ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

THE SYNTHESIS OF NEW POLYMERIC SORBENTS FOR REMOVAL OF ACIDIC AND BASIC DYES

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

Programme : Polymer Science and Technologies

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June 2009

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ASİDİK VE BAZİK BOYALARIN GİDERİLMESİ İÇİN YENİ POLİMERİK ABSORBANLARIN SENTEZLENMESİ

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FOREWORD

First of all, I want to thank my advisor, Prof. Dr. Bahire Filiz Şenkal, for her guidance during my research and study at Istanbul Technical University. Her perpetual energy and enthusiasm in research had motivated me.

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If I had a chance to choose my own family, I think I couldn't have found such a valuable one; I thank to my family for their support in my thesis studies, like the support they gave in all areas of my life.

June 2009

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Chemical Engineer

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ABBREVIATIONS

VI	**:** Vinyl imidazole
EGDMA	**:** Ethylene glycol dimethacrylate
TAB	**:** Tetraallyl ammonium bromide
PVBC	**:** Poly (vinyl benzyl chloride) resin
VBC	**:** Vinyl benzyl chloride
AIBN	**:** Azobisisobutyronitrile
TEMED	**:** Tetramethylethylenediamine
NMP	**:** 2-methyl pyrrolidone
PVI	**:** Poly (vinyl imidazoline) resin
QPVI	**:** Quaternized polyvinyl imidazoline resin

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THE SYNTHESIS OF NEW POLYMERIC SORBENTS FOR REMOVAL OF ACIDIC AND BASIC DYES

SUMMARY

Dye molecules, according to their charge, can be classified as: anionic (direct, acid, reactive), cationic (basic) and nonionic (disperse). Depending upon their structure, azo- and anthraquinonic- dyes are the two major classes and together represent 90% of all organic colorants. Most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin. The extensive use of dyes often poses pollution problems in the form of coloured wastewater discharge into environmental water bodies, which interferes with transmission of sunlight into streams therefore reduces photosynthetic activity. 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. Granular activated carbon is the most popular adsorbent and has been used with great success. However, although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents.
In this study, four different sorbents were synthesized and chracterized by using analitical and spectrophotometric methods. These sorbents were used for removal of dyes from water.

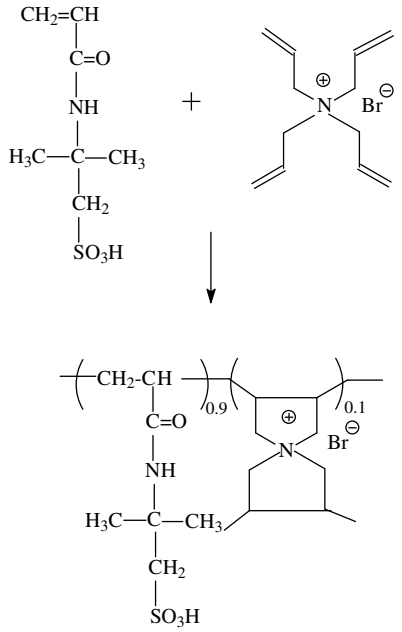
Preparation of Hydrogel

Copolymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid with TAB in aqueous solutions (20%) with $K_2S_2O_8$-TEMED initiator system at 0 ^{0}C was performed by using redox polymerization. The rigid gel obtained is completely homogeneous and transparent.
The structures of the crosslinked polymer gels can be depicted as shown below:

The hydrogel has high dye sorption capacity (Table 1).

Table 1: Dye sorption capacities of the hydrogel

Dye	Capacity (g dye / g gel)	Λ_{max} , nm
Methylene Blue	0.97	664
Crystal violet	0.85	590



Scheme 1: Preparation of Hydrogel

The concentration – time plot (Figure 1.) shows that within about 50 minutes contact time, the dye concentration falls to zero.

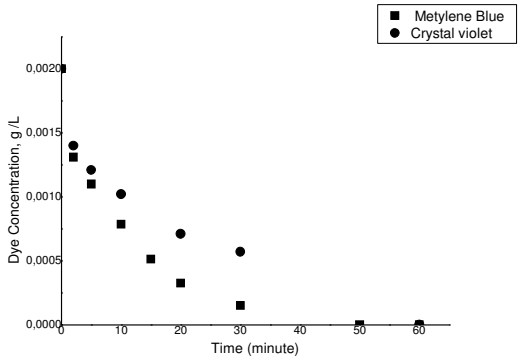
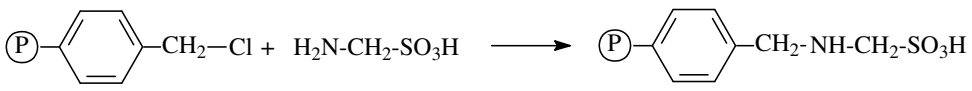


Figure 1: Dye sorption kinetics of the hydrogel from dilute aqueous solution

Preparation of Aminosulfonic Acid Based Resin (PVBC)

This resin was synthesized starting from crosslinked polyvinyl benzyl chloride-EGDMA (10%). The crosslinked co-polymer was reacted with aminosulfonic acid to obtain aminosulfonic acid containing resin.



Scheme 2

The resin was used to remove acidic and basic dyes from water. The maximum sorption was given in Table 2.

Dyes concentration–time plot in Figure 2 shows that within about 60 min of contact time, the resin can remove dyes completely.

Table 2: Sorption capacities of the PVBC resin

Dye	Capacity (g dye / g resin)	λ (nm)
Crystal Violet	0.15	590
Methylene Blue	0.11	664
Everzol Black	0.11	598
Everzol Blue	0.12	591
Ramazol Black	0.16	597
Calcon	0.13	545

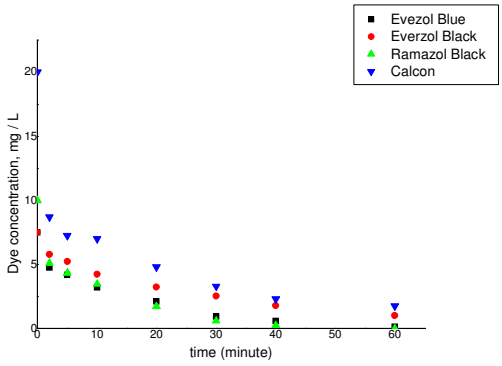
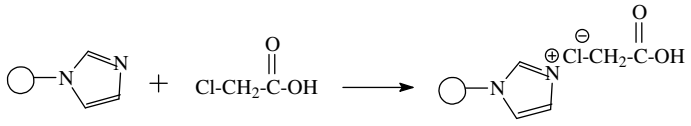


Figure 2: Acidic dye sorption kinetics of PVBC resin

Preparation of the Quaternized Polyvinyl Imidazoline (QPVI) Resin

Crosslinked polyvinylimidazoline resin was prepared reaction with vinylimidazoline-EGDMA (10%) by using suspension polymerization method. Quaternization was performed with chloroacetic acid.



Scheme 3

Quaternary amine containing materials can be used effectively to remove acidic dyes from water. Also, carboxylic acid group on the polymer can interacted with basic dyes. According to the Table 3, the resin can be used to remove both acidic and basic dyes from water.

Table 3: Sorption capacities of the QPVI resin

Dye	Capacity (g dye / g resin)	λ (nm)
Crystal Violet	0.10	590
Methylene Blue	0.40	664
Everzol Black	0.12	598
Ramazol Black	0.14	597
Calcon	0.20	545

According to the concentration-time plots (Figure 3), concentration of the acidic dye in water decreases rapidly because of hydrophilic character of the resin.

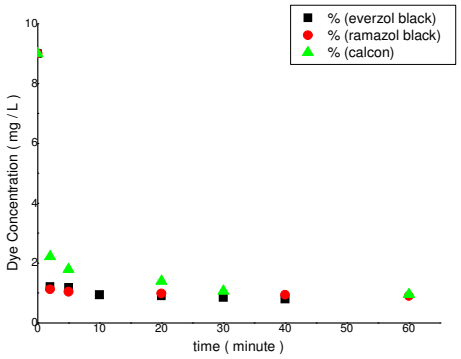


Figure 3: Acidic dye sorption kinetics of QPVI resin

ASİDİK VE BAZİK BOYALARIN GİDERİLMESİ İÇİN YENİ POLİMERİK ABSORBANLARIN SENTEZLENMESİ

ÖZET

Boya molekülleri yüklerine göre şu şekilde sınıflandırılabilir: anyonik, katyonik ve noniyonik. Yapılarına göre ise, azo- ve antrokinon- boyalar olarak iki sınıfa ayrılırlar ve bütün boyar maddelerin %90' ında birlikte bulunurlar. Birçoğunun, kompleks aromatik moleküler yapısı ve sentetik kaynaklı olmasına bağlı olarak biyolojik bozunması zordur. Boyaların kullanımı boyalı suyun çevre suyuyla karışması, kirlilik problemi gibi görünse de, bunun yanında güneş ışığının bu suya iletimini engellediğinden dolayı fotosentez etkinliğini de azaltmaktadır. Sıcaklık ve ışığın sabit olduğu durumda, atık sudaki kompleks boya molekülleri arıtmanın geleneksel metotlarla (birincil ve ikincil arıtma sistemleri gibi) yapılması imkansızdır. Adsorbsiyon işlemi cazip, alternatif arıtma sağlayan diğer bir yöntemdir. Aktif karbon en çok bilinen ve iyi sonuç alınan bir adsorbandır. Ancak aktif karbonun pahalı oluşu, her ne kadar tercih edilen bir adsorban olsa da, yaygın olarak kullanılışını sınırlamaktadır. Boyar maddelerin atıktan giderilmesinin ekonomik maliyetini azaltmak için alternatif ve ucuz adsorbanların elde edilme çalışmaları yaygınlaşmaktadır.
Bu çalışmada, dört farklı adsorban sentezlenerek, elde edilen malzemeler analitik ve spektrofotometrik yöntemlerle karakterize edilmiştir. Taşıdıkları fonksiyonel gruplara bağlı olarak adsorbanlar sulu çözeltilerden asidik ve bazik boyaların giderilmesi için kullanılmıştır.

