

**MODIFICATION OF POLY(GLYCIDIYLMETHACRYLATE) GRAFTED ONTO
CROSSLINKED PVC WITH TERTIARY AMINE GROUP AND USE FOR
REMOVING OF ACIDIC DYES FROM WATER**

**M.Sc. Thesis by
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Department : Polymer Science and Technologies

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**POLİ (GLİSİDİL METAKRİLAT) AŞILANMIŞ ÇAPRAZ BAĞLI PVC’NİN
TERSIYER AMİN GRUBU İLE MODİFİKASYONU VE ASİDİK BOYALARIN
ASİDİK BOYALARIN SUDAN GİDERİLMESİNDE KULLANIMI**

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FOREWORD

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ABBREVIATIONS

ATRP	: Atom Transfer Radical Polymerization
bpy	: 2, 2-bipyridyl
COD	: Chemical Oxygen Demand
Cu	: Copper
CuBr	: Copper(I)Bromide
DHPVC	: Dehydrochlorinated Poly(vinyl)chloride
FT-IR	: Fourier Transform Infrared
GMA	: Glycidyl Methacrylate
g	: mass unit, gram
h	: time unit, hour
k_{act}	: Activation constant
k_{deact}	: Deactivation constant
L	: Ligand
ml	: Volume unit, mililiter
PVC	: Poly(vinyl)chloride
PGMA	: Poly (Glycidyl Methacrylate)
nm	: nanometer unit
Pn[·]	: Polymer symbol
R[·]	: Radical
Rpm	: Round per meter
T	: Transmission
UV	: Ultraviolet
X	: Alkyl halide symbol
λ_{max}	: maximum wavelength

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MODIFICATION OF POLY(GLYCIDYL METHACRYLATE) GRAFTED ONTO CROSSLINKED PVC WITH TERTIARY AMINE GROUP AND USE FOR REMOVING ACIDIC DYES FROM WATER

SUMMARY

Surface initiated polymerizations have been widely used to overcome inadequate properties of some polymers like poly(vinylchloride) (PVC). Atom transfer radical polymerization (ATRP) is one of the most investigated methods of controlled graft polymerization, due to the radical nature of ATRP, a wide range of functional monomers can be polymerized, yielding polymers with pendant functional groups. One of these monomers is glycidylmethacrylate (GMA). Poly(glycidylmethacrylate) (PGMA) or PGMA-based polymers are particularly attractive because of their reactive oxirane pendant groups which provides a large number of subsequent reactions offering a variety of opportunities for chemical modification.

Among the various chemical functional groups, epoxy group is one of the most important type to be integrated into polymers. This functional group can be modified using various chemical reactions to introduce different functional properties onto the polymeric surfaces. They undergo ring opening reaction with various compounds like amine groups. For this reason, polymers with epoxy groups offer numerous functionalization possibilities.

In this study, glycidylmethacrylate is grafted onto partially dehydrochlorinated poly(vinyl chloride) (DHPVC) using ATRP method. Polymerization kinetic of this reaction is studied. Then reacting this polymeric resin with excess of diethylamine, gives a tertiary amine containing resin.

Conversion-time plot of the resin was studied and grafting degree of the resin was found as 1580 % for 16 h.

This polymeric resin will be characterized by using spectrophotometric methods such as FT-IR , UV and analytical methods.

Dye loading capacities of the resin was studied in water and different pH medium. The resin shows reasonably high dye sorptions as high as 0.3 – 0.45 per gram polymer.

There are no big differences depending on pH. It is important to note that the resin can be used in a wide pH range. This property is important in utilization of the resin in industrial applications.

Dye sorption kinetics of the resin was studied. This material is able to remove the anionic dyes completely even from highly diluted aqueous dye solutions which are highly important. Dye loading capacity with respect to time shows maximum sorption capacities within 60 min of contact time.

Regeneration of the resin was investigated and the desorption capacity of the resin was found as 0.23 g dye / g resin for calcon.

POLI(GLİSİDİL METAKRİLATIN) ÇAPRAZ BAĞLI PVC ÜZERİNDEN GRAFT KOPOLİMERİNİN TERSİYER AMİN İLE MODİFİKASYONU VE SUDAN ASİDİK BOYAR MADDELERİN GİDERİLMESİNDE KULLANIMI

ÖZET

Yüzeyden başlama polimerizasyonu polivinil klorür (PVC) gibi birçok polimerin yetersiz kalabilen yüzey özelliklerini geliştirmede yüzey fonksiyonlandırma tekniği olarak yaygın bir şekilde kullanılmaktadır.

Atom transfer radikal polimerizasyonu (ATRP), radikalın doğasından ötürü, birçok fonksiyonel monomerin polimerleştirilebilmesiyle fonksiyonel grup içeren polimerler oluşturabilmesi bakımından en çok incelenen kontrollü graft polimerizasyon yöntemlerinden biridir.

Glisidil metakrilat (GMA) bu tip polimerlere örnek olarak verilebilir. Poli(glisidilmetakrilat) (PGMA) ya da PGMA-bazlı polimerler reaktif oksiran gruplarından dolayı farklı reaksiyonlara girebilmekte ve kimyasal olarak modifiye edilebilmektedirler.

Polimerlere takılabilen birçok fonksiyonel grup arasında epoksi grup, birçok kimyasal reaksiyon ile modifiye edilebildiğinden, oldukça önemli sayılmaktadır. Epoksi gruplar amin gibi çeşitli reaktiflerle halka açılması reaksiyonuna uğrarlar. Bu yüzden epoksi grup taşıyan polimerler birçok fonksiyonlandırma olanağı sunarlar.

