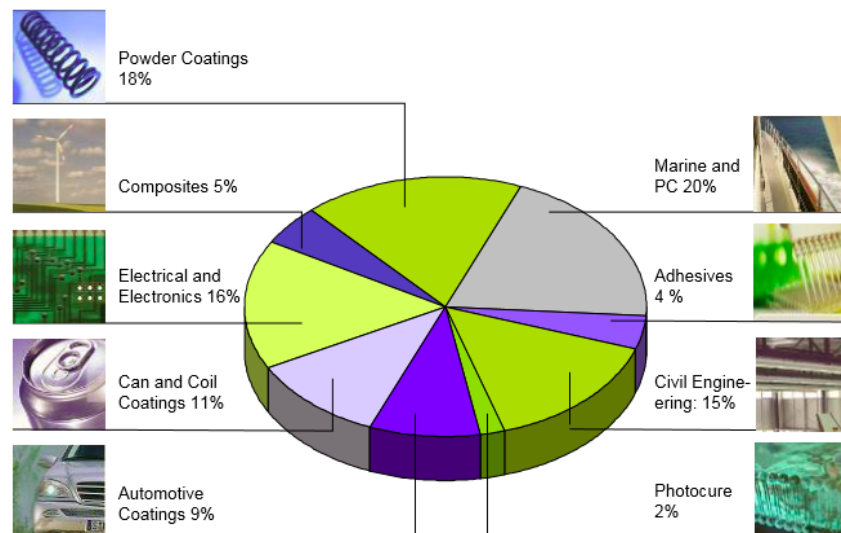


**Figure 2.11 :** Polycarbonate resins



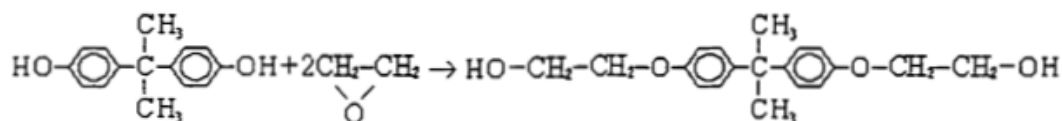
**Figure 2.12 :** Application areas of polycarbonate

The diglycidylether of BPA (BADGE) is used in the manufacture of epoxy resins, and its are liquid resins that cure to form hard, insoluble, chemical resistant plastics when hardening agents are added. Cured epoxy resin is used for coatings such as corrosion protectors, lacquers in the automotive industry, housings for electrical equipment, laminates, industrial floorings, construction parts, composites, adhesives, lacquers on food and beverage cans [51].



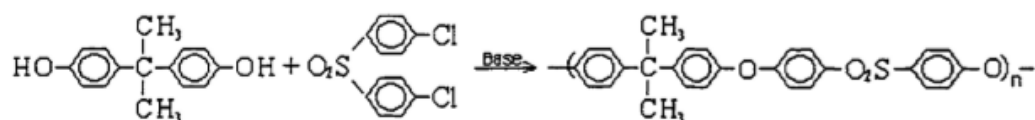
**Figure 2.13 :** Application areas of epoxy resin

Dow and ICI Amencia produced ethers for use as components of unsaturated polyesters, (polyesters of fumaric acid for example), and for coatings applications by reacting BPA with epoxides. In this reaction the phenolic groups are hydroxyalkylated.[41].



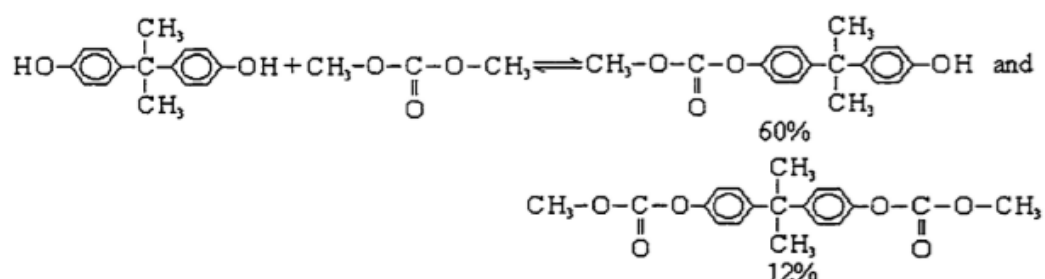
**Figure 2.14 :** Synthesis of unsaturated polyesters

Polymers with terminal phenolic groups are obtained when reacting BPA with less than one molar equivalent of a dihalide such as bis (2-chloroethyl ether) or 1,4-bis(chloromethyl)benzene. Commercial polysulfone resins are manufactured when reacting stoichiometric amounts of BPA and bis(4-chlorophenyl)sulfone:



**Figure 2.15 :** Synthesis of polysulfone resin

Poly(arylenecarbonate)s oligomers can be obtained by carbonate interchange reaction of dimethyl carbonate with BPA [41,52]:



**Figure 2.16 :** Synthesis of poly(arylenecarbonate)

### 2.2.6 Hazards of BPA

Most domestically produced BPA is used as an intermediate in the production of polycarbonate and epoxy resins, flame retardants, and other specialty products. Polycarbonate plastic is used to make a variety of common products, including baby and water bottles, sports equipment, and medical device. Epoxy resins are used as coatings to line the inside of almost all food and beverage cans to prevent the contents from reacting with the metal. BPA can migrate into foods from cans and from polycarbonate plastic products such as baby bottles, tableware, and food containers. The use of BPA in food and beverage containers accounts for the majority of daily human exposure; estimated human consumption of BPA from epoxy-lined food cans alone was 6.6 µg/person-day [54].

The primary route of BPA contamination in the aquatic environment is effluent from wastewater treatment plants and landfill sites [55]. Wastewaters from kraft pulp, printing paper, and packing-board paper plants contain high concentration of BPA [56]. Plants can rapidly absorb BPA through their roots from water and metabolize it to several glycosidic compounds. Glycosylation, the main route of BPA metabolism in plants, leads to loss of estrogenicity of the parent compound. BPA mono- and di-b-D-glucopyranosides show reduced or no estrogenic activity in in vitro tests [57].

Photolysis and photo-oxidation are the main non-biological pathways of BPA breakdown in the aquatic environment. Photodegradation of BPA is slow in pure water, but can be accelerated in the presence of: a) dissolved organic matter, including humic and fulvic acid, [58-60] b) reactive oxygen species, including hydroxyl radicals, peroxy radicals and singlet oxygen [60-62], and/or c) ions, including ferric and nitrate ions [59-63]. In artificial indoor streams, DT50 values (time when 50% of initial BPA disappeared) were about 1 day [64].

The most probable routes of human exposure to bisphenol A are inhalation and dermal contact of workers involved in the manufacture, use, transport or packaging of this compound or use of epoxy powderpaint. Furthermore the exposure through the leaching of BPA from flasks and cans into food, may be important route of exposure.

BPA is slightly toxic to mammals by the intraperitoneal route, eyes and skin. On the other hand BPA is very slightly toxic to mammals by ingestion. BPA is furthermore

an experimental teratogen but not proven to be a carcinogen. BPA is furthermore estrogenic in the in-vitro E-screen, stimulates cell proliferation and induces expression of estrogen responsive genes. In-vivo, BPA increase prolactin release and stimulates uterine, vaginal and mammary growth and differentiation [65].

### **2.3 Removal of phenolic compound**

Organic pollution is the term used when large quantities of organic compounds. It originates from domestic sewage, urban run-off, industrial effluents and agriculture wastewater. sewage treatment plants and industry including food processing, pulp and paper making, agriculture and aquaculture. During the decomposition, process of organic pollutants the dissolved oxygen in the receiving water may be consumed at a greater rate than it can be replenished, causing oxygen depletion and having severe consequences for the stream biota. Wastewater with organic pollutants contains large quantities of suspended solids, which reduce the light available to photosynthetic organisms and, on settling out, alter the characteristics of the riverbed, rendering it an unsuitable habitat for many invertebrates. Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, proteins and carbohydrates [66,67].

Toxic organic pollutants cause several environmental problems to our environment.

Phenols are generally considered one of the important organic pollutants discharged into the environment causing unpleasant taste and odor of drinking water. The major source of phenol pollution in the aquatic environment are wastewaters from paint, pesticide, coalconversion, polymeric resin, petroleum and petrochemical industries [68,69].

There are several reported methods for the removal of pollutants from the effluents. The technologies can be separated into three categories: biological, chemical and physical. All of them have advantages and drawbacks. Because of the high cost and disposal problems, many of these conventional methods for treating phenol bearing wastewater have not been widely applied at large scale in the textile and paper industries.

Physical operations:

- Screening
- Comminution
- Flow equalization
- Sedimentation
- Flotation
- Granular-medium filtration
- Adsorption

Chemical operation:

- Chemical precipitation
- Disinfection
- Dechlorination
- Other chemical application

Biological operations:

- Activated sludge process
- Aerated lagoon
- Trickling filters
- Rotating biological contactors
- Pond stabilization
- Anaerobic digestion
- Biological nutrient removal [70,71].

Biological treatment is often the most economical alternative when compared with other physical and chemical processes.

Chemical processes contain coagulation or flocculation combined with flotation and filtration, precipitation–flocculation with  $\text{Fe(II)/Ca(OH)}_2$ , electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques have high cost and although the phenols are removed, mass of concentrated sludge creates a disposal problem. This technique has a secondary pollution problem will arise because of excessive chemical use.

There are different physical methods are also widely used, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis, etc.) and adsorption techniques. The membrane processes have major disadvantage that they have a limited life time before membrane fouling occurs and the cost of periodic

replacement must thus be contained in any analysis of their economic viability. Consistency with the very abundant literature data, liquid-phase adsorption is one of the most important methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high quality treated effluent.

Adsorption process has attractive alternative for the treatment of contaminated waters, especially if the adsorbent has low cost and does not necessarily require an additional pre-treatment step before its application [70,71].

## 2.4 Adsorption

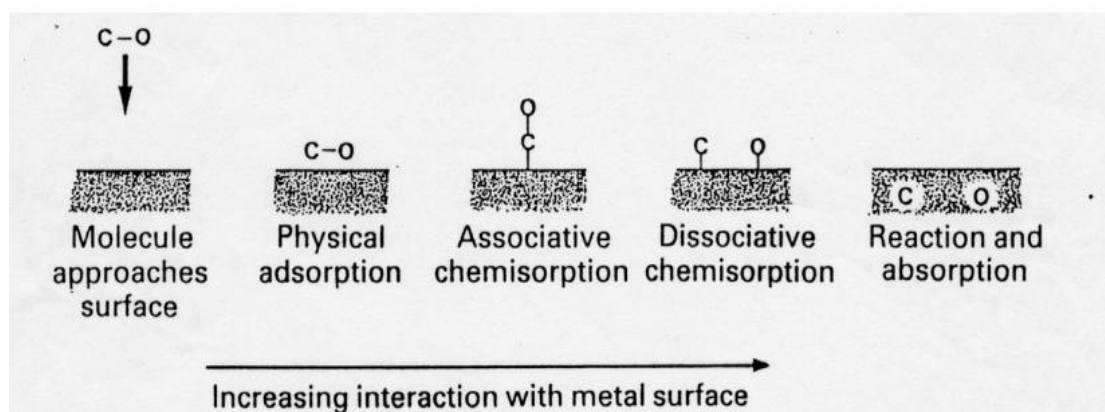
Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutants removal. The adsorption method is a process in which a substance (adsorbate), in gas or liquid phase, collects on a solid surface (adsorbent). It is based on the capability of porous materials with large surfaces to selectively retain compounds on the surface of the solid (adsorbent). The adsorption process of the adsorbate molecules from the bulk liquid phase into the adsorbent surface is presumed to involve the following stages:

- Mass transfer of the adsorbate molecules across the external boundary layer towards the solid particle.
- Adsorbate molecules transport from the particle surface into the active sites by diffusion within the pore-filled liquid and migrate along the solid surface of the pore.
- Solute molecules adsorption on the active sites on the interior surfaces of the pores.
- Once the molecule is adsorbed, it may migrate on the pore surface through surface diffusion [72].