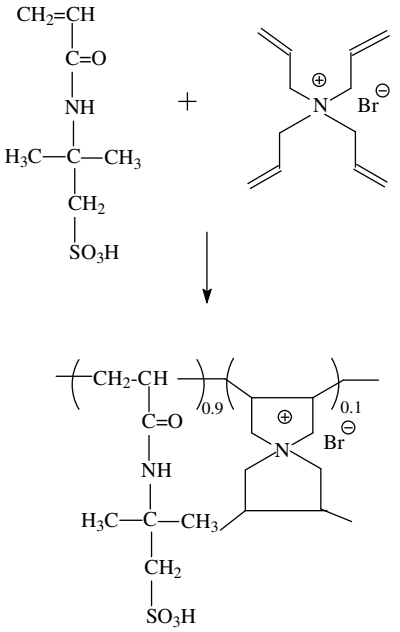
Hidrojelin Hazırlanışı

0 ^{o}C'de $K_2S_2O_8$-TEMED başlatıcı sistem ile sulu ortamda (20%) akrilamido-2-metil-1-propansülfonik asit ile TAB (tetraallil amonyum bromür) 'ın kopolimerizasyonu redoks polimerizasyonu kullanılarak gerçekleştirilmiştir. Elde edilen jel tamamen homojen ve şeffaftır. Çapraz bağlı polimer jelinin yapısı aşağıda verilmiştir.

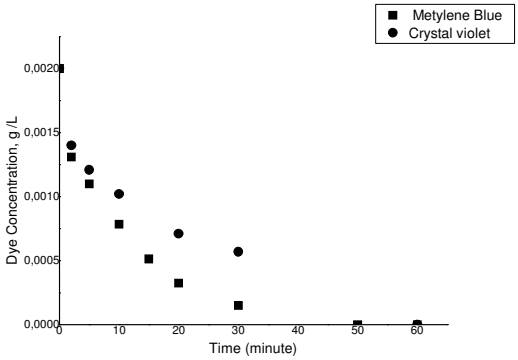
Hidrojel yüksek boya adsorbsiyon kapasitesine sahiptir (Tablo 1).

Tablo 1: Hidrojelin boya adsorblama kapasiteleri

Boya	Kapasite (g boya / g jel)	$\Lambda_{maksimum}$, nm
Metilen Blue	0.97	664
Kristal Violet	0.85	590



Şema 1: Hidrojelin hazırlanışı

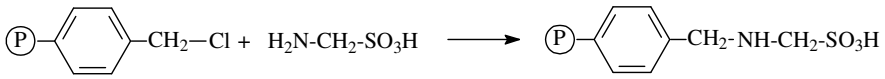


Şekil 1: Hidrojelin boya adsorblama kinetik sonuçları

Konsantrasyon-zaman grafiğinden, hidrojelin 50 dakika içerisinde, boya konsantrasyonunu sıfıra düşürdüğü görülmektedir.

Aminosülfonik Asit Bazlı Reçinenin Hazırlanışı (PVBC)

Reçinenin sentezi poli(vinil benzil klorür) - EGDMA (%10) ile süspansiyon polimerizasyonu ile gerçekleştirilmiştir. Çapraz bağlı kopolimer aminosülfonik asit içeren reçine eldesi için aminometansülfonik asit ile tepkimeye sokulur.

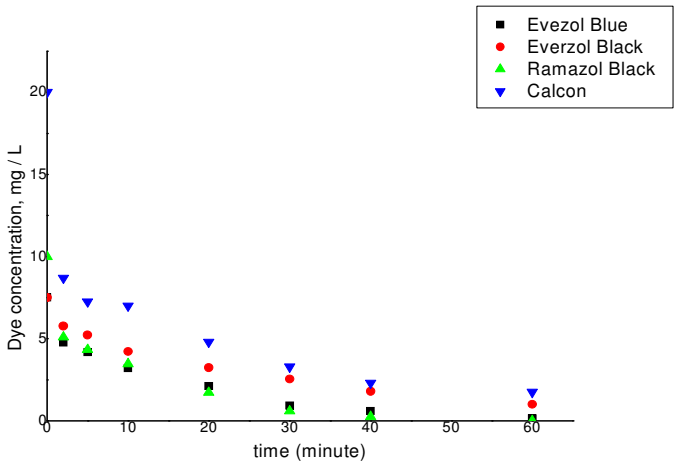


Şema 2.

Reçine asidik ve bazik boyaların giderilmesi için kullanılmıştır. Maksimum adsorpsiyon sonuçları Tablo 2' de verilmiştir.

Tablo 2: PVBC reçinesinin adsorpsiyon kapasiteleri

Boya	Kapasite (gr boya / gr reçine)	λ (nm)
Kristal Violet	0.15	590
Metilen Blue	0.11	664
Everzol Black	0.11	598
Everzol Blue	0.12	591
Ramazol Black	0.16	597
Calcon	0.13	545

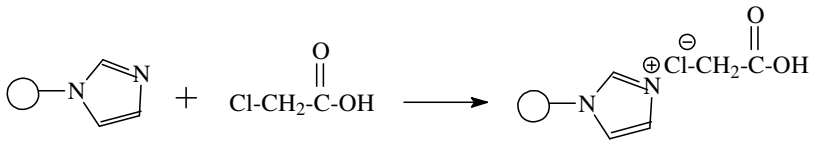


Şekil 2: PVBC reçinesinin asidik boya adsopblama kinetik sonuçları

Boya konsantrasyonu- zaman grafiği ile (Şekil 2) 60 dakika gibi bir zamanda reçinenin boyayı tamamen giderdiği görülmektedir.

Kuarterner Polivinil İmidazol Reçinenin Hazırlanışı (QPVI)

Çapraz bağlı polivinil imidazol reçine süspansiyon polimerizasyon metodu kullanılarak vinil imidazol ile EGDMA(%10) 'ın kopolimerizasyonu ile hazırlanmıştır. Kuarternizasyon kloroasetik asit ile gerçekleştirilmiştir.

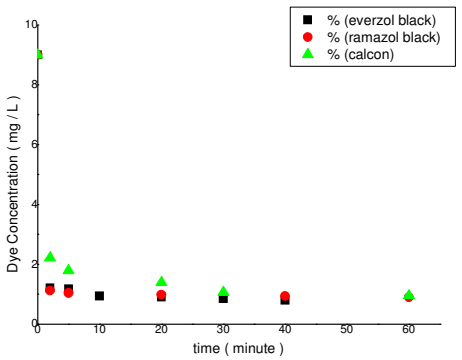


Şema 3.

Kuarterner amin içeren malzemeler asidik boyaların sudan ayrılması için etkin olarak kullanılabilir. Polimerdeki karboksilik asit grupları da bazik boyalarla etkileşebilir. Tablo 3' e göre reçine asidik ve bazik boyaların giderilmesi için kullanılmıştır.

Tablo 3: QPVI reçinenin adsorbsiyon kapasiteleri

Dye	Capacity (g dye / g resin)	λ (nm)
Crystal Violet	0.10	590
Methylene Blue	0.40	664
Everzol Black	0.12	598
Ramazol Black	0.14	597
Calcon	0.20	545



Şekil 3: QPVI reçinenin asidik boya adsorplama kinetik sonuçları

Boya konsantrasyonu-zaman grafiğine göre, (Şekil 3) reçinenin hidrofilik karakterinden dolayı sudaki asidik boya konsantrasyonunun hızla düştüğü görülmektedir.

1. INTRODUCTION

Many industries, such as dyestuffs, textile, paper, and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater. It is recognized that public perception of water quality is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that 2% of dyes that are produced are discharged directly in an aqueous effluent. Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms. However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat, and oxidizing agents. During the past three decades, several physical, chemical, and biological decolorization methods have been reported; few, however, have been accepted by the paper and textile industries. The choice of suitable coloring methods, from the many that are available, is therefore important.

In this study, four different polymeric sorbents have prepared for the removal of dyes from aqueous solutions. These sorbents have been characterized by using analytical methods and spectroscopic methods. Also, dye removal characteristics of the resins have been investigated.

2. TEORITICAL PART

2.1. Properties and Characterization of Functionalized Polymers

There are a number of considerations in the choice of the functional polymers to be used in a specific application functionalized polymer must posses 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 in soluble in our solvents, they offer the greatest is of processing.
2- They can be prepared in the form of spherical beads and can be separated from low molecular weight contamined by simple filtration and washing with very use solvents.
3- Polymer beads with very low degrees of crosslinking swell extensively, exposing their inner reactive groups to the soluble reagents.
4- More highly crosslinked resins may be prepared with very porose 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 encouraged with enhanced properties.

a) Microporose 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 containing no additional solvent.
Swellable polymers are found to offer advantage over non-swellable polymers of particular interest is their lower fragility, 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 also prepared by suspension polymerization using higher amounts of crosslinking agents but with the inclusion of an inert solvent as diluents for the monomer phase.