Bu çalışmada, ATRP yöntemiyle, glisidil metakrilat kısmen dehidroklorine edilmiş PVC (DHPVC) üzerine aşılınmış ve bu reaksiyonun polimerizasyon kinetiği incelenmiştir. Daha sonra elde edilen polimerik reçinenin dietilaminin aşırısı ile reaksiyonunda, tersiyer amin içeren polimerik reçine elde edilmiştir.

Reçine oluşumunun dönüşüm-zaman grafiği oluşturulmuş ve reçinenin graft derecesi 16 saat için 1580 % olarak hesaplanmıştır.

Polimerik reçine FT-IR ve UV gibi spektrometrik ve analitik yöntemlerle karakterize edilmiştir. Polimerik reçinenin değişik pH ortamlarında boya tutma kapasiteleri çalışılmıştır.

Polimerik reçinenin 0.3-0.45 g boya / g reçine gibi yüksek miktarda boya tutabildiği tespit edilmiştir. Farklı pH'larda çalışılması boya tutma özelliğini çok etkilememektedir. Polimerik reçinenin değişik pH aralıklarında çalışabilmesi, reçinenin endüstriyel uygulamalarda kullanılabilirliği açısından önemlidir.

Polimerik reçinenin boya tutma kinetiği çalışılmış olup, anyonik boyaların seyreltik ortamda dahi tamamen tutulduğu anlaşılmıştır. Zamana bağlı boya tutma kapasitesi tayini çalışmaları, 60 dakikalık temas sonucunda boya tutma kapasitesinin maximum olduğunu göstermektedir.

Polimerik reçinenin rejenerasyonu incelenmiş ve polimerik reçinenin desorpsiyon kapasitesi calcon için 0.23 g boya / g reçine olarak hesaplanmıştır.

1. INTRODUCTION

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.

In recent years, surface modification has been of importance to provide chemicals with desired properties for practical applications, though many surface modification methods have been developed. [1]

Graft copolymerization has proved to be a practical method of overcoming a number of inadequate properties of polyvinyl chloride (PVC). Chemical modification of the PVC to provide more active side groups at random positions along the length of the polymer chain to form a multifunctional initiator for grafting reactions. Ghaemy and Gharaebi [1] have studies on grafting PSt onto DHPVC.

Atom transfer radical polymerization (ATRP) is one of the most investigated methods of controlled graft polymerization,

In our previous works, poly (vinylpyrrolidone) and poly (glycidylmethacrylate) were grafted sulfonamide based polymeric sorbents to obtain acidic dye removal. [2,3]

In the present work, polyglycidyl methacrylate was grafted onto partially DHPVC beads by using ATRP method. Epoxy group on the polymeric sorbent can be functionalized via ring opening of epoxide group by using amine and acid. Diethylamine was used to obtain tertiary amine containing polymeric sorbent. Tertiary amine and quaternized amine containing resins are important to remove acidic dyes from aqueous solutions.

Obtained polymeric resin was used for acidic dye removal studies. Also, experiments were carried out at different pH media. Kinetic studies and regeneration studies were also studied in this thesis.

2. THEORETICAL PART

2.1 Poly (vinyl chloride)

PVC is produced by polymerization of vinylchloride by free-radical mechanisms, mainly in suspension and emulsion, but bulk and solution processes are also employed to some extent.

The control of vinyl chloride monomer escaping into the atmosphere in the PVC production plant has become important because cases of angiosarcoma, a rare type of liver cancer, were found among workers exposed to the monomer. This led to setting of stringent standards by governments and modification of manufacturing processes by the producers to comply with the standards.

At processing temperatures used in practice (150–200⁰C), sufficient degradation may take place to render the product useless. Evidence points to the fact that dehydrochlorination occurs at an early stage in the degradation process and produces polyene structures.(Figure 2.1)

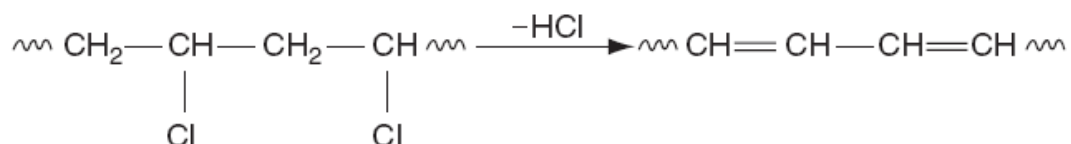


Figure 2.1 : Degradation of PVC [4]

It is believed that the liberated hydrogen chloride can accelerate further decomposition and that oxygen also has an effect on the reaction. However, incorporation of certain materials known as stabilizers retards or moderates the degradation reaction so that useful processed materials can be obtained. Many stabilizers are also useful in improving the resistance of PVC to weathering, particularly against degradation by UV radiation. [4]

2.2 Atomic Transfer Radical Polymerization

Atom transfer radical polymerization is a controlled/“living” polymerization based on the use of radical polymerization to convert monomer to polymer.

This type of polymerization is an alternative to other types of living polymerizations because of their limitations by many factors: only a small number of monomers can be used, the reactions are sensitive to moisture, and two or more monomers can not be randomly copolymerized. Radical polymerization, in contrast, can polymerize hundreds of monomers, can co-polymerize two or more monomers, and can be performed in water as emulsions or suspensions. Controlled/“living” radical polymerization promised to overcome these limitations and provide a method to maximize the potential of living polymerizations.