There are two types of adsorption :

- Physical adsorption
- Chemical adsorption





**Figure 2.17 :** Adsorption of carbon monoxide on various solid surface

### 2.4.1 Physical adsorption

Physical adsorption is obtained by Van der Waals forces, dipole interactions and hydrogen binding. There is no electron exchange between adsorbent and adsorbate. Because this method has no activation energy necessary for physical adsorption, the time needed to reach equilibrium is very short. Physical adsorption is reversible process and a non-specific methods.

### 2.4.2 Chemical adsorption

Chemical adsorption is occurred by the chemical link between adsorbent and adsorbate molecule, for this reason it is specific as well as irreversible and chemical as well as electronic properties of adsorbent are changed.

Binding between adsorbent and adsorbate by covalent bond is called weak chemical adsorption, and that by ionic bonds is called strong chemical adsorption [72].

### 2.4.3 Adsorbents type in adsorption of the phenolic compounds

Different types of adsorbents are classified into natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential formodification and ultimately enhancement of

their adsorption capabilities. Synthetic adsorbents are adsorbents prepared from agricultural product sand wastes, household wastes, Industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces [73].

#### **2.4.3.1 Clay**

Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high adsorption properties and potential for ion-exchange, clay materials are strong candidates as adsorbents. Clay materials possess a layered structure and are considered as host materials. They are classified by the differences in their layered structures. The clays have different class of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite [74].

Montmorillonite clay has biggest surface area and the high cation exchange capacity. Its current market cost (about US\$ 0.04–0.12/kg) is considered to be 20 times lower cost than that of activated carbon [70]. In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and Fuller's earth for their capacity to adsorb not only inorganic but also organic molecules. The potential of bentonite for phenol adsorption from aqueous solutions was studied by Banat et al. [75]. The adsorption process was significantly influenced by the solvent type in which phenol was dissolved. The affinity of phenol to bentonite in the presence of cyclohexane was greater than that in water and was lowest in the presence of methanol [76].

#### **2.4.3.2 Zeolites**

Zeolites are a naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms [77,78]. Zeolites have been receiving increasing attention for pollution control. An important property of zeolites is the capacity to be easily regenerated while keeping their initial properties [79].

### **2.4.3.3 Activated carbon**

Adsorption on activated carbon is currently the most frequently used technology for removing organic pollutants from aqueous industrial effluents, surface water, sand, drinking water [80].

Adsorption of phenolic compounds from aqueous solutions by activated carbon is one of the most investigated of all liquid-phase applications of carbon adsorbents [81].

In particular, the effectiveness of adsorption on commercial activated carbons (CAC) for the removal of a wide variety of phenolic compounds from waste waters has made it an ideal alternative to other expensive treatment options. Because of their large capacity to adsorb phenols, CAC are the most effective adsorbents. This capacity is mainly due to their structural characteristic and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages [70]. The regeneration of saturated carbon is also expensive, not straight forward, and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications [82].

### **2.4.3.4 Synthetic polymers**

The adsorption of phenols onto a polymeric sorbent such as; SP206, a polystyrene matrix crosslinked with divinyl benzene [72]. Laszlo investigated the adsorption of phenol and 2,3,4-trichlorophenol on carbon prepared from polyethylene (terephthalate). Pan investigated the role of amination of a polymeric adsorbent on phenol adsorption from aqueous solution. They investigated the adsorption on a hypercrosslinked polymeric adsorbent (CHA- 111) and its dimethyl amine derivative [83].

The phenols are phenol, p-cresol, 2-Naphthol, p-nitro phenol, 2,4-Dichlorophenol, 2,4-Dinitrophenol. It was observed that dimethyl amine derivative showed a higher adsorption capacities than ordinary polymeric adsorbent due to hydrogen bonding interaction with the amino groups and the adsorbate molecules.

The removal of phenolics species onto  $\beta$ -cyclodextrin modified poly (hydroxy-ethyl methacrylate ethyleneglycol dimethacrylate, poly HEMA-EGDMA) micro beads was studied by Abay [84]. They investigated the adsorption of phenol, o-chlorophenol, p-chlorophenol, o-nitrophenol, p-nitrophenol on plain micro beads of  $\beta$ -cyclodextrin polymer and its modified derivative poly (HEMA-EGDMA).

#### **2.4.4 Effecting factors of adsorption**

##### **2.4.4.1 Solvent effect**

The solvent effects should be taken into consideration in adsorption studies. The hydrogen bonding absorb water molecule on the surface oxygen groups which is unfavorable for the adsorption of phenols as some activated sites are occupied. Assuming that water molecules, adsorbed on oxygen groups, become secondary adsorption centres retaining other water molecules by means of H-bonds. The adsorbed water molecules block the entry of organic molecules to significant parts of the surface [85,86].

##### **2.4.4.2 Molecular size**

The molecular size is important factor for the adsorption. The molecules has suitable size would be adsorbed more favourably since they have more contact sites with the carbon surface. Contrarily, if the substance has molecular size is relatively large, it will have difficulties in moving within pores with size not large enough, according to the as known steric effects. The steric effects are possibly caused by the following reasons: some extremely low size pores might be inaccessible for big molecules; the interior part of the pores might not be reached due to the blockage of the adsorbed molecules; the molecules could not be so compact in pores due to the introduction of the substituent groups [87,88].

##### **2.4.4.3 Adsorbate**

The characteristics of ion, molecules (size, shape, charge, etc.) present in wastewater and their concentration have profound influence on the extend of adsorption. Phenols

are dissociated in aqueous medium to form anionic species at  $\text{pH} > 6$ . These anionic species adsorb at positively charged surface centers on adsorbents [89].

#### **2.4.4.4 Solubility**

Both, solubility and chemical structure of organics are important factors in adsorption. If the substance has more the solubility in water the lower the adsorption capacity of a given compound. The dissolution of adsorbate generally relates to its polarity; also, the more polar adsorbate has higher solubility in a polar solution. The adsorption capacities are known to depend on the solubility of the phenols compounds in water [90].

#### **2.4.4.5 Hydrophobicity**

The hydrophobic interactions are believed to make contributions to the adsorption of phenols [73]. The adsorbate with higher hydrophobicity in aqueous solution has stronger tendency to be adsorbed and sorbate on the carbon surface or in the pores. Hydrophobic compounds tend to be pushed to the adsorbent surface and; therefore, they are more adsorbed than hydrophilic compounds [72].

#### **2.4.4.6 Solution pH**

Solution pH is played an important role in the adsorption performance. Acidic or alkali species may change the surface chemistry of the adsorbent by reacting with the surface groups. These effects may bring about significant alterations in the adsorption equilibrium depending on the pH [91]. The functional groups exhibit pH-dependent interactions with water, which result in the transformation of the active sites [92,93]. The removal of acidic/basic species may thence bring about a concomitant shift in pH of both the medium and the surface. The adsorbate is mainly in protonated form at  $\text{pH} < \text{pK}_a$  and in deprotonated form at  $\text{pH} > \text{pK}_a$ . These effects may give rise to significant alterations in the adsorption equilibrium depending on the pH [94].

#### **2.4.4.7 Temperature**

The solvent effects are closely related to temperature, since temperature influences not only the hydration degree of the phenolic molecules but also the adsorption of water [95]. This negative effect of temperature on the adsorption of phenol is expected for physical adsorption that is exothermic in nature in most cases [96-98].

#### 2.4.5 Adsorption kinetics

The kinetic study of the adsorption equilibrium and kinetics is essential to supply the basic information required for the design and operation of adsorption equipment. A mass transfer consist during the adsorption process; the first step is the solute transfer through the adsorbent external surface film, and the others are the solute fluid diffusion into the pore holes and the adsorbed molecules migration along the pore surfaces, if it takes place. The former is characterized by the external mass transfer coefficient, and the last ones, by the internal pore and surface diffusivities. Available bulk adsorbate concentration in the liquid phase and adsorbed solute concentration in the solid phase are considered time-dependent [99].

Diffrent type models of kinetic are used fort he adsorption method, such as Pseudo-First-Order Equation and Pseudo-Second-Order Rate Equation.

##### 2.4.5.1 Pseudo-first-order rate equation

Pseudo-first-order equation was given by Langergren and Svenska (1898) to determine the rate constant of adsorption process as:

$$\log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t \quad (2.1)$$

where  $q_e$  and  $q_t$  are the amounts of the adsorbed (mg/g) at equilibrium and at time  $t$  (min), respectively, and  $k_1$  is the rate constant of adsorption ( $\text{min}^{-1}$ ). Values of  $k_1$  and  $q_e$  were calculated from the slope and the intercept of the plots of  $\log(q_e - q_t)$  versus  $t$  respectively at different concentrations.

#### 2.4.5.2 Pseudo-second-order rate equation

Equation of pseudo-second-order based on equilibrium adsorption can be expressed as:

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \quad (2.2)$$

$$\frac{t}{q_t} = \frac{1}{(k_2 \times q_e^2)} + \left( \frac{1}{q_e} \right) \times t \quad (2.3)$$

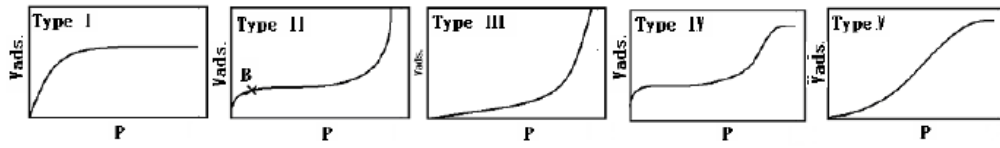
where  $k_2$ (g/mg·min) is the adsorption rate constant of pseudo-second-order adsorption rate. The value of  $q_e$  and  $k_2$  can be obtained from the slope and the intercept of the plot of  $t/q_t$  versus  $t$  respectively [100,101].

#### 2.4.6 Adsorption isotherm

Adsorption isotherm expresses the quantity of material adsorbed per unit mass of adsorbent as a function of the equilibrium concentration of the adsorbate. The necessary data are derived from experiments where a specified mass of adsorbent is equilibrated with a known volume at a specific concentration of a chemical and the resultant equilibrium concentration is measured in solution by the mass balance equation:

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (2.4)$$

Where  $C_o$  is initial liquid-phase concentration of solute,  $m$  is the mass of adsorbent and  $V$  is the isotherm solution volume. At a given temperature, the relationship between the equilibrium concentration of adsorbate in the solution and the amount of adsorbate on adsorbent is called the adsorption isotherm. Adsorption isotherms are commonly categorized into five types which are shown in Figure 16 [102].



**Figure 2.18 :** Classification of adsorption isotherms

- **Type I Isotherm:** These isotherms are used to characterize the sorption caused by predominantly microporous structure. This is also called the Langmuir isotherm and is used to describe monolayer adsorption.
- **Type II isotherm:** These isotherms are used to describe multilayer physical adsorption on macroporous structure and are also called sigmoid isotherm. Point B expresses the formation of a monolayer adsorption and multilayer coverage starts right after the point B. Solids with mixed micro- and mesoporosity show Type II isotherms.
- **Type III and Type IV:** These isotherms are found with microporous or mesoporous adsorbents and are convex at the high relative concentration. These are favoured by weak interactions between adsorbate-adsorbent systems and strong interaction between the adsorbate molecules lead to multilayer formation.
- **Type V isotherm:** These isotherms are commonly shown for mesoporous materials. After the formation of monolayer, the multilayer coverage starts. The total pore volume governs the upper limit of adsorption [72].