Macroreticular resin is non-swelling and a macro pores a rigid material with a high crosslinking it retains its overall shapes and volume when the precipitate is removed.

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 sever 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 rubit and extreme change in the nature of the solvating media and can not be subjected to study and high pressures. Macropores resins with less than %1 crosslinking generally have low mechanical stability while macropores resins with more than %8 crosslinking are mechanically stable but unfortunately give rise to acute.

2.2. Hydrogels

Hydrogel is a network of hydrophilic polymers that can hold a large amount of water. A tree-dimensional network is formed by crosslinking polymer chains. Crosslinking can be provided by covalent bonds, hydrogen bonding, van der Waals interactions, physical entanglements, or hydrophobic interactions [1].

Hydrogels are three-dimensional hydrophilic polymer networks that absorb water but do not dissolve in water. The extent of volume change due to water absorption varies with the degree of ionization of the gel and for a superabsorbent it may be as large as 500 fold. The volume change is understood as a phase transition which is a manifestation of competition among three forces on the gel—the positive osmotic pressure of counterions, the negative pressure due to polymer-polymer affinity, and the rubber elasticity of the polymer network. The balance of these forces varies with changes in temperature or solvent properties [2].

The interaction between polymer and dye leading to polymer–dye complex formation exhibits many interesting and important practical features. Coulombic, hydrophobic, and steric interactions are major factors governing the thermochemical and dynamic aspects of complex formation. The interactions of the hydrogels with dyes are of principal interest [3].

Since the environmental pollution is increasing day-by-day due to the increase in industrialization and urbanization, the need to reduce the pollution particularly in wastewater streams of hydrometallurgical and other industries is important. Among the environmental pollutions, heavy metal ions and dyes have gained relatively more significance due to their toxicity. Heavy metal ions in wastewater come from battery manufacturing, automobile emissions, mining activities and alloy industries. Also, many industries such as plastics, paper, textile and cosmetics use dyes in order to colour their products. Moreover, the colour they impart is very desirable to the water consumers. Therefore, colour removal from wastewater is a major environmental problem. Several treatment techniques such as precipitation, filtration and neutralization have been developed in recent years, but adsorption is generally preferred for the removal of metal ions and dyes from wastewater because of its high efficiency, easy handling and availability of different adsorbents [4].

2.2.1. Usage of hydrogel as polymeric sorbent

Removal of heavy metal ions and dyes by using polymers having different functional groups would be of great importance in environmental applications due to their high adsorption capacities, especially regeneration abilities and reuse for continuous processes. For this purpose, different polymeric adsorbents especially hydrogels having different functional groups, which have complexing ability with metal ion and dyes, have been investigated in the preceding literature. Hydrogels can be defined as three-dimensional networks of polymers that are water-swollen. According to the type of the functional group in polymer matrix, the properties of hydrogels can be changed with temperature, pH, solvent composition and salt concentration. The hydrogels having functional groups can be obtained by copolymerization of the monomers with different functional groups or post-modification of polymerized products. The second option is generally preferred to prepare materials, which are difficult to obtain by direct polymerization of the corresponding monomers [4].

2.3. Hazardous of Dyes

Many textile manufacturers use dyes that release aromatic amines (e.g., benzidine, toluidine). Dyebath effluents may contain heavy metals, ammonia, alkalai salts, toxic solids and large amounts of pigments - many of which are toxic. About 40 percent of globally used colorants contain organically bound chlorine, a known carcinogen. Natural dyes are rarely low-impact, depending on the specific dye and mordant used. Mordants (the substance used to "fix" the color onto the fabric) such as chromium are very toxic and high impact. The large quantities of natural dyestuffs required for dyeing, typically equal to or double that of the fiber's own weight, make natural dyes prepared from wild plants and lichens very high impact [5].

Synthetic dyes have been increasingly used in the textile, paper, rubber, plastic, cosmetics, and pharmaceutical and food industries because of their ease of use, inexpensive cost of synthesis, stability and variety of colour compared with natural dyes. Today 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 extensive use of dyes often poses pollution problems in the form of coloured wastewater discharge into environmental water bodies, which interferes with transmission of sunlight into streams therefore reduces photosynthetic activity. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic. 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. Use of variety of dyes and chemicals in the dyeing processes causes considerable variation in the wastewater characteristics like pH, colour and chemical oxygen demand (COD). 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 and readily available. Granular activated carbon is the most popular adsorbent and has been used with great success, but is expensive. Consequently, many investigators have studied the feasibility of using low cost substances, such as plum kernels, chitin, chitosan, perlite, natural clay, bagasse pith, fly ash, boiler bottom ash, bagasse fly ash, rice husk, peat, banana pith orange peel, Eichhornia ash, saw dust, walnut shells charcoal, etc. as adsorbents for the removal of dyes from wastewaters [6].

2.4. Dye Removal Techniques

Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater. It is recognized that public perception of water quality is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater [7]. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [8].

Over 100.000 commercially available dyes exist and more than 7×10^5 tonnes per year are produced annually [9,10]. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that two per cent of dyes that are produced are discharged directly in aqueous effluent. Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms [11,12]. However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents [13,14].

During the past three decades, several physical, chemical and biological decolorization methods have been reported; few, however, have been accepted by the paper and textile industries [15]. Amongst 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 coloring materials [16-18]. If the adsorption system is designed correctly, it will produce a high-quality treated effluent. Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies. However, although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents.

Recently, numerous 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 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).

2.5. Technologies Available for Color Removal

2.5.1. General considerations

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 wastewater have not been widely applied at large scale in the textile and paper industries.

Table 2.1: Principal existing and emerging processes for dye removal

	Technology	Advantages	Disadvantages
Conventional treatment proceses	Coagulation Flocccculation Biodegradation	Simple,economically feasible Economically, attractive,publicly acceptable treatment	High sludge production,handling and disposal problems Slow process,necessary to create an optimal favorable environment,maintance and nutrition requirements
	Adsorbtion 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 seperations	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 efective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost,chemical 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)

At the present time, there is no single process capable of adequate treatment, mainly due to the complex nature of the effluents [19,20]. In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way.

There are several reported methods for the removal of pollutants from effluents (Table 2.1).

2.5.2. Biological treatments

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 [21]. 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 [20]. In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

2.5.3. 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.

2.5.4. 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 [22]. 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.

2.6. Color Removal Using Commercial 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, amongst all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater [23, 24]. 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 straightforward, and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications [25]. This has led many workers to search for more economic adsorbents.

2.6.1. Non-conventional low-cost adsorbents and removal of dyes

Due to the problems mentioned above, 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. According to Bailey et al. [26], 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.

2.6.2. Waste materials from agriculture and industry

The by-products from the agricultural and industrial industries could be assumed to be low-cost adsorbents since they are abundant in nature, inexpensive, require little processing and are effective materials.

2.6.3. Activated carbons from solid wastes

Commercially available activated carbons (AC) are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents [27]. Because of its availability and cheapness, coal is the most commonly used precursor for AC production [28]. Coal is a mixture of carbonaceous materials and mineral matter, resulting from the degradation of plants. The sorption properties of each individual coal are determined by the nature of the original vegetation and the extent

of the physical–chemical changes occurring after deposition [29]. Coal based sorbents have been used for dye removal. However, since coal is not a pure material, it has a variety of surface properties and thus different sorption properties.

Plentiful agricultural and wood by-products may also offer an inexpensive and renewable additional source of AC. These waste materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low-cost by-products. So, their conversion into AC would add economic value, help reduce the cost of waste disposal and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbons.

A wide variety of carbons have been prepared from agricultural and wood wastes, such as bagasse, coir pith, banana pith, date pits, sago waste, silk cotton hull, corn cob, maize cob, straw, rice husk, rice hulls, fruit stones, nutshells, pinewood, sawdust, coconut tree sawdust, bamboo, cassava peel. There are also several reports on the production of AC from various city wastes and industrial by – products such as waste PET bottles, waste tires, refuse derived fuel, wastes generated during lactic acid fermantation from garbage, sewage sludges, waste newspaper, waste carbon slurries and blast furnace slag [30-35].

The excellent ability and economic promise of the activated carbons prepared from by-products have been recently presented and described. However, the adsorption capacities of a carbon depend on the the different sources of raw materials, the history of its prepartion and treatment conditions such as pyrolysis temperature and activation time.

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 posses not only a porous texture, but also high surface area. Guo et al. showed that the adsorption does not always increase with surface area. Besides the physical structure, the adsorption capacitiy of a given carbon is strongly influenced by the chemical nature of the surface. The acid and base character of a carbon character influences the nature of the dye isotherms. The adsorption capacitiy depends also on the accessibility of the pollutants to the inner surface of the adsorbent, which depends on their size. The specific sorption mechanisms by which the adsortion of dye takes place on these adsorbents are still not clear. This is because adsorption is a complicated process depending on several interactions such as electrostatic and non-electrostatic (hydrophobic) interactions.

Although much has been accomplished in terms of sorption properties and kinetics, much work is stil necessary to identify the sorption mechanisms clearly.