The Matyjaszewski research group was the first to develop a controlled/“living” polymerization that used a simple, inexpensive polymerization system. It is capable of polymerizing a wide variety of monomers, is tolerant of trace impurities (water, oxygen, inhibitor), and is readily applicable to industrial processes. The system that was developed was termed *atom transfer radical polymerization*.

ATRP is a robust system that has generated much interest among polymer chemists in both industry and academia. The control of the polymerization afforded by ATRP is a result of the formation of radicals that can grow, but are reversibly deactivated to form dormant species. Reactivation of the dormant species allows for the polymer chains to grow again, only to be deactivated later. Such a process results in a polymer chain that slowly, but steadily, grows and has a well-defined end group (for ATRP that end group is usually an alkyl halide).

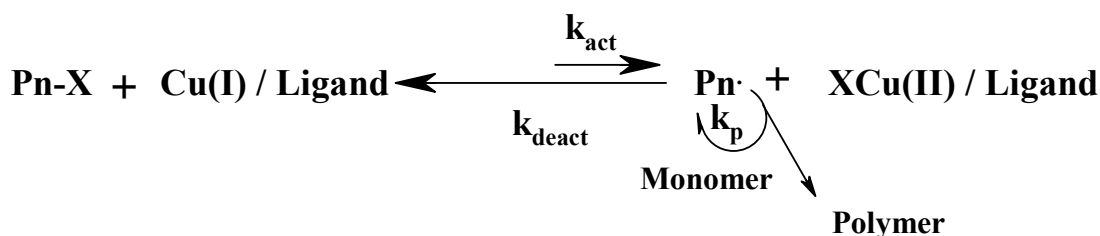


Figure 2.2 : ATRP Reaction Mechanism [5]

An ATRP system consists of an initiator-generally simple, commercially available alkyl halide. The catalyst is a transition metal that is complexed by one or more

ligands, and monomer. The catalyst does not need to be used in one-to-one ratio with the initiator, but can be used in much smaller amounts.

ATRP occurs as a repetitive addition of a monomer to a growing radicals generated from dormant alkyl halides by a reversible redox process catalyzed by transition metal compounds complexed by amine ligand. Nitrogen-based ligands generally work well for Cu-mediated ATRP. Our study has considered this issue in working with 2, 2-bipyridyl and Cu(I) Bromide system. (Figure 2.3)

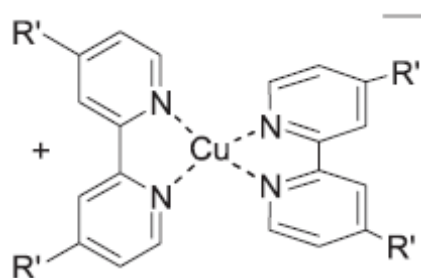
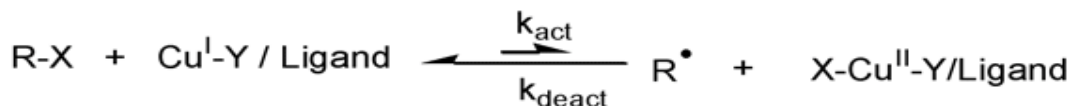


Figure 2.3 : 2, 2-bipyridyl and Cu(I) Bromide system [5]

Although other controlled radical polymerization systems have been reported by various groups, ATRP remains the most powerful, versatile, simple, and inexpensive. One advantage of ATRP over other CRP processes is the commercial availability of all necessary ATRP reagents (alkyl halides, ligands and transition metals). Additionally, the dynamic equilibrium between dormant species and propagating radicals can be easily and appropriately adjusted for a given system by modifying the complexing ligand of the catalyst

Only ATRP has been able to polymerize a wide range of monomers including various styrenes, acrylates and methacrylates as well as other monomers such as acrylonitrile, vinyl pyridine, and dienes. ATRP commonly uses simple alkyl halides as initiators and simple transition metals (iron, copper) as the catalysts. These catalysts can be used in very low amounts, whereas, other controlled polymerization systems require the use of expensive reagents in much higher concentrations [5].

Atom Transfer (Overall Equilibrium)



Contributing Reactions

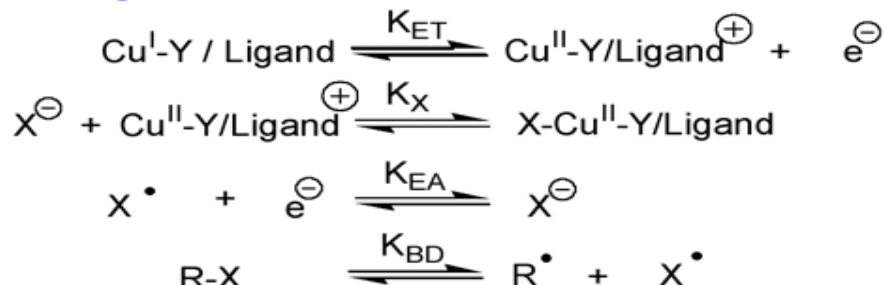


Figure 2.4: ATRP reaction progress [5]