#### 2.4.6.1 Langmuir model

The most widely used isotherm equation for modeling of the adsorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number identical site and is given by:

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \quad (2.5)$$

Where  $q_0$  and  $K_L$  are Langmuir parameters related to maximum adsorption capacity and free energy of adsorption, respectively  $C_e$  is the equilibrium concentration in the



aqueous solution and  $q_e$  is the equilibrium adsorption capacity of adsorbent. The linearized form of Langmuir equation can be written as

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L} \cdot \frac{1}{C_e} \quad (2.6)$$

The Langmuir constant  $q_0$  and  $K_L$  can be calculated by plotting  $1/q_e$  versus  $1/C_e$  [103].

#### 2.4.6.2 Freundlich model

The Freundlich model is an empirical equation based on sorption on heterogeneous surface. It is given as:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (2.7)$$

Where  $K_f$  and  $n$  are the Freundlich constants that indicate adsorption capacity and adsorption intensity, respectively.

The linearized form of Freundlich isotherm can be written as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2.8)$$

The value of  $K_f$  and  $n$  can be calculated by plotting  $\ln q_e$  versus  $\ln C_e$  [103].

## 2.5 Polymerization

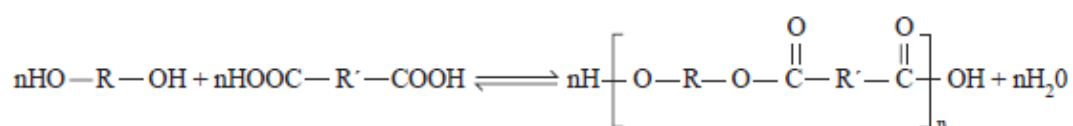
### 2.5.1 Synthesis of polymer

Polymers are macromolecules occurred by the linking together of large numbers of much smaller molecules. The small molecules that linked with each other to form polymer molecules are termed monomers, and the reactions by which they combine are termed polymerizations.

Polymers may be classified broadly as condensation, addition, or ring-opening polymers, depending on the type of polymerization reaction inclusive in their formation.

Condensation polymers are formed from a series of reactions, often of condensation type, in which any two species (monomers, dimers, trimers, etc.) can react at any time leading to a larger molecule. In condensation polymerization, the stepwise reaction consist of between the chemically reactive groups or functional groups on the reacting molecules. In the condensation polymerization, a small molecule, usually water or ammonia, is eliminated.

A typical condensation polymerization reaction is the formation of a polyester through the reaction of a glycol and a dicarboxylic acid. Examples of condensation polymers include polyamides polyesters and urea-formaldehyde and phenol-formaldehyde resins [104].



**Figure 2.19 :** The condensation reaction of polyester

Addition polymers are obtained by reactions in which monomers are added one after another to a rapidly growing chain. The growing polymer in addition polymerization proceeds with chain mechanism. The chain reactions has, three fundamental steps are involved: initiation, propagation, and termination. Monomers generally employed in addition polymerization are unsaturated (usually with carbon-carbon double bonds). For instance addition polymers are polystyrene, polyethylene, polyacrylonitrile, poly(methyl methacrylate), and poly(vinyl chloride) [105].

Addition polymerization is occurred on the radical or ionic mechanism. The radical chain polymerization is suitable mechanism for synthesis of addition polymers.

### 2.5.2 Radical chain polymerization

Unsaturated monomers are converted to polymers through chain reactions. In chain polymerization processes, the active center is retained at the end of a growing polymer chain and monomers are added to this center in rapid succession. The rate of addition of monomers to the active center relative to the overall conversion of the

monomer to polymer is quite fast. This means that high-molecular-weight polymers are generated even while most of the monomers remain intact [106].

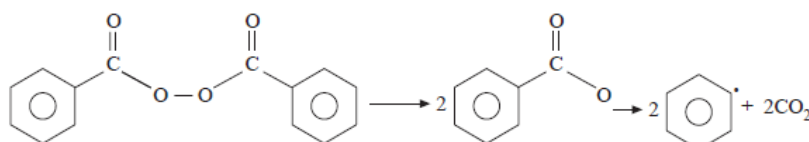
### 2.5.2.1 Mechanism of chain polymerization

Chain-reaction polymerization, like all chain reactions, consists of three fundamental steps. These are initiation, which involves the acquisition of the active site by the monomer; propagation, which is the rapid and progressive addition of monomer to the growing chain without a change in the number of active centers; and termination, which involves the destruction of the growth activity of the chain leaving the polymer molecule(s). In addition to the above three processes, there is the possibility of another process known as chain transfer during which the growth activity is transferred from an active chain to a previously inactive species [107].

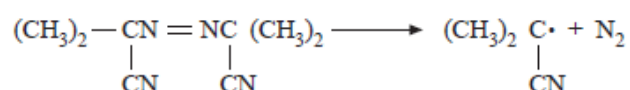
Initiation:

Initiation is generation of active species, which can be through free-radical, ionic, or coordination mechanism. Free radicals can be generated by a number of ways, including thermal or photochemical decomposition of organic peroxides, hydroperoxides, or azo or diazo compounds. Other methods of generation of free radicals include dissociation of covalent bonds by high-energy irradiation and oxidation–reduction (redox) reactions. The active species produced by these processes are referred to as initiators.

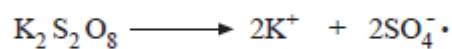
➤ Benzoyl peroxide:



➤ Azobis-isobutyronitrile (AIBN):



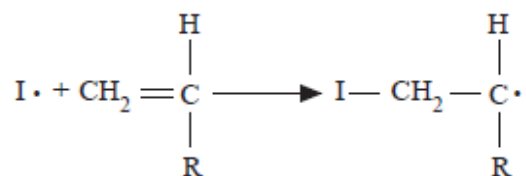
➤ Potassium persulfate:



➤ t-Butylhydroperoxide



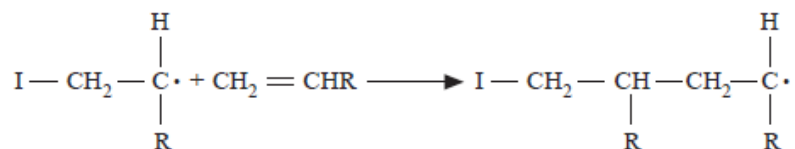
The final initiation stage is: Initiator is added in monomer and first monomeric active center is occurred.



**Figure 2.20 :** Monomeric active center

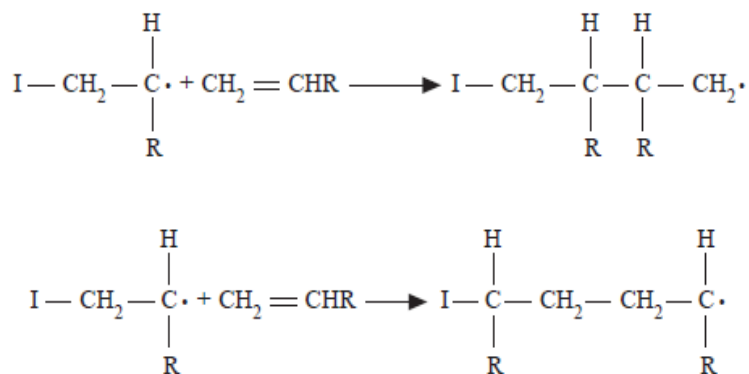
Propagation:

This involves the addition of a free radical to the double bond of a monomer, with regeneration of another radical. The active center is thus continuously relocated at the end of the growing polymer chain.



**Figure 2.21 :** Monomeric active center is added in the other monomer

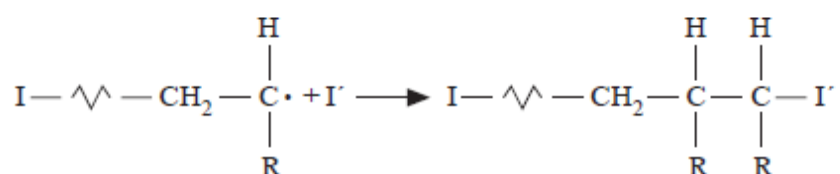
The substituted carbon atom is regarded as the head and the unsubstituted carbon atom the tail of the vinyl monomer. There are, therefore, three possible ways for the propagation step to occur: head-to-tail, head-to-head.



**Figure 2.22 :** Monomeric active center is added in the other monomer

Termination:

In termination, the growth activity of a polymer chain radical is destroyed by reaction with another free radical in the system to produce polymer molecule(s). Termination can occur by the reaction of the polymer radical with initiator radicals. This type of termination process is unproductive and can be controlled by maintaining a low rate for initiation.

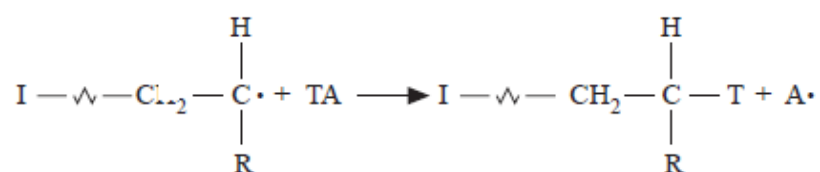


**Figure 2.23 :** Dead polymer by transferred on the initiator

Chain Transfer:

Ideally, free-radical polymerization involves three basic steps: initiation, propagation, and termination. However, a fourth step, called chain transfer, is usually

involved. In chain-transfer reactions, a growing polymer chain is deactivated or terminated by transferring its growth activity to a previously inactive species.



**Figure 2.24 :** Dead polymer by transferred on the monomer, polymer or solvents

The species, TA, could be a monomer, polymer, solvent molecule, or other molecules deliberately or inadvertently introduced into the reaction mixture [104,108].

### 2.5.2.2 Redox polymerization

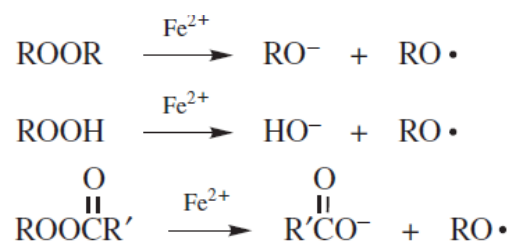
Many oxidation–reduction reactions produce radicals that can be used to initiate polymerization. This type of initiation is referred to as redox initiation, redox catalysis, or redox activation. A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0–50°C and even lower. This allows a greater freedom of choice of the polymerization temperature than is possible with the thermal homolysis of initiators. Some redox polymerizations can be initiated photolytically as well as thermally [109].

Types of redox initiator:

- Peroxides in combination with a reducing agent are a common source of radicals; for example, the reaction of hydrogen peroxide with ferrous ion

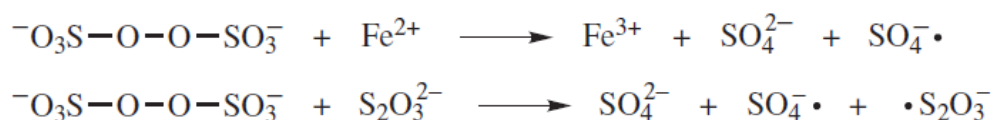


Ferrous ion also promotes the decomposition of a variety of other compounds including various types of organic peroxides [110].



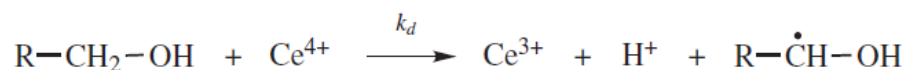
Other reductants such as  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Ti}^{+3}$ ,  $\text{Co}^{+2}$ , and  $\text{Cu}^{+2}$  can be employed in place of ferrous ion in many instances. Most of these redox systems are aqueous or emulsion systems. Redox initiation with acyl peroxides can be carried out in organic media by using amines as the reductant [111,112].

