

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**PREPARATION OF NEW POLYMERIC SORBENTS FOR REMOVAL OF
ORGANIC WASTES**

Ph.D. THESIS

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Department of Chemistry

Chemistry Programme

DECEMBER 2016

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**ORGANİK ATIKLARIN GİDERİLMESİ İÇİN YENİ POLİMERİK
SORBENTLERİN HAZIRLANMASI**

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To my FAMILY

FOREWORD

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TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	ix
ABBREVIATIONS	xv
LIST OF TABLES	xvii
LIST OF FIGURES	xix
SUMMARY	xxi
ÖZET	xxiii
1. INTRODUCTION	1
2. THEORETICAL PART	5
2.1 Hazards of Organic Waste	5
2.1.1 Health hazards of dye effluents	6
2.1.2 Hazards of phenol	6
2.1.3 Hazards of pesticides and herbicides	7
2.2 Technique for the Removal of Organic Pollutants from Wastewater.....	7
2.3 Classifications and Properties of Dyes	9
2.4 Technologies Available for Dye and Phenolic Compounds Removal	10
2.4.1 Dye and phenolic compounds removal using activated carbons	12
2.4.2 Low-cost adsorbents for removal of dyes and phenolic compounds	12
2.4.3 Natural materials	12
2.4.3.1. Clay	12
2.4.3.2. Siliceous materials	13
2.4.3.3. Zeolites	14
2.4.3.4. Bioadsorbents	14
2.4.3.5. Biopolymers: chitin and chitosan	14
2.4.3.6. Peat	15
2.4.3.7. Biomass	16
2.5 Dye Removal Ability of Polymeric Adsorbent	17
2.6 Phenol Removal Ability of Polymeric Adsorbent	21
2.7 Atrazine Removal Ability of Polymeric Adsorbent	22
2.8 Crosslinked Polymers and Grafted Polymer and Their Properties	24
2.8.1 Ion exchange resins	26
2.8.2 Chelating polymers	26
2.8.3 Hydrogels	27
2.8.4 Affinity polymers	27
2.9 Properties of the Crosslinked Polymers	27
2.9.1 Grafting techniques	29
2.9.1.1 Grafting from strategy	30
2.9.1.2 Grafting through strategy	30
2.9.1.3 Grafting onto strategy	30
2.10 Suspension Polymerization	30
2.11 Emulsion Polymerization	31
2.12 Controlled-Living Radical Polymerization	32

2.12.1 Atom transfer radical polymerization (ATRP).....	33
2.12.2 Controlled radical polymerization (CRP)	34
2.12.3 Degenerative transfer (DT) processes	35
2.12.4 Reversible addition-fragmentation transfer (RAFT).....	35
3. EXPERIMENTAL PART	37
3.1 Materials and Methods.....	37
3.2 Instruments.....	37
3.3 Preparation of the Polymeric Sorbents	37
3.4 Preparation of the Sorbents for Dye Removal	37
3.4.1 Preparation of polyvinyl benzyl chloride (PVBC) resin	37
3.4.2 Modification of PVBC with ethyl piperazine (EP-PS)	38
3.4.2.1 Determination of amine content of the (EP-PS) modified resin	38
3.4.2.2 Quaternization of cross-linked ethyl piperazine modified polystyrene based resin (QEP-PS)	38
3.4.2.3 Estimation of the carboxyl content of the (QEP-PS)	38
3.5 Modification of PVBC with Imidazole.....	39
3.5.1 Quaternization of the imidazole containing PVBC resin with chloroacetic acid	49
3.6 Poly (vinyl imidazole) (PVI) Grafted onto PVBC resin.....	39
3.6.1 Determination of amine of the PVI grafted resin	40
3.7 Extraction of Dyes	40
3.7.1 Kinetics of the dye sorption	40
3.8 Regeneration of the sorbents.....	40
3.9 Preparation of the Quaternized Tertiary Amine Containing Sorbents for Phenol Removal	41
3.9.1 Quaternization of the imidazole modified PVBC with chloroacetamide..	41
3.9.2 Preparation of the chloroacetamide quaternized ethyl piperazine	41
3.9.3 Modification of PVBC with N,N-dimethylethylenediamine	41
3.9.4 Reaction of (PVBC-DMEA) with chloroacetamide.....	49
3.9.5 Determination of chlorine content of the resin.....	49
3.10 Extraction of Phenol from Water	42
3.10.1 Kinetics of the phenol sorption	42
3.11 Poly (2-acrylamido-2-methylpropane sulfonic acid) (AMPS) Grafted onto Crosslinked Poly (vinylbenzyl chloride) Resin for Removal of Atrazine from Water	43
3.11.1 Extraction of atrazine	49
3.11.2 Kinetics of the atrazine sorption.....	49
4. RESULTS AND DISCUSSION.....	45
4.1 Preparation of the New Polymeric Sorbents for Removal of Dyes	45
4.1.1 Preparation of the quaternary carboxylic acid containing piperazine based resin	45
4.1.2 Preparation of the PVI grafted resin and imidazole modified (IP-PVBC) onto PVBC	46
4.1.3 Extraction of dyes.....	49
4.1.4 Dye sorption kinetics of the resin.....	52
4.1.5 Kinetic models.....	53
4.1.6 Regeneration of the dye loaded resins.....	57
4.2 Preparation of the New Polymeric Sorbents for Removal of Phenol	57
4.2.1 Preparation of the quaternary amide containing imidazole based resin....	57

4.2.2 Preparation of the N,N-dimethylethylenediamine modified resin and quaternization with chloroacetamide poly(styrene) based sorbent	59
4.2.2.1 Determination of chlorine content of the resin	59
4.2.3 Characterization of the resins.....	59
4.2.4 Extraction of phenol.....	60
4.2.5 Phenol sorption kinetics of the resins	62
4.2.6 Kinetic models	63
4.3 Preparation of the New Polymeric Sorbents for Removal of Atrazine	66
4.3.1 Preparation poly (2-acrylamido-2-methylpropane sulfonic acid) (AMPS) grafted onto crosslinked poly (vinylbenzyl chloride) resin for removal of atrazine from water	66
4.3.2 Characterization of the resin poly(2-acrylamido-2-methylpropane sulfonic acid) (AMPS)	67
4.3.3 Atrazine extraction experiments	68
4.3.4 Atrazine sorption kinetics of the (poly(2-acrylamido-2-methylpropane sulfonic acid) (AMPS) resin	70
4.3.5 Kinetic models	70
5. CONCLUSION.....	73
REFERENCES.....	75
CURRICULUM VITAE.....	85

ABBREVIATIONS

EGDMA	: Ethylene Glycole Dimethacrylate
AMPS	: 2-Acrylamido-2-Methylpropane Sulfonic Acid
PMDETA	: N,N,N',N'',N''-Pentamethyldiethylenetriamine
PVBC	: Poly(vinyl benzyl chloride)
VBC	: Vinyl Benzyl Chloride
PVA	: Poly(vinyl alcohol)
PVI	: Poly(vinyl imidazole)
ATRP	: Atom Transfer Radical Polymerization
PGMA	: Poly (glycidyl methacrylate)
CAC	: Commercial Activated Carbons
DVB	: Divinylbenzene
NMP	: N-Methyl-2-Pyrrolidone
XAD	: Polystyrene-Divinylbenzene Copolymer
CRP	: Controlled Radical Polymerization
EP-PS	: Ethyl Piperazine Modified Polystyrene Resin
QEP-PS	: Quaternized Ethyl Piperazine Modified Polystyrene Resin
DMEA	: N,N-Dimethylethylenediamine
DMEA-CAM	: N,N-Dimethylethylenediamine Modified Chloroacetamide Quaternized resin
DMF	:Dimethylformamide
AIBN	:Azobisisobutyronitrile
FESEM	: Field Emission Scanning Electron Microscopy
FTIR	: Fourier Transform Infrared Spectroscopy
QIP-PS	: Quaternized Imidazole Modified Polystyrene Resin
IP-PVBC	: Imidazole Modified Poly(vinyl benzyl chloride) Resin

LIST OF TABLES

	<u>Page</u>
Table 2.1 : Principal existing and emerging processes for organic pollutant	8
Table 2.2 : Waste-water treatment unit operations and processes.....	11
Table 2.3 : Some synthetic polymer adsorbents,targeted dyes and corresponding adsorption capacities.....	20
Table 4.1 : Dye sorption capacity of the quaternary resins	49
Table 4.2 :Sorption capacities of the imidazole based resins.	50
Table 4.3 : Maximum dye sorption capacities of the resins depending on pH.....	51
Table 4.4 : Maximum dye sorption capacities of the PVI grafted PVBC resin depending on pH	52
Table 4.5 : Pseudo-first-order and second-order kinetics models for adsorption of dyes on the (QEP-PS) resin.	55
Table 4.6 : Pseudo-first-order and second-order kinetics models for adsorption of dyes on the (QIP-PS) resin.	56
Table 4.7 : Pseudo-first-order and second-order kinetics models for adsorption of dyes on the PVI grafted PVBC resin.	56
Table 4.8 :Maximum phenol sorption capacities of the resins.	61
Table 4.9 : Phenol sorption capacity of the resin depending on pH.....	61
Table 4.10 : Pseudo-first-order and second-order kinetics models for adsorption of phenol the resins	65
Table 4.11 : Maximum atrazine sorption capacities of the resin.	69
Table 4.12 : Atrazine sorption capacities of the resin depending on pH.....	69
Table 4.13 : Pseudo-first-order and second-order kinetics models for atrazine sorption of the resin	71

LIST OF FIGURES

	<u>Page</u>
Figure 2.1 : Illustration of adsorption process [50].....	18
Figure 2.2 : A schematic representation for various classifications of grafted and/or crosslinked polymers [96].	25
Figure 2.3 : A schematic representation for various types of grafted and/or crosslinked polymers [96].....	26
Figure 2.4 : Grafting techniques[109].....	29
Figure 2.5 : Suspension polymerization.....	31
Figure 2.6 : Scheme of emulsion polymerization.	32
Figure 2.7 : The mechanism of transition metal-catalyzed ATRP [122, 123].	33
Figure 2.8 : Mechanism of normal ATRP and reverse ATRP (M: Cu, Fe, Ni etc.)	34
Figure 2.9 : Controlled polymerization via deactivation/activation process	35
Figure 2.10 : Schematic of the RAFT polymerization [133].	35
Figure 4.1 : Preparation of the resin.....	45
Figure 4.2 : (a) PVBC resin (b) Ethyl piperazine modified PVBC (EP-PS) (c) Quaternary amine containing resin (QEP-PS).	46
Figure 4.3 : Preparation of the IP-PVBC resin	46
Figure 4.4 : Preparation of the PVI grafted resin.	47
Figure 4.5 : FT-IR spectra of the (a) PVBC resin; (b) Resin 1; (c) Resin 2.	48
Figure 4.6 : SEM image of the (a) PVBC resin (b) PVI grafted PVBC resin.....	48
Figure 4.7 : Dye sorption kinetics of the (QEP-PS) resin.....	53
Figure 4.8 : Sorption kinetic of the PVI grafted PVBC resin	53
Figure 4.9 : The pseudo-second-order model plots of dyes sorption of (QEP- PS) resin	54
Figure 4.10 : The pseudo-second-order model plots of dyes sorption of PVI grafted PVBC resin.....	55
Figure 4.11 : Preparation of the quaternary amide containing resins	58
Figure 4.12 : PVBC resin (b) Imidazole modified PVBC (c) Quaternary chloroacetamide containing resin.	58
Figure 4.13 : Preparation of PVBC-DMEA-CAM resin.	59
Figure 4.14 : FT-IR spectra of (a) PVBC (b) PVBC+N,N-dimethylethylenediamine c) N,N- dimethylethylenediamine Modified chloroacetamide quaternized PVBC Resin	60
Figure 4.15 : Phenol sorption kinetics of imidazole modified chloroacetamide quaternized resin.....	62
Figure 4.16 : Phenol sorption kinetics of ethyl piperazine modified chloroacetamide quaternized resin	63
Figure 4.17 : Phenol sorption kinetics of the (PVBC-DMEA-CAM) resin.....	63
Figure 4.18 : The pseudo -second-order model plots for phenol sorption of chloroacetamide quaternized imidazole modified resin	64

Figure 4.19 : Pseudo-second-order model plots for adsorption of phenol quaternary amide containing piperazine based resin	64
Figure 4.20 : Pseudo-second-order model plots for adsorption of phenol on the (PVBC-DMEA-CAM) resin	65
Figure 4.21 : Chemical structure of atrazine	66
Figure 4.22 : Preparation of core-shell type crosslinked polymeric resin.....	67
Figure 4.23 : FT-IR spectra of a) PVBC resin b) AMPS resin c) Atrazine loaded AMPS resin.	68
Figure 4.24: SEM image of the (a) AMPS grafted onto PVBC resin (b) Atrazine loaded resins	68
Figure 4.25 : Atrazine sorption kinetics of the poly(2-acrylamido-2-methylpropane sulfonic acid) (AMPS) resin.	70
Figure 4.26 : Pseudo-second-order model plots of adsorption of atrazine on the (Poly(2-acrylamido-2-methylpropane sulfonic acid) (AMPS) resin. ..	71

PREPARATION OF NEW POLYMERIC SORBENTS FOR REMOVAL OF ORGANIC WASTES

SUMMARY

The environmental protection becomes a difficult task while many industries produce wastes that cause serious pollution.

In the textile industry, large quantities of aqueous wastes and dye effluents are discharged from the dyeing process with strong persistent color. Most of these dye wastes are toxic and may be carcinogenic, and this poses a serious hazard to aquatic living organisms. As a result, the removal of dyestuffs from effluents becomes important, and many governments have established environmental restrictions with regard to the quality of colored effluents and have forced dye-using industries to decolorize their effluents before discharging. In this study, poly(styrene) based quaternary ammonium carboxylate based resins were prepared to remove acidic and basic dyes from aqueous solutions.

In this study, a beaded polymer with quaternary amine functions were prepared in two steps, starting from poly(vinyl benzyl chloride-co-ethylene glycol dimethacrylate) based beads, according to the synthetic protocol; modification of ethyl piperazine and imidazole quaternization of chloroacetic acid, respectively.

Poly (vinyl imidazole) grafted onto PVBC resin was prepared by using reverse ATRP technique. The grafting degree of the resin was found about 59% after 72 h. Therefore, core-shell type polymeric sorbent was obtained for removal of acidic dyes from water.

Linear polymers grafted onto crosslinked polymer resin particles offer numerous potential applications due to the combination of the non-solubility resin and the flexibility of the graft polymer side-chains as the functional group carrier.

The flexible side-chains can provide pseudo-homogeneous reaction conditions and better accessibility of the involved functional groups. The atom transfer radical polymerization (ATRP) technique, for instance, provides chain growing mostly on the solid surface if the initiator function is covalently bound to the surface.

Dye sorption and desorption experiments were investigated under various operating conditions.

Phenols are generally considered as one of the important organic pollutants discharged into the environment causing unpleasant taste and odor of drinking water. Three mechanisms of phenolic compounds adsorption is postulated namely, π - π dispersion interaction, electron-donor acceptor complex formation and hydrogen bond formation. This methodology was used to prepare new polymeric sorbents for phenol removal.

Ethyl piperazine and imidazole modified PVBC beads were quaternized with chloroacetamide. The resulting polymer resins, which had a total nitrogen content of about 4.50 mmol/g, was effective in extracting phenol from aqueous solutions. The phenol sorption capacity was around 0.208 g phenol/g resin in non-buffered conditions.

Another sorbent was prepared starting from the reaction of PVBC beads with N,N-dimethylethylenediamine. The resulting beads were quaternized with chloroacetamide to obtain quaternary amide containing sorbent. The phenol sorption capacity was around 0.220 g phenol / g resin in non-buffered conditions. The adsorption conditions (initial phenol concentration and pH) were varied to evaluate mechanism of adsorption of phenol on the prepared resins. These resins are also able to remove phenol completely even from highly diluted aqueous phenol solutions.

Atrazine is another important organic pollutant. Many techniques have been researched and developed for the removal of hazardous agricultural chemicals that migrate to the environment, including photocatalytic degradation, biological repair, sorption, etc. Sorption is recognized as one of the most applicable technologies for contamination removal. Regarding that adsorption on solid substrates, such as activated carbon, biosorbents or clay, are a widely used method for removing atrazine from waters.

In this study, poly (2-acrylamido-2-methylpropane sulfonic acid) (AMPS) grafted onto crosslinked PVBC resin by ATRP polymerization technique for removal of atrazine from water. Atrazine is a basic compound. Therefore, acidic type of sorbents can be used to remove atrazine.

Atrazine sorption capacities of the polymeric sorbent was determined depending on different waste concentration and pH.

Trace contaminants of atrazine removal experiments were also investigated and different kinetic models were applied. Prepared sorbents were characterized by using analytical and spectroscopic techniques to determine functional groups. Morphological characterization of core-shell type resins were studied with scanning electron microscope (SEM).

ORGANİK ATIKLARIN GİDERİLMESİ İÇİN YENİ POLİMERİK SORBENTLERİN HAZIRLANMASI

ÖZET

Çok sayıda endüstrinin ürettiği atıklar ciddi bir kirliliğe neden olmasından dolayı çevrenin korunması daha zor hale geliyor.

Organik kirlilikler pestisid, hidrokarbonlar, fenoller, plastizerler, bifeniller, deterjanlar, yağlar, gresler, farmasötikler, proteinler ve karbonhidratları içerirler.Yüksek derece organik bileşiklerin sudan uzaklaştırılmasında etkin yöntemler önem kazanmaktadır.Çok sayıda metod koagulasyon, filtrasyonlu koagulasyon, ozonlama, adsorbsiyon, iyon değişimi, ters osmoz ve inert oksidasyon gibi prosesler sudan ve atık sulardan organik atıkların giderilmesinde kullanılmıştır.Bu metodlar yüksek yatırım ve maliyet gerektirir.Diğer taraftan adsorbsiyon ve iyon değişimi metodları organik atıkların giderilmesinde etkili olduğu gibi uygun ve düşük maliyetli yöntemlerdir.

Tekstil endüstrisinin en büyük sorunlarından biri boya atıklarının uzaklaştırılmasıdır. Boya atıkları insan sağlığını ciddi şekilde etkileyebilir. Bazı boyalar metabolizma üzerinde mutajenik ya da kanserojenik etkiye sahiptir. Boyaların uzaklaştırılması çevre açısından önemlidir. Renkli atık suları, boya imal endüstrileri ve boya tüketen endüstrilerde seri üretim süreçleri sonucunda oluşur.Üretim fazlası boyalar direkt olarak pis suya boşaltılır.Bu amaçla çeşitli sorbentler aktif karbon, modifiye çitosan ve bazı yüzey modifiye zeolitler boya artıklarının uzaklaştırılmasında kullanılmışlardır.Her ne kadar aktif karbon organik kirleticilerin uzaklaştırılmasında etkili bir şekilde kullanılsa da düşük adsorpsiyon kapasitesi olması, rejenerasyonunun uygun ve düşük maliyetle olması gerekmektedir.

Boya giderilmesinde bir çok sorbent denemiştir.Ancak bu maddelerden birçoğu rejenere edilmedikleri için okalıptüs kabuğu gibi bir kere kullanılıp atılmaktadır.Reaktif boyaların selüloz, pirinç kabuğu, hindistan cevizi kabuğu gibi kuarternize organik maddelerle adsorbsiyon kapasitesi 60-240 mg arasında değişmekte olup rejenerasyonları ile ilgili başarılı sonuç alınamamıştır.

Polimer ve boyanın etkileşimiyle polimer-boya kompleks oluşumunun pek çok ilginç ve önemli özelliği vardır.Kulombik, hidrofobik ve sterik etkileşimler, kompleks oluşumunu sağlayan termodinamik ve dinamik etkilerdir.Hidrojellerin boya ile etkileşimleri ise en önemli unsurdur.Bu çalışmada poli(stiren) esaslı polimerik kuarternler amonyum karboksilik asit içeren reçine hazırlanarak asidik ve bazik boyaların giderilmesinde kullanılmıştır.

Bu çalışmada kuarterner amin fonksiyonlu polimerik kürecikler iki basamakta hazırlanmıştır. İlk olarak poli (vinil benzil klorür-etilen glikol dimetakrilat) (PVBC) esaslı kürecikler sentetik protokole göre sentezlenmiştir. PVBC kürecikler etil piperazin ve imidazolle modifikasyonu yapıldıktan sonra kloroasetik asit ile kuaternizasyonu gerçekleştirilmiştir.

Ters atom tranfer radikal polimerizasyon tekniği (ATRP) kullanılarak PVBC küreleri üzerine poli(vinil imidazol) aşılantısı. Aşılantı derecesi 72 saatte yaklaşık % 59'a ulaşmıştır. Bu nedenle "core-shell" yapısındaki polimerik sorbent sudan asidik boyaların giderilmesinde kullanılmıştır.

Çapraz bağlı polimerik reçinelerin üzerine aşılantısı lineer polimerler, reçinenin çözücü ile etkileşmesini ve fonksiyonel grup taşıyan yan zincirlerin esnekliğinin birleşmesinden dolayı sayısız uygulama alanına sahiptir.

Yan zincir esnekliği homojen bir reaksiyon şartı sağladığı gibi fonksiyonel grupların daha etkili kullanımına olanak sağlar.

Atom tranfer radikal polimerizasyon(ATRP) tekniği, çoğunlukla katı yüzey üzerinde büyüyen zincirler verir. Başlatıcı gruplar yüzeye kovalent bağ ile bağlanmışlardır.

Boya adsorpsiyon deneyleri farklı boya konsantrasyonları, pH ve kinetik ölçümlere bağlı olarak çalışılmıştır. Aynı zamanda desorpsiyon deneyleri de yapılmıştır.