2.3 Dye Sorption

Dyes are used in many industries, such as food, paper, rubber, plastics, cosmetics, and textile to color their products. There are more than 10,000 dyes available commercially. Most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin. The discharge of colored waste water from these industries into natural streams has caused many significant problems, such as increasing the toxicity and COD (Chemical Oxygen Demand) of the effluent, also reducing the light penetration, which results a harmful effect on photosynthetic phenomenon. The presence of dyes, in particular carcinogenic compounds, in surface and underground waters is not safe, pleasant, or welcomed. A lot of cases throughout the world are reported about the role of dyes in connection with variety of skin, lung, and other respiratory disorders. Recently, all governments have been under severe pressure by their people to stop this type of effluent to the public watercauses, unless it is treated properly. So the removal of color waste from waste effluents has become environmentally important. [6]

Several treatment techniques such as precipitation, filtration and neutralization have been developed in recent years. There are many studies dealing with dye removal, and many physico chemical methods have been tested but only that of adsorption is considered to be superior to other techniques. This is attributed to its low cost, easy

availability, simplicity of design, high efficiency, ease of operation, biodegradability, and ability to treat dyes in more concentrated form. Activated carbons are widely used as adsorbents because of their high adsorption capabilities for a large number of organic compounds. However, the price of activated carbons is relatively high, which limits their usage. As a result, many researchers investigate low cost substitutes to remove organic contaminants such as dyes from wastewater.

One possibility to address reactive dye removal is sorption onto suitable sorbents in fixed bed filters. Many sorbents have been tested for dye removal; however, most of them are non-regenerable throw-away products.

Ho et al. [7] studied sugarcane bagasse pith and Tunç et al.[8] studied cotton plant wastes as adsorbent. Some of other reported sorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin).

Acid dyes are sodium salts of organic sulfonic acids. Brightly colored, water soluble and reactive acid dyes are composed of ionizable anionic groups such as sulfonates, carboxylates or sulfates (Figure 2.5 and 2.6).

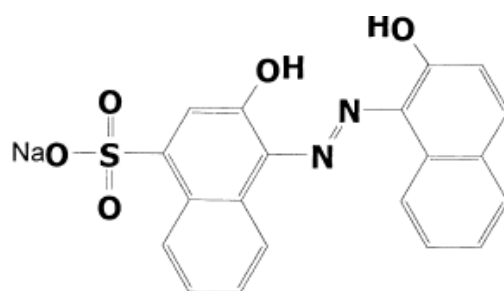


Figure 2.5 : Chemical Structure of calcon [10]

Moreover acid dyes are the most problematic with their high molecular weight, as they tend to pass through conventional treatment systems unaffected. [9]

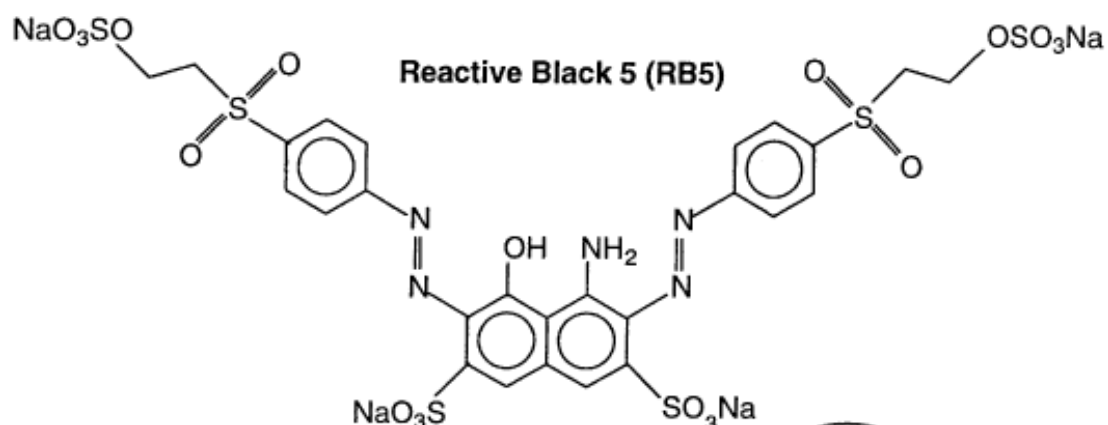


Figure 2.6: Chemical Structure of Ramazol Black Dye [3]

2.4 Dye Removal Technologies

The technologies can be divided into three categories: Biological, chemical and physical. All of them have advantages and disadvantages. Because of the high cost and disposal problems, many of these traditional methods for treating dye wastewater have not been widely applied at large scale in the textile and paper industries.

At the present time, there is no single process capable of adequate treatment, mainly due to the complex nature of the effluents [10,11]. In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way. (Table 2.1)

Table 2.1 Existing and emerging dye removal techniques [16]

	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation	Simple, economically feasible, attractive, publicly acceptable treatment	High sludge production, handling and disposal problems
	Flocculation		Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements
	Biodegradation		
	Adsorption on activated carbons	The most effective adsorbent, great capacity, produce a high-quality treated effluent	Ineffective against disperse 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
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemical utilization required
Emerging removal process	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

2.4.1 Biological methods

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants. However, their application is often restricted because of technical constraints. Biological treatment

requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin. In particular, due to their xenobiotic nature, azo dyes are not totally degraded [12, 13].

2.4.2 Chemical methods

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with Fe(II)/Ca(OH)_2 , electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

2.4.3 Physical methods

Different physical methods are also widely used, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis, etc.) and adsorption techniques. The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated waters, especially if the

sorbent is inexpensive and does not require an additional pre-treatment step before its application.

Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances [13].

3. EXPERIMENTAL

3.1 Materials and Instruments

3.1.1 Materials

DHPVC has been prepared from PVC powder supplied from SOLVIN S.A. (suspension polymer, with a K value of 64, granule diameter smaller than 180 μm).

GMA (Fluka), 2,2-Bipyridine (Aldrich), CuBr (Aldrich), Diethylene amine (Fluka), and all the other chemicals, solvents utilised were analytical grade commercial products.

For adsorption analysis Calcon (E-Merck) (empirical formula $\text{C}_{20}\text{H}_{13}\text{N}_2\text{NaO}_5\text{S}$), Ramazol Black (Dystar) and Everzol Black B and Everzol Turquoise Blue were obtained from Everlight Company, Taiwan.

3.1.2 Instruments

Perkin Elmer 25 UV-vis Spektrometer were used for analytical measurements, and spectra of the resins and the sorbed chemicals were obtained using Perkin Elmer Spectrum One Fourier Transform Infrared Spectrum in between wavenumbers of 650-4000 cm^{-1} . A total of 4 scans was collected for each spectrum.

3.2 Dehydrochlorination of PVC

13.5 g of PVC was dispersed in 100 mL of 10% KOH solution containing isopropyl alcohol-water. This mixture was refluxed for 10 h. The colour of the reaction mixture was changed from colorless to dark brown during the reaction. Then, degraded PVC was filtered and washed with excess of water, ethanol, and diethyl ether respectively. Then, the product was dried under vacuum at room temperature. The yield of the reaction is 9 g.

The soluble fractions in the degraded PVC were extracted with tetrahydrofuran (360 mL) by using Soxhlet extractor for 7 h. The insoluble part of the product was dried under vacuum.

3.2.1 Determination of Chlorine Content

To determine the chlorine content 0.2 g of DHPVC was added to the solution of 4.08 g of NaOH in 20 ml of distilled water. The mixture was shaken for 24 h in a continuous shaker with 270 rpm. At the end of the given time, the mixture was heated up to 60°C in a silicon bath for 2 h to complete the chlorine elimination and then cooled to room temperature and filtered.

Analysis of the chloride ions was performed by the mercuric thiocyanate method as described in the literature [14]. The chloride content was found as 3.4 mmol · g⁻¹ resin.

3.3 Graft Copolymerization of Poly (GMA) onto DHPVC by ATRP method

Graft polymerization of glycidyl methacrylate was achieved through chlorine initiation sites on the crosslinked PVC. A typical procedure is as follows:

0.105 g, (0.73 mmol) of CuBr, 0.344 g (2.2 mmol) of bipyridine ligand and 5 ml (0.036 mol) of glycidyl methacrylate (GMA) were put in a three necked flask equipped with a reflux condenser under nitrogen atmosphere. Polymer sample (0.1g) was added to the flask and the mixture was heated to 65 °C for 24 h. Vacuum dried sample weighed 1.96 g.

3.3.1 Determination of Epoxy Content

0.2015 GMA-*g* -PVC has been added to 20 ml of pyridine - HCl solution with 10 % HCl content. The mixture was refluxed for 1 hour to complete the ring opening reaction of the epoxy rings. Then the solution was filtered.

20 mL of Pyridine-HCl solution and then 2 ml of the filtered solution were titrated with 0.1 M NaOH solution. The epoxy content of the resin was calculated with respect to the differences between the NaOH consumptions in titrations.

The calculated epoxy content of the resin is 7.7 mmol · g⁻¹ resin.

3.4 Modification of Poly (GMA) graft copolymer by Diethyl amine

4 g of GMA-*g*-PVC was added to 35 mL of diethylamine (C₄H₁₁N) in a 100 ml of flask. The mixture was stirred for 24 h at room temperature, and then it was heated at 90°C in a thermo stated oil bath for 4 h.

The reaction content was poured into water, filtered and washed with an excess of water. The product was dried at room temperature in vacuum 24h. The yield was 5.8 g.

3.4.1 Determination of Amine Content

For determination of the amine content, 0.104 g of the polymer sample was left in contact with 10 ml of HCl (0.1 M) for 24 h. After filtration, 2 ml of the filtrate was taken and the acid content of the solution was determined by titration with 0.122 M NaOH solution in the presence of phenolphthalein color indicator.

10 ml of HCl solution and then 2 ml of the filtered solution were titrated with 0.1 M NaOH solution. The amine content of the resin was calculated with respect to the differences between the NaOH consumptions in titrations. A total amine content of the polymer was calculated as $4.69 \text{ mmol} \cdot \text{g}^{-1}$ resin.

3.5 Extraction of Dyes

Dye capacities of the resin were determined by mixing weighed amount of polymer sample (0.5 g) with 50 mL aqueous dye solution (0.5 g dye /50 mL buffer solution). In these experiments ramazol black, everzol black and everzol turquoise blue were used as dyes. For calcon 0.2 g dye / 50 ml buffer solution has been prepared. The mixture was stirred for 24 h and then filtered. Capacities were assigned by colorimetric analysis of residual dye contents.

3.6 Kinetics of dye sorption

In order to estimate the efficiency of the resin for trace dye, batch kinetic experiments were performed using highly diluted dye solutions 1 g dye / 100 mL distilled water. Then, 0.1 g of resin was added to the dye solution for this purpose. 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.