2.7. Natural Materials

2.7.1. Clays

Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ionexchange, clay materials are strong candidates as adsorbents. Clay materials possess a layered structure and are considered as host materials. They are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite [36]. 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 sorption properties also come from their high surface area and high porosity [37]. Montmorillonite clay has the largest surface area and the highest cation exchange capacity.

In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and Fuller's earth for their capacity to adsorb not only inorganic but also organic molecules. Clay minerals exhibit a strong affinity for both heteroatomic cationic and anionic dyes. 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 dyes on clay minerals is mainly dominated by ion-exchange processes.

2.7.2. Siliceous materials

The use of natural siliceous sorbents such as silica beads, glasses, alunite, perlite and dolomite for wastewater is increasing because of their abundance, availability and low price. Among inorganic materials, silica beads deserve particular attention [38], 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. Moreover, the surface of siliceous materials contains acidic silanol (among other

surface groups) which causes a strong and often irreversible non-specific adsorption. For that reason, it is necessary to eliminate the negative features of these sorbents. In order to promote their interaction with dyes, the silica surface can be modified using silane coupling agents with the amino functional group.

Another sorbent from siliceous materials to adsorb dye is alunite [39]. Alunite is one of the minerals of the jarosite group and contains approximately 50% SiO_2. However, untreated alunite does not have good adsorbent properties. After a suitable process, alunite-type layered compounds are useful as adsorbents for removing color. Alunite is so cheap that regeneration is not necessary. The surface charge on the sorbent and the pH play a significant role in influencing the capacity of alunite towards dyes.

Other siliceous materials such as dolomite, perlite and glass have been proposed for dye removal**.** Dolomite is both a mineral and a rock. Outstanding removal capability of dolomite for dye uptake has been demonstrated [40].

It was suggested that 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.

2.7.3. Zeolites

Zeolites are highly porous aluminosilicates with different cavity structures. Their structures consist of a three dimensional framework, having a negatively charged lattice. The negative charge is balanced by cations which are exchangeable with certain cations in solutions. 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. Its characteristic tabular morphology shows an open reticular structure of easy access, formed by open channels of 8–10 membered rings. Clinoptilolite has been shown to have high selectivity for certain pollutants. 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. Several studies have been conducted on the sorbent behavior of natural zeolites [41-43]. However, raw clinoptilolite was not suitable for the removal of reactive dyes due to extremely low sorption capacities [44].

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

2.8. Biosorbents

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 from solutions. These biosorbents and their derivatives contain a variety of functional groups which can complex dyes. The biosorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons, and can reduce dye concentration to ppb levels. Biosorption is a novel approach, competitive, effective and cheap.

2.8.1. Chitin and chitosan

The sorption of dyes 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. Chitin, a naturally occurring mucopolysaccharide, has been found in a wide range of natural sources such as crustaceans, fungi, insects, annelids and molluscs. However, chitin and chitosan are only commercially extracted from crustaceans (crab, krill, and crayfish) primarily because a large amount of the crustacean's exoskeleton is available as a by-product of food processing [45]. Utilization of industrial solid wastes for the treatment of wastewater from another industry could be helpful not only to the environment in solving the solid waste disposal problem, but also to the economy.

Chitin contains 2-acetamido-2-deoxy-b-D-glucose through a β (1→ 4) linkage. This waste product is second only to cellulose in terms of abundance in nature. Chitosan contains 2-acetamido-2-deoxy-b-D-glucopyranose and 2-amino-2-deoxy-b-D-glucopyranose residues. 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 hydroxy functional groups showing high potential for adsorption of a wide range of molecules, including phenolic compounds, dyes and metal ions [46]. This biopolymer represents an attractive alternative to other biomaterials because of its physico-chemical characteristics, chemical stability, high reactivity, excellent chelation behavior and high selectivity toward pollutants.

Both batch contacting and column processes are available for chitosan materials with solution containing dyestuffs [47]. In sorption columns, chitin and chitosan are often used as powder or flake forms. This technique usually causes a significant pressure drop in the column. Moreover, another limitation of chitosan is that it is soluble in acidic media and therefore cannot be used as an insoluble sorbent under these conditions, except after physical and chemical modification. To avoid these problems, crosslinked beads have been developed. 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 and become 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.

There are, of course, disadvantages of using chitosan in wastewater treatment. 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. These parameters, determined by the conditions selected during preparation, control swelling and diffusion properties of the biopolymer and influence its characteristics. Performance is dependent on the type of material used and the efficiency of adsorption depends on the accessibility of sorption sites. The uptake is strongly pH-dependent. Dye molecules have many different and complicated structures. This is one of the most important factors influencing adsorption. There is, as yet, little information in the

literature on this topic. The traditional and commercial source of chitin is from shells of crab, shrimp and krill that are wastes from the processing of marine food products. However, this traditional method of extraction of chitin creates its own environmental problems as it generates large quantities of waste and the production of chitosan also involves a chemical deacetylation process. These problems can explain why it is difficult to develop chitosan-based materials as adsorbents at an industrial scale.

The results presented above show that chitosan-based materials may be promising biosorbents for adsorption processes since they demonstrated outstanding removal capabilities for dyes.

2.8.2. Peat

Peat is a porous and rather complex soil material with organic matter in various stages of decomposition. Based on the nature of parent materials, peat is classified into four groups, namely moss peat, herbaceous peat, woody peat and sedimentary peat. This natural material is a plentiful, 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.

However, when raw peat is used directly as an adsorbent, there are many limitations: Natural peat has a low mechanical strength, a high affinity for water, poor chemical stability, a tendency to shrink and/or swell, and to leach fulvic acid [48,49]. Chemical pretreatment and the development of immobilized biomass beads can produce a more robust medium. As with other sorbents, chemical processes are also used for improving sorption properties and selectivity.

The mechanism by which dyes are adsorbed onto peat has been a matter of considerable debate. Different studies have reached different conclusions. Various pollutant- binding mechanisms are thought to be involved in the biosorption process, including physical adsorption, ion-exchange, complexation, adsorption–complexation and chemisorption [50]. 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.

2.8.3. Biomass

Decolorization and/or bioadsorption of dye wastewater by (dead or living) biomass, white-rot fungi and other microbial cultures were the subject of many studies reviewed in several recent papers. In particular, these studies demonstrated that biosorbents derived from suitable microbial biomass can be used for the effective removal of dyes from solutions since certain dyes have a particular affinity for binding with microbial species [51,52]. The use of biomass for wastewater is increasing because of its availability in large quantities and at low price. Microbial biomass is produced in fermentation processes to synthesize valuable products such as antibiotics and enzymes. In such processes, a large amount of by-products is generated, which can be used in biosorption of pollutants.

The major advantages of biosorption technology are its effectiveness in reducing the concentration of dyes to very low levels and the use of inexpensive biosorbent material. Fungal biomass can be produced cheaply using relatively simple fermantion techniques and inexpensive growth media [53]. The use of biomass is especially interesting when the dye-containing effluent is a very toxic. Biosorption is also an emerging technology that attempts to overcome the selectivity disadvantage of conventional adsorption processes. The use of that rather than live biomass eliminates the problems of waste toxicity and nutrient requirements. Biomass adsorption is effective when conditions are not always favorable for the growth and maintenance of the microbial population.

Dyes vary greatly in their chemistries and their interactions with microorganisms depend on the chemistry of a particular dye. There is also limited information available on the interactions between biomass and dyes [54]. This can be explained by the fact that decolorization by living and dead cells involves several complex mechanisms such as surface adsorption, ion-exchange, complextion (coordination), complextion-chelationand microprecipitation. Cell walls consisting mainly of pollysaccharides, proteins and lipids offer many functional groups. The dyes can interact with these active groups on the cell surface in a different manner. The accumulation of dyes by biomass may involve a combination of active, metabolism-dependent and passive transport mechanisms starting with the diffusion of the adsorbed solute to the surface of the microbial cell [55]. Once the dye has diffused to the surface, it will bind to sites on the cell surface.The precise binding mechanisms

may range from physical (i.e.electrostatic or van der Walls forces) to chemical binding (i.e.ionic and covalent). However, it is now recognized that the efficiency and the selectivity of adsorption by biomass are due to ion-exchange mechanisms.

Biosorption processes are particularly suitable for the treatment of solutions containing dilute (toxic) dye concentration. Biosorption is a promising potential alternative to convertional processes for the removal of dyes [56]. However, these technologies are still being developed and much more work is required.

2.9. Miscellaneous Sorbents

Other materials have been studied as low-cost sorbents, such as starch [57] and cyclodextrins [58]. Next to cellulose, starch is the most abundant carbohydrate in the world and is present in living plants as an energy storage material. Starches are mixtures of two polyglucans, amylopectin and amylose, but they contain only a single type of carbohydrate, glucose. They are composed of α-D-glucose units linked together in 1,4-position. Amylose is nearly unbranched, while amylopectin is highly branched with the branches connected via the a-1,6-position of the anhydroglucose unit. Starch is used mostly in food applications, but there is a growing interest in its utilization as a renewable raw material for non-food industrial applications. Starches are unique raw materials in that they are very abundant natural polymers, inexpensive and widely available in many countries. They possess several other advantages that make them excellent materials for industrial use. They have biological and chemical properties such as hydrophilicity, biodegradability, polyfunctionality, high chemical reactivity and adsorption capacities. However, the hydrophilic nature of starch is a major constraint that seriously limits the development of starch based-materials. Chemical derivatisation has been proposed as a way to solve this problem and to produce water resistant sorbents.