Fenoller en önemli organik kirleticilerden biridir. Çevreye verildiklerinde suda istenmeyen renk ve koku bırakırlar. Düşük konsantrasyonda bile organizma üzerindeki zararlarından dolayı fenoller kirleticiler arasında önemli yere sahiptir.

Fenolik bileşiklerin adsorpsiyonu 3 mekanizma üzerinden ilerler.

Şöyleki, π - π etkileşimi, elektron-dönör akseptör kompleks formasyonu ve hidrojen bağ oluşumudur. Fenollerin uzaklaştırılmasında yeni sorbentler hazırlanarak kullanılmıştır.

Etil piperazin ve imidazol PVBC ile modifiye edilerek kloroasetamid ile kuaternizasyonu gerçekleştirilmiştir. Kloroasetamid içeren polimerik reçine 4.50 mmol/g amin fonksiyonu elde edilmiştir.

İşlem sonunda fenolün adsorpsiyon kapasitesi 0.208 g fenol/ g bulunmuştur. Bu sonuç fenolün çözüldüden etkili bir şekilde uzaklaştırıldığını gösterir.

Diğer bir sorbent N,N dimetiletilenamin ile PVBC küreciklerinden başlayarak hazırlanmıştır. Daha sonra kloroasetamid ile kuaternize edilerek kuarterner amid grubu içeren kürecikler hazırlanmıştır. Elde edilen sorbentin adsorpsiyon kapasitesi 0.22 g fenol/ g reçine olarak bulunmuştur. Adsorpsiyon şartlarına bağlı olarak reçinenin fenol adsorpsiyon mekanizması çeşitlilik gösterir. Bu reçine fenol içeren seyreltik çözeltilerde bile fenolu tamamen ortamdan uzaklaştırır.

Bu çalışmada ATRP (atom tranfer radikal polimerizasyon) tekniği ile polimer yüzeyine aşılama yapılabilmiştir. Poli (2-akrilamido-2-metilpropen sülfonik asit) çapraz bağlı PVBC reçine üzerine aşılama yapılarak, atrazinin sudan giderilmesinde kullanılmıştır. Atrazin bazik bir bileşiktir. Bu nedenle atrazinin uzaklaştırılmasında asidik türden sorbentler kullanılmıştır. Farklı pH ve konsantrasyona bağlı olarak polimerik sorbentlerin atrazini tutma kapasiteleri incelenmiştir.

Eser miktarda atrazinin uzaklaştırılması üzerinde deneysel alıřmalar yapılmıř ve farklı kinetik modeller uygulanmıřtır. Spektroskopik ve analitik yntemler kullanarak hazırlanan sorbentin fonksiyonel grupları karakterize edilmiřtir. Core-shell tipi reinelerin SEM ile morfolojileri ve yapıları karakterize edilmiřtir.

1. INTRODUCTION

The environmental protection becomes a difficult task while many industries produce wastes that cause serious pollution.

In the textile industry, large quantities of aqueous wastes and dye effluents are discharged from the dyeing process with strong persistent color. Most of these dye wastes are toxic and may be carcinogenic, and this poses a serious hazard to aquatic living organisms. As a result, the removal of dye stuffs from effluents becomes important, and many governments have established environmental restrictions with regard to the quality of colored effluents and have forced dye-using industries to decolorize their effluents before discharging. Different kinds of conventional treatment technologies have been investigated for dye removal extensively, such as the trickling filter, activated sludge, chemical coagulation, carbon adsorption, and photo degradation processes [1]. Among these chemical and physical methods, the adsorption process is effective to produce a high-quality effluent without the formation of harmful substances, such as ozone and free radicals in the photo degradation process using UV [2].

Phenols are generally considered one of the important organic pollutants discharged into the environment causing unpleasant taste and odor of drinking water. They are harmful to organisms at low concentrations. The major sources of phenol pollution in the aquatic environment are wastewaters from paint, pesticide, coal conversion, polymeric resin, and petroleum and petrochemicals industries. Introducing phenolic compounds into the environment or degradation of these substances means the appearance of phenol and its derivatives in the environment. The chlorination of natural waters for disinfection produces chlorinated phenols.

There are several reported methods for the removal of pollutants from the effluents. The technologies can be divided 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

waste water have not been widely applied at large scale in the phenol and textile industries.

Atrazine is one of the most difficult herbicides to remove from water. The harmful influence of atrazine on environment and human health has resulted in prohibition of its usage in EU since 2005. However, atrazine is still observed in ground water, due to the fact that it has been degradation half-life in soil range from 2 months to 6 years and applied for pre-emergence control in the agriculture. Its resistance to biological degradation and its physicochemical properties (low soil sorption coefficient and solubility in water). Therefore, these herbicides removal from water is widely studied utilizing these various materials. It kills weeds in corn and inhibiting photosynthesis. Many techniques have been developed for removal of toxic agricultural chemicals that migrate to the environment, including photo catalytic degradation, biological repair, sorption, etc. Sorption is recognized one of the most applicable technologies for contamination removal [3]. Regarding that adsorption on solid substrates, such as activated carbon, biosorbents or clay, is a widely used method for removing atrazine from waters.

Functional polymers are important to removal organic and inorganic wastes. There are a number of considerations in the choice of functional polymers to be used in a specific application. Functionalized polymer must possess a structure that permits adequate of reagent in the reactive sites. This depends on the extent of swelling compatibility the effective pore size, pore volume (porosity), chemical, thermal and mechanical stability of the resins under the conditions of a particular chemical reaction on reaction sequence. This in turn depends on the degree of the crosslinking of the resin and the conditions employed during its preparation [4].

The use of crosslinked polymers in chemical applications is associated with some advantages, such as the following.

1. Due to their insolubility, they are easy to process in common solvent.
2. They can be prepared in the form of spherical beads and can be separated from low molecular weight contaminants by simple filtration and washing solvents.
3. Polymer beads with very low degrees of crosslinking swell extensively, exposing their inner reactive groups to the soluble reagents.

4. Crosslinked resins may be prepared with very porous structures, which allow solvents and reagents to penetrate inside of the beads to contact reactive groups.

Adsorption is an important method for separation and purification and is widely used in industrial applications of water treatment using adsorbents such as activated carbon, synthetic resins and zeolites.

Functional group carrying polymeric sorbents are important to remove organic and inorganic wastes selectively. Also, polymeric sorbents could be regenerate by using suitable reagent without losing their activity compared with other sorbents like activated carbon and natural materials [5].

In this study, new polymeric sorbents such as ethyl piperazine, imidazole based sorbents and their quaternary derivatives were synthesized to remove organic wastes (acidic and basic dyes, phenol and derivatives, herbicides like atrazine, etc) from water and organic mixtures.

Vinyl benzyl chloride and ethylene glycol dimethacrylate (crosslinker) was copolymerized to obtain crosslinked poly (vinyl benzyl chloride) (PVBC) by using suspension polymerization technique.

PVBC resin was modified with imidazole and ethyl piperazine. A beaded polymer with quaternary amine functions were prepared in two steps, starting from poly(vinyl benzyl chloride-ethylene glycol dimethacrylate) based beads, according to the synthetic protocol; modification of ethyl piperazine and imidazole quaternization of chloroacetic acid, respectively. These resins were used to remove both acidic and basic dyes from water.

Poly (4-vinyl imidazole) (PVI) was grafted onto the PVBC resin to obtain core-shell type structure for removal of acidic dyes.

Imidazole, ethyl piperazine and N,N-dimethylethylene diamine modified resins were quaternized by using chloroacetamide to remove phenol.

Poly (2-Acrylamido-2-Methylpropane Sulfonic Acid) (AMPS) grafted on to PVBC resin was used to remove atrazine.

2. THEORETICAL PART

2.1 Hazards of Organic Waste

Waste is defined as any object or substance that the holder is required to discard; and is produced in huge quantities. For example, it is estimated that the European Union generates approximately three billion tons of waste, including hazardous organic waste every year and it is expected that this figure continues rising [6]. Approximately, hazardous organic waste represents 3% of the waste generation. The generation and management of the wastes and particularly hazardous organic waste, has led to a serious environmental concern.

Different types of organic wastes, taking into account their origins, agriculture, wood processing, leather industries, municipal wastes, etc., and further subclasses based on the productive process or the presence of dangerous substances. The actual organic waste has to display one or more of the defined hazardous properties or should contain dangerous substances in a concentration, which makes the waste exhibits one or more of the hazardous properties to be really considered hazardous organic waste [7].

The hazardous properties listed in the WFD (waterframe work directive) , include different characteristics that can be classified as follows:

- Physicochemical properties:
 - Explosive
 - Oxidizing,
 - Highly flammable
 - Flammable
- Toxicity properties
 - Irritant
 - Harmful
 - Carcinogenic
 - Corrosive
 - Infectious

- Toxic for reproduction
- Mutagenic
- Sensitizing

2.1.1 Health hazards of dye effluents

The most critical and fundamental component in the world for vital activities of living beings is water. Hence, water pollution has become an important issue now, effecting all living creatures, household, recreation, fishing, transportation and other commercial activities. Thus, government authorities, scientists, and academicians are concern about the threading threats to both humans and aquatic lives.

Some water contaminants such as organic, inorganic, and biological pollutants have serious side effects and toxicities with a few being lethal and carcinogenic. Aquatic conditions and the ecosystem of the earth as a whole are threatened by these pollutants.

Dyes which are used by many textile manufacturers release aromatic amines (benzidine, toluidine, etc.). Dye bath effluents may contain heavy metals, ammonia, alkali salts, toxic solids and large amounts of pigments-many of which are toxic. Due to their complex aromatic molecular structure and synthetic origin, most of synthetic dyes are not biodegradeble. The broad use of dyes generally poses pollution problems in the form of coloured waste water discharge into environmental water bodies, which interferes with transmission of sunlight into streams thus reduces photosynthetic activity. Besides, some dyes or their metabolites are either toxic or mutagenic and carcinogenic. The presence of these heat and light stable complex dye molecules in wastewater made the conventional methods of sewage treatment, such as primary and secondary treatment systems unsuitable. The adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive [8].

2.1.2 Hazards of phenol

Phenol is widely used and is a basic structural unit for a variety of synthetic organic compounds including agricultural chemicals and pesticide. This compound is one of the most common organic water pollutants, because it is toxic even at low concentrations and also its presence in natural waters can lead further to the formation of substituted compounds during disinfection and oxidation processes

which is encountered most frequently in the petroleum refining and chemical processing industries. It is mutagenic substance at high concentrations and may be absorbed through skin and causes various health hazards. Exposure to phenol by any route can produce systemic poisoning. Phenol is corrosive and causes chemical burns at the contact site [9,10].

2.1.3 Hazards of pesticides and herbicides

Once pesticides and herbicide are introduced into the environment, whether by application, disposal, or a spill, it can be influenced by many processes. These processes determine ultimate fate of the herbicide by affecting its persistence and movement in the environment. There has been increasing concern about the release of pesticides and other organic compounds to the environment as a result of agricultural activities and the fact that many are finding their way into drinking water supplies [11,12].

Contamination of water and soil by pesticide and herbicide has a negative impact on aquatic ecosystems which is generally characterized by high toxicity and long environmental half-life and induce severe hormonal disturbances in amphibians and malignant tumors in rats [13]. The presence of atrazine metabolites is an indication of herbicide degradation. The harmful influence of atrazine on human health and environment has resulted in prohibition of its usage in European Union since 2004. They represent a serious concern for the remediation of contaminated waters and have long been reported to be priority pollutants. However, even now this herbicide is still observed in groundwater, due to the fact that in the past it has been heavily applied for pre-emergence control in the agriculture [14,15].

2.2 Technique for the Removal of Organic Pollutants from Wastewater

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. 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 during the decomposition process of organic pollutants.

Wastewaters with organic pollutants contain large quantities of suspended solids which reduce the light available to photosynthetic organisms and, on settling out, alter the characteristics of the river bed, rendering it an unsuitable habitat for many invertebrates [16].

Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, proteins and carbohydrates [17]. Efficient techniques for the removal of highly toxic organic compounds from water have drawn significant interest. A number of methods such as coagulation, filtration with coagulation, precipitation, ozonation, adsorption, ion exchange, reverse osmosis and advanced oxidation processes have been used for the removal of organic pollutants from polluted water and wastewater. These methods involve relatively high investment and operational cost. On the other hand reverse osmosis and ion exchange are more effective processes which can be recovered along with their removal from organic pollutants. Advanced oxidation processes, reverse osmosis and ion exchange seem to be economically feasible [18].

The adsorption process is relatively efficient for the treatment and removal of organic contaminants in wastewater treatment. Materials locally available such as natural materials, agricultural wastes and industrial wastes can be utilized as low-cost adsorbents [19].

Table 2.1 : Principal existing and emerging processes for organic pollutant [20].

	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation	Simple, economically feasible	High sludge production, handling and disposal problems
	Flocculation		Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements
	Biodegradation	Economically, attractive, publicly acceptable treatment	
	Technology	Advantages	Disadvantages
	Adsorption on activated carbons	The most effective adsorbent, great capacity, produce a high-quality treated effluent	Ineffective against dispersed and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery process	Membrane separations	Removes all the dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes

2.3 Classifications and Properties of Dyes

Some properties of dyes classified on their usage are discussed in brief here.

i) Acid dyes

They are used for wool, silk, nylon, modified acrylics, leather, ink-jet printing, cosmetics and food. They are usually water soluble. The principal chemical classes of these dyes are azo (premetallized), azine, triphenylmethane, xanthene, anthraquinone, nitroso and nitro.

ii) Cationic (basic) dyes

They are used for modified nylons, paper, modified polyesters, polyacrylonitrile and some extent in medicine. Originally, they were used for tannin-mordanted cotton silk and wool. The principal chemical classes are thiazine, triarylmethane, oxazine, acridine, diazahemicyanine, cyanine and hemicyanine.

iii) Disperse dyes

They are used mainly on nylon and to some extent on polyester, acrylic fibers, cellulose and cellulose acetate. These are generally water-insoluble that used for hydrophobic fibers from aqueous dispersion. They generally contain nitro, azo, styryl, benzodifuranone groups and anthraquinone.

iv) Direct dyes

They are used in the dyeing of rayon and cotton, leather, nylon and to some extent to paper. They are water-soluble.

v) Anionic dyes

These dyes in aqueous solution in the presence of electrolytes have more affinity for cellulosic fibers. Generally, the dyes in this class are azo compounds, along with some oxazines, stilbenes and phthalocyanines.

vi) Reactive dyes

They are usually used for cellulosics and nylon, but are also used to a small extent on cotton. These dyes form a covalent bond with the fibers and contain chromophoric groups such as anthraquinone, azo, phthalocyanine, oxazine, triarylmethane form etc. Their absorption spectra shown in the figure, the dyeings are brighter making them advantageous over direct dye and chemical structures are simpler.

vii) Solvent dyes

They are used for lubricants, oils, gasoline, waxes and plastics. These dyes are water insoluble and generally nonpolar or little polar, i.e., lacking polar solubilizing groups such as quaternary ammonium, sulfonic acid or carboxylic acid. The principal chemical classes are predominantly phthalocyanine, butatriarylmethane, azo and anthraquinone are also used.

viii) Sulfur dyes

They are used for cotton and polyamide fibers and have limited use with rayon, leather, wood, silk and paper. They have a relatively small group of dyes and though they form intermediate structures, good wash fastness and the low cost properties make this class major important from an economic point of view.

ix) Vat dyes

They are used for cellulosic fibers mainly to cotton as soluble for rayon and wool and leuco salts too. These water-insoluble dyes are with principal chemical class containing indigoids and anthraquinone (including polycyclic quinones). Besides these, there are some other classes too having azoic groups used for other cellulosic materials and cotton; fluorescent brighteners having naphthalimides, pyrazoles, stilbene and coumarin used for detergents and soaps and paints, oils, plastics fibers and mordant having azo and anthraquinone used for natural fibers, leather, wool after pretreating with anodized aluminium and metals.

2.4 Technologies Available for Dye and Phenolic Compounds Removal

There are several reported methods for the removal of pollutants from the effluents. The technologies can be divided 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 dye and phenol bearing wastewater have not been widely applied at large scale in the agriculture and industries.

Physical, chemical and biological methods are used to remove the contaminants from wastewater. In order to achieve different levels of contaminant removal, individual wastewater treatment procedures are combined into a variety of systems. These can be classified as primary secondary and tertiary wastewater treatment. Wastewater

treatment methods are broadly classifiable into physical, chemical and biological processes and shown below [21]:

Table 2.2 : Waste-water treatment unit operations and processes.

Physical unit operations	Chemical unit operations	Biological unit operations
Screening	Chemical precipitation	Activated sludge process
Comminution	Adsorption	Aerated lagoon
Flow equalization	Disinfection	Trickling filters
Sedimentation	Dechlorination	Pond stabilization
Flotation		Anaerobic digestion
		Biological nutrient removal

Attention has been focused on various natural solid materials, which are able to remove the pollutants from the contaminated wastewater at low cost. Cost is actually an important parameter for comparing the adsorbent materials.

The numerous techniques of dye removal is the procedure of choice and gives the best results as it can be used to remove different types of contaminant materials. New approaches have been studied for the development of cheaper and effective adsorbents.

Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from industry and agriculture, have been proposed by several workers.

These materials could be used as sorbents for the removal of dyes and phenol from solution. Some of the reported sorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton) [22-25].

2.4.1 Dye and phenolic compounds removal using activated carbons

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. However, among all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater [26]. In particular, the effectiveness of adsorption on commercial activated carbons (CAC) for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options. Because of their great capacity to adsorb dyes, CAC are the most effective adsorbents. This capacity is mainly due to their structural characteristics 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. It is quite expensive, the higher the quality, the greater the cost, non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straight forward, and results in loss of the adsorbent [27,28].

2.4.2 Low-cost adsorbents for removal of dyes and phenolic compounds

Research interest into the production of alternative sorbents to replace the costly activated carbon has intensified in recent years. Attention has focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials. A sorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for dye removal [29].

2.4.3 Natural materials

2.4.3.1. Clay

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 adsorption capabilities result from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species. Their adsorption properties also come from their high-surface-area and high porosity. In particular, interactions between dyes, phenol compounds and clay particles have been extensively studied [30-32].

Clay minerals exhibit a strong affinity for both heteroatomic cationic and anionic dyes and phenols. However, the sorption capacity for basic dye is much higher than for acid dye because of the ionic charges on the dyes and character of the clay. The adsorption of phenols by organoclays and a coal/mineral complex (ARO) was also studied. The adsorption of dyes and phenolic compounds on clay minerals is mainly dominated by ion-exchange processes. This means that the sorption capacity can vary strongly with pH. As with other materials, clay materials can be modified to improve their sorption capacity. They showed that the adsorption capacities are substantially improved upon modifying their surfaces with quaternary amines. The adsorption capacity of kaolinite can be improved by purification and by treatment with NaOH solution. The acid-treated bentonite showed a higher adsorption capacity than non-modified bentonite [33].

2.4.3.2. Siliceous materials

Among inorganic materials, silica beads deserve particular attention considering chemical reactivity of their hydrophilic surface, resulting from the presence of silanol groups. Their porous texture, high surface area and mechanical stability also make them attractive as sorbents for decontamination applications. However, due to their low resistance toward alkaline solutions their usage is limited to media of pH less than 8. Moreover, the surface of siliceous materials contains acidic silanol (among other surface groups) which causes a strong and often irreversible non-specific adsorption [34,35]. It was suggested that phenols and dyes are physically adsorbed onto the perlite. Perlite is a good adsorbent for decontamination purposes.

However, perlites of different types (expanded and unexpanded) and of different origins have different properties because of the differences in composition.

2.4.3.3. Zeolites

Zeolites consist of a wide variety of species, more than 40 natural species. However, the most abundant and frequently studied zeolite is clinoptilolite, a mineral of the heulandite group. Clinoptilolite has been shown to have high selectivity for certain pollutants which high ion-exchange capacity and relatively high specific surface areas and more importantly their relatively cheap prices, make zeolites attractive adsorbents. Another advantage of zeolites over resins is their ion selectivities generated by their rigid porous structures. Zeolites are becoming widely used as alternative materials in areas where sorptive applications are required. They have been intensively studied recently because of their applicability in removing trace quantities of pollutants such as heavy metal ions and phenols thanks to their cage-like structures suitable for ion exchange. Zeolites also appear as suitable sorbents for dyes. The sorption mechanism on zeolite particles is complex because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity and other imperfections on the surface [36,37].

Although the removal efficiency of zeolites for dyes and phenols may not be as good as that of clay materials, their easy availability and low cost may compensate for the associated drawbacks.

2.4.3.4. Bioadsorbents

The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials is termed biosorption. In this instance, biological materials, such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass, are used as chelating and complexing sorbents in order to concentrate and to remove dyes and phenols from solutions. These biosorbents and their derivatives contain a variety of functional groups which can complex dyes and phenolic compounds.

The biosorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons and can reduce contaminants concentration to ppb levels. Biosorption is a novel approach, competitive, effective and cheap.

2.4.3.5. Biopolymers: chitin and chitosan

The sorption of dyes and phenols using biopolymers such as chitin and chitosan is one of the reported emerging biosorption methods for the removal of dyes, even at

low concentration (ppm or ppb levels). Chitin and chitosan are abundant, renewable and biodegradable resources. The performance of chitosan as an adsorbent to remove acid dyes has been demonstrated by Wong et al [38].