3.7 Regeneration of the beads

This process was performed by using 10% KOH in ethanol-water mixture. 0.1 g everzol black loaded resin was placed into 10 mL of KOH solution. This mixture was stirred for 24 h at room temperature and refluxed for 3 h. Regeneration capacity was found as 0.23 g per gram polymer.

4. RESULTS AND DISCUSSION

Thermal dehydrochlorination of commercial PVC was carried out heating in concentrated NaOH containing isopropanol 80 % - water 20 % mixture for 6 h. This method gave a black product and soluble polymer fraction was removed by using soxhlett extraction with THF. (Figure 4.1)

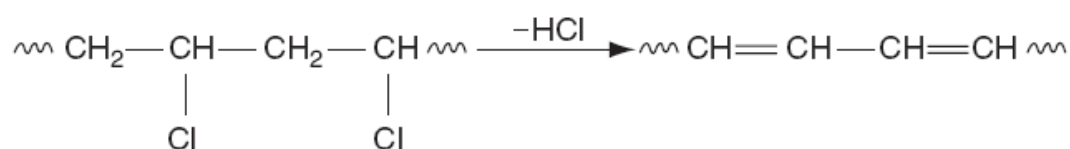


Figure 4.1 : Dehydrochlorination of PVC

Partial dehydrochlorination of PVC generates new double bonds, and these increase the availability of allylic chlorine atoms in the backbone. This shows that thermal stability of PVC decreases upon increase in dehydrochlorination. Unstable chlorine atoms in PVC in conjunction with suitable catalyst provide initiation sites for grafting . Chlorine content of the crosslinked PVC was found as 3.4 mmol/g polymer.

In this study ATRP method has been utilized for grafting glycidyl methacrylate onto DHPVC. Graft polymerization of glycidyl methacrylate can be achieved from chlorine atoms onto crosslinked PVC (Figure 4.2).

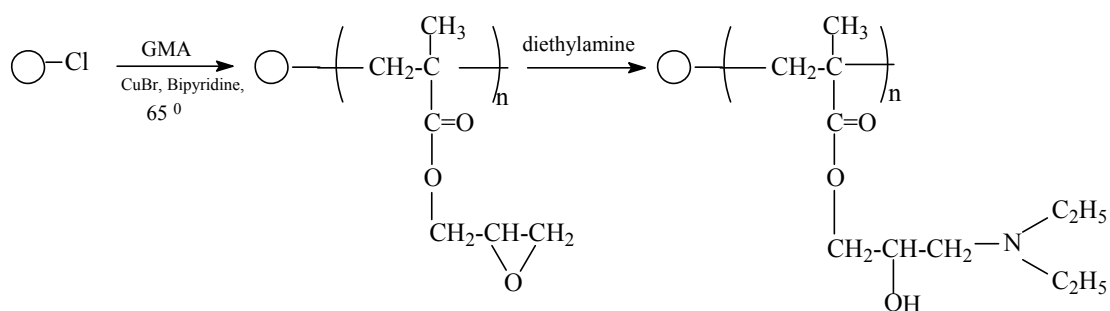


Figure 4.2 Synthesis of polymeric sorbent

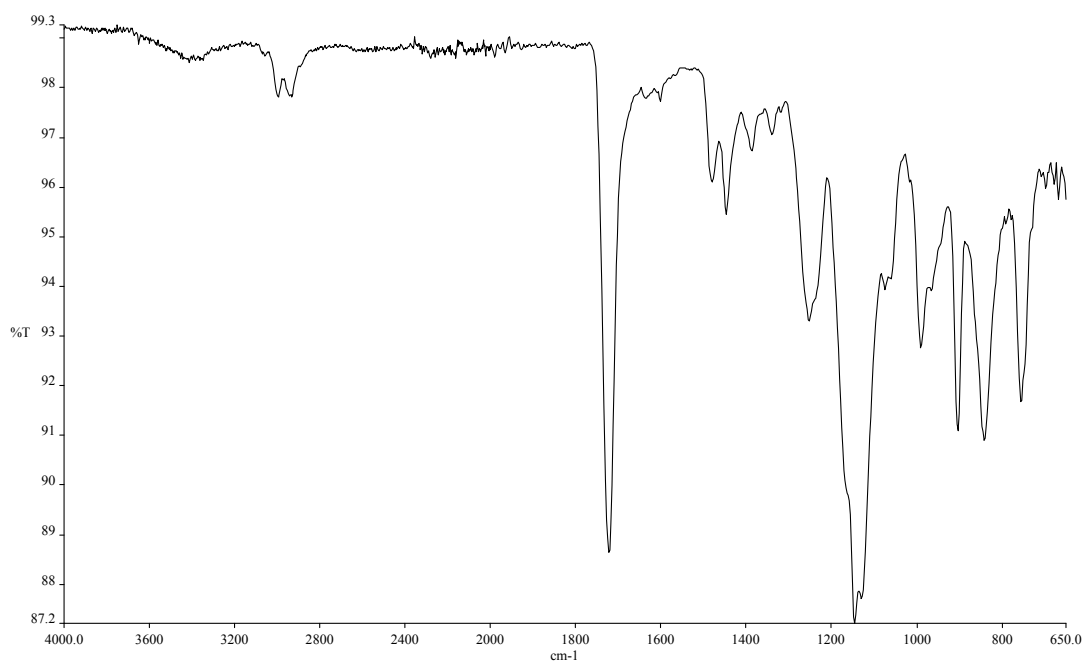


Figure 4.3 FT-IR spectrum of poly(GMA) grafted sorbent

In the polymerizations [CuBr]/[L] ratio was chosen as 1/3. The graft degree of the reaction reaches to 1580 % for 16 h.