More important than starch is its cyclic derivative, cyclodextrin. Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to twelve glucose units. The CD molecules are natural macrocyclic polymers, formed by the action of an enzyme on starch [59]. Beta-cyclodextrins containing seven glucose units are available commercially at a low cost. The most characteristic feature of CDs is the ability to form inclusion compounds with various aromatic molecules, including dyes. CDs possess a hydrophobic cavity in which a pollutant can be trapped.

Like other polysaccharides, starches and cyclodextrins can be crosslinked by a reaction between the hydroxyl groups of the chains with a coupling agent to form water-insoluble crosslinked networks. Due to the hydrophilic nature of their crosslinking units, crosslinked starches also possess a remarkably high swelling capacity in water, and consequently their networks are sufficiently expanded to allow a fast diffusion process for the pollutants. Crosslinked cyclodextrin polymers also have interesting diffusion properties and possess an amphiphilic character. It is precisely this character of these sorbents what makes them so appealing, since they are hydrophilic enough to swell considerably in water allowing fast diffusion processes for the dyes, while at the same time they possess highly hydrophobic sites which trap non-polar dyes efficiently. It is well known that synthetic resins have a poor contact with aqueous solutions and their modification is necessary for enhanced water wettability. Activated carbons adsorb some hydrophilic substances poorly.

3. EXPERIMENTAL

3.1. Materials and Method

Vinyl imidazole (VI) (Aldrich), chloroacetic acid (E-Merck), aminomethane sulfonic acid (Fluka), vinyl benzyl chloride (Fluka), ethylene glycol dimethacrylate (EGDMA) (Fluka), 2-acrylamido-2-methyl-1-propanesulfonic acid (Fluka), triallyl amine (Fluka), allyl bromide (Fluka), polyvinyl alcohol (Fluka), calcon(E-Merck), crystal violet (E-Merck), methylene blue (E-Merck), ramazol black (Dye staff) and all chemicals used were analytical grade commercial products. Also, everzol blue and everzol black were supplied from Everlight Company.

Perkin Elmer lamda 25 UV/VS and Perkin Elmer specturm one FT-IR spectrophotometer were used as instruments.

3.2. Preparation of Polymeric Sorbents

Three different polymeric sorbents were synthesized for dye removal.

3.2.1. Preparation of hydrogel for removal of basic dyes

The hydrogel was prepared by capolymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid –TAB (10%) according to the following procedure.

3.2.1.1. Preparation of tetraallylammonium bromide

Tetraallyl ammonium bromide (TAB) was prepared according to the literature [60].

3.2.1.2. Copolymerization of TAB with 2-acrylamido-2-methyl-1-propanesulfonic Acid

2-acrylamido-2-methyl-1-propanesulfonic acid (10 g, 48.25 mmol) and 1.245 g (9.3 mmol) of TAB were placed in a flask and 45 mL of water added. Then, 0.261 g(0.965 mmol) of $K_2S_2O_8$ and TEMED (0.1 mL) were added to the solution under nitrogen. The reaction mixture was stirred at 0 ^{0}C until gelation occurred. The

obtained gel was washed with excess water and acetone and then was dried under vacuum at room temperature for 24 h. The yield was 10.5 g (93.37%).

3.2.1.3. Dye uptake measurements of the hydrogels

Dye capacities of the hydrogels were determined by mixing a weighed amount of polymer sample (0.2 g) with 20 mL aqueous dye solution (2 g dye/50 mL water). In these experiments, the dyes Methylene blue and Crystal violet were used. The mixture was stirred for 24 h and then filtered. The dye concentrations were determined colorimetrically at different wavelengths and the dye loading capacities were calculated from the initial and final dye contents of the solution. 1ml of the filtrate was used for determination of the residual dye.

3.2.1.4. Kinetics of the dye sorption

To estimate the efficiency of the hydrogels for trace dye removal, batch kinetic experiments were performed using highly diluted dye solutions ($2x10^{-4}$ g dye /L water). For this purpose, gel (0.1 g) was wetted with distilled water (1.5 mL) and added to a solution of dye (100 mL). The mixtures were stirred magnetically and aliquots of the solution (5 mL) were taken at appropriate time intervals for analysis of the residual dye.

3.2.1.5. Regeneration of the gel

The dye loaded samples (0.1 g) were interacted with 10 mL of H_2SO_4 (5 mol L^{-1}) and stirred at room temperature for 24 h. After cooling, the mixtures were filtered, and 2 mL of the filtrate was removed for colorimetric analysis of the dyes. Regeneration capacity of the hydrogel was found as 0.90 g / g resin (92.8 %) for Methylene blue.

3.2.2. Preparation of polyvinyl benzyl chloride (PVBC) beads

Crosslinked PVBC microspheres were prepared by suspension polymerization according to the literature. 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 diluents and unreacted monomer. They were subsequently dried in vacuo at 50 °C. The microspheres were sieved and a proper size fraction (200-500 µm diameters) was isolated.

3.2.2.1. Modification of PVBC with amino methane sulfonic acid

PVBC resin (9.5 g) was added portion wise to a stirred of aminomethane sulfonic acid (7 g, 6.3 mmol) in 30 ml of 2-methyl pyrrolidone (NMP) at 0 ^{o}C. The mixture was shaken with a continuous shaker for at room temperature. Then, the reaction mixture was stirred at 60 ^{o}C for 12 h.

The reaction content was poured into water (1L), filtered and washed with excess water and methanol respectively. The resin dried under vacuum at room temperature for 24 h. The yield was 8.0 g.

3.2.2.2. Determination of amine content of resin

For the determination of the amine content, 0.206 g of the resin was left in contact with 15 ml of HCl (0.1 M) for 1 day. After filtration, 2 ml of the filtrate was taken and acid content of the solution was determined by filtration with 0.1 M NaOH in the presence of phenol-phatalein color indicator. A total amine content was found 1.11 mmol.g^{-1} resin.

3.2.3. Preparation of polyimidazole (PVI) resin

Synthesis of crosslinked poly (N-vinyl imidazole) was carried out by suspension polymerization method. For this purpose, 0.17 mol (15 mL) of VIm, 0.018 mol (3.5 mL) of EGDMA (crosslinking reagent) , 0.5 g of AIBN as initiator and 10 mL of Toluene as porogen were added to 200 mL of water containing 1 g of polyvinyl alcohol. The reaction was kept under nitrogen at 70 °C for 24 h. The resin was filtered and washed with abundant water and dried up to constant weight. Yield was 18 g.

Afterward, resin was sized by screening, and the fraction with mesh size in the range of 180–250 mµ was chosen to carry out the dye sorption studies.

3.2.3.1. Modification of PVI resin with chloroacetic acid

Quarternization of PVI resin was carried out by reaction with potassium salt of monochloroacetic acid solution. For this purpose, 9.5 g (0.1 mol) chloro acetic acid

was dissolved in 10 ml H_2O. Then 6,9 g (0,05 mol) of K_2CO_3 in 15 ml of distilled water was added drop wise to the ice cooled solution of the chloro acetic acid while stirring.

5 g of the PVI resin was placed in this solution and the mixture was stirred by a continuous shaker for 48 h at room temperature. The reaction content was filtered and washed with excess of distilled water and acetone respectively.

The vacuum-dried sample weighed 9.2 g.

3.2.3.2. Determination of chlorine content

The quarternization yield was followed by analysis of the chloride ions of the resin. 0.102 g querternized resin bead was placed in 10 ml of 10% NaOH solution for 24 h. Analysis of the chloride ions was performed by the mercuric thiocyanate method as described in the literature [61]. The chloride content was found as 3.52 $mmol.g^{-1}$ resin.

3.2.4. Dye sorption experiments

Quaternary amine containing materials can be used to remove acidic dyes. Also, the resin has carboxylic acid group and this group can bind basic dyes. Therefore, dye experiment studies were investigated by using acidic and basic dyes. All experiments were performed according to the PVBC resin described above.

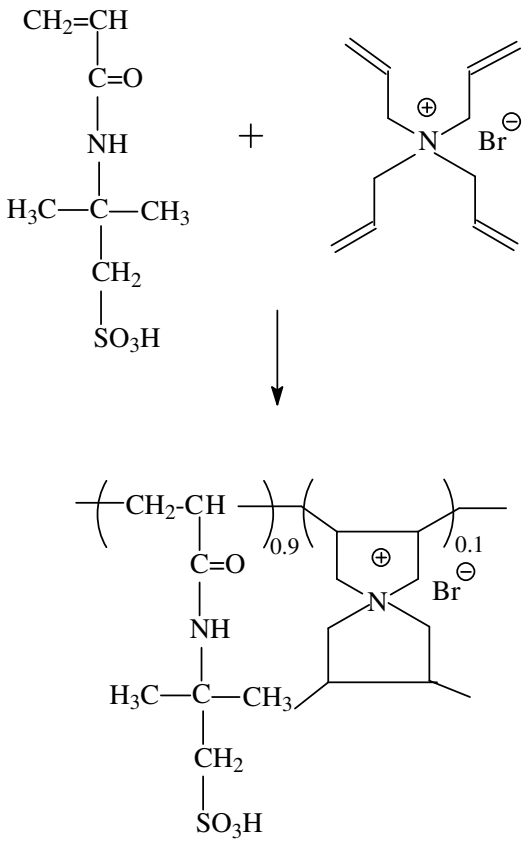
4. RESULTS AND DISCUSSION

In this study three different polymeric sorbents were synthesized and were characterized by using spectroscopic and analytical methods.