Chitosan-based biosorbents are easy to prepare with relatively inexpensive reagents. These materials are insoluble in acidic and alkaline media as well as in organic solvents. They are more resistant to high temperature and low pH compared to their parent biopolymer. After crosslinking, they maintain their properties and original characteristics. Chemical modifications of chitosan have also been made to improve its removal performance and selectivity for dyes, to control its diffusion properties and to decrease the sensitivity of sorption to environmental conditions. In comparison with commercial activated carbon, the beads exhibited excellent performance for adsorption of anionic dyes: The adsorption values were 3–15 times higher at the same pH. Hence chitosan chelation is the procedure of choice for dye and phenols removal from aqueous solution. Its adsorption properties depend on the different sources of chitin, the degree of N-acetylation, molecular weight and solution properties and vary with crystallinity, affinity for water, percent deacetylation and amino group content [39,40].

Chitosan has drawn particular attention as a complexing agent due to its low cost compared to activated carbon and its high contents of amino and hydroxyl functional groups showing high potential for adsorption of a wide range of molecules, including phenolic compounds [41].

The uptake of dyes on chitosan may also proceed through ion-exchange mechanisms. The major adsorption site of chitosan is a primary amine group which is easily protonated to form -NH_3^+ in acidic solutions.

The strong electrostatic interaction between the -NH_3^+ groups and dye anions can be used to explain the sorption mechanism. The difference in the degree of adsorption may also be attributed to the chemical structure of each dye [42].

2.4.3.6. Peat

This natural material is a relatively inexpensive and widely available biosorbent, which has adsorption capabilities for a variety of pollutants. Raw peat contains lignin, cellulose, fulvic and humic acid as major constituents. These constituents, especially lignin and humic acid, bear polar functional groups, such as alcohols, aldehydes,

ketones, carboxylic acids, phenolic hydroxides and ethers that can be involved in chemical bonding [43].

Various pollutant-binding mechanisms are thought to be involved in the bioadsorption process, including physical adsorption, ion exchange, complexation, adsorption–complexation and chemisorptions [44]. Batch kinetic and isotherm studies were carried out to determine the adsorptive characteristics of peat and bentonite mixtures for pentachlorophenol. Batch isotherm studies showed that the adsorption of PCP by the peat–bentonite mixture from aqueous solution was described by the Freundlich isotherm equation [45].

Because of its polar character, peat can effectively remove dyes and phenols from solution. It was observed that peat tends to have a high cation exchange capacity, and is an effective sorbent for the removal of dyes. For acid and basic dyes, the removal performance was comparable with that of activated carbon, while for disperse dyes, the performance was much better. Their studies demonstrated that modified peat can be used for the removal of a variety of basic dyes. Variations in peat type and sorbent preparation also make the comparison of results difficult. However, it is now recognized that ion-exchange is the most prevalent mechanism [46,47].

2.4.3.7. Biomass

Biomass has a high potential as a sorbent due to its physico-chemical characteristics. A wide variety of microorganisms including algae, yeasts, bacteria and fungi are capable of decolorizing a wide range of dyes with a high efficiency. In fungal decolorization, fungi can be classified into two kinds according to their life state: Living cells to biodegrade and biosorb dyes and dead cells (fungal biomass)[48].

The biosorption capacity of fungal biomass could be increased by some pretreatment (by autoclaving or by reacting with chemicals). Other types of biomass such as yeasts have been studied for their dye and phenols uptake capacities.

The biosorption capacity of fungal biomass could be increased by some pretreatment (by autoclaving or by reacting with chemicals). Other types of biomass such as yeasts have been studied for their dyes and phenols uptake capacities. Yeasts are extensively used in a variety of large-scale industrial fermentation processes and waste biomass from these processes is a source potential for cheap adsorbent. Biosorption was also influenced by the functional groups in the fungal biomass and

its specific surface properties [49]. Biosorption performance depends on some external factors such as salts and ions in solution, which may be in competition. Other limitations of the technology include the fact that the method has only been tested for limited practical applications since biomass is not appropriate for the treatment of effluents using column systems, due to the clogging effect. Because of major limitations regarding its efficient utilization in a column reactor, there is a need for it to be immobilized. This step forms a major cost factor of the process.

Biosorption processes are particularly suitable for the treatment of solutions containing dilute (toxic) dye concentration. Biosorption is a promising potential alternative to conventional processes for the removal of dyes [50]. However, these technologies are still being developed and much more work is required.

2.5 Dye Removal Ability of Polymeric Adsorbent

Reactive dyes pollutant has the lowest biodegradability. Thus, biological wastewater processes cannot play role in adsorption. The chemical oxidation, flocculation, adsorption and membrane separation can only be caused to treatment reactive dyes pollutants. Recently, adsorption method has been chosen by several workers because of their simple equipment and relatively efficiency. Adsorption is usually reversible method, which adsorbed dyes from wastewater. It can be efficiency desorbs under specific conditions further treatment [51]. Some adsorbents such as clay and eucalyptus bark are only utilized once and disposed off products. Especially, polymeric adsorbents have regenerability, wide variations in porosity and continuous process which can increasingly utilized remove organic and wastewater pollutants treatment recently.

Polymeric adsorbents have been ability to remove inorganic and organic pollutants. It has improve adsorption capacity which used to waste treatment such as organic pollutants. It has been reported that surface functionalization can included being effective process due to interaction of polymeric matrixes bound to specific functional groups with target pollutants. Some of polymeric adsorbents have been studied for removal of dyes [52].

Polymeric adsorbents have the ability to remove inorganic and organic pollutants. Polymeric adsorbent has improved adsorption capacity, which used to waste treatment such as organic pollutants. It has been reported that surface

functionalization can included being effective process due to interaction of polymeric matrixes bound to specific functional groups with target pollutants. Some of polymeric adsorbents have studied for remove dyes. Different functional groups on polymer structure are various interactions between dye molecules. Especially, these interactions occur to between dye molecules and polymeric adsorbents [53].

Polymeric adsorbents show more significant advantages over other adsorbents such as activated carbon ,ion-exchangers due to simple and strong processing. They can be tunable, variety of ligands can be inserted to produce specific structure and they are produced in wide range of polymerization techniques (conventional ring opening polymerization, free- radical polymerization-radiation polymerization, single-electron transfer radical polymerization, atom transfer radical polymerization (ATRP), reversible addition fragmentation, chain transfer etc.) [54]. The most utilized adsorbents are hydrogels. This type of polymeric form with cross-linked structure which allow to large amount of aqueous solution while chemical or physical crosslinks could be swelling process of hydrogels. The network expansion of polymeric material changes be able to access of aggregates to yielding maximum removal dye molecules [55].

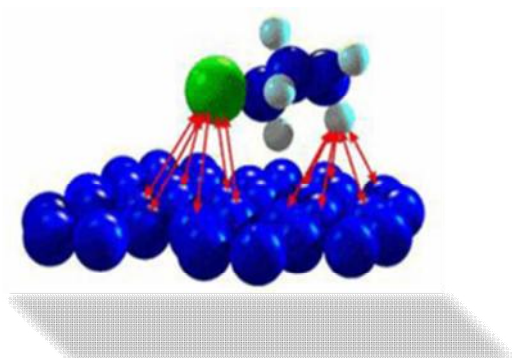


Figure 2.1 : Illustration of adsorption process [56].

The mechanical properties of polymer gels have increased through polymer networks which combinations of polymers are defined network without any covalent bonds. The sorption capacity of polymeric material specify group of dyes would be improved by monomers which have various functional groups due to specific several groups interaction of polymeric structure with different pollutants. Crosslinked polymer grafted on to linear polymers resins that have a potential applications all experiments because of side chain used as functional group transfer and interactions

of non-solubility particles. The side-chains involve pseudo-homogeneous reaction and better accessibility promote modified center. Senkal et.al. have prepared poly (glycidyl methacrylate) (PGMA) grafted on to polystyrene groups with tertiary amine which can be efficiency materials enable to removal of dyes from wastewater. It is listed tertiary amine involved through dye molecules. PGMA shell could be modified specific several step, treated from poly (styrene –co-divinyl benzene) beads [57].

It has expected that hydrogen bonding together with electrostatic interactions involved between anionic groups and cationic groups of dyes. Hydrophobic effect interacts with aqueous solution which present could occur to methyl groups on the dye molecules and aromatic rings. Hydrogen bonding would interactions between carbonyl groups on monomer unit and amine groups of oxygen atom on dye structure. The most of the used polymer materials, which show wide pH, range behavior. It has reported that many of polymers sorbent are ionic structure [58].

It is assumed that pH influence structures of polymeric materials as well as structure of reactive dyes have effects on surface modified of sorbent.

Thereby, the degree of interactions of functional groups would be promoting adsorption process. Many authors proven that the electrostatic attraction both the polymeric materials and dye molecules, charged groups on polymer structure and high over pH range can be increase electrostatic interactions on dye molecules [59]. The pH of system decreases, the positively charged center increased. The significantly limitation high reactivity sorbent which reacts with non-selectivity compounds tent to inorganic salts due to inorganic compounds small molecules. It is accomplish higher sorbents amount that results showed increase dye removal efficiency [60].

Table 2.3 show the sorption capacities of polymer structure for reactive dyes.

Table 2.3 : Some synthetic polymer adsorbents, targeted dyes and corresponding adsorption capacities [56].

Polymeric adsorbent	Dye	Maximal adsorption capacity	Reference
Poly(glycidyl methacrylate) grafted sulfonamide based polystyrene resin with tertiary amine	Everzol black	980 mg g ⁻¹	[58]
Poly(glycidyl methacrylate) grafted sulfonamide based polystyrene resin with tertiary amine	Everzol red	1000 mg g ⁻¹	[61]
Poly(glycidyl methacrylate) grafted sulfonamide based polystyrene resin with tertiary amine	Calgon	1000 mg g ⁻¹	[61]
Poly(ether sulfones)/ poly(ethyleneimine) (PES/PEI) nanofibrous membrane	Sunset Yellow FCF	1000 mg g ⁻¹	[63]
Poly(ether sulfones)/ poly(ethyleneimine) (PES/PEI) nanofibrous membrane	Amaranth	454 mg g ⁻¹	[62]
Porous poly(vinyl alcohol) gels	Congo red	35%	[64]
Porous poly(vinyl alcohol) gels	Methly Orange	Not available	[58]
poly(amidoamine-co-acrylic acid)copolymer	Direct Red 31	3400 mg g ⁻¹	[65]
poly(amidoamine-co-acrylic acid)copolymer	Direct Red 80	3448 mg g ⁻¹	[63]
Macroporous polystyrene cross-linked with divinylbenzene(Purolite A-520E)	Acid Blue29	48.2 mg g ⁻¹	[66]
poly(1-naphtylamine)	Acid Orange 10 (orange G)	328 mg g ⁻¹	[64]
poly(1-naphtylamine)-camphorsulphonic acid	Acid Orange 10 (orange G)	315 mg g ⁻¹	[64]
poly(N-vinyl-2-pyrrolidone)	Congo Red	Not available	[67]
poly(N-vinyl-2-pyrrolidone)	Methly orange	Not available	[65]
Cross-linked poly(styrene) resin	Acid red 14	Not available	[68]
poly(N,N-dimethylacrylamide-co-sodium acrylate)hydrogel	Basic Blue 41	710 mg g ⁻¹	[69]
poly(N-vinyl-2-pyrrolidone-co-acrylonitrile)treated with hydroxylamine-hydrochloride	Acid fast yellow G	7.6 mg g ⁻¹	[70]
poly(N-vinyl-2-pyrrolidone-co-acrylonitrile)treated with hydroxylamine-hydrochloride	Direct blue 3B	7 mg g ⁻¹	[68]
poly(N-vinyl-2-pyrrolidone-co-acrylonitrile)treated with hydroxylamine-hydrochloride	Reactive red SH	7.4 mg g ⁻¹	[68]
poly(acrylamide-co-acrylic acid)hydrogels	Janus Green B	44 mg g ⁻¹	[71]
poly(acrylamide-co-sodium acrylate)hydrogels	Janus Green B	7x10 ⁻⁴ mol g ⁻¹	[72]
poly(acrylamide-co-sodium acrylate)/poly(ethylene glycol)semi-IPN	Janus Green B	6.33x10 ⁻⁴ mol g ⁻¹	[70]
poly(acrylamide-co-sodium 4-styrenesulfonate)	Janus Green B	67%	[73]
poly(acrylamide-co-sodium 4-styrenesulfonate)/poly(ethylene glycol) semi IPN	Janus Green B	62%	[71]
poly(acrylamide-co-sodium methacrylate)hydrogels	Janus Green B	90%	[74]
poly(acrylamide-co-sodium methacrylate)/poly(ethylene glycol) semi IPN	Janus Green B	87%	[75]

2.6 Phenol Removal Ability of Polymeric Adsorbent

Synthetic polymeric adsorbents include materials with hydrophobic or hydrophilic nature, such as divinyl benzene-ethyl vinyl benzene copolymers, polystyrene–divinyl benzene copolymers, polymethacrylate polystyrene–divinylbenzene copolymers and vinyl pyridine. Polymeric adsorbents are chemically inert, durable and stable, and possess high adsorption capacity, efficiency, selectivity, with relatively low cost and limited toxicity, and ease of regeneration. Although the effective surface areas are smaller than in the case of ACs

Ion-exchange resins are structure of a polymer matrix, based on polysaccharides, or synthetic resins or inorganic compounds and a functional group. Depending on the negative or positive charge of the ion-active group, the resins act as anion or cation exchangers and each type can be act as strong or weak exchangers. The strong anion exchange resins have quaternary ammonium groups and the weak anion exchangers have tertiary amine substitutes. The strong cation exchangers contain sulfonic acid functional groups, and weak cation exchange resins with carboxylic acid functional groups. Phenols and natural extracts were adsorbed onto strong and weak cation and anion exchange resins [76-78].

Some authors have studied removal of phenol from water utilizing strong-base anion exchanger. It is shown that the removal capacities of adsorbents are higher than other well-known adsorbents. pH dependent equilibrium isotherm was explained according to molecular adsorption and ion exchange processes.

Polymerization techniques to prepare macroporous polymer particles with large specific surface areas have come through three generations. The first-generation technique was prepared by divinylbenzene (DVB) copolymerization in the presence of the inert solvent. The specific surface area of the resulting product was often limited by the purity of DVB and the mechanism of the pore formation induced by phase separation in the process of polymerization [79,80]. The second-generation technique, called hypercrosslinked resin, was first introduced in the 1970s by Davankov et al. [81-83]. The hypercrosslinked resins were obtained by an extensive post-crosslinking of a preformed linear polystyrene or low-crosslinked polystyrene using a bifunctional crosslinking agent and a Friedel-Crafts catalyst [84].

Elution of the adsorbed phenol from polymer has evaluated by treatment with organic solvent such as methanol and acetone that easier than anion exchange resin. Thus, the styrene copolymer has efficiently regenerated. The adsorption capacity for phenol on MIP's (molecularly imprinted polymers) depend on the utilize of functional monomers. Moreover, the pH was affected adsorption capacity of MIPs.

2.7 Atrazine Removal Ability of Polymeric Adsorbent

Atrazine is one of the most difficult herbicides to be removed from water. The harmful effects of atrazine on environment and human health has prohibition of its usage in EU since 2005. However, atrazine is still observed in ground water, due to fact that it has been degradation half-life in soil range from two months to six years and applied for preemergence control in the agriculture.

Its resistance to biological degradation and its physicochemical properties (low soil sorption coefficient and solubility in water). Therefore, this herbicides removal from water is widely studied utilizing various materials [85,86]. It kills weeds in corn and inhibiting photosynthesis. In recent years, the problem of contamination with herbicides has been investigated many research groups [87,88].

Degradation of atrazine by biological, physical and, above all, chemical means, has risen to a prolific literature during the last decades. Many techniques undergoing development and research, those emerging as potentially real applications are very anecdotic [89]. These techniques have been research and developed for the removal of hazardous agricultural chemicals that migrate to the environment, including photocatalytic degradation, biological repair, sorption, etc. Sorption is recognized one of the most applicable technologies for contamination removal [90]. Regarding that adsorption on solid substrates, such as activated carbon, biosorbents or clay, is a widely used method for removing atrazine from waters.

Techniques suitable for concentration are very limited, with adsorption on AC (activated carbon) being widely used industrial sorbent. It is obtain usually have high sorption capacity and a much higher surface area at specific temperature. It is also easily available and low-cost materials. Chemical activation involves precursor in an inert stream which can be catalyst ZnCl_2 , KOH and H_3PO_4 . Many other factors can also affect the adsorption capacity in the same sorption conditions such as surface chemistry (heteroatom content), surface charge and pore structure.

A suitable carbon should possess not only a porous texture, but also high surface area. The good ability and economic promise of the activated carbons prepared from by-products have been recently presented and described. It reported that the adsorption capacities of activated carbons large values of 240-80 l/g (mg of atrazine per g of carbon). However, the adsorption capacities of a carbon depend on the different sources of raw materials, the history of its preparation and treatment conditions such as pyrolysis temperature and activation time [91].

Good removal capability of clay materials to take up herbicide has been demonstrated. Many authors reported that an adsorption capacity of 20.5-40.2 mg atrazine / g clay (bentonite) was achieved. The adsorption isotherms revealed that adsorption equilibrium was reached within 180 min. They showed that this naturally occurring material could substitute for activated carbon as an adsorbent due to its availability and low cost, and its good sorption properties.

It was suggested that bentonite is a good adsorbent for atrazine due to their sorption properties also come from their high surface area and high porosity [92].

Biosorbents are compounds of biological origin, composed of organic wastes, agricultural by-products, or secondary industrial or, such as bacteria, algae, plants, fungi or yeast. These biosorbents, particularly originating from agricultural by-products, such as seed wastes, are particularly interesting because of their ubiquity and low-cost. Vegetal material can be important as containing many binding sites, very heterogeneous, thereby resembling a adsorption chromatography and multichromatographic system with partition (absorption) on various polarity supports. Atrazine is lipophilic materials [Log K_w =2.68]. Indeed vegetal high lipophilic contents (waxes, rubber, oil). Thus, these sorbents are expected to be more efficient for the sorption of atrazine. Among vegetal materials, oilseeds show the highest adsorption of herbicide [93].

Diels-Alder modification of vinyl groups poly (divinyl benzene) with maleic anhydride polymer structure issue leading to selective sorption of atrazine. These mechanism involve carboxylic groups on the polymer surface and the presence of amino groups in herbicide structure the possibility of specific interactions related to hydrogen bond formation [94]. Therefore, the sorption studies using atrazine an adsorbate and preparation of modified poly (divinylbenzene) adsorbent.

Another method is choice of appropriate monomer which containing suitable functional group(s). These polymers have been applied commercially available Chromosorb 104 and Amberlite XAD-7 that have nitrile and ester groups. Typical materials of this groups are permanently porous with large surface area and become available for different affinities and capacities [95, 96].

Amberlite XAD-7, a cross-linked acrylic ester polymer is characterized as a hydrophilic adsorbent having a somewhat more hydrophobic structure comparing to Amberlite XAD-4 (polystyrene-divinylbenzene copolymer) resins. The each of these adsorbents, equilibrium isotherm data are involved, in particular shape and type of the isotherm, their dependence on the conditions of the adsorption (such as the presence of other components in the mixture pH and ionic strength) as well as mass transfer processes [97].

Also, other copolymers with nitrile groups e.g., copolymers of divinyl benzene and acrylonitrile and divinylbenzene and methacrylonitrile have been used to synthesize polymeric sorbent.

It was reported that sorbents a large proportion of strongly polar functional groups and large specific surface area are performed sorption of selected herbicides (atrazine) [98].

2.8 Crosslinked Polymers and Grafted Polymer and Their Properties

Crosslinked and /or grafted polymers are obtained by the modification of polymers. They are attractive materials because of their new or enhanced properties compared to corresponding conventional polymers. These new or enhanced properties arise principally from the introduction of new functionalities and /or interlinkages to the original polymers structures by grafting reactions. Because their chemical and physical properties may be tail wide range of characteristics. They are used a permanent place in various fields such as environmental applications, energy conversion, biomedical and solid state [99-101]. They are available in different forms that as shown in (Figure 2.2).

These polymers can be found in various physical forms including resins, gels, fibers, films, and fabrics that have widely differing chemical and physical properties and can be chemically active. Especially, they are made of modified synthetic polymers such as polyethylene, polystyrene, and polyvinyl fluoride.

Some of the more obtained from modified natural polymer sources including cellulose, chitosan and starch.

Considering the separation function, grafted and/or crosslinked polymers can be classified into various categories including ion exchangers, chelating adsorbents, hydrogels, and affinity polymers, as shown in (Figure 2.3).

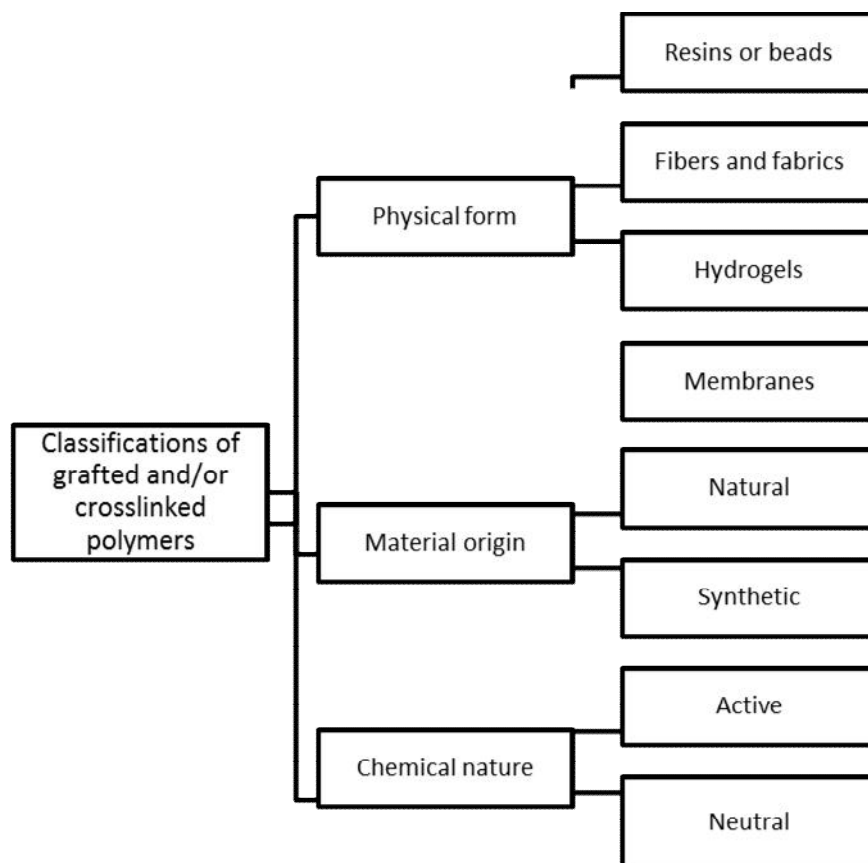


Figure 2.2 : A schematic representation for various classifications of grafted and/or crosslinked polymers [102].