The polymeric sorbent was characterized by using analytical and spectrophotometric methods. Epoxy content of the resin was determined as 7.7 mmol g⁻¹resin, by the pyridine–HCl method given in the literature [15]

FT-IR spectra of the resulting graft beads (Figure 4.3) represent strong C–O stretching vibrations at 1726 cm⁻¹, which indicate incorporation of the poly (glycidylmethacrylate) chains.

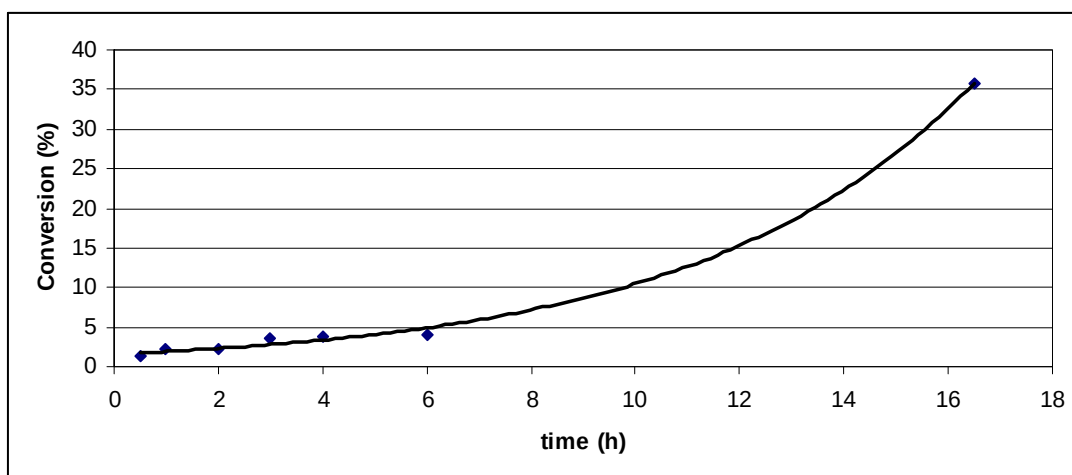


Figure 4.4 : Conversion of the graft copolymerization of glycidylmethacrylate onto DHPVC at 65 °C

[GMA]₀ = 7.6 mol/l; [CuBr] = 0.15 mol/l; [bpy] = 0.44 mol/l ; [DHPVC] = 20 g /lt

Figure 4.4 represents the conversion of graft copolymerization of GMA onto DHPVC in the presence of Cu (I) Br (1 equivalent) and bpy (3 equivalent) at 65 °C. The plot indicates that the concentration of growing radicals is constant during the polymerization. The reaction of epoxy rings in grafted PGMA with excess of diethylamine gives a tertiary amine containing resin with 4.69 mmol g⁻¹ resin amine functions .

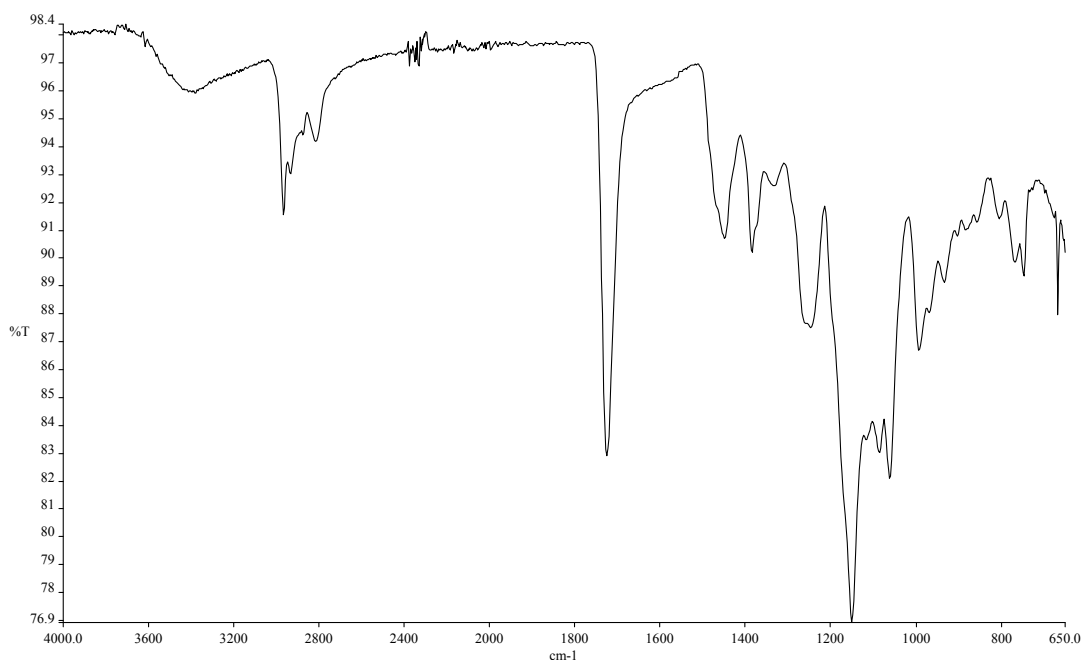


Figure 4.5 : FT-IR Spectrum of tertiary amine containing polymeric sorbent

Figure 4.5 shows the FT-IR spectrum of the resulting tertiary amine modified graft beads. N-H stretching vibration of the tertiary amine containing resin at 3440 cm^{-1} appears and epoxide ring vibration band disappears at 950 cm^{-1} .