- The combination of a variety of inorganic reductants and inorganic oxidants initiates radical polymerization, for example



Other redox systems include reductants such as  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{S}_2\text{O}_5^{2-}$  in combination with oxidants such as  $\text{Ag}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{ClO}_3^-$ , and  $\text{H}_2\text{O}_2$ .

- Organic-inorganic redox pairs initiate polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol by  $\text{Ce}^{4+}$ ,



or by  $\text{V}^{5+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Mn}^{3+}$  [113-115].

- There are some initiator systems in which the monomer itself acts as one component of the redox pair. Examples are thiosulfate plus acrylamide or methacrylic acid and N,Ndimethylaniline plus methyl methacrylate [116,117].

### 2.5.3 Polymerization process

The conditions under which radical polymerizations are carried out are of both the homogeneous and heterogeneous types. This classification is usually based on whether the initial reaction mixture is homogeneous or heterogeneous. Some

homogeneous systems may become heterogeneous as polymerization proceeds as a result of insolubility of the polymer in the reaction media. Mass and solution polymerizations are homogeneous processes; suspension and emulsion polymerizations are heterogeneous processes [118,119]

### **2.5.3.1 Suspension polymerization**

Suspension polymerization is used for the commercial produce of many important polymers included poly(vinyl chloride), poly(methyl methacrylate), expandable polystyrene, styrene–acrylonitrile copolymers and a variety of ion exchange resins. In suspension polymerization, drops of a monomer-containing phase are dispersed in a continuous liquid phase and polymer is obtained inside the drops. In many cases, the monomer include no diluent and the chemical reactions that take place inside the drops are very similar to those that are found in bulk polymerization [120].

Suspension polymerization (also referred to as bead or pearl polymerization) is carried out by suspending the monomer (discontinuous phase) as droplets (50–500  $\mu\text{m}$  in diameter) in water (continuous phase). The water: monomer weight ratio varies from 1 : 1 to 4 : 1 in most polymerizations. The monomer droplets (subsequently converted to polymer particles) are prevented from coalescing by agitation and the presence of suspension stabilizers (also referred to as dispersants or surfactants).

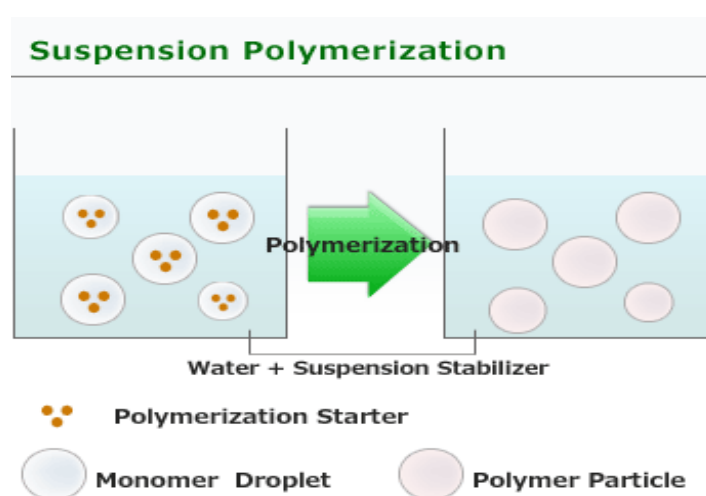
Two types of stabilizers are used—water-soluble polymers (often in the presence of electrolyte or buffer) and water-insoluble inorganic compounds. The former type includes poly (vinyl alcohol), hydroxypropyl cellulose, sodium poly(styrene sulfonate), and sodium salt of acrylic acid–acrylate ester copolymer; the latter type includes talc, hydroxyapatite, barium sulfate, kaolin, magnesium carbonate and hydroxide, calcium phosphate, and aluminum hydroxide. The levels of suspension stabilizers are typically less than 0.1 weight percent (wt%) of the aqueous phase (although the water-soluble polymers are sometimes used at higher concentrations). This is much lower than the surfactant concentrations used in emulsion polymerizations (typically as high as 1–5%) and accounts for the higher monomer droplet sizes in suspension polymerization. Also, unlike emulsion polymerization, the two-phase system cannot be maintained in suspension polymerization without



agitation. Another difference is that the dispersants used in suspension polymerization seldom form colloidal micelles as in emulsion polymerization.

The initiators used in suspension polymerization are soluble in the monomer droplets. Such initiators are often referred to as oil-soluble initiators.

An inverse suspension polymerization involves an organic solvent as the continuous phase with droplets of a water-soluble monomer (e.g., acrylamide), either neat or dissolved in water. Microsuspension polymerizations are suspension polymerizations in which the size of monomer droplets is about 1 mm [121-123].



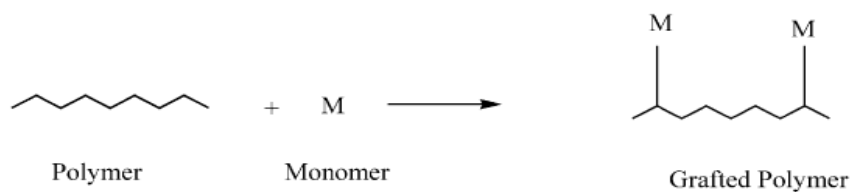
**Figure 2.25 :** Suspension polymerization

#### **2.5.4 Graft copolymerization**

One trend in modern civilization is to effect gradual replacement of natural materials with either all synthetic materials or modified natural materials. In the polymeric age, it is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications. There are several means to modify polymers properties blending, grafting, and curing.

Grafting is a method where in monomers are covalently bonded (modified) onto the polymer chain, whereas in curing, the polymerization of an oligomer mixture forms a coating which adheres to the substrate by physical forces.

Considerable work has been done on techniques of graft co-polymerization of different monomers on polymeric backbones. These techniques include chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting [124,125].



**Figure 2.26 :** Graft polymerization

### **3. EXPERIMENTAL PART**

#### **3.1.1 Materials**

Hydroxyethyl methacrylate (HEMA) (Aldrich), Ethylene glycole dimethacrylate (EGDMA) (Aldrich), acrylamide (Aldrich), Phenol (Aldrich), BisPhenolA (Aldrich), Methyl methacrylate (MMA) (Aldrich), All chemicals were analytical grade and were used without further purification

#### **3.1.2 Instruments**

FT-IR (Nicolet) and UV-Vis spectrophotometer (Perkin Elmer lamda 25).

### **3.2 Preparation of Polymeric Resins**

#### **3.2.1 Preparation of poly(HEMA-MMA-EGDMA) beads**

Poly(HEMA-MMA-EGDMA) beads were prepared by suspension polymerization of HEMA (6.1 mL, 0.05 mol), MMA (4.3 mL, 0.04 mol), EGDMA (1.9 mL, 0.01mol) as a cross-linker and AIBN (0.16 g,  $9.74 \times 10^{-4}$  mol) as initiator in toluene (50 mL), using 50 mL of aqueous poly(vinyl alcohol) (0.2 g) as stabilizer. The reaction carried out at 65°C for 4 hours. The yield was 9.65 g.

#### **3.2.2 Preparation of poly(acrylamide) grafted poly(HEMA-MMA-EGDMA)**

Grafting of poly(acrylamide) onto poly(HEMA-MMA-EGDMA) beads was carried out by using redox polymerization method. Therefore, 2.0 g of crosslinked polymer was interacted with 0.54 g of cerium ammonium nitrate as redox initiator in 10 mL of 0.1 M HNO<sub>3</sub>. Then, 6.0 g of acrylamide in 10 mL of water was added to the reaction mixture at room temperature under nitrogen. The mixture was shaken with a continuous shaker for 24 hours at room temperature. To remove homopolymer fraction of polyacrylamide, the reaction content was poured into water (100 mL) and was stirred for 24 hours. Then this mixture was filtered and washed with excess of water and acetone. The product was dried under vacuum at 40°C for 24 hours. The yield was 3.64 g.

### **3.2.3 Determination of the total nitrogen content of the sorbent**

The amine content of the resin was determined by Kjeldahl nitrogen analysis as follows. The polymer sample (0.2 g) was put into 20 mL H<sub>2</sub>SO<sub>4</sub> (80%) and refluxed for 8 h. After cooling the mixture was diluted cautiously to 50 mL and filtered. The filtrate was used the Kjeldahl analysis the consumption of 5 mL 0.1 M HCl for the neutralization of the evolved ammonia

## **3.3 Experiment of Phenol and BPA Adsorption on the Resins**

### **3.3.1 Extraction of phenol and BPA from water**

The adsorption experiments were performed at 25 °C, using 0.10 g resins (resin 1 and resin 2) added 10 mL solution of phenol with different initial concentrations of 0.0085–0.085 M for phenol. All experiments were performed at a shaking speed of 200 rpm for 24 h to ensure the equilibrium of the sorption process. Then, the mixture was filtered and the concentration of phenol was monitored by spectrophotometric analysis using UV–VIS Spectrophotometer. The absorbance values were measured according to the maximum UV-absorption, at the wavelength of 270 nm.

Similar experiments were carried out for BPA with different initial concentrations (1.71.10<sup>-4</sup> M-1.71.10<sup>-3</sup>M).

Also, pH depending sorption experiments were investigated.

### **3.3.2 Kinetic measurements for phenol and BPA solution**

Batch kinetic experiment was carried out as follows:

Batch kinetic experiments were performed using highly diluted phenol and BPA solutions (0.03 mg phenol /mL water) to estimate the efficiency of the resins. For this purpose, 0.1 g of resin was wetted with distilled water (1.5 mL) and added to a solution of phenol (100 mL). The mixtures were stirred with a magnetic stirring bar and aliquots of the solution (5 mL) were taken at appropriate time intervals for the analysis of the residual phenol contents. Phenol and BPA were determined by UV-Vis. spectrophotometer ( $\lambda_{\text{phenol}}=270$  nm, and  $\lambda_{\text{BPA}}=265$  nm).

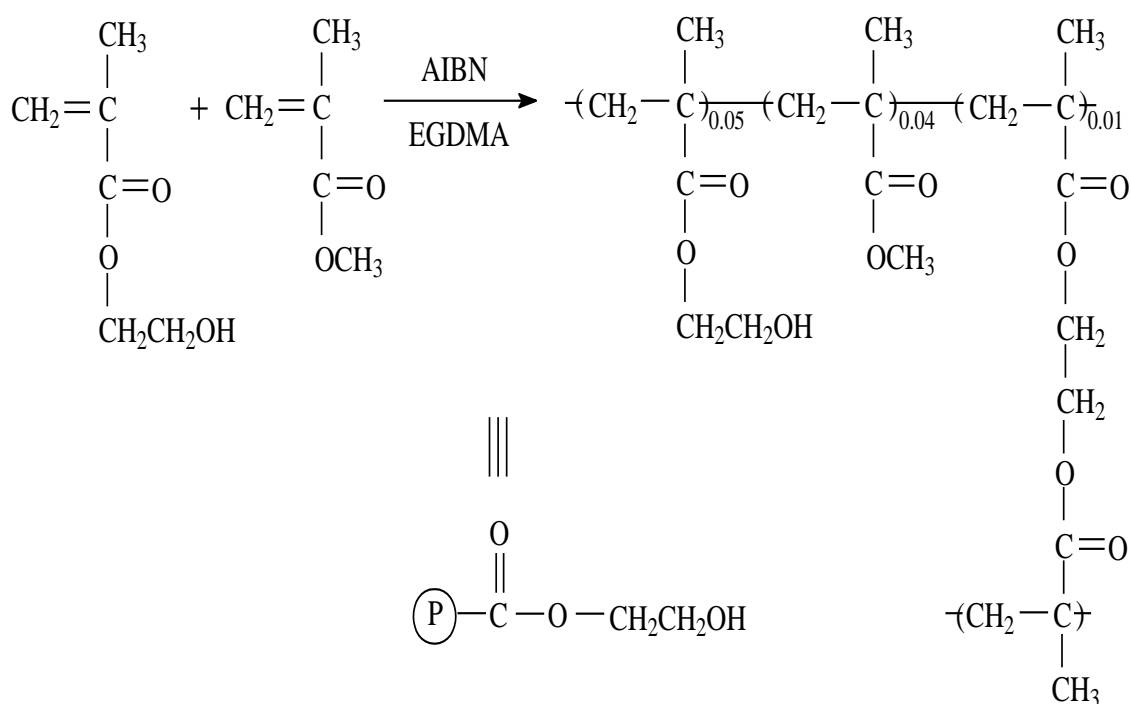
Kinetic models were applied both resins for sorption of phenol and BPA.