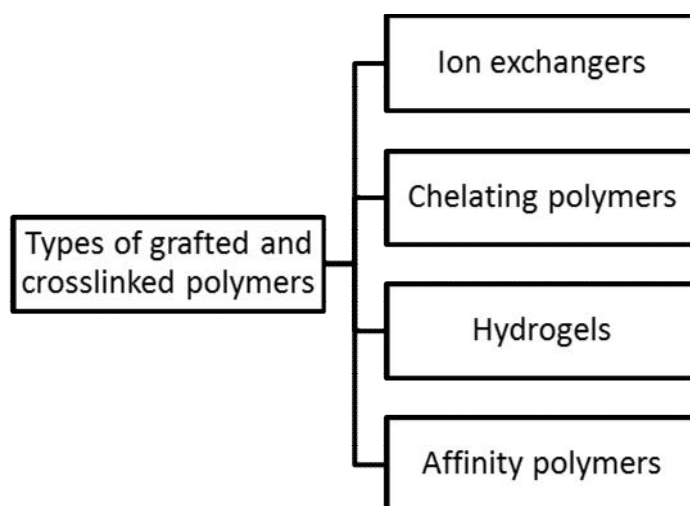


Figure 2.3 : A schematic representation for various types of grafted and/or crosslinked polymers [102].

2.8.1 Ion exchange resin

IER (Ion exchange resin) is network polymer of high molecular weight. They have fixed ionic groups. Ion exchange resins are capable of exchanging anions or cations. The ionic components with two types of resin: anion and cation exchange. Each resin has a maximum capacity of exchanges per unit weight of resins. They are also available in weakly or strongly basic form and weakly or strongly acid form. In addition, ion exchange resins are commercially available two physical form; gel and macroporous resins. The macroporous resins have major advantages permanent pore diameter with uniform distribution, which lead to arising from their high degree of crosslinking and more stability.

Ion exchange resins are applied in various fields including waste water treatments; electronic, gas and oil, electroplating industries and improvement of soil water retention [103,104].

2.8.2 Chelating polymers

Chelating polymers bind metals ions by ionic interactions and/or coordinating interactions. They are characterized by two components; the polymer backbone which provides the functional groups and stability, which the ligands require to metal complexation. Chelating polymers can undergo selective absorption for metal ions by fixing the ligand groups on the polymer structure.

Practically, they are very useful for recovery of soluble metal ions from solutions and selective adsorption of certain metal ions from their mixtures [105]. Chelating polymers have great importance, especially environmental application which lead to availability of different adsorbents, the advantage of high efficiency, easy handling and cost effectiveness [106,107].

They are characterized into two components depending on the origin of their backbone, graft biosorbents and graft adsorbents.

2.8.3 Hydrogels

Hydrogels are hydrophilic three-dimensional network structures that capable of absorbing significant amount of water. They can be divided two classes depending on the nature of their network.

(i) Reversible hydrogels having formed by molecular entanglements and/or hydrophobic forces or H-and ionic bonding, making them free chain ends and lack homogeneity that causes network are defect [108]. (ii) Permanent hydrogels network which using ionizing and UV radiation [109,110].

Hydrogels have entangled network macromolecular structures and various crosslinked including block copolymers, graft copolymers, linear copolymers, bonded complexes or polyions-multivalent ions. The physicochemical properties of hydrogels depend not only on degree of crosslinking and molecular gel structure but also content of water in the hydrogel.

2.8.4 Affinity polymer

Affinity polymers include of porous structures having synthetic molecules such as ion exchange ligands and dye or selective affinity ligands. Preparation of affinity polymers usually involves coupling of affinity ligands to the activated polymers and preparation of the basic polymer. They can be used for specific classes of depending on the chemicals structures of matrices [111].

2.9 Properties of the Crosslinked Polymer

There are a number of considerations in the choice of the functional polymers to be used in a specific application. Functionalized polymer must possess a structure which permits adequate of reagent in the reactive sites. This depends on the extent of

swelling compatibility the effective pore size, pore volume (porosity) and the chemical, thermal and mechanical stability of the resins under the conditions of a particular chemical reaction on reaction sequence. This in turn depends on the degree of the crosslinking of the resin and the conditions employed during its preparation.

We studied crosslinking polymers in this thesis. The use of crosslinked polymers in chemical applications is associated with some advantages, such as the following.

- 1-) Since they are insoluble in our solvents, they offer the ease of processing.
- 2-) They can be prepared in the form of spherical beads and can be separated from low molecular weight contaminants by simple filtration and washing with very useful solvents.
- 3-) Polymer beads with very low degrees of crosslinking swell extensively, exposing their inner reactive groups to the soluble reagents.
- 4-) Crosslinked resins may be prepared with very porous structures which allow solvents and reagents to penetrate inside of the beads to contact reactive groups.

The following is a classification of the types of crosslinked polymers which are most frequently encountered with enhanced properties.

- a) Microporous pore gel-type resins are generally prepared by suspension polymerization using a mixture of vinyl monomer and small amounts (less than 10% ; in most cases less than 0.5% - 2%) of a crosslinking agent.

Swellable polymers are found to offer advantage over non-swellable polymers of particular interest is their lower sensitivity.

- b) Macropores and macroreticular resins

The mechanical requirements in industrial applications force the use of higher crosslinking densities for preparing density with enhanced properties. Macropores and macroreticular resins are prepared by suspension polymerization using higher amounts of crosslinking agents but with the inclusion of an inert solvent as diluents for the monomer phase.

To sudden shock and their potential to achieve a higher leading capacity during functionalization however, a degree in crosslinking density will increase swelling but will also result in soft gels, which generally have low mechanical stability, and readily in fragment even under careful handling. Gels with lower density of

crosslinking are difficult to filter and under severe conditions can degrade to produce soluble linear fragments in addition gel type resins that are likely crosslinked may suffer considerable mechanical damage as a result of rapid and extreme change in the nature of the solvating media and cannot be subjected to study and high pressures. Macro pores resins with less than 1% crosslinking generally have low mechanical stability while macro pores resins with more than 8% crosslinking are mechanically stable but unfortunately give rise to acute.

2.9.1 Grafting techniques

Today, there is great interest to the polymers having nonlinear architecture with different composition and topology such as star, micro arm star, graft, hyper branched, dendrimer, and cyclic structures [112].

An important category of three-dimensional macromolecular architectures with many examples detailing their single molecule visualization is consisted by brush and block graft copolymers and thanks to their unique properties, these graft polymers take great attention [113,114].

Block graft copolymers might be classified through one of three general synthetic methods: “grafting from”, “grafting through,” and “grafting onto” (Figure 2.4).

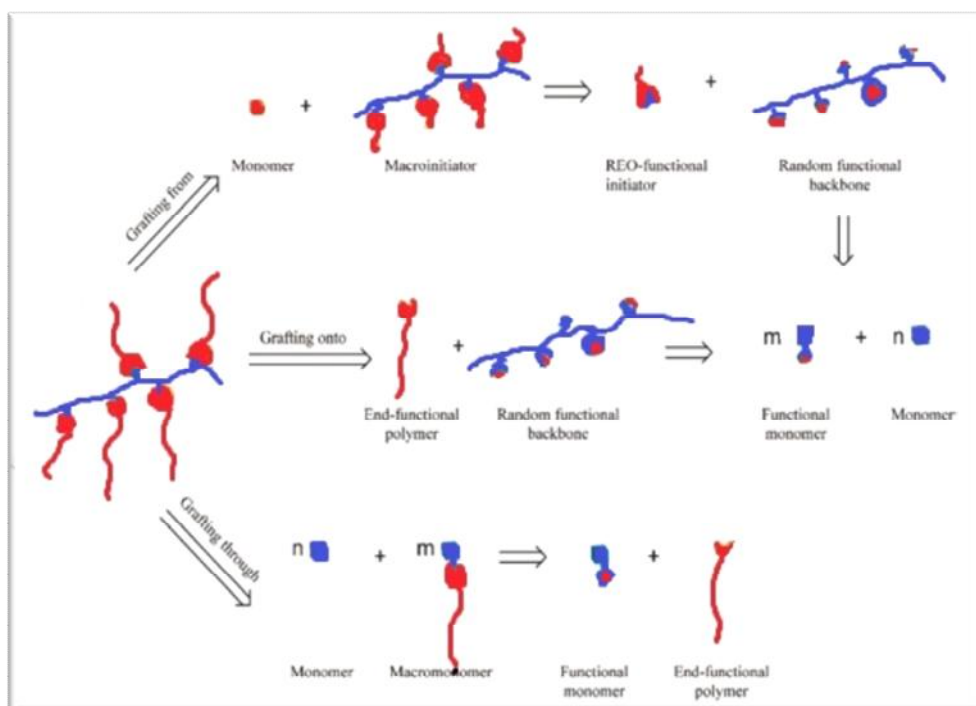


Figure 2.4 : Grafting techniques [115].

2.9.1.1 Grafting from strategy

In “grafting from” strategy, there is a backbone which has active sites and they initiate the polymerization. Therefore, graft copolymer can occur due to these initiating sites. This approach has been used widely to obtain brush or comb-like copolymers. A number of graft copolymers can be synthesized using only a single grafting from method [116].

2.9.1.2 Grafting through strategy

The “grafting from” method comprises preformed macro monomers that will be polymerized to produce graft polymer. Due to the macro monomers which are polymeric or oligomeric chains with a polymerizable end group, the backbone is formed in situ. This method has been utilized to synthesize graft copolymers using a variety of controlled polymerization techniques.

Owing to requirement of specific polymerizable chain end functionality and the steric effects that can effective polymerization of high molecular weight or bulky macro monomers the grafting through technique is complicated.

2.9.1.3 Grafting onto strategy

The grafting density of polymeric brushes made using the “grafting onto” technique is typically low due to the steric closeness that happens when trying to couple polymer chains onto a backbone. One strategy used to increase the grafting density is the employment of highly efficient organic chemistries that will enhance the range of reaction between the polymeric grafts and the backbone.

2.10 Suspension Polymerization

Suspension polymerization is a popular method that combines positive effects both bulk and solution polymerization techniques. Water is commonly used as suspension medium for all water insoluble monomers. Mostly polystyrene, poly (methylmethacrylate), poly (vinylchloride) and poly (vinylacetate) are obtained via suspension polymerization [117].

In suspension polymerization some additives (stabilizers) are needed, enabling the dispersion of monomer droplets and preventing coagulation [118]. Water soluble

polymers at low concentrations such as carboxymethyl cellulose or methyl cellulose, poly(vinyl alcohol), gelatin are used as stabilizers.

By forming a thin layer on the monomer-polymer droplets, they stabilize the polymerization and increase the medium viscosity. Bentonite, kaolin, magnesium silicate, and aluminium hydroxide are common water insoluble inorganic compounds that are used to avoid agglomeration of the monomer droplets. Monomer soluble initiators such as organic peroxides, hydroperoxides or azo compounds are preferred instead of oil-soluble initiators.

As it is showed in Figure 2.5, the reaction occurs in the monomer droplets in which the initiator is dissolved. Each monomer droplets act as miniature bulk polymerization system. The products are obtained as “pearls” that are handy for further processes such as functionalization. The size of the droplets varies from 0.1-5 μm in diameter. Final product may contain trace amount of initiator and stabilizers. Efficient drying and elimination of dispersing additives are crucial [118].

As compared to bulk polymerization, heat and viscosity control is easier in the suspension polymerization because the water absorbs heat and provides good control of temperature [117].

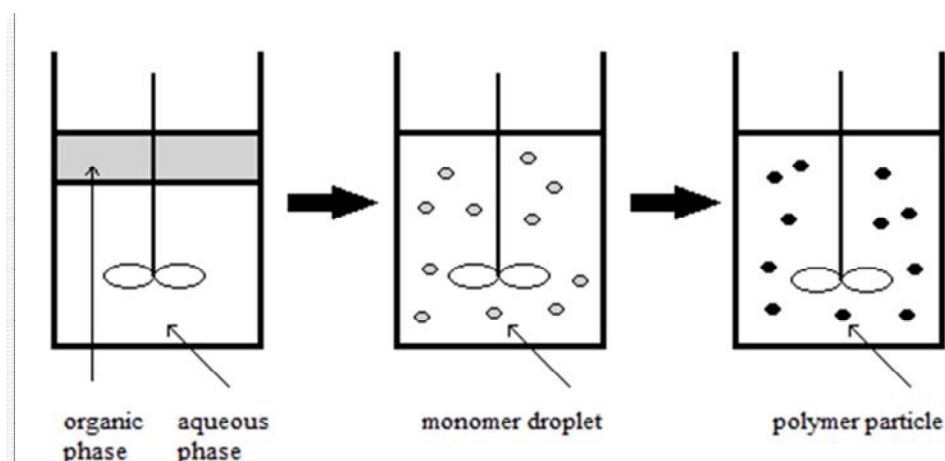


Figure 2.5 : Suspension polymerization.

2.11 Emulsion Polymerization

In general, an emulsion polymerization system would consist of the following ingredients: monomer(s), dispersing medium, emulsifying agent, water-soluble initiator, and, possibly, a transfer agent. Water is used as the dispersing medium and

acts as a heat transfer medium. Monomers such as styrene, acrylates, methacrylates, vinyl chloride, and butadiene show only a slight solubility in water and are able to polymerize via emulsion polymerization [117].

The initiator is water soluble and the monomer molecules diffuse into the hydrophobic interior of the micelles while water is attracted to the hydrophilic exterior zone. Thus, the micelles serve as the core of growing polymer particles.

Emulsion polymerization provides improved thermal control, results in a higher rate of production. This method is preferred to obtain higher molecular weights and a narrow molecular weight distribution [118].

The product of an emulsion polymerization, referred to as latex, can be used directly without further separations.

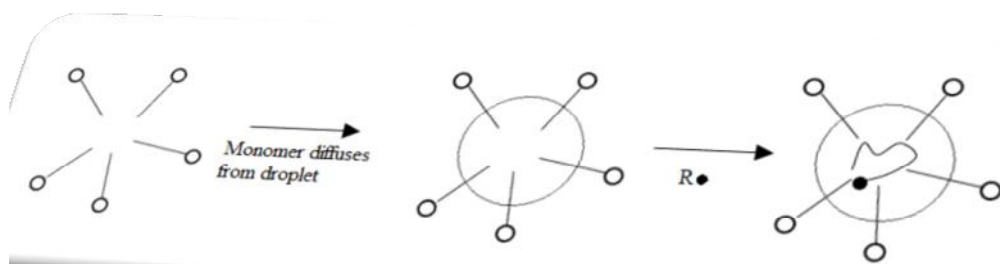


Figure 2.6 : Scheme of emulsion polymerization.

2.12 Controlled-Living Radical Polymerization

We can refrain from chain termination step with two ways in controlled-living radical polymerization. These are increasing rate of initiation with respect to the rate of propagation or getting rid of chain termination and transfer reactions. Every chain length is approximately same and polymer chains grow at a more constant rate. These conditions can provide many types of reactions, e.g., atom transfer, nitroxide mediated.

Characteristics:

- Unless all monomers have consumed, there action continues. Polymerization resumes by adding monomer.
- Instead of $R_i \ll R_p$ in where conventional free-radical polymerization, in living polymerization $R_i > R_p$ (R_i and R_p are the rate of initiation and propagation).

- Between a propagating radical and dormant species dynamic equilibrium occurs.
- Opportunity of mono and/or narrow dispersities of the products.
- Molar mass of the grafted/crosslinked polymer molecules can be predicted.
- Usage of accurate terminating reagents can allow to synthesize telechelic polymers.

2.12.1 Atom transfer radical polymerization (ATRP)

Atom Transfer Radical Polymerization (ATRP) is a type of controlled radical polymerization (CRP) technique which is the most powerful and versatile method [119–122]. M_w , M_{wd} , and functionality can be controlled accurately [123] and it can be carried out in a range of different solvents and conditions even in water at room temperature. We can synthesize products including functional groups by ATRP. The reaction conditions and parameters can be adjusted providing reaction kinetics. Polymers can be grown from surfaces, proteins, organic materials, and inorganic materials including nanoparticles, additively homogeneous and heterogeneous solution polymerization [124]. We can synthesize hydrogels with it in imaging, diagnostics and biosensors.

In 1995, ATRP was first announced in primary publications [120-124]. In many fields of polymer science, it has powerfully affected, inspiring quite interest in living polymerizations. The basic characteristic of ATRP [121–127] is the equilibrium between a low concentration of active propagating species and a larger number of dormant chains, via an inner sphere electron transfer process encouraged by a transition metal complex (Figure 2.7) [128,129].

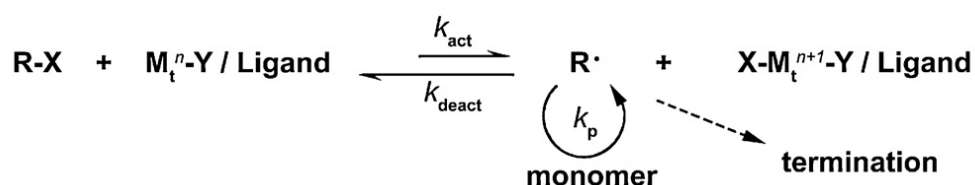


Figure 2.7 : The mechanism of transition metal-catalyzed ATRP [128, 129].

In conventional free radical polymerization, due to k_p and k_t , produced radicals propagate and terminate but in ATRP, reversible redox process catalyzed by a transition metal complex ($M_t^n\text{-Y / Ligand}$, where Y may be another ligand or the counter ion) generates radicals that undergoes an one electron oxidation with

consequent abstraction of a (pseudo) halogen atom, X, from a dormant species, RX. This procedure occurs with rate constants of activation k_{act} , and deactivation k_{deact} . Polymer chains grow with the rate constant of propagation k_p , with adding radicals to monomers.

By radical coupling and disproportionation, termination happens and very small percentage of polymer chains go through termination in a well-controlled ATRP process, because concentration of active propagating radicals is low and dormant species' concentration is high.

Despite the fact that copper is most usually used metal catalyst in ATRP, iron compounds like iron also can be used [130-133].

The polymerization begins alkyl halide and the transition metal in its lower oxidation state in normal ATRP. Moreover, reaction can be started with conventional radical initiator like AIBN, and the transition metal in its higher oxidation state. This reaction is named reverse ATRP [134] which radicals occurs from the (thermal) dissociation of the initiator are reversibly terminated by transition metal. Therefore, it ends up an alkyl halide and the reduced transition metal (Figure 2.8).

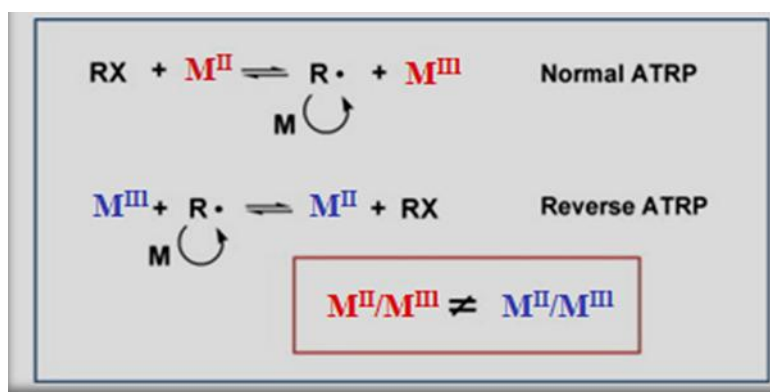


Figure 2.8 : Mechanism of normal ATRP and reverse ATRP (M: Cu, Fe, Ni etc.).

2.12.2 Controlled radical polymerization (CRP)

All CRP systems have a dynamic equilibrium between propagating radicals and various dormant species [135]. There are two types of equilibria. Radicals may be reversibly trapped in a deactivation/activation process, according to Scheme 2.1 or they can be involved in a degenerative exchange process (Figure 2.10).

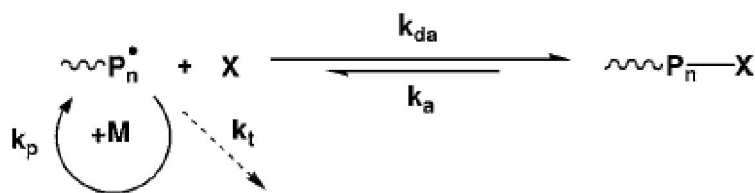


Figure 2.9 : Controlled polymerization via deactivation/activation process.

2.12.3 Degenerative transfer (DT) processes

Conventional free radical initiators are used in DT processes, and control is by the presence of Transfer agents- TAs- (RX) which exchange a group/atom X between all growing chains.