4.1. Preparation of Hydrogel

Copolymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid with TAB in aqueous solutions (20%) with $K_2S_2O_8$-TEMED initiator system at 0 ^{0}C was performed by using redox polymerization. The obtained rigid gel is completely homogeneous and transparent.

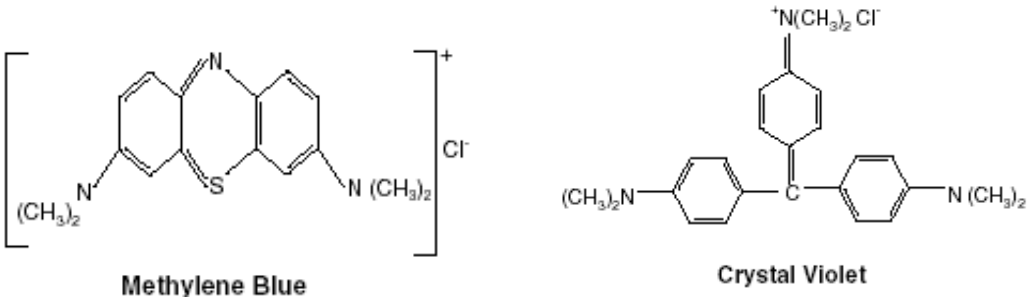
The structures of the crosslinked polymer gels can be depicted as shown below:



Scheme 4.1: Preparation of Hydrogel

4.1.1. Extraction of basic dyes

Dye extraction experiments were performed by contacting wetted polymer samples with aqueous dye solutions (1 g dye/100 mL) at room temperature. Capacities were determined by colorimetric analysis of residual dye contents. Methylene blue and crystal violet were used as basic dyes for determining of the resin capacity and kinetic studies.



Scheme 4.2: Basic Dyes

Dye sorptions capacities are given in Table 4.1.

Table 4.1: Dye sorption capacities of the hydrogel

Dye	Capacity (g dye / g gel)	Λ_{max} , nm
Methylene Blue	0.97	664
Crystal violet	0.85	590

Basic dyes possess cationic properties originating from positively charged nitrogen or sulfur atoms; they have an affinity to materials with net negative charges [62].

The swollen hydrogel in water shows reasonably high dye sorptions as high as 0.97 g g^{-1}. It is important to note that the hydrogel can be used over a wide pH range (Table 4.2.), with little differences in sorption. This property is important for industrial applications.

Table 4.2: Maximum dye sorption capacity of the hydrogel dependence on pH

Dye	pH	Capacity (g dye / g resin)
Methylene Blue	4.0	0.98
	6.0	0.97
	8.0	0.98
Crystal violet	4.0	-
	6.0	0.90
	8.0	0.95

4.1.2. Dye sorption kinetics of the hydrogel

This material is able to remove the basic dyes completely even from highly diluted aqueous dye solutions which are industrially highly important. Here batch kinetic sorption experiments were performed with very dilute dye solutions ($2x10^{-4}$ g L^{-1}) to investigate the efficiency of the gel in the presence of trace quantities of dyes, The concentration – time plot (Figure 4.1.) shows that within about 50 minutes contact time, the dye concentration falls to zero.

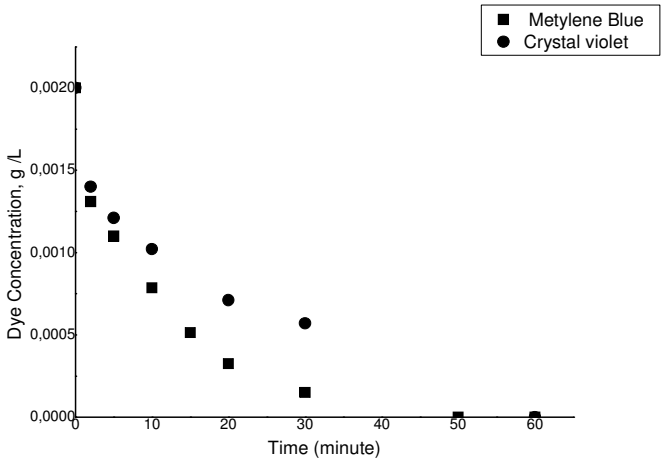
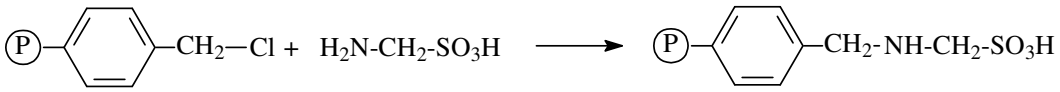


Figure 4.1: Dye sorption kinetics of the hydrogel from dilute aqueous solution

4.2. Preparation of Aminosulfonic Acid Based Resin (PVBC)

This resin was synthesized starting from crosslinked polyvinyl benzyl chloride-EGDMA (10%). The crosslinked co-polymer was reacted with aminosulfonic acid to obtain aminosulfonic acid containing resin.



Scheme 4.3.

The resin was characterized by using titrimetric method and FT-IR spectrophotometer. Nitrogen content of the resin was calculated as 1.11 mmol.g^{-1}.

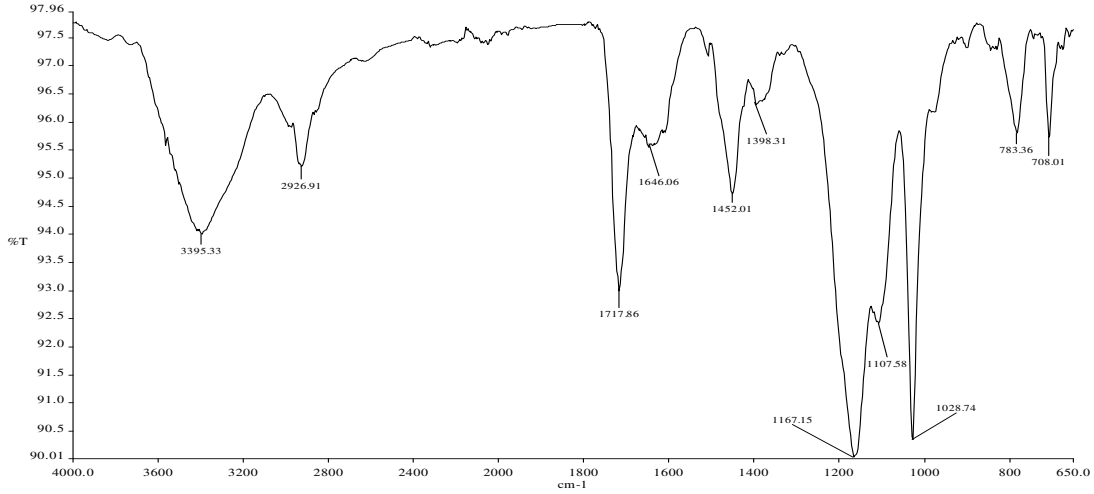


Figure 4.2: FT-IR spectra of the aminosulfonic acid containing resin

The resin was characterized by FT-IR spectroscopy (Figure 4.2.). In the resin, N-H stretching vibration occurs at 3395 cm^{-1} and 1398 cm^{-1} and 1028 cm^{-1} peak belong to sulfonic acid groups.

4.2.1. Extraction of dyes

Dye extraction experiments were carried out simply by contacting wetted bead samples with aqueous dye solutions at room temperature. Capacities were assigned by colorimetrical analysis of residual dye contents. Dye sorption capacities of the PVBC resin were given in Table 4.3. According to the Table 4.3. acidic and basic dyes sorption capacities of the resin were found as 0.11 g dye / g resin-0.16 g dye / g resin. Acidic and basic dyes can be removed successfully because the resin has both acidic and basic groups.

Table 4.3: Sorption capacities of the PVBC resin

Dye	Capacity (g dye / g resin)	λ (nm)
Crystal Violet	0.15	590
Methylene Blue	0.11	664
Everzol Black	0.11	598
Everzol Blue	0.12	591
Ramazol Black	0.16	597
Calcon	0.13	545

It has been reported that the basic mechanism in dyeing protein fibers with acid dyes is salt formation with amino groups as follows [63]:

$$^{+}NH_3 + {}^{-}Dye \longrightarrow NH_3Dye$$

Scheme 4.4: Salt formation of dyes with amino groups

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 [64].

It is important to note that the resin can be used in a wide pH range (Table 4.4.). This property is important in utilization of the resin in industrial applications.

The resins can be used in lower pH values. 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 [65,66].

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 [63]:

$$DyeSO_3Na + H_2O \rightarrow DyeSO_3^- + Na^+ \qquad (1)$$

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

$$-NH^{+3} + DyeSO_3- = -NH^{+3}\,{}^{-}O_3\,SDye. \qquad (2)$$

Table 4.4: Maximum dye sorption capacity of the PVBC resin depending on pH

Dye	pH	Capacity (g dye / g resin)
Everzol Black	2	0.30
	4	0.10
	8	0.05
Ramazol Black	2	0.10
	4	0.06
	8	0.10
Methylene Blue	2	-
	4	0.10
	8	0.24
Calcon	2	-
	4	-
	8	0.17

4.2.2. Dye sorption kinetics of the resin (PVBC)

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 (7.5-20 mg 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 4.3. shows that within about 60 min of contact time, the resin can remove dyes completely.