## 4. RESULTS AND DISCUSSION

### 4.1 Preparation of Polymeric Sorbents

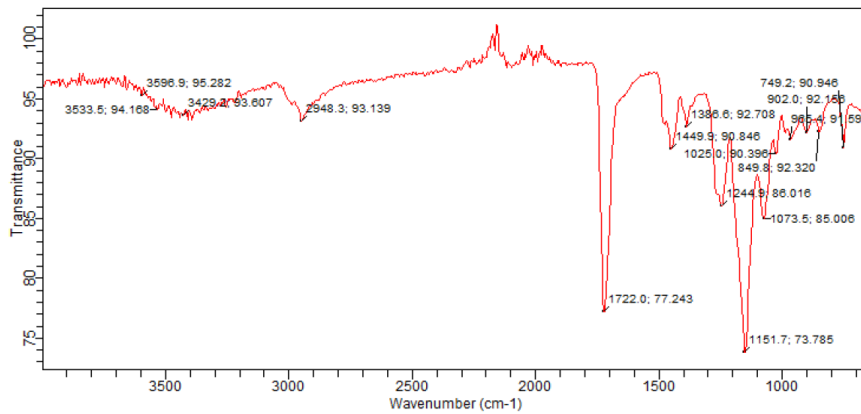
#### 4.1.1 Preparation of poly(HEMA-MMA-EGDMA) beads (resin 1)

Resin1 was prepared starting from copolymerization of hydroxyethyl methacrylate (HEMA) (50%)-methyl methacrylate (MMA) (40%) and ethylene glycol diethacrylate (EGDMA) (10%) by using suspension polymerization method at 65°C for 4 hours



**Figure 4.1** : Crosslinked poly (HEMA-co-MMA) beads.

The resin was characterized by FT-IR. According to the FT-IR spectrum of the resin 1 (Fig 4.2), the broad range at 3300-3500 cm<sup>-1</sup> range indicates -OH stretching vibrations and the sharp peak at 1722 cm<sup>-1</sup> corresponds to carbonyl groups in the terpolymer.



**Figure 4.2 :** FT-IR spectrum of the resin 1

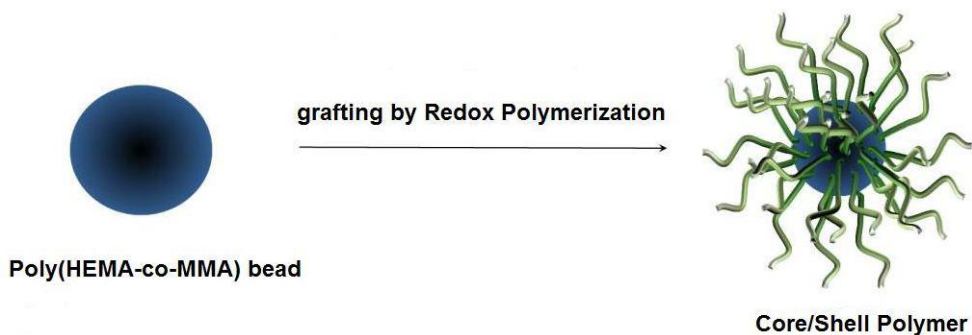
#### 4.1.2 Grafting of poly(acrylamide) on resin1

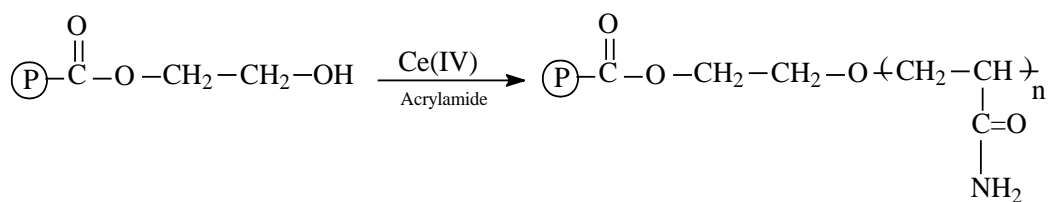
Grafting of poly(acrylamide) onto resin 1 was performed by using redox polymerization method in the presence of Ce (IV) salt as redox initiator in 1 M of HNO<sub>3</sub>. After the reaction, the poly(acrylamide) grafted onto crosslinked poly(HEMA-co-MMA) (resin 2) (3.6367 g) was obtained .

The grafting percentage (GP) was determined by calculating the percentage increase in weight by using following equation:

$$GP = \left[ \frac{(m_{gf} - m_0)}{m_0} \right] 100\% \quad (4.1)$$

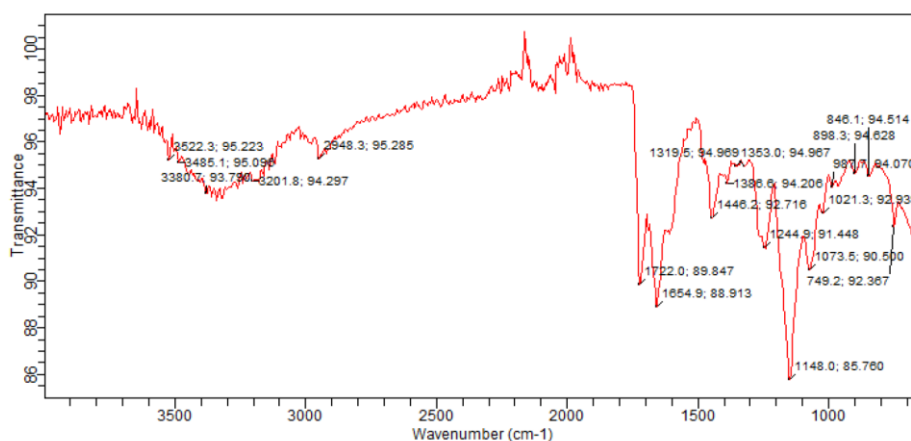
where,  $m_0$  and  $m_{gf}$  are the weights of the beads before and after grafting, respectively and grafting degree was found as about 82 % for 24 h.





**Figure 4.3 :** Grafting of poly (acrylamide) onto resin1 core-shell beads

The total nitrogen content of the grafted polymer was assayed by the Kjeldahl method. Total nitrogen content was found as 7.0 mmol.g<sup>-1</sup>. Also, resin 2 was characterized with FT-IR. According to the Fig.4.4, appearance of the new broad peak of N-H stretching observed between 3300-3500cm<sup>-1</sup> and in addition, the sharp peak at about 1655 cm<sup>-1</sup> corresponds to C=O stretching vibration of the amide group in the Resin 2 (Figure 4.4).



**Figure 4.4 :** FT-IR spectrum of the resin 2

## 4.2 Experiment of Phenol and BPA Adsorption on the Resins

### 4.2.1 Extraction of phenol and BPA from water

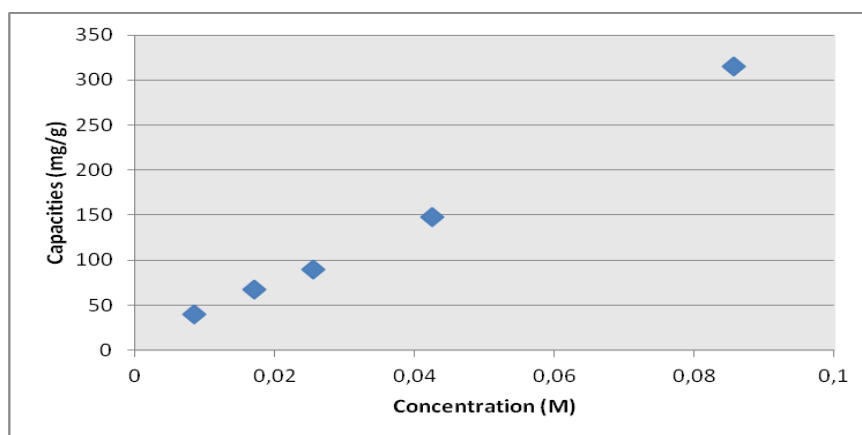
Phenol and Bisphenol A extraction experiments were carried out simply by contacting wetted resin1 and resin2 samples with aqueous phenol and bisphenol A solutions at room temperature. The phenol and BPA sorption capacities of the sorbent were determined by mixing weighed amount of polymer sample (0.1 g) with 10 mL aqueous phenol and BPA solutions.

The phenol and BPA loading capacities of the resins were calculated from the initial and final phenol and BPA contents of the solutions. The results were given in Table 4.1. and Table 4.2. According to the Table 4.1. and Table 4.2.,

**Table 4.1 : Maximum phenol sorption capacities of the resins.**

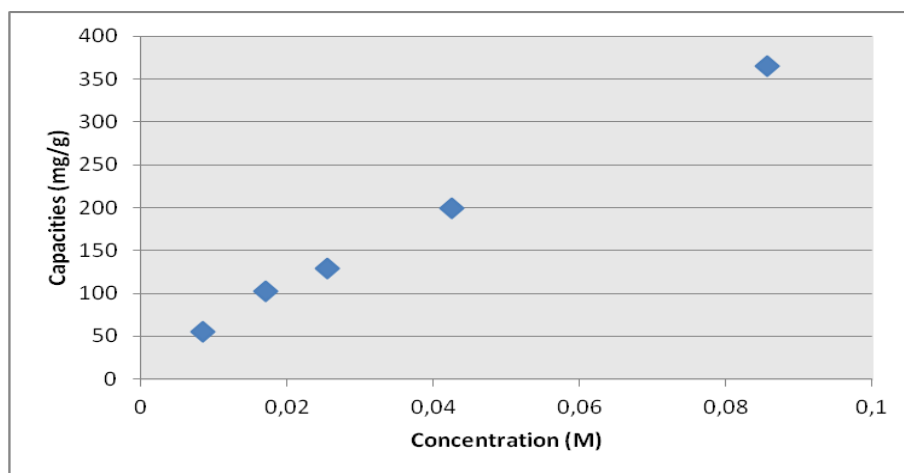
Concentration, M	Capacities (mg/g)	
	Resin1	Resin2
0.00850	40.15	55.83
0.01700	67.10	102.87
0.02550	89.77	129.25
0.04251	147.52	199.63
0.085700	315.14	365.00

According to the Tables and Figures, adsorption of phenol and BPA on the resins were found to be concentration dependent. The sorption capacity of phenol increases proportionally with increase in initial concentration (Fig.4.5, Fig.4.6, Fig.4.7, Fig.4.8).