This thermodynamically neutral (degenerative) transfer reaction should be fast in comparison to propagation ($k_{exch} > k_p$). At any instant, the concentration of dormant species $\text{P}_n\text{-X}$ is much larger than that of the active species P_n^* . Degrees of polymerization are defined by the ratio of concentrations of consumed monomer to the sum of concentrations of the consumed TA and the decomposed initiator.

2.12.4 Reversible addition-fragmentation transfer (RAFT)

RAFT polymerization is among the most successful DT processes [136]. While addition-fragmentation chemistry was originally applied to the polymerization of unsaturated methacrylate esters (prepared by catalytic chain transfer) [137]. RAFT employs various dithioesters, dithiocarbamates, trithiocarbonates, and xanthates as TAs leading to polymers with low polydispersities and various controlled architectures for a broad range of monomers [138].

The polymer chains successively pass from a dormant state to an active state during which they can add monomer units. In contrast to a conventional free radical polymerization, chains grow in parallel during the whole polymerization duration (Figure 2.10) [139].

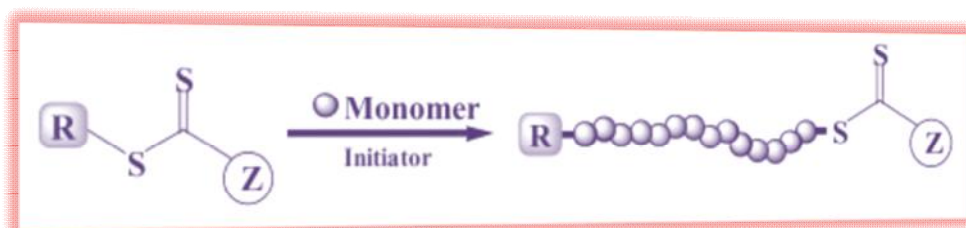


Figure 2.10 : Schematic of the RAFT polymerization [139].

3. EXPERIMENTAL PART

3.1 Materials and Methods

All chemicals used were analytical grade: Vinyl benzyl chloride (Aldrich), Ethylene glycole dimethacrylate (EGDMA) (Aldrich), Ethyl piperazine (Aldrich), Imidazole (Aldrich), 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) (Aldrich), Chloro acetic acid (Aldrich), Chloro acetamide (Aldrich), Calcon (Aldrich), Malachite green chloride (Aldrich), Reactive red 120 (Aldrich), Phenol (Aldrich), Vinyl imidazole (Aldrich), N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA) (Fluka), CuBr (Aldrich), CuBr₂ (Aldrich), CuCl (Aldrich), CuCl₂ (Aldrich). All chemicals were analytical grade and were used without further purification.

3.2 Instruments

FT-IR (Nicolet), scanning electron microscopy (FE-SEM) (FEI Quanta 250 FEG) and UV-Vis spectrophotometer (Perkin Elmer lamda 25).

3.3 Preparation of the Polymeric Sorbents

In this thesis, crosslinked polystyrene based sorbents were prepared to remove dyes, phenol and atrazine as organic wastes from water.

3.4 Preparation of the Sorbents for Dye Removal

For this purpose, quaternary chloroacetic acid containing ethyl piperazine and imidazole modified poly (styrene) based sorbents and poly (vinyl imidazole) grafted onto PVBC were prepared and characterized accordingly.

3.4.1 Preparation of polyvinyl benzyl chloride (PVBC) resin

Crosslinked PVBC microspheres were prepared by suspension polymerization according to the literature [32]. The details are as follows:

VBC (5.0 mL, 31.9 mmol), EGDMA (1.5 mL, 7.8 mmol), and AIBN (0.12 g, 0.71 mmol) were dissolved in toluene (7.2 mL). The resulting solution was dispersed in an aqueous medium, prepared by dissolution of PVA (0.25 g) in water (80 mL). The polymerization was carried out in a magnetically stirred glass flask (100 mL) at 78 °C for 8 h. After polymerization, the PVBC microspheres were washed exhaustively with ethanol, and then with water, to remove the diluent and unreacted monomer. They were subsequently dried in vacuum at 50 °C. The microspheres were sieved and a proper size fraction (200-500 µm diameter) was isolated.

3.4.2 Modification of PVBC with ethyl piperazine (EP-PS)

PVBC resin (5 g.) was added portion wise to a stirred of ethyl piperazine 15 mL in 2-methyl pyrrolidone (NMP) 30 mL at 0 °C. The mixture was shaken with a continuous shaker for at room temperature. The reaction content was poured into water (1L), filtered and washed with excess water and methanol respectively. The EP-PS resin dried under vacuum at room temperature for 24 h. The yield was 8.4 g.

3.4.2.1 Determination of amine content of the (EP-PS) modified resin

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 H₂SO₄ (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 4 mL 1 M HCl for the neutralization of the evolved ammonia.

3.4.2.2 Quaternization of cross-linked ethyl piperazine modified polystyrene based resin (QEP-PS)

Quaternization of polymer beads was carried out by reacting the potassium salt of monochloro acetic acid solution, while 18.9 g (0.2 mol) chloroacetic acid was dissolved in 20 mL H₂O. Then 13.8 g (0.1 mol) K₂CO₃ in 25 ml of distilled water was added drop wise to the ice cooled solution of the chloroacetic acid while stirring. 10 g of the EP-PS containing resin sample was placed in this solution and the mixture was shaken by means of a continuous shaker for 48 h at room temperature. The mixture was heated to 70 °C for 3 h, filtered and washed with water. The product was filtered washed with excess of water and acetone, respectively. The vacuum-dried sample weighed 14.0 g.

3.4.2.3 Estimation of the carboxyl content of the (QEP-PS)

0.1g of the quaternized resin was added to 40 ml of 0.1 M NaOH solution and left to stand over- night. The mixture was filtered. The filtrate was titrated with 0.05 M HCl solution.

3.5 Modification of PVBC with Imidazole

PVBC resin (5.00 g) was added portion wise to a stirred of 2.50 g of imidazole and 6.0 mL of triethylamine as acid capture in 30 mL of 2-methyl-1- pyrrolidone (NMP) at 0 °C. The mixture was shaken with a continuous shaker for at room temperature. The reaction content was poured into water (1 L), filtered and washed with excess water and methanol respectively. The resin1 was dried under vacuum at room temperature for 24 h. The yield was 5.80 g. A total amine content of the polymer was found to be about 2.35 mmol per g of the resin.

3.5.1 Quaternization of the imidazole containg PVBC resin with chloroacetic acid

Quaternization of the resin was performed as described above.

3.6 Poly (vinyl imidazole) (PVI) Grafted onto the PVBC Resin

Graft polymerization of vinyl imidazole was achieved through 2-chloroethyl functional group initiation sites on the crosslinked bead polymer.

A typical procedure is as follows:

0.144 g, (0.01 mol) CuBr, 0.0672 g (0.30 mmol) CuBr₂, 0.62 mL (4.31 mmol) of the PMDETA ligand and 10 mL (0.11 mol) vinyl imidazole in an under nitrogen were successively put in a three necked flask equipped with a reflux condenser and a nitrogen inlet. Crosslinked PVBC resin sample (2 g) was added to the flask and the mixture was heated to 130 °C for 72 h. At the end of the reaction period, the reaction content was poured into 100 mL of distilled water. The mixture was filtered and interacted with 5 % of EDTA solution to remove copper salts. Then, PVI grafted resin (resin 2) was filtered and washed with excess of water (300 mL) and alcohol (20 mL). The resin 2 was dried under vacuum for 24 h at room temperature. Dried sample weighed 3.186 g.

The grafting percentage was determined from the mass of dried beads before and after grafting as follows:

$$\text{Percentage grafting} = [(W_2 - W_1)/W_1] \times 100 \quad (3.1)$$

where W_1 and W_2 are the masses of the PVBC beads and PVI grafted beads, respectively.

3.6.1 Determination of amine of the PVI grafted resin

Amine content of the resin 2 was determined procedure described above. The amine content of the resin was found as 4.50 mmol per g of the resin.

3.7 Extraction of Dyes

The adsorption of reactive dyes on the resins was investigated in a batch system. In these experiments, Calcon, Remazol Black B and Reactive red were used as acidic dyes and also malachite green and methylene blue as basic dyes. Capacities of the resins were determined by mixing weighed amount of polymer sample (0.2 g) with 10 mL of different dye solutions of different initial concentrations (1.00 g dye /50 mL water -0.555 g /50 mL).

The mixtures were stirred at room temperature for 24 h and after centrifugation; the amounts of un-adsorbed dyes in supernatant solutions were analyzed for dye concentration using a double-beam UV-vis spectrophotometer. Also, pH depending on the resin experiments was conducted.

3.7.1 Kinetics of the dye sorption

Batch kinetic experiments were performed using highly diluted dye solutions (0.02 mg dye/mL water) to estimate the efficiency of the resin for trace dye. For this purpose, resin (0.1 g) was wetted with distilled water (1.5 ml) and added to a solution of dye (90 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 dye contents by the method as described above.

3.8 Regeneration of the Sorbents

Desorption experiment was conducted with dye loaded resins, in which resins were treated with dyes for around 24 h. Before subjecting to the desorption experiment, the dye loaded resin was separated from the solution by centrifuge, washed with distilled water several times, and finally dried under a vacuum. Then, the acidic dye loaded sample (0.2 g) was mixed with 50 mL 10% KOH in methanol solution and was refluxed for 6 h.

Then, the solution was cooled and the resin was separated by centrifuge, and the dye containing solution was diluted with water properly and neutralized with HCl solution. The concentrations of the dyes were determined by UV–vis spectroscopy at their respective absorbance maxima.

To determine the reusability of resin 2 consecutive adsorption–desorption cycles were repeated 5 times using the same adsorbent.

Desorption of the 0.1 g of basic dye loaded resin was interacted with 20 mL 5 M H₂SO₄ solution for 24 h at room temperature.

3.9 Preparation of the Quaternized Tertiary Amine containing sorbents for Phenol Removal

Imidazole, ethyl piperazin and N,N-dimethyl ethylene diamine modified resins were modified with PVBC resin.

3.9.1 Quaternization of the imidazole modified PVBC with chloroacetamide

Imidazole modified resin (5.0 g) was interacted with 3.5 g chloro acetamide in 25 mL of DMF solution while stirring. The reaction mixture was shaken by means of a continuous shaker for 24 h at room temperature. The mixture was heated to 70 °C for 8 h, filtered and washed with DMF, water and ethanol respectively. The product was filtered and dried under vacuum for 24 h at room temperature. sample weighed 7.20 g.

3.9.2 Preparation of the chloroacetamide quaternized ethyl piperazine containing resin

Quaternization reaction of the (EP-PS) modified resin with chloroacetamide was performed according to given procedure above.

3.9.3 Modification of PVBC with N,N-dimethylethylenediamine (PVBC-DMEA)

PVBC resin (2 g) was added portion wise to (20 mL) in 1-methyl-2-pyrrolidone (NMP) (10 mL) at 0°C. Then, N,N-dimethylethylenediamine (7.20 mL) was added drop wise the mixture was shaken continuously for 48 h at room temperature. The reaction content was filtered and washed with excess water and methanol and then dried under vacuum at room temperature for 24 h. The yield was 3.66 g.

3.9.4 Reaction of (PVBC-DMEA) with chloroacetamide (PVBC-DMEA-CAM)

N,N-dimethylethylenediamine modified resin (2.0 g) was interacted with 2g chloroacetamide in 20 mL of DMF solution while stirring. The reaction mixture was shaken by means of a continuous shaker for 24 h at room temperature.

The mixture was heated to 65 °C for 24 h, filtered and washed with DMF, water and ethanol respectively. The quaternized resin was filtered and dried under vacuum for 24 h at room temperature. Sample weighed 3.72 g.

3.9.5 Determination of chlorine content of the resin

The amine content of the resin was determined with chlorine content determination by using spectroscopic method: the polymer sample (0.1 g) was put into 10 mL NaOH (10%) and stirred for 8 h. The mixture was diluted and neutralized by using 9 M HNO₃ cautiously to 50 mL by water and filtered. The filtrate was used for the chlorine determination by using colorimetric method described in the literature [63].

3.10 Extraction of Phenol from Water

The adsorption experiments were performed at 25 °C, using 0.10 g resin added 10 mL solution of phenol with different initial concentrations of 0.25–1.00 g/100 mL 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. Also, pH depending sorption experiments were investigated.

3.10.1 Kinetics of the phenol sorption

Batch kinetic experiments were performed using highly diluted phenol solutions (0.03 mg phenol /mL water) to estimate the efficiency of the resin for trace phenol. For this purpose, resin (0.1 g) was wetted with distilled water (1.5 mL) and added to a solution of phenol (90 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 by the method as described above.

3.11 Poly (2-acrylamido-2-methylpropane sulfonic acid) (AMPS) Grafted onto Crosslinked Poly (vinylbenzyl chloride) Resin for Removal of Atrazine from Water

Graft polymerization of vinyl imidazole was achieved through 2-chloroethyl functional group initiation sites on the crosslinked bead polymer.

A typical procedure is as follows:

0.068 g, (0.01 mmol) CuCl, 0.0670 g CuCl₂, 2.30 mL, (1.88 mmol) of the PMDETA ligand and 10 g (0.094 mol) AMPS in an under nitrogen were successively put in a three necked flask equipped with a reflux condenser and a nitrogen inlet. Polymer sample (2 g) was added to the flask and the mixture was heated to 60 °C for 90 h. At the end of the reaction period, the reaction content was poured into 20 mL acetic acid solution to obtain colorless product. The mixture was filtered and washed with excess of water (300 mL) and alcohol (20 mL).

$$\text{Percentage grafting} = [(W_2 - W_1)/W_1] \times 100 \quad (3.1)$$

3.11.1 Extraction of atrazine

Atrazine was dissolved in water-ethanol (10% volume) mixture. Extraction experiments were carried out simply by contacting wetted polymer samples (0.2 g) with aqueous atrazine solutions at room temperature.

Capacities were assigned by spectroscopic analysis of residual atrazine contents by using UV-Vis spectrophotometer at 223 nm. Atrazine sorption capacities were found as 57.21 mg atrazine per gram resin.

More importantly, this material is able to remove the atrazine completely even from highly diluted solutions. No trace absorbance was detected after processing.

3.11.2 Kinetics of the atrazine sorption

In order to estimate the efficiency of the resin for atrazine, batch kinetic experiments were performed using highly diluted atrazine solutions (0.2 mg atrazine / 500 mL ethanol-water mixture). For this purpose, polymer (0.2 g.) was wetted with distilled water (1.5 mL) and added to a solution of atrazine (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 atrazine contents by the method as described above.

4. RESULTS AND DISCUSSION

In this study, the new polymeric sorbents were prepared and characterized to remove organic wastes from water solution. Acidic, basic dyes, phenol and atrazine were used as organic pollutants.

4.1 Preparation of the New Polymeric Sorbents for Removal of Dyes

In this study, tertiary amine and quaternary amine containing polymeric sorbents were synthesized for removal of dyes.

4.1.1 Preparation of the quaternary carboxylic acid containing piperazine based resin

This resin was synthesized starting from crosslinked vinyl benzyl chloride and EGDMA (10%). The crosslinked co-polymer was reacted with ethyl piperazine to obtain piperazine containing resin (EP-PS). The amine content of the EP-PS resin was found as 4.1 mmol/g as the total nitrogen content by using Kjeldahl analysis method. Quaternization of the EP-PS resin was performed with chloroacetic acid.

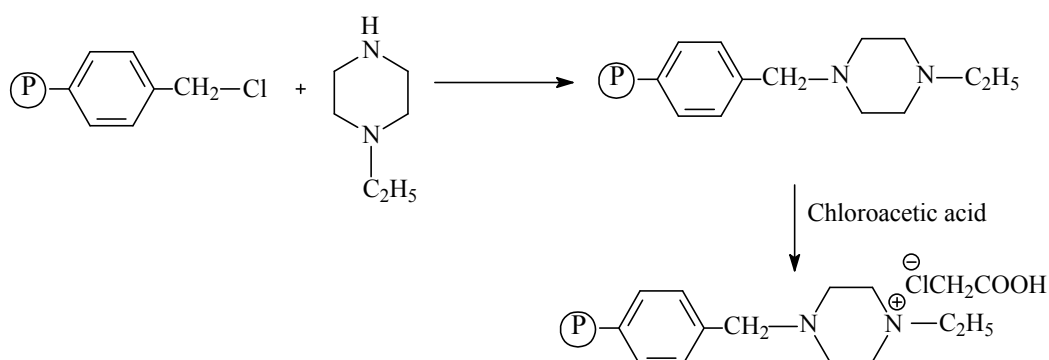


Figure 4.1 : Preparation of the EP-PS resin.

At the end of reaction carboxylic acid content of the sorbent was found as 2.34 mmol g^{-1} resin.

The resin was characterized using FT-IR spectra. According to the Fig 1.a, PVBC-co-EGDMA resin showed a sharp band 1720 cm^{-1} corresponding to the ester

carbonyl group of the crosslinking agent. Also, resin showed characteristic C-Cl stretching at about 669 cm^{-1} .

Also symmetric stretching of methylene was found at 2815 cm^{-1} and the bands at $2900\text{--}2831\text{ cm}^{-1}$ and 1159 cm^{-1} belong to the methyl symmetric stretching and C-N symmetric stretching vibrations in the piperazine ring respectively. In the carboxylic acid modified sorbent, C=O stretching vibration bands are observed at about 3364 cm^{-1} and 1615 cm^{-1} (Figure 4.2.).

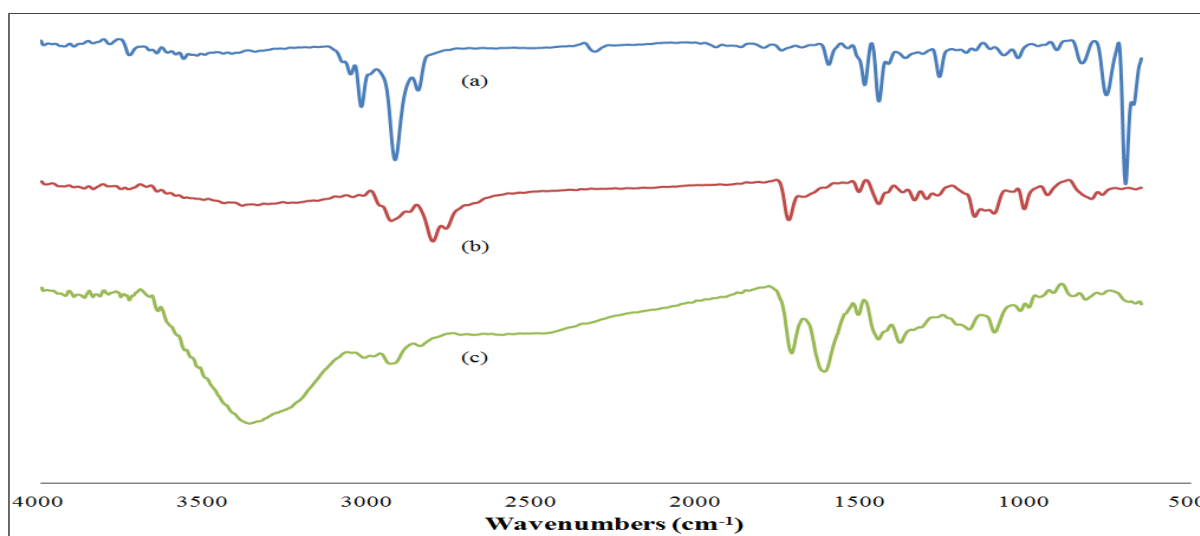


Figure 4.2 : (a) PVBC resin (b) Ethyl piperazine modified PVBC (EP-PS) (c) Quaternary amine containing resin (QEP-PS).

4.1.2 Preparation of the PVI grafted resin and imidazole modified (IP-PVBC) onto PVBC

In this study, crosslinked with $200\text{--}400\text{ m}\mu$ in size of poly (PVBC-co-EGDMA) beads were used. The (IP-PVBC) resin was synthesized starting from reaction with crosslinked PVBC resin and imidazole (Figure 4.3).

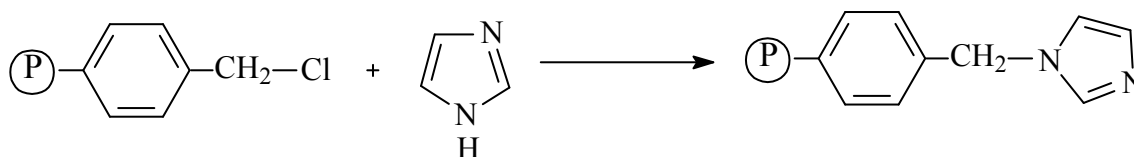


Figure 4.3 : Preparation of the IP-PVBC resin.

The amine content of the IP-PVBC was found as 2.35 mmol/g as the total nitrogen content by using titrimetric method.

Core-shell type of polymer with polyvinyl imidazole shells were obtained by reverse ATRP method. Graft polymerization of vinyl imidazole was obtained from 2-chloroethyl groups on PVBC beads (Figure 4.4).

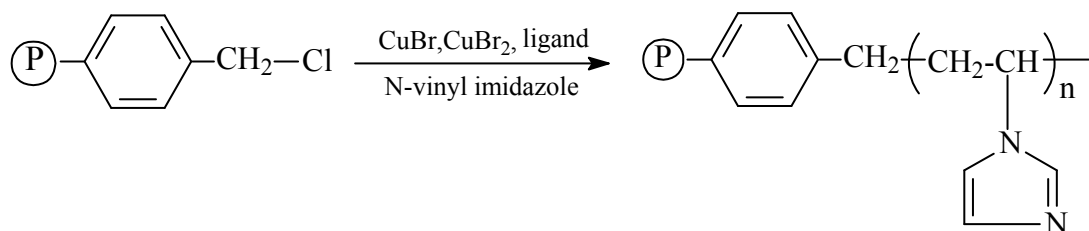


Figure 4.4 : Preparation of the PVI grafted resin.