4.1 Extraction of dyes

Dye extraction experiments were carried out simply by contacting wetted polymer samples with aqueous dye solutions at room temperature. Capacities were assigned by colorimetric analysis of residual dye contents. (Table 4.1)

Table 4.1 : Maximum Dye Sorption Capacities of the Resin

Dye	Capacity (g dye/g resin)	λ_{max} (nm)
Ramazol Black	0.45	597
Everzol Black	0.36	598
Calcon	0.30	545
Everzol Turquoise Blue	0.35	666

It has been reported that the basic mechanism in dyeing protein fibers with acid dyes is salt formation with amino groups as shown in Figure



Figure 4.6: Dye sorption Mechanism [2]

In a similar manner, the unshared electrons on tertiary amine of the resin will create a positive charge, due to the hybridization of the nitrogen atom, capable of forming the salt linkage with the anionic groups of the acid dye molecules [16].

Table 4.2 Maximum dye sorption capacities of the resin depending on pH

Dye	pH	Capacity (g dye / g resin)
Ramazol Black	2.0	0.40
	4.0	0.50
	8.0	0.50
Everzol Black	2.0	0.40
	4.0	0.50
	8.0	0.50
Calcon	2.0	-
	4.0	-
	8.0	0.20
Turquoise Blue	2.0	0.34
	4.0	0.70
	8.0	0.55

The resin shows reasonably high dye sorptions as high as 0.3-0.45 g dye / gram polymer resin. It is important to note that the resin can be used in a wide pH range (Table 4.2). There are no big differences depending on pH. This property is important in utilization of the resin in industrial applications.

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 [17,18].

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 sorbent includes many functional groups, so the net charge on sorbent, is also pH dependant.

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

4.2 Dye Sorption Kinetics of the Resin

This material is able to remove the anionic dyes completely even from highly diluted aqueous dye solutions which are highly important. We performed batch kinetic sorption experiments with highly diluted dye solutions (0.01 g dye / L water) to investigate the efficiency of the resin in the presence of trace quantities of dyes. Dye loading capacity–time plot in Figure 4.4 shows maximum sorption capacity within 60 min of contact time.

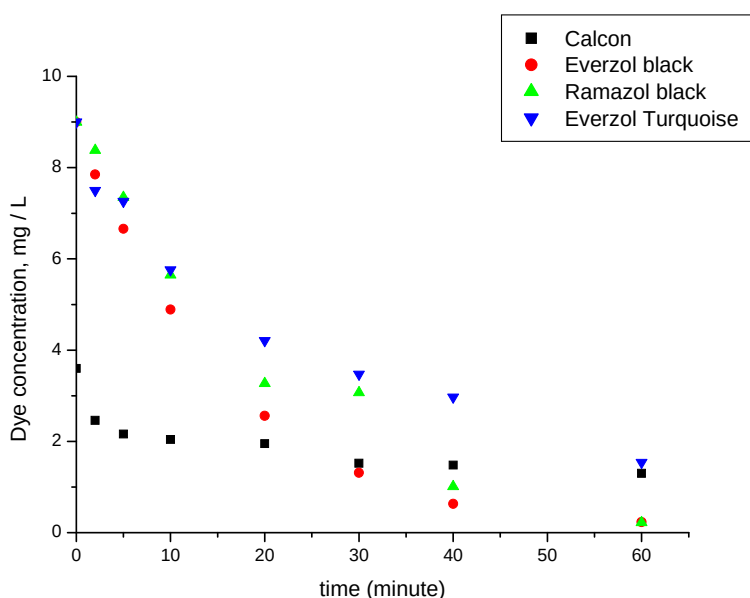


Figure 4.7: Dye loading capacity –time

More importantly, this material is able to remove the anionic dyes completely even from highly diluted aqueous dye solutions.

4.3 Regeneration of the Resin

Loaded polymer samples were treated with basic ethanol-water (80 % - 20 %) solution for 2 days at room temperature. The desorption capacity of the resin was found as 0.23 g dye / g resin for calcon. Loaded polymer samples, when treated with % 10 KOH become desorbed in a different range when compared with each other.

Alkaline regeneration works well for strong and weak basic sorbents and acid regeneration works for most dyes [19].

5. CONCLUSION

In this work, the tertiary amine modified DHPVC polymeric resin was synthesized to prepare an alternative adsorbent for removal of reactive dyes from wastewater. For this purpose graft copolymerization of GMA onto DHPVC was carried out using ATRP method. The epoxy rings in grafted PGMA reacted with excess of diethylamine to give a tertiary amine containing resin.

Flexibility of the side chains 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 textile dyes from aqueous mixtures. The polymeric resin has a potential as an adsorbent for removal of reactive dyes from textile wastewater because it can adsorb reactive dyes over a wide pH range.

The polymeric resin exhibited reasonably high dye sorptions as 0.3-0.45 g dye / gram showing that the resin can be used in a wide pH range.

The desorption capacity of the resin was found as 0.23 g dye / g resin for calcon.

The resulting graft polymer resin is highly effective for dye sorption and the resin format of the material makes it a possible column packing material.

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