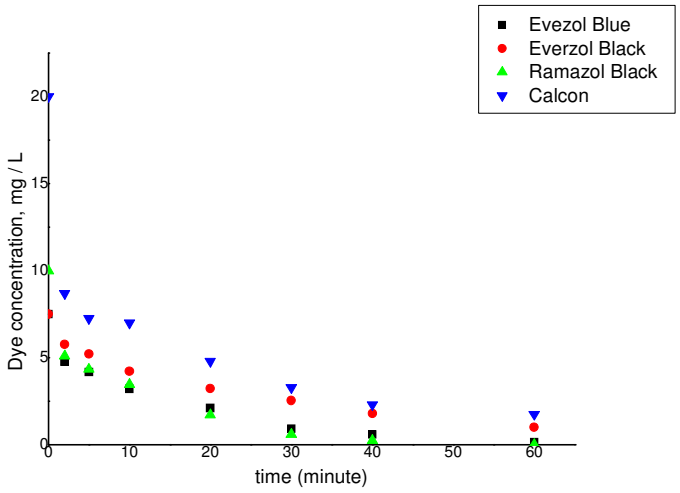


Figure 4.3: Acidic dye sorption kinetics of PVBC resin

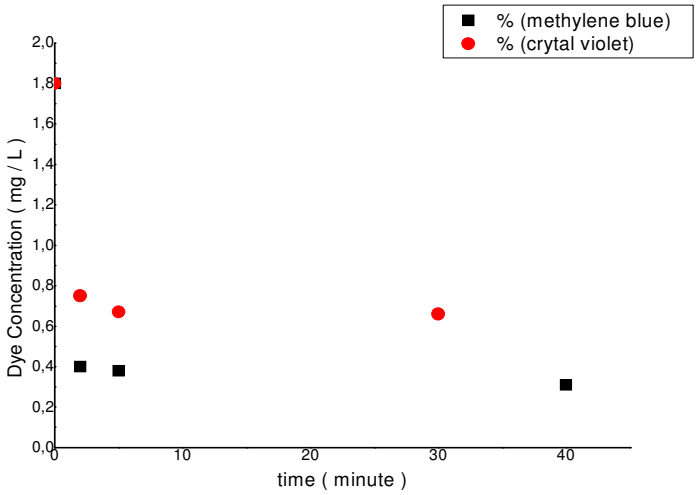
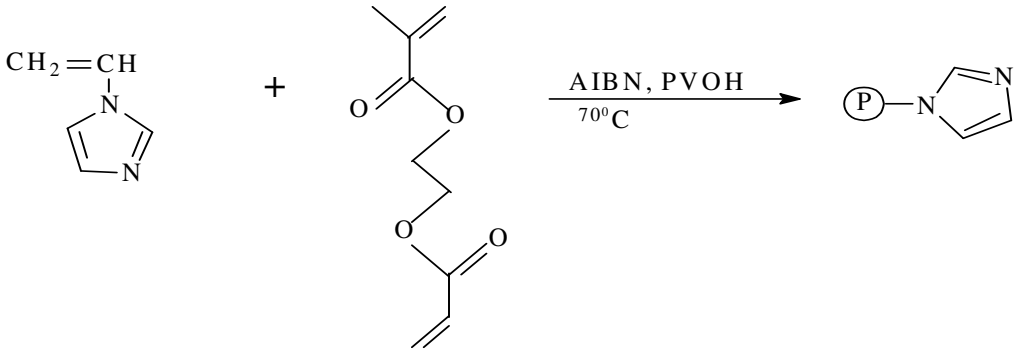


Figure 4.4: Basic dye sorption kinetics of PVBC resin

4.3. Preparation of polyimidazole (PVI) resin

The resin was prepared reaction with vinylimidazoline-EGDMA monomers by using suspension polymerization method.



Scheme 4.5: Preparation of PVI resin

4.3.1. Extraction of dyes

Dye extraction experiments were investigated according to the given procedure described above.

Dye sorption capacities of the PVI resin were given in Table 4.5. According to the Table 4.5., acidic dyes sorption capacities of the resin were found as 0.26 g dye/g resin – 0.67 g dye/g resin. Acidic dyes can be removed successfully.

Table 4.5: Sorption capacities of the PVI resin

Dye	Capacity (g dye / g resin)	λ (nm)
Everzol Black	0,26	598
Everzol Red	0,16	591
Ramazol Black	0,20	597
Calcon	0,67	545

Table 4.6: Maximum dye sorption capacity of the PVI resin depending on pH

Dye	pH	Capacity (g dye / g resin)
Everzol Black	2	0.14
	4	0.29
	8	0.19
Everzol Red	2	0.21
	4	0.31
	8	0.26
Ramazol Black	2	0.15
	4	0.25
	8	0.22
Calcon	2	-
	4	-
	8	0.68

4.3.2. Dye sorption kinetics of the resin (PVI)

Sorption kinetic studies were performed acidic dyes.

This resin is able to remove dyes completely even from highly diluted aqueous dye solutions which are highly important. We performed batch kinetic sorption experiments with highly diluted dye solutions (9 mg 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 4.5. shows that within about 60 min of contact time, the resin can remove dyes completely.

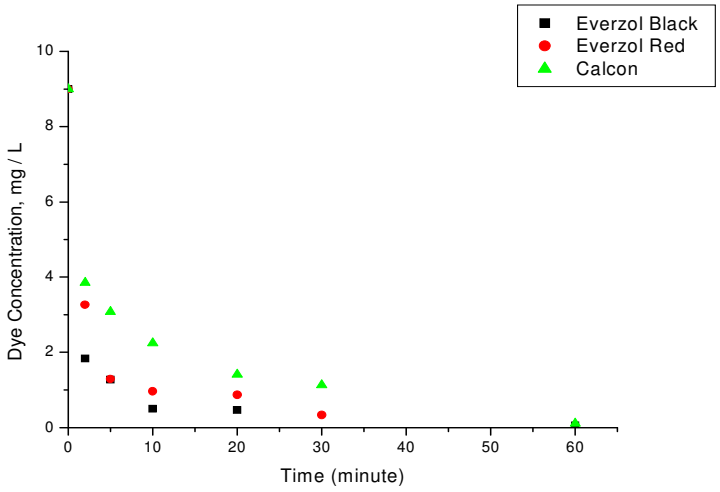
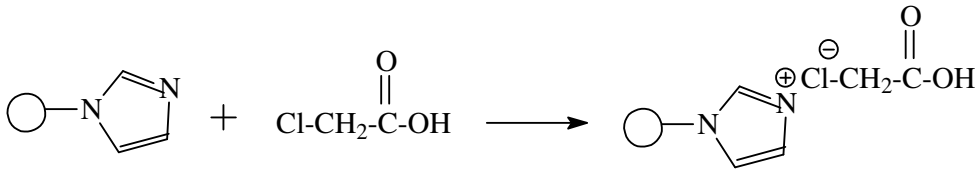


Figure 4.5: Acidic dye sorption kinetics of PVI resin

4.4. Preparation of the Quaternized Polyvinyl Imidazoline Resin

Crosslinked polyvinylimidazolne resin was prepared reaction with vinylimidazoline-EGDMA (10%) by using suspension polymerization method. Quaternization was performed with chloroacetic acid.



Scheme 4.6: Preparation of QPVI resin

The resin was characterized by using chlorine analysis method and FT-IR spectrophotometer. Chlorine content of the resin was calculated as about 3.52 mmol.g^{-1}.

The resin was characterized by FT-IR spectroscopy (Figure 4.6.). In the resin, C=O stretching vibration occurs at 1632 cm^{-1}, 1392 cm^{-1} and 1152 cm^{-1} peak belong to quaternary amine group.

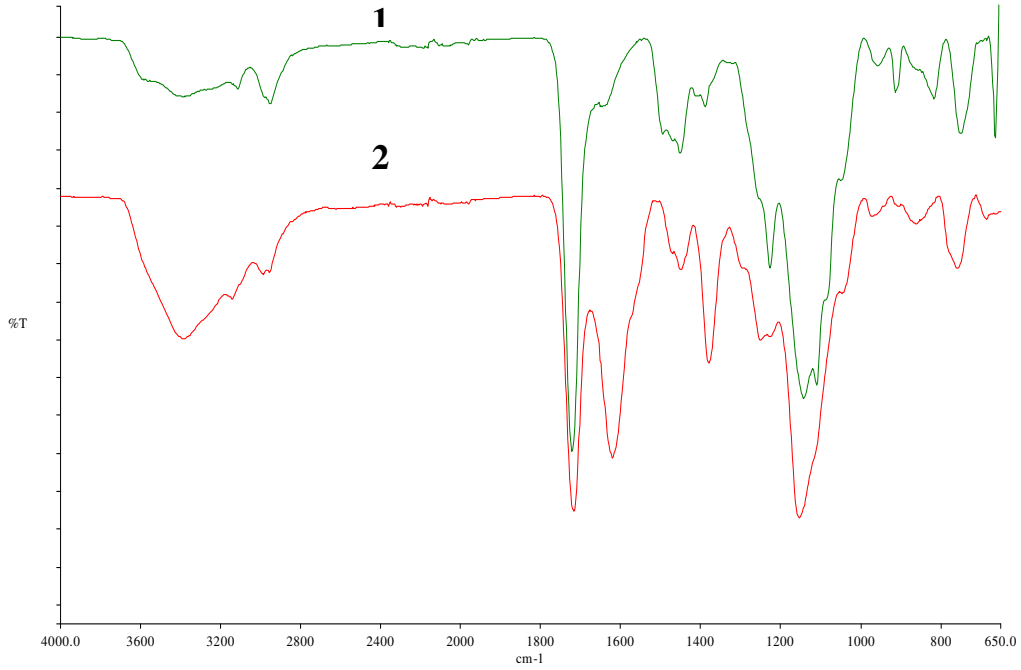


Figure 4.6: FT-IR spectrum of the Quaternized polyvinyl imidazoline and Poly (vinyl imidazoline) resin resins

(1) Poly (vinyl imidazoline) resin

(2) Quaternized polyvinyl imidazoline resin

4.4.1. Extraction of dyes

Dye extraction experiments were investigated according to the given procedure described above.