Although polymerization is heterogeneous in nature, it proceeds with progressive mass increase at 130 °C. The grafting degree reaches to about 59.3% for 72 h. The resins were characterized using FT-IR spectra.

The resins were characterized using FT-IR spectra. According to the Fig 4.5(a), PVBC resin showed a characteristic C-Cl stretching at about 698 cm⁻¹. According to the FT-IR spectrum, C=N stretching mode of ring including conjugated C=C occur at 1651 cm⁻¹, C-C and C=N (ring) stretching modes at 1508 cm⁻¹ and 1159 cm⁻¹ belong to the C-N (ring) stretching vibrations in the imidazole ring respectively (Fig1.b). In the resin 2, asymmetric stretching of methyl and methylene groups observed at 2988 and 2918 cm⁻¹, respectively. Symmetric stretching of methylene was found at 2835 cm⁻¹ and the bands at 2900–2810 cm⁻¹ and 1422 cm⁻¹ belong to the methyl symmetric stretching and C-N symmetric stretching vibrations in the imidazole ring respectively. Also, C=N stretching mode of ring including conjugated C=C occur at 1646 cm⁻¹ (Figure 4.5).

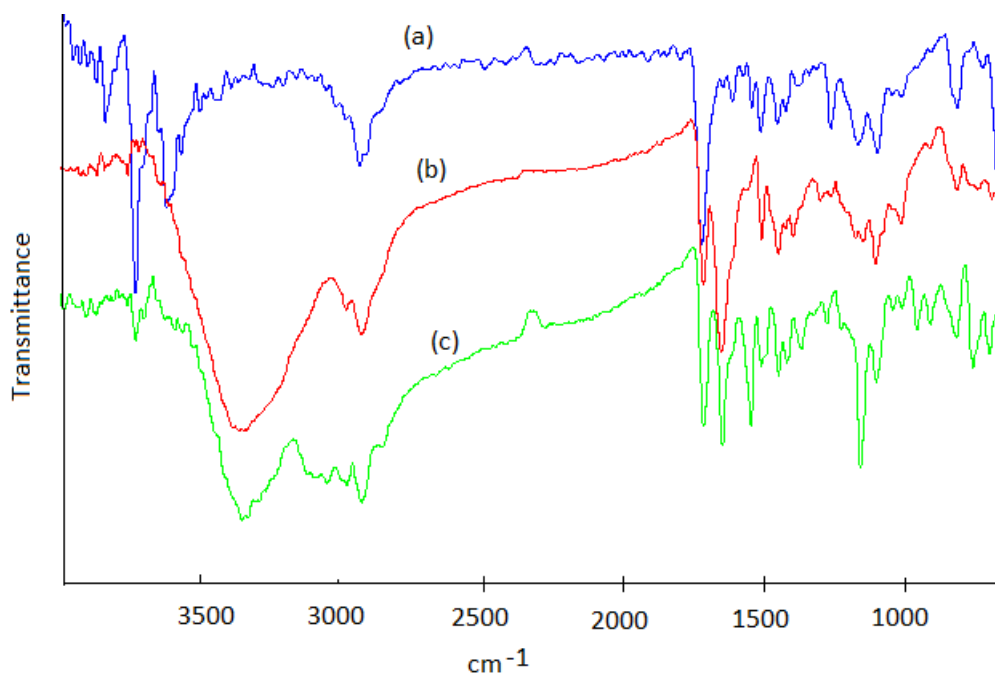


Figure 4.5 : FT-IR spectra of the (a) PVBC resin; (b) IP-PVBC ; (c) PVI grafted.

Morphological characterizations of the resins were investigated by SEM. After grafting with PVI, the pores of the PVBC beads seem to be filled with grafted polymer and the surface of the polymer.

(GMA)-grafted beads are smoother than that of the plain beads Figure 4.6. It can also be seen in the SEM images that the shapes of the grafted beads (Figure 4.6) cracked, because of heating and stirring during polymerization.

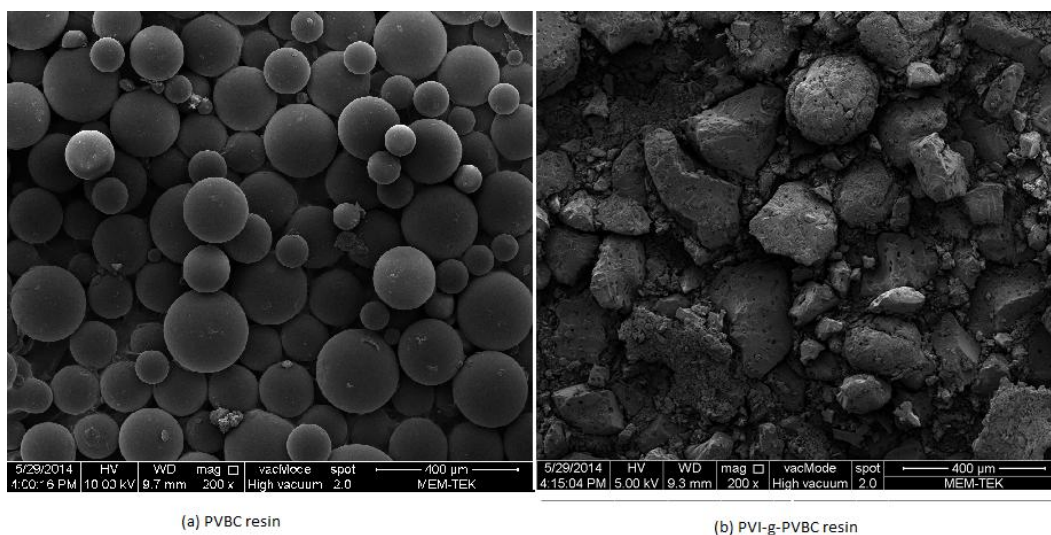


Figure 4.6 : SEM image of the (a) PVBC resin (b) PVI-g-PVBC resin (Resin 2).

4.1.3 Extraction of dyes

Dye extraction experiments were carried out simply by contacting wetted resin samples with aqueous dye solutions at room temperature.

Capacities were assigned by colorimetric analysis of residual dye contents. Dye sorption capacities of the quaternary resins (QEP-PS and QI-PS) depending of the dye concentration were given in Table 4.1 and 4.2.

Table 4.1 : Dye sorption capacity of the quaternary resins (QEP-PS and QI-PS).

Dye	Dye Concentration (g dye/ 100mL)	Capacities (g dye / g resin)	
		QEP-PS	QI-PS
<i>Reactive Red</i>	0.250	0.340	0.370
	0.500	0.350	0.380
	0.750	0.380	0.400
	1.000	0.390	0.410
<i>Malachite green</i>	0.250	0.350	0.360
	0.500	0.370	0.380
	0.750	0.390	0.390
	1.000	0.410	0.400

According to the Table 4.1, acidic and basic dyes sorption capacities of the resins were found as 0.34g dye / g resin-0.41 g dye / g resin and. Acidic and basic dyes can be removed successfully because the resin has both acidic and basic groups.

The poly (vinyl) imidazole grafted resin in water shows reasonably high dye sorptions, as high as 0.77 g per gram resin for dye. On the other hand, dye sorption capacity of the resin 1 was found as 0.67 g dye /g resin.

Dye sorption capacity of the resin 2 is higher than the resin 1. According to as can be seen from the table that dye sorption (Table 4.2). The sorption capacity of the flexibility of the side chains in the resin 2 is expected to provide pseudo homogeneous reaction conditions and easy accessibility of the functional groups involved. It is expected that the adsorbents have the advantage of mobility of the graft chains in the removal of dyes from aqueous mixtures.

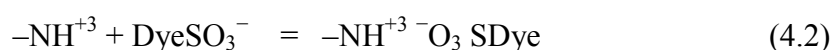
Table 4.2 : Sorption capacities of the imidazole based resins.

Dyes	Capacity (g dye/g resin)		$\lambda_{\max}$ (nm)
	PVI resin (Resin1)	PVI-g-PVBC resin (Resin 2)	
Calcon	0.67	0.77	552
Remazol Black	0.40	0.82	597
Reactive Red	0.25	0.55	591

In aqueous solutions, the synthetic reactive dye was dissolved and the sulfonate group of the reactive dye was dissociated and converted to anionic dye ions [22]:



The adsorption process then proceeded due to the electrostatic interaction between these two counter ions:



There are no big differences depending on pH (Table 4.3). This property is important in utilization of the resin in industrial applications.

Table 4.3 : Maximum dye sorption capacities of the resins depending on pH.

Dyes	pH	Capacities (g dye / g resin)	
		QEP-PS	QI-PS
Reactive red	2	0.25	0.31
	4	0.30	0.33
	6	0.33	0.29
	8	0.35	0.30
Malachite green	2		-
	4	0.30	0.32
	6	0.40	0.38
	8	0.45	0.42

The sorption capacity of the resin does not change very much in lower pH. The explanation for this is that under acidic conditions hydrogen atoms (H^+) in the solution could protonate the amine group and thus cause an increase in pH [37,38].

The interaction between sorbate and sorbent is affected by the pH of an aqueous medium in two ways : firstly, since dyes are complex aromatic organic compounds having different functional groups and unsaturated bonds, they have different ionization potentials at different pH, resulting in the pH dependant net charge on dye molecules. Secondly, the surface of the resin includes many functional groups, so the net charge on sorbent, is also pH dependant.

Therefore the interaction between dye molecules and sorbent resin are basically a combined result of charges on dye molecules and the surface of sorbent.

The PVI grafted PVBC resin can be used in lower pH values and a wide pH range (Table 4.4). The explanation for this is that under acidic conditions hydrogen atoms (H^+) in the solution could protonate the amine group and thus cause an increase in pH [42,44].

Table 4.4 : Maximum dye sorption capacities of the PVI grafted PVBC resin depending on pH.

Dye	pH	Capacity
		(g dye / g resin)
Reactive Red	2.0	0.42
	4.0	0.46
	6.0	0.55
	8.0	0.40
Remazol Black	2.0	0.46
	4.0	0.48
	6.0	0.80
	8.0	0.48
Calcon	2.0	0.71
	8.0	0.86

4.1.4 Dye sorption kinetics of the resin

This material is able to remove the anionic and cationic dyes completely even from highly diluted aqueous dye solutions, which are highly important. Batch kinetic sorption experiments were performed with highly diluted dye solutions (0.02 mg dye/mL water) to investigate the efficiency of the resin in the presence of trace quantities of dyes.

Dye loading capacity–time plot in (Figure 4.7) shows that within about 60 min of contact time for (QEP-PS) resin and (Figure 4.8) shows that within about 40 minutes contact time the dye concentration falls to zero for resin 2.

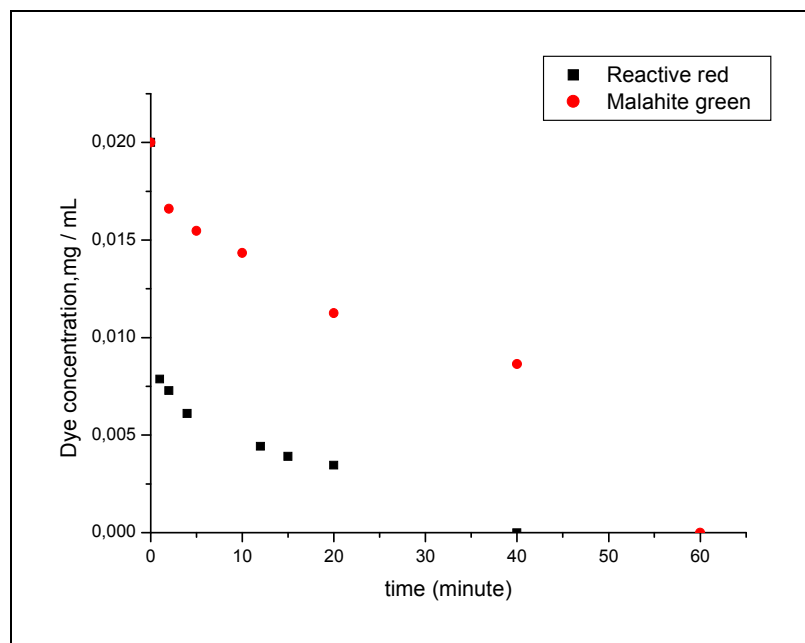


Figure 4.7 : Dye sorption kinetics of the (QEP-PS) resin.

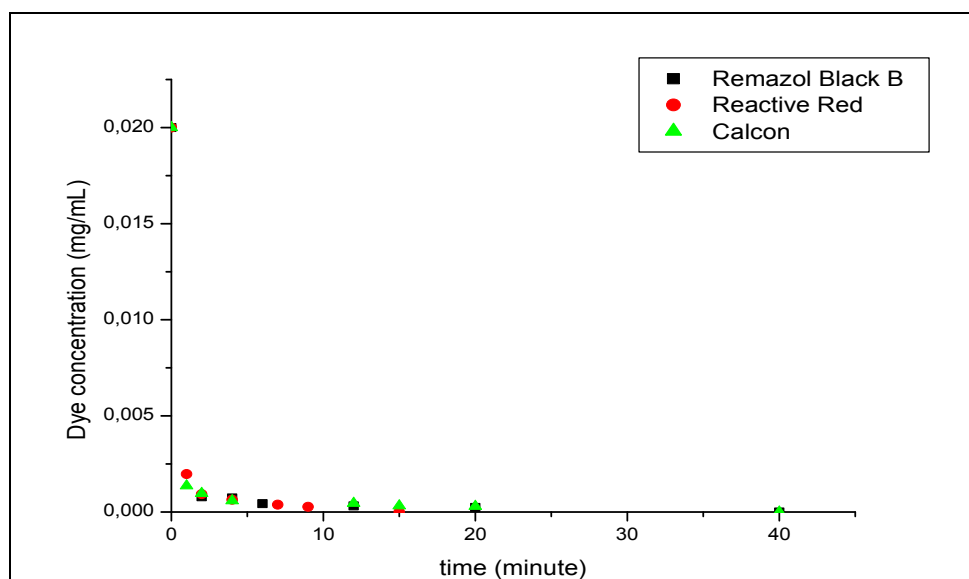


Figure 4.8 : Sorption kinetic of the PVI grafted PVBC resin (resin 2).

4.1.5 Kinetic models

The kinetics of sorption are an important aspect of the process control of removal of pollutants. The pseudo-first-order and pseudo-second-order kinetic models were used in order to evaluate dyes sorption kinetics on the resin.

The Lagergren first-order rate equation is one of the most widely used equations for the sorption of solute from a liquid solution. For this model, the following relation was used for the variation of adsorbed concentration with respect to time.

The pseudo first-order kinetic model given by Lagergren [46] as follows:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (4.3)$$

where k_1 (1/min) is the pseudo-first-order rate constant, q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and time t .

The linear form pseudo second-order kinetic model is based on chemical adsorption [47] and can be expressed as follows:

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \quad (4.4)$$

where q_e is the amount of dye adsorbed at equilibrium (mg. g^{-1}); q_t is the amount of dye adsorbed at time t (mg. g^{-1}); and k_2 is the equilibrium rate constant of pseudo-second-order sorption ($g \cdot mg^{-1} \cdot min^{-1}$). The rate parameters k_2 and q_e can be directly obtained from the intercept and slope of the plot of t/q_t versus t (Figure.4.9, Figure 4.10).

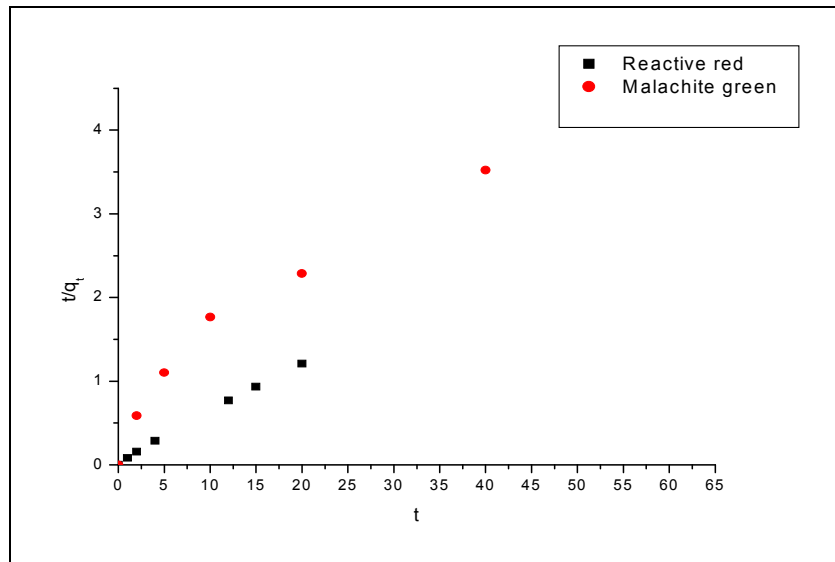


Figure 4.9 : The pseudo-second-order model plots of the dyes sorption of (QEP-PS) resin.

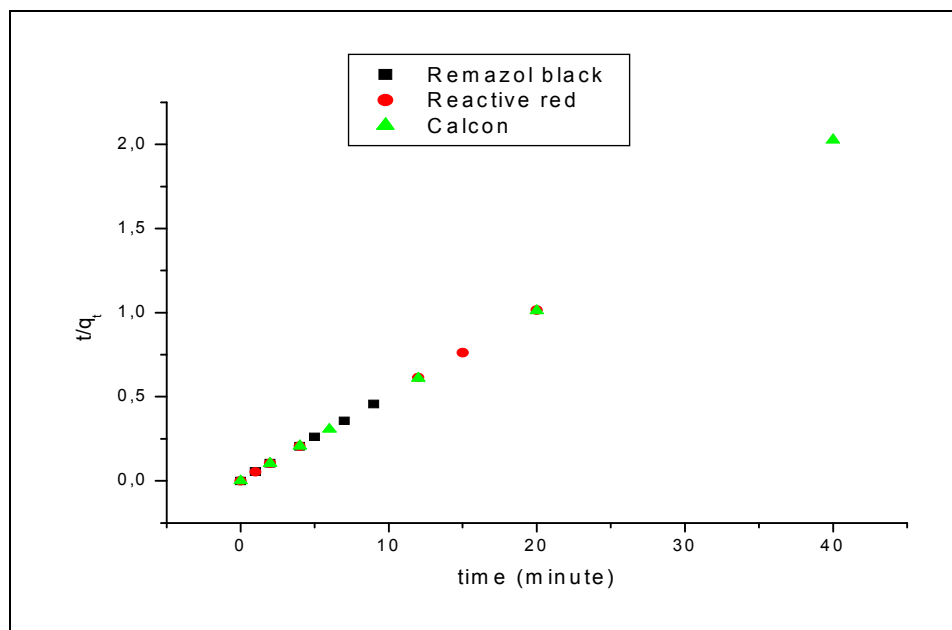


Figure 4.10 : The pseudo-second-order model plots of dyes sorption of resin PVI grafted PVBC resin.

The kinetic values obtained by linear regression are reported in (Table 4.5, Table 4.6). According to experimental and theoretical kinetic data in Table 4.5 and Table 4.6 the experimental results obtained for the adsorption of reactive red and malachite green dyes on resin were found to obey second-order kinetics. Also, PVI grafted PVBC resin obeys second order kinetic model (Table 4.7). In this case, the theoretical q_{eq} values for the resin were very close to the experimental q_{eq} values. In addition, high values of correlation coefficients showed that the data fitted well the kinetic model (Table 4.5, Table 4.6 and Table 4.7).

Table 4.5 : Pseudo-first-order and second-order kinetics models for adsorption of dyes on the (QEP-PS) resin.

DYES	FIRST ORDER				SECOND ORDER		
	q_{exp}	q_e	$k_1 \times 10^2$	R^2	k_2	q_e	R^2
	$(mg\ g^{-1})$		(min^{-1})		$(mg\ g^{-1}\ min^{-1})$	$(mg\ g^{-1})$	
Malahit Green	14.41	13.07	0.041	0.960	8.3×10^{-3}	14.98	0.972
Reactive Red	16.54	7.59	0.188	0.879	0.128	16.64	0.999

Table 4.6 : Pseudo-first-order and second-order kinetics models for adsorption of dyes on the (QIP-PS) resin.

DYES	FIRST ORDER				SECOND ORDER		
	q_{exp} (mg g ⁻¹)	q_e (mg g ⁻¹)	$k_1 \times 10^2$ (min ⁻¹)	R^2	k_2 (mg g ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
Malahit Green	14.83	14.18	0.042	0.976	7.3×10^{-3}	15.08	0.986
Reactive Red	16.39	8.63	0.190	0.885	0.152	16.89	0.998

Table 4.7 : Pseudo-first-order and second-order kinetics models for adsorption of dyes on the PVI grafted PVBC resin.

DYES	FIRST ORDER				SECOND ORDER		
	q_{exp} (mg g ⁻¹)	q_e (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	k_2 (mg g ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
Reactive Red	19.94	2.77	0.29	0.730	0.95	19.72	0.999
Ramazol Black	19.52	5.68	0.57	0.910	0.70	20.70	0.999
Calgon	19.98	3.90	0.41	0.730	0.99	19.76	0.999

The pseudo-second-order model is based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

The theoretical q_{eq} values estimated from the first-order kinetic model gave significantly different values from the experimental values, and the correlation coefficients were also lower. These results showed that the first-order kinetic model did not describe these adsorption systems.

Thus, the results obtained suggest that the pseudo-second-order adsorption kinetic model well describe the adsorption process, and so implies that adsorption rates of both dyes onto the resin is probably controlled by the chemical process.