**Figure 4.5 : The resin1 capacity of phenol solution at different concentration**

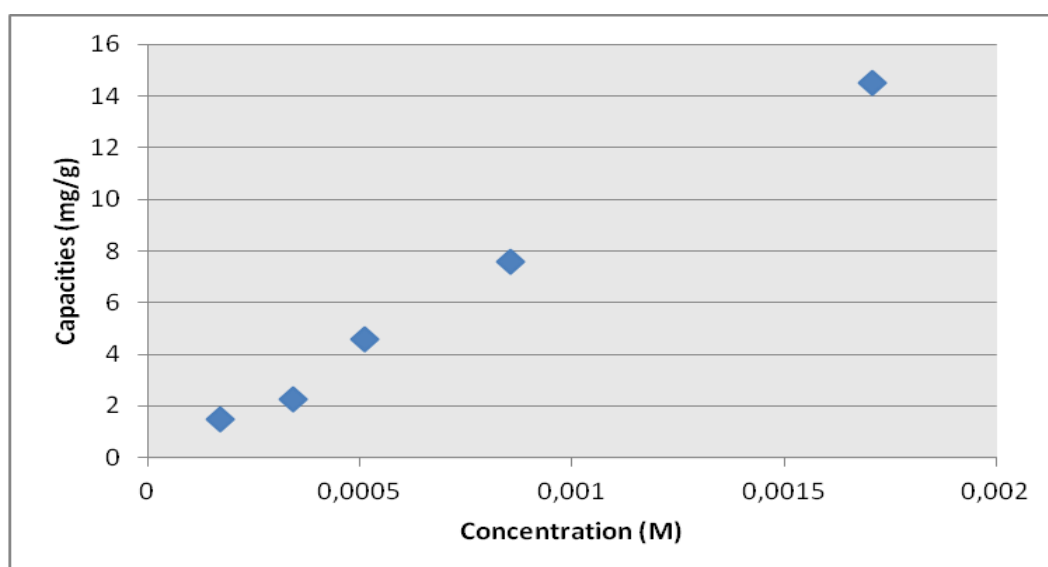




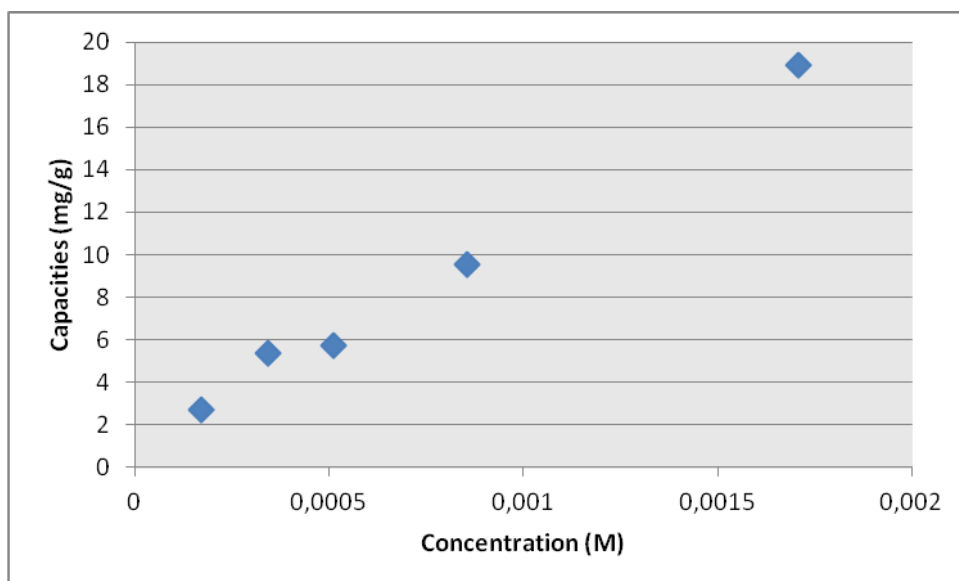
**Figure 4.6 :** The resin2 capacity of phenol solution at different concentration.

**Table 4.2 :** Maximum BPA sorption capacities of the resins.

Concentration, M	Capacities (mg/g)	
	Resin1	Resin2
$1.71 \cdot 10^{-4}$	1.490	2.691
$3.42 \cdot 10^{-4}$	2.27	5.340
$5.13 \cdot 10^{-4}$	4.595	5.750
$8.54 \cdot 10^{-4}$	7.563	9.560
$1.71 \cdot 10^{-3}$	14.483	18.940



**Figure 4.7 :** The resin1 capacity of BPA solution at different concentration.



**Figure 4.8 :** The resin2 capacity of BPA solution at different concentration.

Three mechanisms of phenolic compound adsorption are postulated, namely  $\pi$ - $\pi$  dispersion interaction, electron-donor-acceptor complex formation and hydrogen bond formation.

Sorption mechanism of the resin assumes the formation of a donor-acceptor complex between the surface electron donor groups (e.g. carbonyls and nitrogen on the polymer, N) and an OH group of phenol molecule that acts as the acceptor.

If we compare the results, we can say sorption capacity of the resin 2 higher than resin1. Resin 2 has amide group and it forms strong hydrogen bonds with phenolic groups comparing to the resin1.

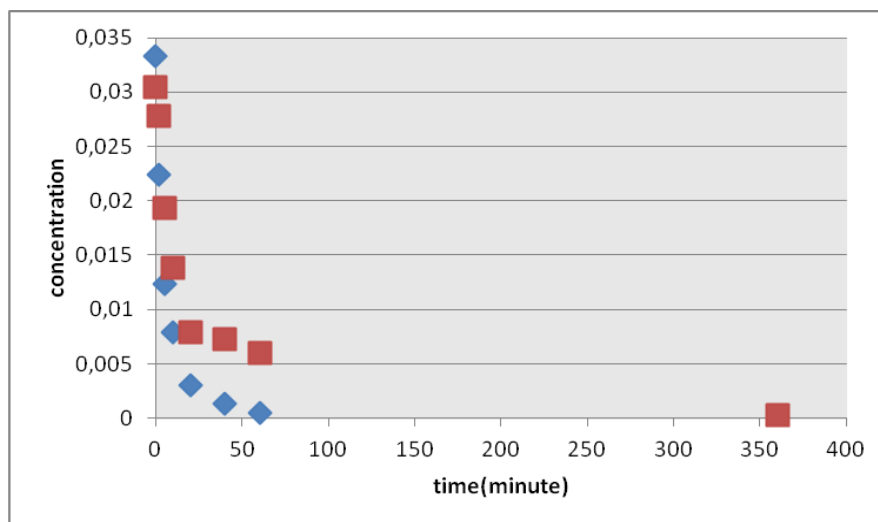
**Table 4.3 :** Phenol sorption capacity of the resins depending on pH

pH	Capacities (mg/g)	
	Resin1	Resin2
2.44	281	352
4.02	319	387
6.21	339	420
8.25	188	300
10.28	151	301

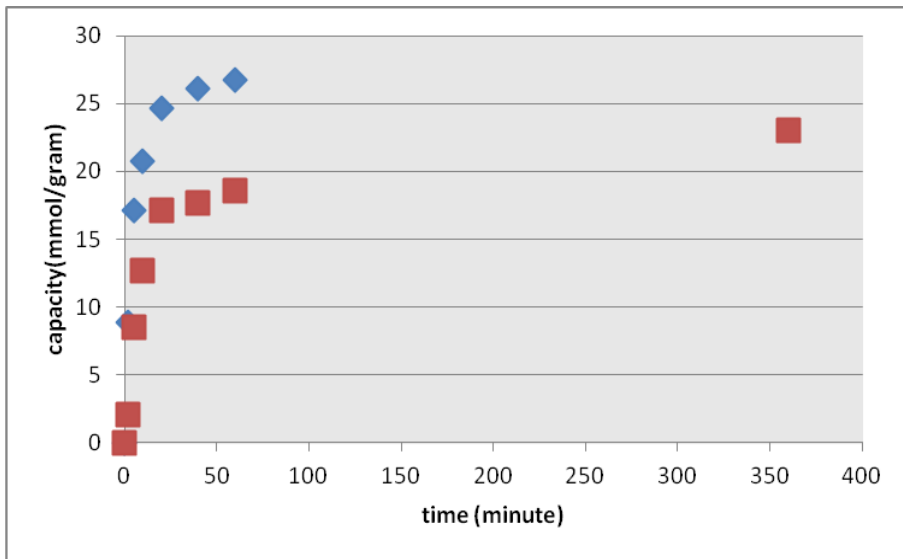
The effect of pH for the adsorption of phenol onto the resins were studied in the pH range 2.0-10.0. It is apparent from (Table 4.3) that the adsorption of phenol first increased from pH 2.0 to 6.0 and then declined with further increase of pH. The highest adsorption of phenol was noted at pH 6. In basic solution, phenol makes phenolate ions. The reduction in the adsorption of phenol at high pH was due to the electrostatic repulsions between the negative surface charge of resin and phenolate-phenolate anions in solution.

#### 4.2.2 Kinetic measurements

Batch sorption kinetics of the polymeric sorbents were performed by using dilute solutions of phenol (0.0305 g / L) and BPA (0.00086 g/L). According to the Fig.4.13 and Fig 4.13 the concentration – time and capacities-time plots for the resin 1 and resin 2 show that, phenol concentrations falls to zero within for 350 minute and 60 minute respectively.

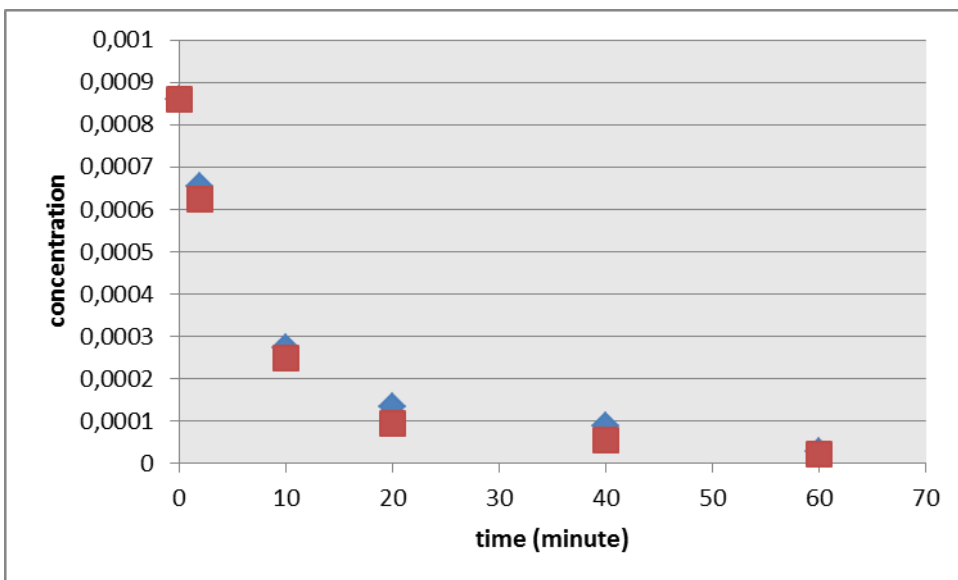


**Figure 4.9** : Phenol sorption kinetic of sorbent

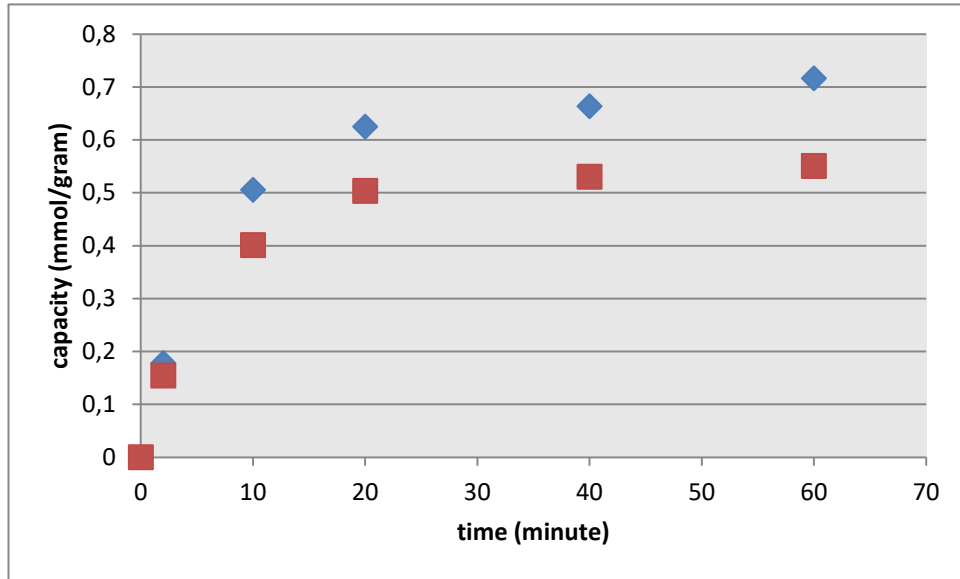


**Figure 4.10 :** Phenol sorption kinetic of sorbent

BPA concentration is very diluted according to phenol due to solubility in water. Therefore, BPA concentrations fall to zero within 60 minute.