Dye sorption capacities of the QPVI resin were given in Table 4.7. According to the Table 4.7., acidic and basic dyes sorption capacities of the resin were found as 0.10 g dye/g resin – 0.40 g dye/g resin. Acidic and basic dyes can be removed successfully because the resin has both acidic and quaternary amine groups.

Tablo 4.7: Sorption capacities of the QPVI resin

Dye	Capacity (g dye / g resin)	λ (nm)
Crystal Violet	0.10	590
Methylene Blue	0.40	664
Everzol Black	0.12	598
Ramazol Black	0.14	597
Calcon	0.20	545

Table 4.8: Maximum dye sorption capacity of the QPVI resin depending on pH

Dye	pH	Capacity (g dye / g resin)
Everzol Black	2	0.30
	4	0.20
	8	0.29
Ramazol Black	2	0.30
	4	0.10
	8	0.14
Methylene Blue	2	-
	4	0.09
	8	0.23
Calcon	2	-
	4	-
	8	0.19

4.4.2. Dye sorption kinetics of the resin (QPVI)

Sorption kinetic studies were performed both acidic and basic dyes separately.

This resin is able to remove dyes completely even from highly diluted aqueous dye solutions which are highly important. We performed batch kinetic sorption experiments with highly diluted dye solutions (7.5-20 mg 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 4.7. shows that within about 60 min of contact time, the resin can remove dyes completely.

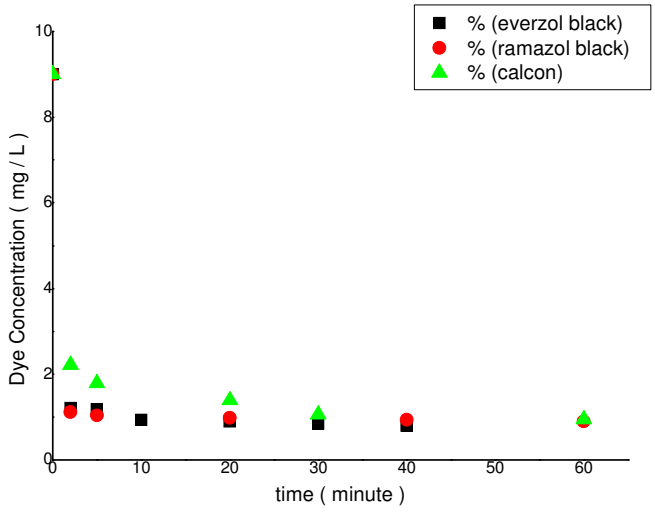


Figure 4.7: Acidic dye sorption kinetics of QPVI resin

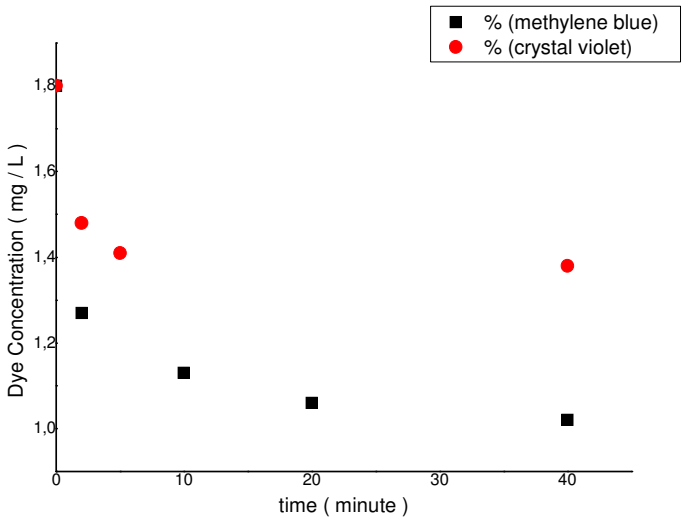


Figure 4.8: Basic dye sorption kinetics of QPVI resin

4.5. Dye Sorption Studies with Different Dye Concentrations

The influences of dye concentration on sorption percentages of dyes were estimated under the condition of 0.2 g sorbent used. As shown in Figure 4.9., the Ramazol Black dyeconcentration was increased from 0.01 to $1.25.10^{-3}$ mg/L.

With the data in Figure 4.8., Langmuir equation was employed to study the sorption isotherm of PVBC and QPVI.

The Langmuir equation is based on the assumption that maximum sorption corresponds to saturated monolayer of sorbate molecule on the sorbent surface, that the energy of sorption is constant and that there is no transmigration of sorbate in the plane of the surface.

The linear Langmuir equation was shown as follows:

$C_e/q_e = 1 / (a.Q_m) + C_e / Q_m$

where C_e (mg/L) is the concentration of the dye solution at equilibrium, q_e (mg/g) is the amount of dye sorbed at equilibrium, Q_m is the maximum sorption capacity and represents a practical limiting sorption capacity when the sorbent surface is fully covered with monolayer sorbate molecules and a is Langmuir constant. The Q_m and a values were obtained from the slopes ($1/Q_m$) and intercepts ($1/a.Q_m$) of linear plots of C_e/q_e versus C_e.

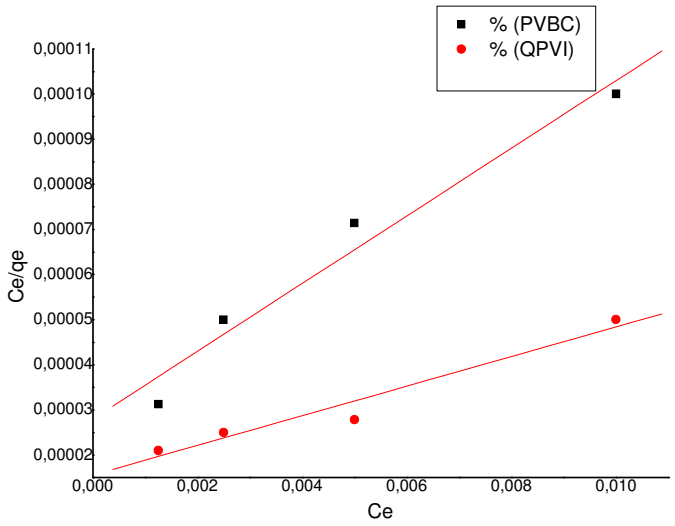


Figure 4.9: Langmuir isotherm plot for ramazol black dye

Table 4.9: Langmuir parameters for ramazol black dye

Resin	Qm (mg dye / g resin)	a	R
PVBC	133	267.7	0.98
QPVI	305	210.73	0.98

4.6. Regeneration of Loaded Resins

4.6.1. Regeneration of the acidic dye loaded resins

Loaded polymer samples, when treated with basic ethanol become almost dye-free. In this way, 0.029 g calcon and 0.044 g calcon were recovered per g of loaded sample for PVBC resin and QPVI respectively.

4.6.2. Regeneration of the basic dye loaded polymeric sorbents

For the regeneration of dyes from loaded hydrogel, 5 mol L^{-1} H_2SO_4 was used according to the literature [67]. When loaded samples were contacted with 5 mol L^{-1} H_2SO_4 for 24 h. The amount of recovered methylene blue was found as around 0.90 g dye / g hydrogel, 0.79 mg dye / g PVBC resin and 0.92 mg dye / g resin QPVI.

5. CONCLUSION

Three types of new crossliked sorbents were prepared for removal of dyes.

Characterizations of the sorbents were performed by using analytical determination metods and spectrophotometric methods.

Hydrogel was prepared by using TAB as a crosslinker. The resulting gel is highly effective in removal of dye and the gel format makes the material of interest as a column packing material for technological use. Under non-buffered conditions, the dye uptake capacity is around 0.97 g dye/g polymer. This provides hydrophilicity to the gel. Additionally, hydrogel does not hydrolyze in acid and base solutions. This property is very important for regeneration.

PVBC resin has both tertiary amine and sulfonic acid groups therefore it can sorb reactive (acidic) and basic dyes. According to the experimental results, PVBC resin can remove dyes successfully.

PVI resin has basic character therefore it can be used to remove acidic dyes from water but QPVI resin contains both quaternary amine and carboxylic acid groups. The resin can be used for removing both acidic and basic dyes.

Basic dyes regeneration of the resins was carried out by 1 M H_2SO_4 succesfully and acid dyes regeneration was performed by KOH solution containing alcohol - water .

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