4.1.6 Regeneration of the dye loaded resins

Acidic dyes loaded resin samples, when treated with basic ethanol become almost dye-free.

For the regeneration of dyes from basic dyes loaded resin, 5 M H_2SO_4 was used according to the literature [38]. The amount of recovered dyes is about 0.30 g dye g^{-1} polymer for reactive red and 0.35 g dye g^{-1} polymer for malachite green. These values are about 85% of the capacity of fresh polymer. Regeneration experiments were repeated twice and five adsorption desorption cycles were performed without significant decrease in the adsorption capacity of the resin for both acidic and basic dyes.

Ramazol Black loaded polymer samples, when treated with basic methanol become almost dye-free. In this way, 0.65 g dye is recovered per g of loaded sample (PVI grafted PVBC), which accounts for 84% of the capacity.

4.2 Preparation of the New Polymeric Sorbents for Removal of Phenol

In this thesis, quaternary chloroacetamide modified polymeric sorbents were synthesized and used to remove phenol from water.

4.2.1 Preparation of the quaternary amide containing imidazole based resin

This resin was synthesized starting from vinyl benzyl chloride and EGDMA (10%). The crosslinked co-polymer was reacted with imidazole to obtain imidazole modified resin. The amine content of the resin was found as 4.50 mmol/g as the total nitrogen content by using titrimetric method. The resin was quaternized with chloroacetamide. Total nitrogen content of the resin was found as 4.50 mmol/g by using Kjeldahl analysis method.

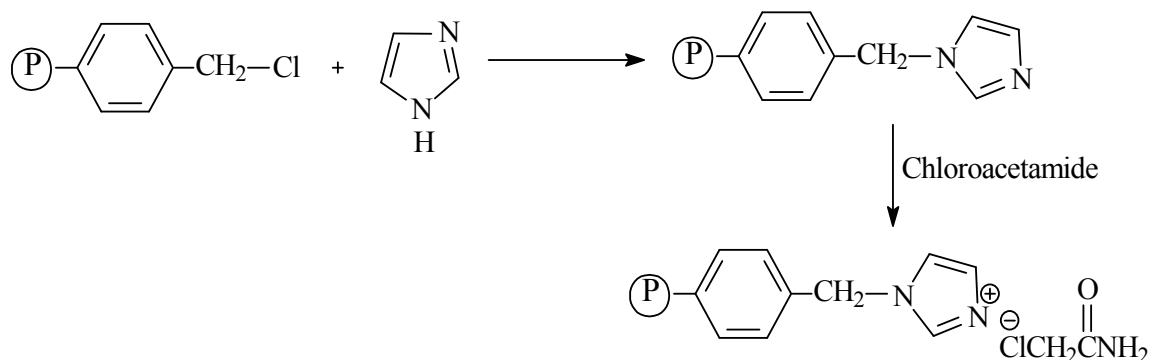


Figure 4.11 : Preparation of the quaternary amide containing resins.

The resin was characterized using FT-IR spectra. According to the (Figure 4.12 a), PVBC-co-EGDMA resin showed a characteristic C-Cl stretching at about 698 cm^{-1} . According to the FT-IR spectrum, C=N stretching mode of ring including conjugated C=C occur at 1651 cm^{-1} , C-C and C=N (ring) stretching modes at 1508 cm^{-1} and 1159 cm^{-1} belong to the C-N (ring) stretching vibrations in the imidazole ring respectively (Figure 4.12 b). In the chloroacetamide quaternized resin, C=O stretching vibration band is observed at about 1683 cm^{-1} (Figure 4.12).

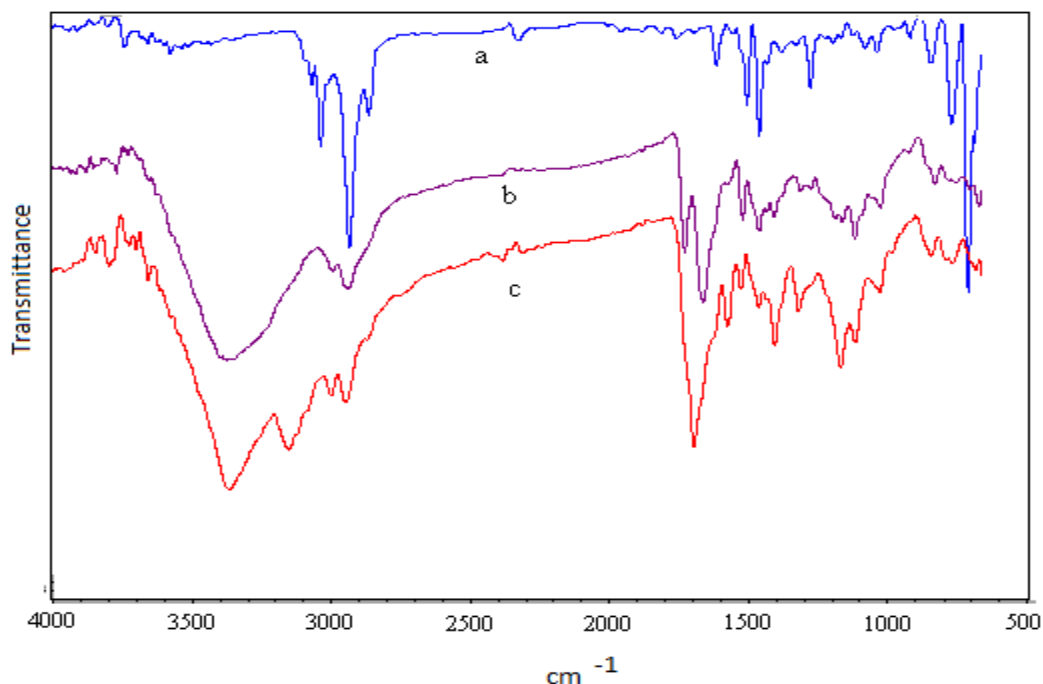


Figure 4.12 : (a) PVBC resin (b) Imidazole modified PVBC (c) Quaternary chloroacetamide containing resin.

4.2.2 Preparation of the N,N-dimethylethylenediamine modified resin and quaternization with chloroacetamide poly(styrene) based sorbent

The resin was synthesized starting from prepared vinyl benzyl chloride and EGDMA (10%) by suspension polymerization. The crosslinked co-polymer was reacted with N,N-dimethylethylenediamine and quaternized with chloroacetamide to obtain the modified resin (Figure 4.13). The amine content of the resin was found as 4.50 mmol/g as the total nitrogen content by using titrimetric method.

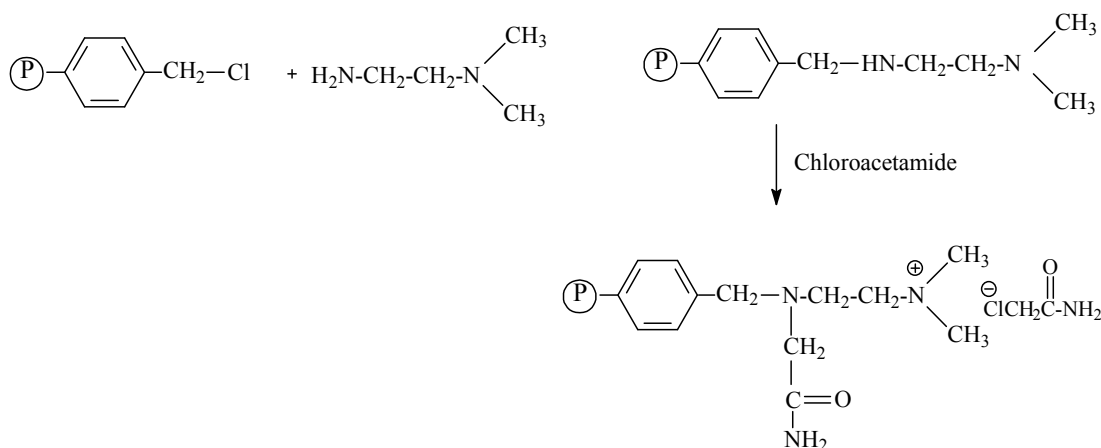


Figure 4.13 : Preparation of PVBC-DMEA-CAM resin.

4.2.2.1 Determination of chlorine content of the resin

The amine content of the resin was determined with chlorine content determination by using spectroscopic method: the polymer sample (0.1 g) was put into 10 mL NaOH (10%) and stirred for 8 h. The mixture was diluted and neutralized by using 9 M HNO₃ cautiously to 50 mL by water and filtered. The filtrate was used for the chlorine determination by using colorimetric method described in the literature [52] and was found as 4.1 mmol

4.2.3 Characterization of the resins

The resin was characterized using FT-IR spectra with asymmetric stretching of methyl and methylene groups observed at 2870 cm⁻¹ and 2924 cm⁻¹ respectively. Appearance of the new broad peak of N-H stretching observed between 3300-3500 (Figure 4.14a) evidenced the successful modification on the resin. In addition, the sharp peak at about 1685 cm⁻¹ corresponds to C=O stretching vibration of the amide group in the Resin (Figure 4.14).

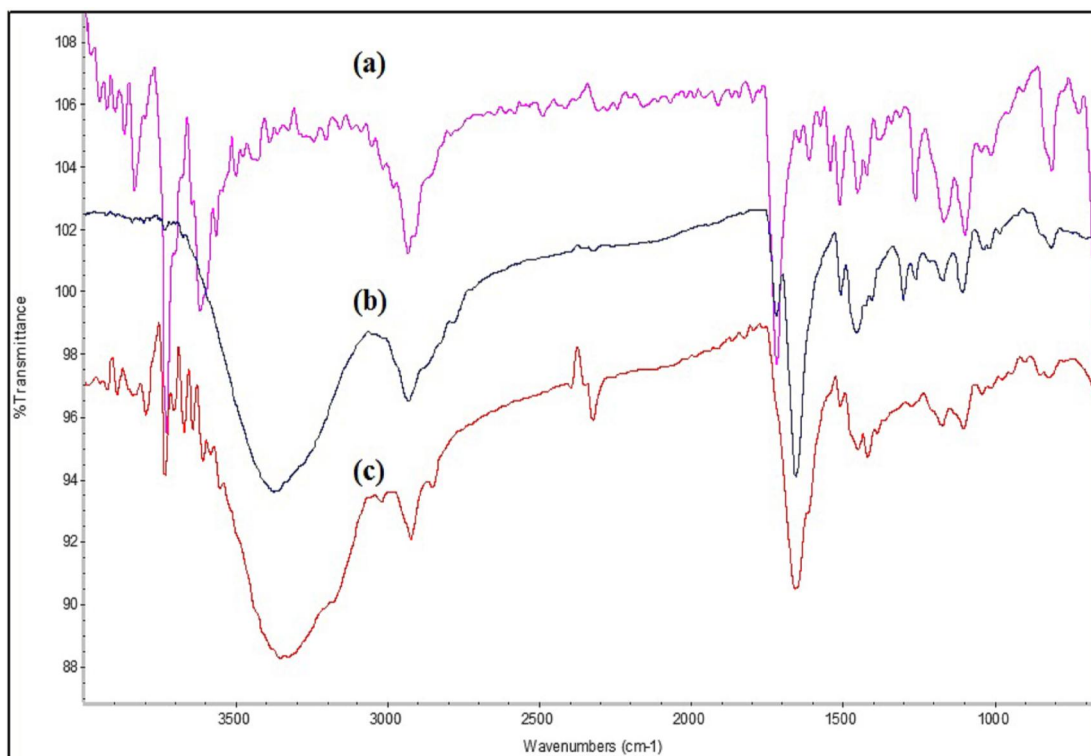


Figure 4.14 : FT-IR spectra of (a) PVBC (b) PVBC+N,N-dimethylethylenediamine (c) N,N- dimethylethylenediamine modified chloroacetamide Ouaternized PVBC resin.

4.2.4 Extraction of phenol

Phenol extraction experiments were carried out simply by contacting wetted resin samples with aqueous phenol solutions at room temperature. The effect of initial concentration of phenol on adsorption was studied at four different concentrations (i.e. 0.25, 0.50, 0.75 and 1.00 g / 100 mL). The effect of phenol on adsorption on the resin was given in (Table 4.8).

According to the (Table 4.8), phenol sorption capacities of the resin were found as 0.25g phenol / g resin-0.20 g phenol / g resin and phenol can be removed successfully because the resin has amide groups.

Table 4.8 : Maximum phenol sorption capacities of the resin.

Phenol Concentration (g phenol / 100 mL)	Ethyl Piperazine chloroacetamide	(PVBC-DMEA-CAM)	Quaternary Chloroacetamide imidazoleModified Resin
	Capacity	Capacity	Capacity
0.25	0.237	0.193	0.188
0.50	0.256	0.220	0.190
0.75	0.280	0.208	0.196
1.00	0.251	0.218	0.208

According to the Table 4.8, adsorption of phenol on the resin was found to be concentration dependent. The sorption capacity of phenol increases with increase in initial concentration.

Three mechanisms of phenolic compound adsorption are postulated, namely π - π dispersion interaction, electron-donor-acceptor complex formation and hydrogen bond formation [55].

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.

Table 4.9 : Phenol sorption capacity of the resins depending on pH.

pH	Chloroacetamide Ethyl piperazine Modified Resin	(PVBC-DMEA- CAM) Resin	Quaternary Chloroacetamide imidazoleModified Resin
	Capacity	Capacity	Capacity
	(g phenol / g resin)	(g phenol / g resin)	(g phenol / g resin)
2.0	0.210	0.202	0.202
4.0	0.220	0.237	0.213
6.0	0.286	0.273	0.234
8.0	0.200	0.197	0.194

The effect of pH for the adsorption of phenol onto the resins was studied in the pH range 2.0-8.0. It is apparent from (Table 4.9) 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[61].

4.2.5 Phenol sorption kinetics of the resins

The resin is able to remove phenol from water completely even from highly diluted aqueous solutions which are highly important. Batch kinetic sorption experiments were performed with highly diluted phenol solutions (0.03 mg phenol /mL water) to investigate the efficiency of the resin in the presence of trace quantities of phenol. Concentration–time plot in (Figure 4.15, Figure 4.16 and Figure 4.17) shows that within about 60 min of contact time, the dye concentration falls to zero.

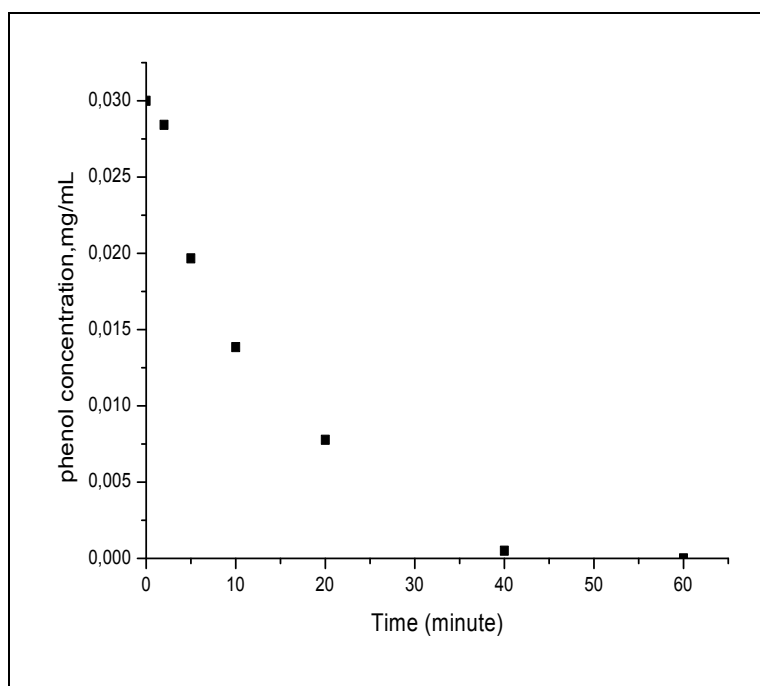


Figure 4.15 : Phenol sorption kinetics of imidazole modified chloroacetamide quaternized resin.

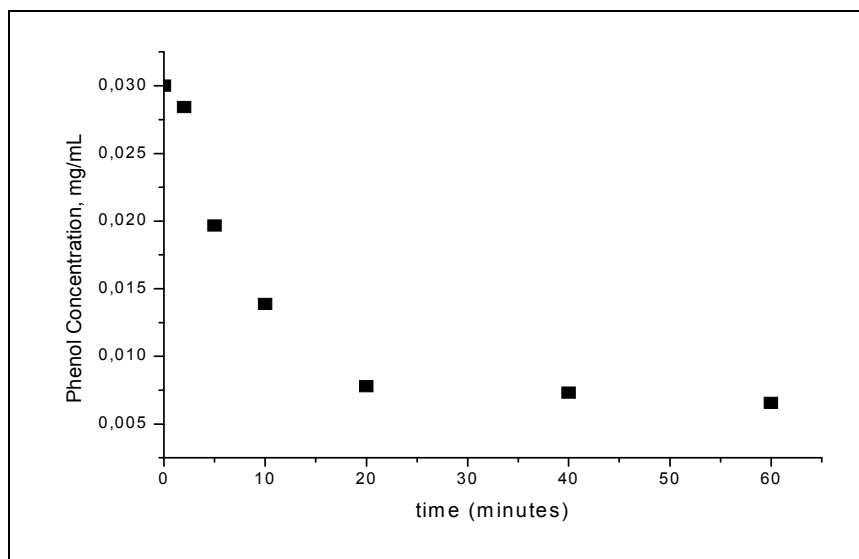


Figure 4.16 : Phenol sorption kinetics of the ethyl piperazine modified chloroacetamide quaternized resin.

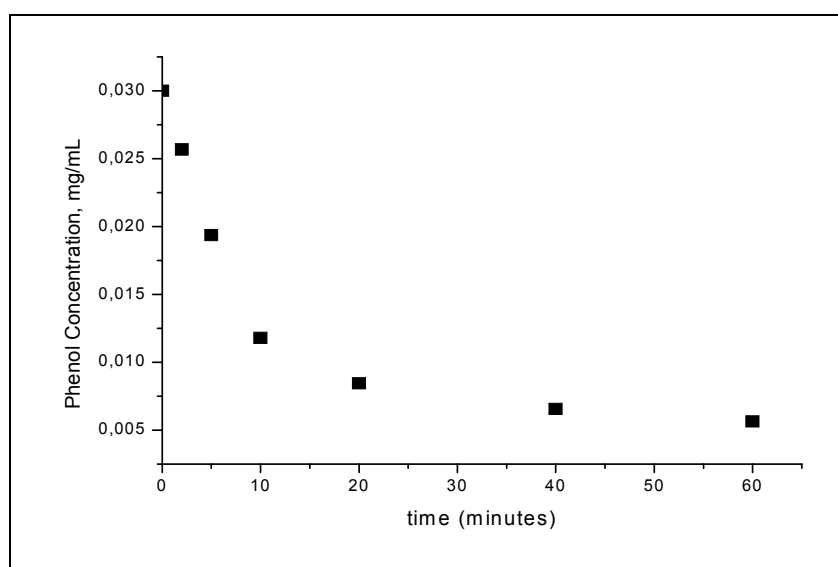


Figure 4.17 : Phenol sorption kinetics of the (PVBC-DMEA-CAM) resin.

4.2.6 Kinetic models

Also, pseudo second and first models were applied as described above. And, the resins obey second order kinetic models.

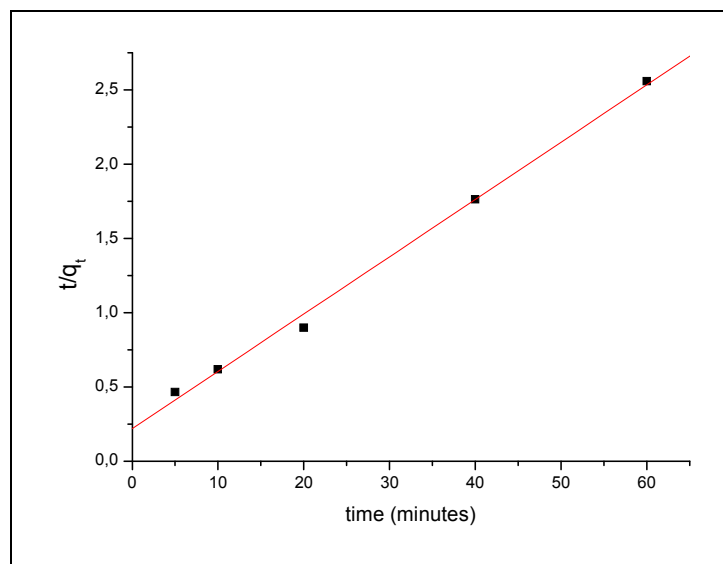


Figure 4.18 : The pseudo-second-order model plots for phenol sorption of chloroacetamide quaternized imidazole modified resin.