**Figure 4.11 :** BPA sorption kinetic of sorbent



**Figure 4.12 : BPA sorption kinetic of sorbent**

◇ poly(acrylamide) grated onto crosslinked poly(HEMA-co- MMA)

□ poly(HEMA-co-MMA)

The kinetics of sorption is an important aspect of the process control of removal of wastes.

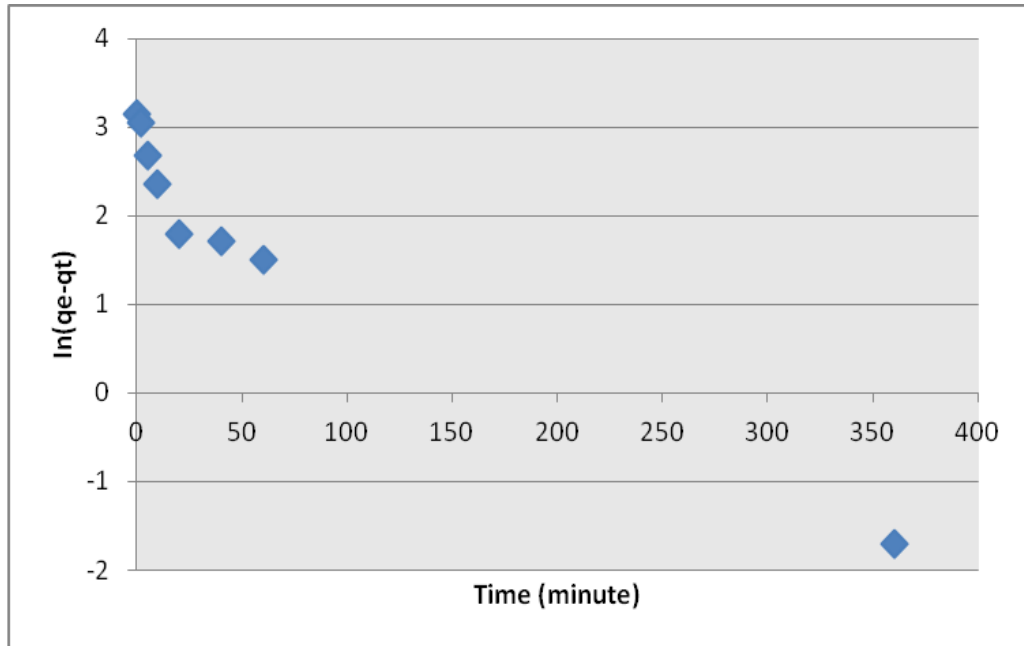
The linearized form of the first-order rate equation by Lagergren and Svenska is given as follows :

$$\ln (q_{eq}-q_t) = \ln q_{eq} - k_1.t \quad (4.2)$$

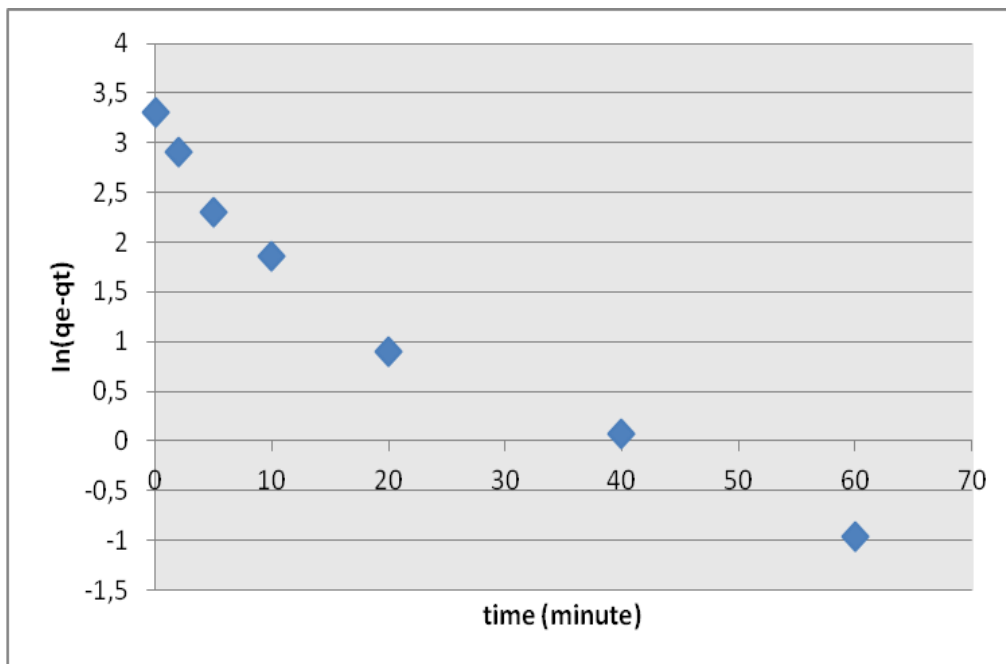
where  $k_1$  is the rate constant of pseudo-first-order adsorption ( $\text{min}^{-1}$ ) and  $q_{eq}$  and  $q_t$  show the amounts of adsorption ( $\text{mmol.g}^{-1}$ ) at equilibrium and at time  $t$ , respectively.

The Lagergren first-order rate equation (1) is one of the most widely used equations for the sorption of solute from a liquid solution.

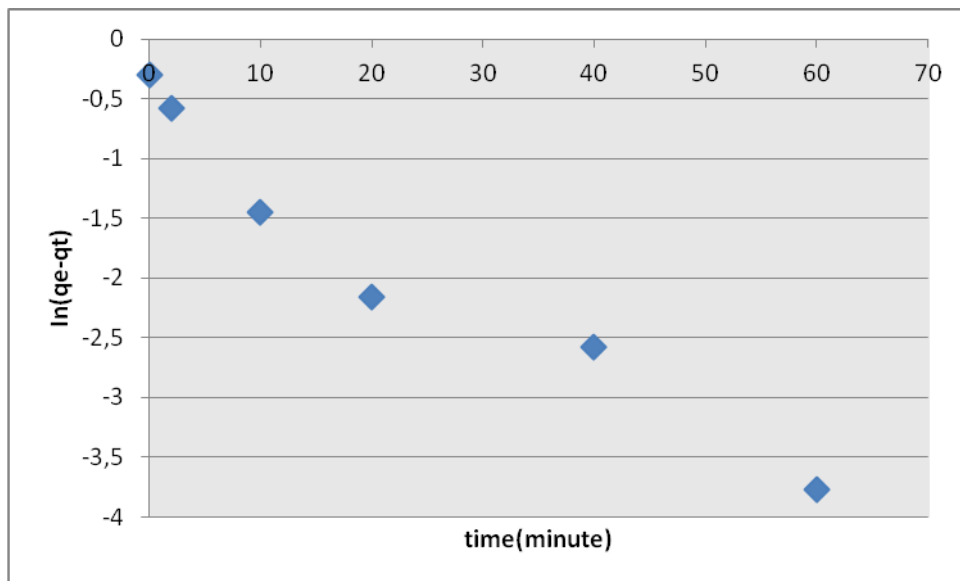
The slopes and intercepts of plots of  $\ln (q_{eq} - q_t)$  versus  $t$  were depicted in Fig.4.13, Fig 4.14, Fig 4.15 and Fig 4.16. The pseudo-first-order rate constant  $k_1$  and theoretical equilibrium adsorption capacities  $q_{eq}$  are presented in Table 4.4 and Table 4.5.



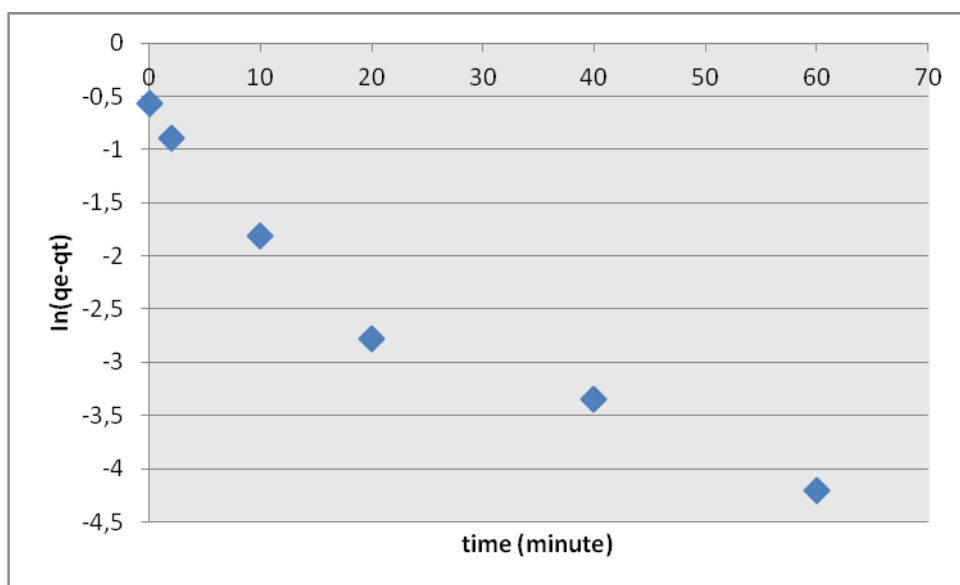
**Figure 4.13 :** The pseudo-first order model plots of phenol by resin1



**Figure 4.14 :** The pseudo-first order model plots of phenol by resin2



**Figure 4.15 :** The pseudo-first order model plots of BPA by resin1



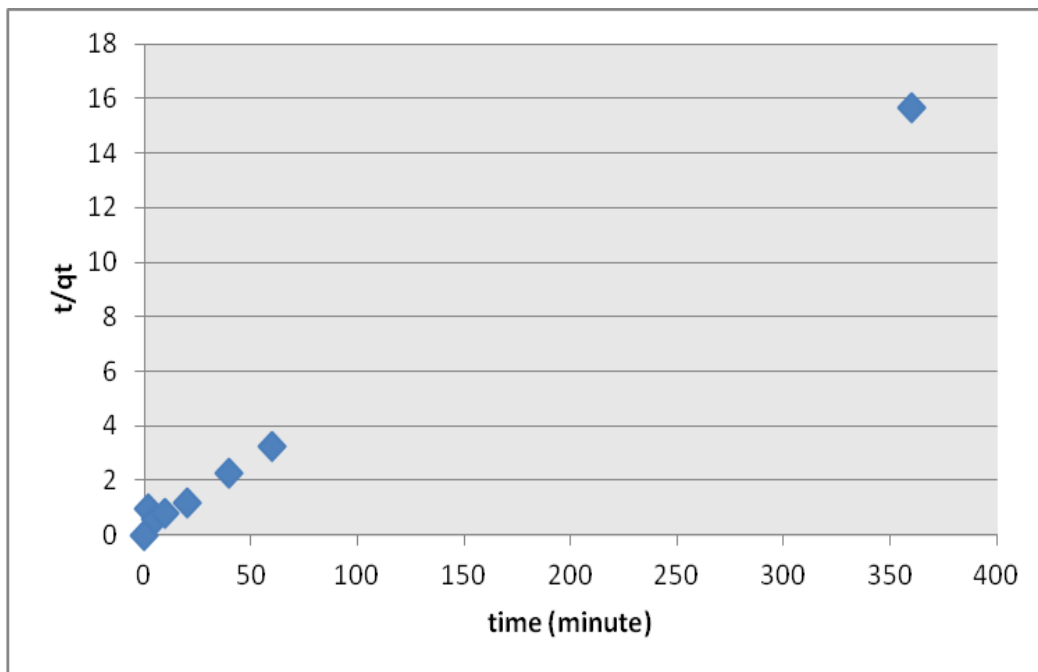
**Figure 4.16 :** The pseudo-first order model plots of BPA by resin2

The experimental data were also fitted by the pseudo-second-order kinetic model given with the equation below:

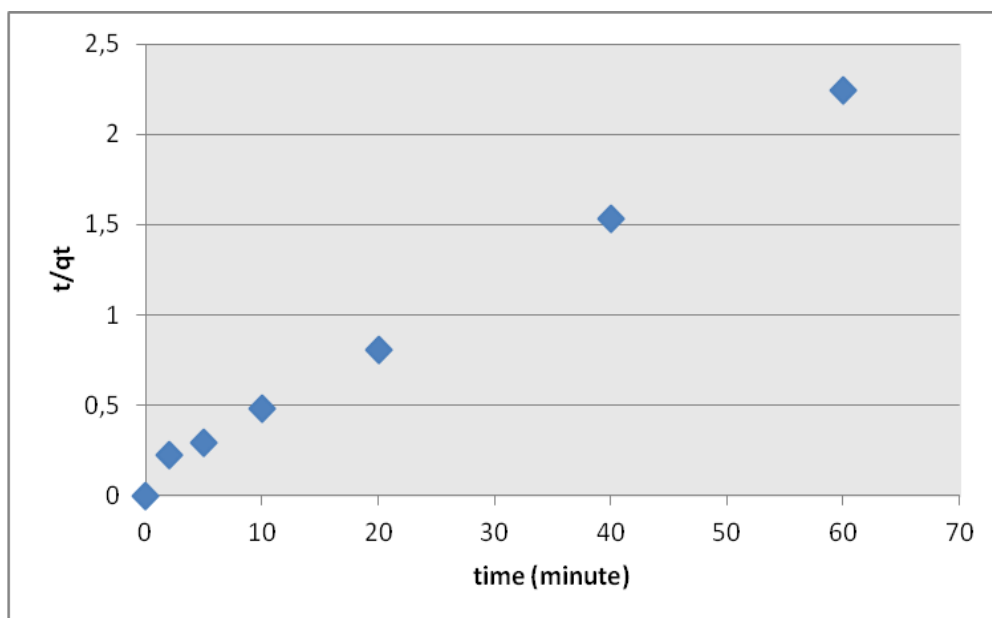
$$t/q_t = 1/k_2q_e^2 + 1/q_e \cdot t \quad (4.3)$$

where  $q_e$  is the amount of phenols adsorbed at equilibrium ( $\text{mmol.g}^{-1}$ );  $q_t$  is the amount of phenols adsorbed at time  $t$  ( $\text{mmol.g}^{-1}$ ); and  $k_2$  is the equilibrium rate

constant of pseudo-second-order sorption ( $\text{g} \cdot \text{mmol}^{-1} \cdot \text{min}^{-1}$ ). The plots of  $t/q_t$  versus  $t$  are shown in Fig. 4.17, Fig.4.18, Fig.4.19, Fig.4.20 and the rate constants ( $k_2$ ) and theoretical equilibrium adsorption capacities,  $q_e$  are presented in Table 4.4 and Table 4.5.

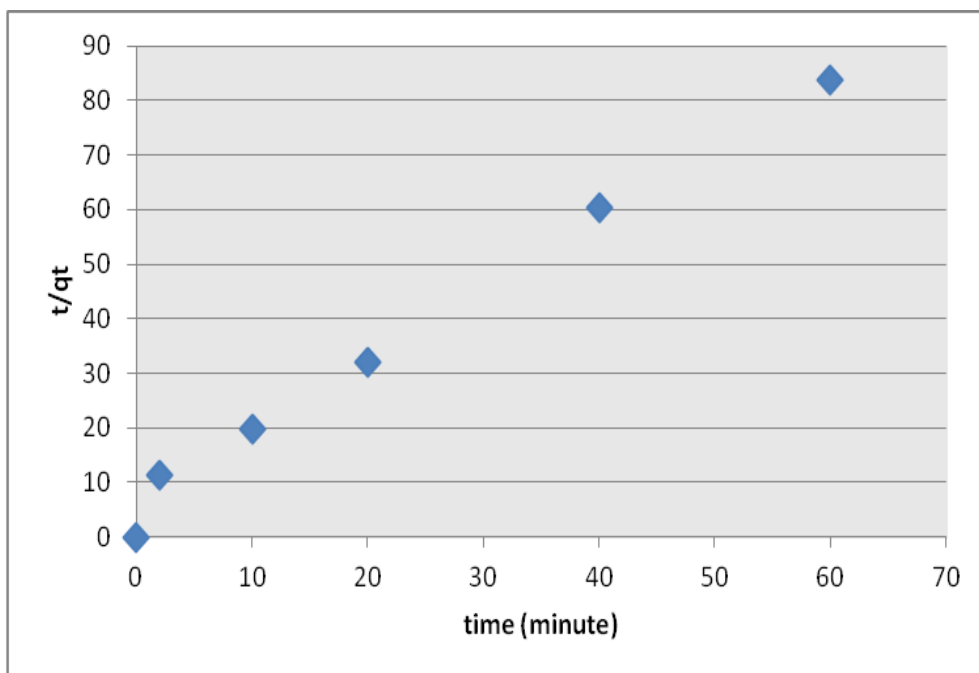


**Figure 4.17 :** The pseudo-second-order model plots of phenol by resin1

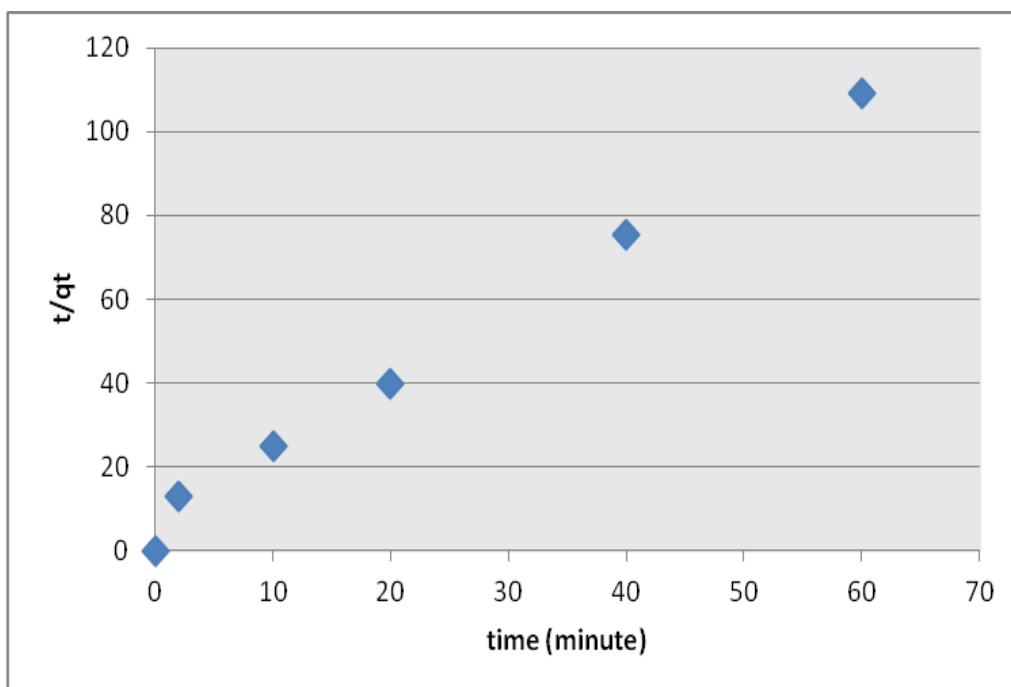


**Figure 4.18 :** The pseudo-second-order model plots of phenol by resin2





**Figure 4.19 :** The pseudo-second-order model plots of BPA by resin1



**Figure 4.20 :** The pseudo-second-order model plots of BPA by resin2

According to experimental and theoretical kinetic data in Table 4.5 and Table 4.6, the experimental results obtained for the adsorption of phenols on the sorbent were found to obey second-order kinetics.

**Table 4.4 :** Pseudo-first-order, second-order kinetics models for adsorption of phenol

SORBENT	FIRST ORDER				SECOND ORDER		
	$q_{ex}$ (mmol g <sup>-1</sup> )	$q_e$	$k_1 \times 10^2$ (min <sup>-1</sup> )	$R^2$	$k^2 \times 10^3$ (min <sup>-1</sup> )	$q_e$ (mmol g <sup>-1</sup> )	$R^2$
<b>Poly(HEMA-co-MMA)</b>	23.16	13.17	1.22	0.93	3.98	23.58	0.99
<b>Poly(acrylamide) grafted onto crosslinked poly(HEMA-co-MMA)</b>	27.14	16.30	6.7	0.94	13.60	27.85	0.99

**Table 4.5 :** Pseudo-first-order, second-order kinetics models for adsorption of BPA

SORBENT	FIRST ORDER				SECOND ORDER		
	$q_{ex}$ (mmol g <sup>-1</sup> )	$q_e$	$k_1 \times 10^2$ (min <sup>-1</sup> )	$R^2$	$k^2 \times 10^3$ (min <sup>-1</sup> )	$q_e$ (mmol g <sup>-1</sup> )	$R^2$
<b>Poly(HEMA-co-MMA)</b>	0.73	0.53	6.30	0.94	3.49	0.74	0.99
<b>Poly(acrylamide) grafted onto crosslinked poly(HEMA-co-MMA)</b>	0.56	0.94	99.07	0.92	5.52	0.57	0.99

From Table 4.4 and Table 4.5 for the pseudo-second-order model, the correlation coefficient is 0.99 and the theoretical  $q_e$  value is close to the experimental  $q_e$  value. These results suggest that the adsorption data were well represented by pseudo-

second order kinetics model and the rate-limiting step of phenols onto the resin might be chemical adsorption



## 5. CONCLUSION

Crosslinked poly(HEMA-MMA-EGDMA) resin was prepared by suspension polymerization and poly (acrylamide) grafting onto resin1 was carried out by redox polymerization from hydroxyl groups by using Ce(IV) as oxidant. The phenol and BPA sorption capacities of the resins was determined and compared. Solubility of BPA in water is lower than phenol and therefore, lower BPA concentrations were used. Phenol sorption capacities of the resins higher than BPA due to solubility and molecular structure.

The results indicated that core-shell type polymeric sorbent has higher sorption capacity.

Sorption kinetics models were applied on the resin 1 and resin 2. According to the results, pseudo second order model was found suitable



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