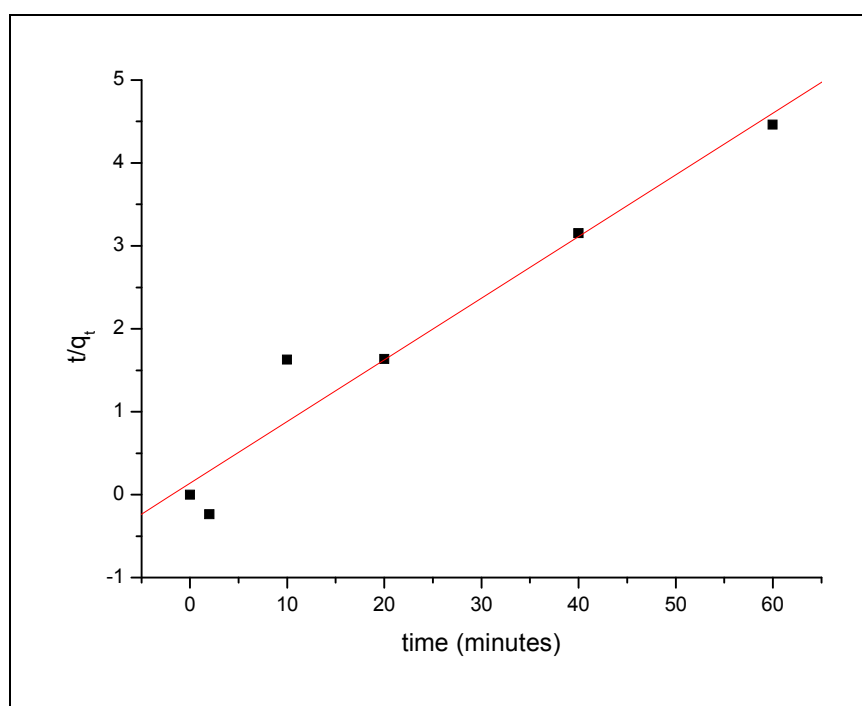


Figure 4.19 : Pseudo-second-order model plots of adsorption of phenol quaternary amide containing piperazine based resin.

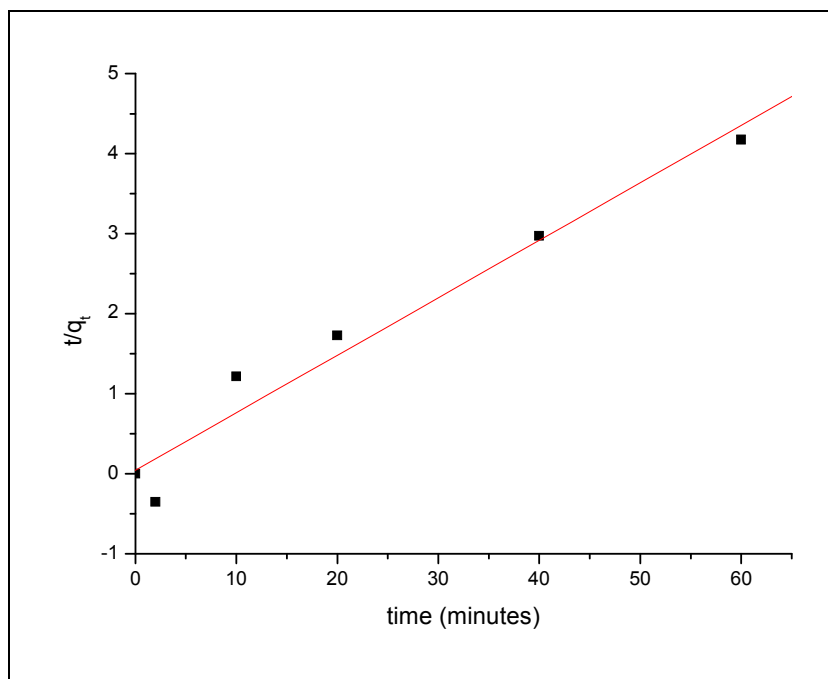


Figure 4.20 : Pseudo-second-order model plots for adsorption of phenol on the (PVBC-DMEA-CAM) resin.

The kinetic values obtained by linear regression are reported in (Table 4.10).

Table 4.10 : Pseudo-first-order and second-order kinetics models for adsorption of phenol the resins.

Sorbents	FIRST ORDER				SECOND ORDER		
	q_{exp}	q_e	$k_1 \times 10^2$	R^2	$k_1 \times 10^2$	q_e	R^2
	(mg g ⁻¹)		(min ⁻¹)		(mg g ⁻¹ min ⁻¹)	(mg g ⁻¹)	
(Quaternary chloroacetamide Modified resin)	23.46	19.63	0.09	0.892	0.68	25.92	0.997
(Ethyl Piperazine chloroacetamide resin)	11.09	15.24	0.07	0.887	0.29	12.63	0.903
(PVBC-DMEA-CAM resin)	13.46	14.83	0.07	0.924	0.15	13.81	0.969

The adsorption of phenol on resin were found to obey second-order kinetics (Table 4.10) (Fig.4.18,4.19 and 4.20). In this case, the theoretical q_{eq} values for the resin were very close to the experimental q_{eq} values.

In addition, high values of correlation coefficients showed (Table 4.10) that the data fitted well the kinetic model. The pseudo-second-order model is based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. The theoretical q_{eq} value estimated from the first-order kinetic model gave significantly different value from the experimental value and the correlation coefficient was lower. These results showed that the first-order kinetic model did not describe these adsorption systems. Thus, the results obtained suggest that the pseudo-second-order adsorption kinetic model well describe the adsorption process, and so implies that adsorption rate of phenol onto the resin is probably controlled by the chemical process.

The fact that the kinetics of phenol adsorption on the resin follows the pseudo-second-order kinetic models suggested phenol adsorption probably occurred via sharing of electrons between the phenolic ring and the polymeric resin.

4.3 Preparation of the New Polymeric Sorbents for Removal of Atrazine

Atrazine is a herbicide of the triazine class (Fig.4.21). There are different kind of methods use to remove atrazine from water.

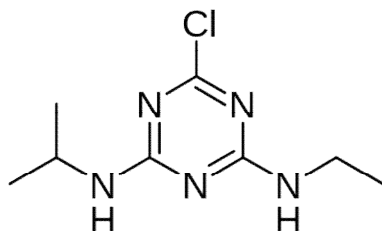


Figure 4.21 : Chemical structure of atrazine.

Sulfonic acid containin core-shell type polymeric sorbent was prepared and used to remove Atrazine.

4.3.1 Preparation poly (2-acrylamido-2-methylpropane sulfonic acid) (AMPS) grafted onto crosslinked poly (vinylbenzyl chloride) resin for removal of atrazine from water

ATRP technique can be used even in heterogeneous conditions successfully and grafting from solid particles can be obtained with moderate or acceptable poly dispersities. More importantly, ATRP is expected to eliminate free polymer

formation during the graft polymerization and provide a relatively easy pathway to core-shell type of polymers. Alkyl halides are common initiators studied in copper mediated ATRP (Fig.4.22).

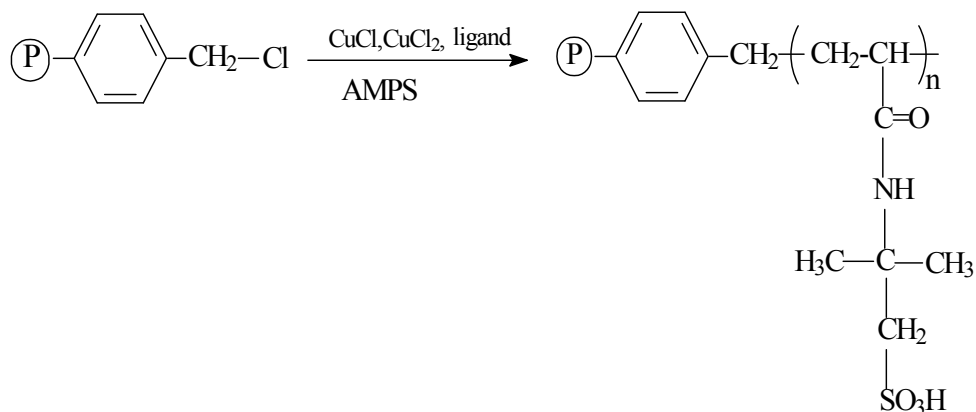


Figure 4.22 : Preparation of core-shell type crosslinked polymeric resin.

The mixture was filtered and washed with excess of water (300 mL) and alcohol (20 mL). Vacuum dried sample weighed 9.62 g. Grafting degree of the resin was calculated as:

$$\text{Grafting degree \%} = (W_f - W_i / W_i) * 100 = (9.62 - 2/2) * 100 = 381\%.$$

The resulting core-shell type polymeric sorbent has been demonstrated to be an efficient sorbent for removal of atrazine. Effects of initial atrazine concentration, pH and temperature on the sorbent with the batch method were investigated.

4.3.2 Characterization of the resin poly(2-acrylamido-2-methylpropane sulfonic acid) (AMPS)

The band at 1106 cm^{-1} and 1033 cm^{-1} were ascribed to the asymmetric and symmetric vibration of S=O, respectively, which were the characteristic absorption of AMPS. The C=O stretching peak of S=O was observed at 1661 cm^{-1} (Figure 4.23).

Morphological characterizations of the AMPS grafted and atrazine loaded resins were studied by SEM. According to the SEM Picture (Fig.4.24 a and b) , the pores of the atrazine loaded resin seem to be filled (Fig.4.24b).

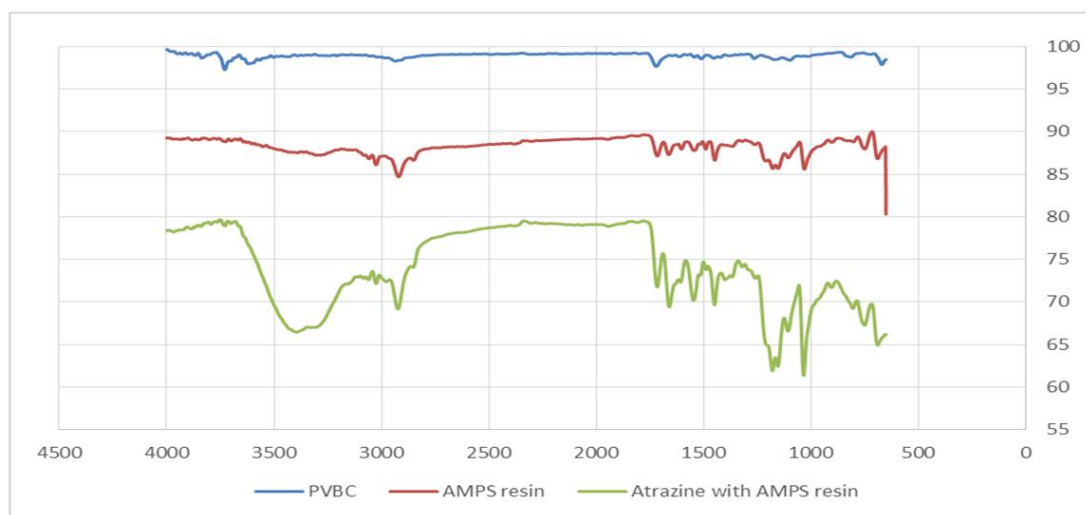


Figure 4.23 : FT-IR spectra of a) PVBC resin b) AMPS resin c) Atrazine loaded AMPS resin.

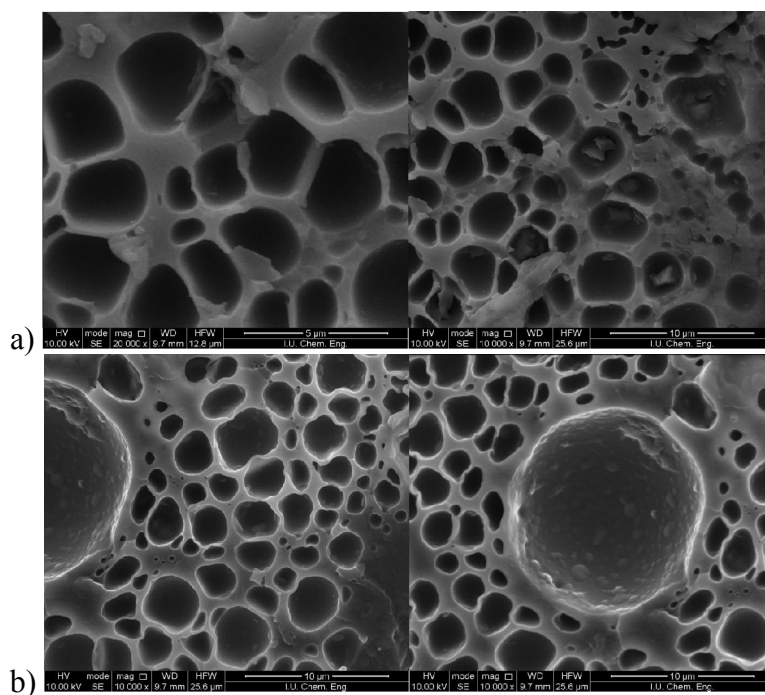


Figure 4.24 : SEM image of the (a) AMPS grafted onto PVBC resin (b) Atrazine loaded resins.

4.3.3 Atrazine extraction experiments

Atrazine extraction experiments were carried out simply by contacting wetted bead samples with aqueous solutions at room temperature. Capacities were assigned by spectroscopic analysis of residual atrazine contents. Atrazine sorption capacities of the sorbent depending of the atrazine concentration were given in (Table 4.11).

According to the (Table 4.11), atrazine sorption capacities of the resin were found as 57.21 mg atrazine / g resin and atrazine can be removed successfully.

Table 4.11 : Maximum atrazine sorption capacities of the resin.

Atrazine	Atrazine Concentration (mg atrazine / 100 mL)	Capacity
		(mg atrazine / g resin)
	10	57.21
	5	29.32
	2.5	11.16
	1.25	6.43

The effect of pH for the adsorption of atrazine onto the resin was studied in the pH range 2.0–8.0. It is apparent from (Table 4.12) that the adsorption of atrazine first increased from pH 2.0 to 6.0 and then declined with the further increase of pH. The highest adsorption of atrazine was noted at pH 6. The reduction in the adsorption of atrazine at high pH was due to the electrostatic repulsions between the negative surface charge of the resin and the anions in solution.

Table 4.12 : Atrazine sorption capacities of the resin depending on pH.

Atrazine	pH	Capacity
		(mg atrazine / g resin)
	2	56.18
	4	49.77
	6	41.51
	8	39.83

4.3.4 Atrazine sorption kinetics of the (poly(2-acrylamido-2-methylpropane sulfonic acid) (AMPS) resin

This material is able to remove atrazine from diluted aqueous dye solutions which is commercially highly important.

In order to estimate the efficiency of the resin for trace atrazine, batch kinetic experiments were performed using highly diluted atrazine solutions (0.2 g atrazine/L ethanol-water mixture) to investigate the efficiency of the resin in the presence of trace quantities of atrazine.

For this purpose, resin (0.2 g) was wetted with distilled water (1.5 ml) and added to a solution of atrazine (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 atrazine contents by the method as described.

The concentration–time plot (Figure 4.25) shows that with about 40 min and 60 min contact the concentration of atrazine fall to zero respectively.

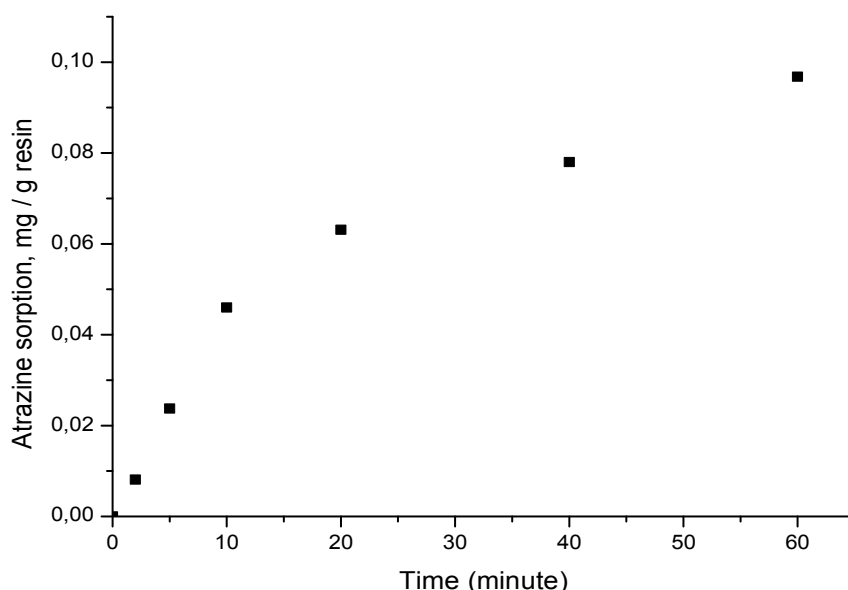


Figure 4.25 : Atrazine sorption kinetics of the (poly(2-acrylamido-2-methylpropane sulfonic acid) (AMPS) resin.

4.3.5 Kinetic models

Also, pseudo second and first models were applied described above. According to experimental and theoretical kinetic data in Table 4.13 and Fig.4.26, the

experimental results obtained for the adsorption of atrazine on the resin were found to obey second-order kinetics.

In this case, the theoretical q_{eq} values for the resin were very close to the experimental q_{eq} values. In addition, high values of correlation coefficients showed that the data fitted well the kinetic model.

The pseudo-second-order model is based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

Table 4.13 : Pseudo-first-order and second-order kinetics models for adsorption of atrazine the resin.

Sorbent	FIRST ORDER				SECOND ORDER		
	q_{exp} ($mg\ g^{-1}$)	q_e ($mg\ g^{-1}$)	$k_{1 \times 10^2}$ (min^{-1})	R^2	$k_{1 \times 10^2}$ ($mg\ g^{-1}\ min^{-1}$)	q_e ($mg\ g^{-1}$)	R^2
Poly(2-Acrylamido-2-Methylpropane Sulfonic Acid)	23.86	19.03	0.08	0.896	0.33	23.48	0.966

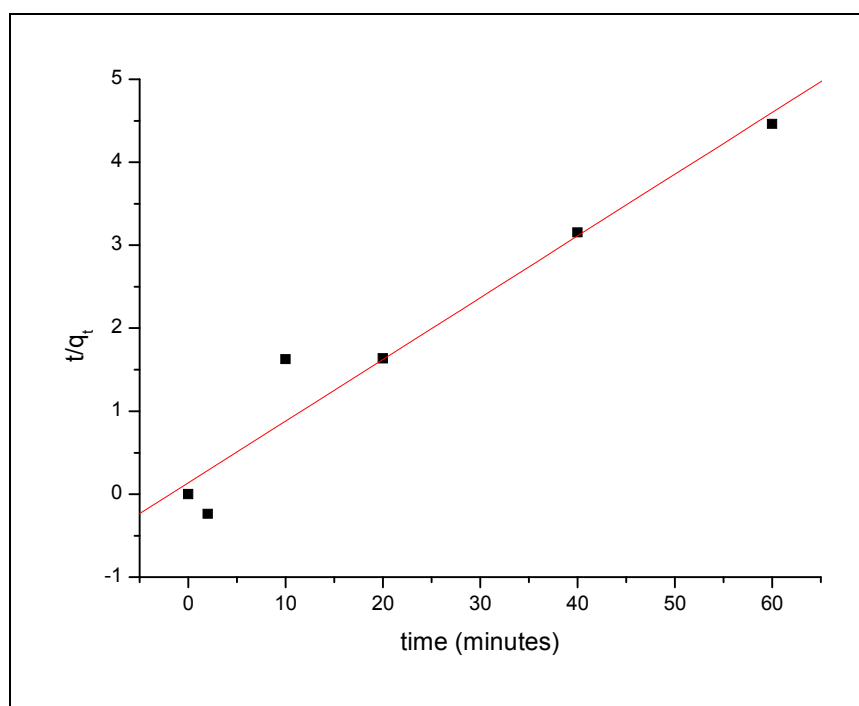


Figure 4.26 : Pseudo-second-order model plots of adsorption of atrazine the (poly(2-acrylamido-2-methylpropane sulfonic acid) (AMPS) resin.

The theoretical q_{eq} values estimated from the first-order kinetic model gave significantly different values from the experimental values, and the correlation coefficients were also lower. These results showed that the first-order kinetic model did not describe these adsorption systems.

5. CONCLUSION

In this work, carboxylic acid modified quaternary amine containing polystyrene based resin was synthesized to prepare an alternative sorbent for removal of both acidic and basic dyes from wastewater. The polymeric resin has a potential as an adsorbent because it can adsorb both acidic and basic dyes over a wide pH range. Dye sorption capacity of the polymeric resin was found as 0.34-0.41 g dye / g in neutral medium.

The desorption capacity of the resin was found as 0.30-0.35 g dye / g resin for reactive red and Malachite green. Desorption experiment was conducted regenerated resin again and the sorbent was desorbed completely.

PVI grafted onto crosslinked PVBC sorbent was synthesized to prepare an alternative adsorbent for removal of acidic dyes from wastewater. For this purpose graft copolymerization of PVI onto PVBC was carried out using inverse ATRP method. The sorption capacity of the flexibility of the side chains in the PVI-g-PVBC (resin 2) is expected to provide pseudo homogeneous reaction conditions and easy accessibility of the functional groups involved. It is expected that the adsorbents have the advantage of mobility of the graft chains in the removal of dyes from aqueous mixtures.

Another organic waste is phenol. In this study, quaternary chloroacetamide containing polystyrene-based resins were synthesized to prepare an alternative sorbent for removal of phenol from wastewater. The polymeric resin has a potential as an adsorbent because it can adsorb phenol over a wide pH range (2.0-8.0). Phenol sorption capacity of the polymeric resin was found as 0.188 g phenol / g resin-0.208 g phenol / g resin. The adsorbed phenol was recovered using 0.1 M NaOH solution and the regenerated resin was effectively used up to three consecutive cycles without any appreciable loss in the adsorptive performance. In view of all these outcomes, it can be used for removal of phenol from water.

Atrazine is herbicide and it is an important organic waste. Poly (2-Acrylamido-2-Methylpropane Sulfonic Acid) (AMPS) was grafted on to PVBC resin by using

inverse ATRP method to remove atrazine from water. Atrazine sorption capacity of the resin was found as about 57 mg atrazine/ g resin.

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- **Bildik,F.**,Yavuz,E.,Senkal,B.F., (2015).Preparation Of The Poly (Styrene) Based Quaternary Chloroacetamide Modified Sorbent For Removal Of Phenol,ICOCEE.(Poster Presentation).

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