İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PREPARATION OF PYRRIDINE SULFONAMIDE AND DICARBOXYLIC ACID CONTAINING RESINS FOR REMOVAL OF DYES

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Department : POLYMER SCIENCE AND TECHNOLOGY

Programme: POLYMER SCIENCE AND TECHNOLOGY

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June 2007 Chemical Engineer E.Tuğrul TEKİN

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SYMBOL LIST

P	: Crosslinked resin
DVB	: Divinyl benzene
FT-IR	: Fourier Transform Infrared
UV-VIS	: Ultraviolet Visible
NaOH	: Sodium Hydroxide
HNO_3	: Nitric Acid
NMP	: 2-Methyl Pyrrolidone
H_2SO_4	: Sulfuric Acid
HCl	: Hydrocholoric Acid
KOH	: Potassium Hydroxide

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PREPARATION OF PYRRIDINE SULFONAMIDE AND DICARBOXYLIC ACID CONTAINING RESINS FOR REMOVAL OF DYES

SUMMARY

Textile industry suffers from huge quantities of aqueous dye-wastes. Among various sorbents activated carbon, clays, modified chitosans and some surface modified zeolites have been found useful in removal of residual dyes in fabric treatments. Although activated carbon is an efficient sorbent in extraction of organic pollutants, it has rather low capacity and needs regeneration to be cost-effective in large scale treatments.

Many sorbents have been tested for dye removal; however, most of them are not regenerable, such as bagasse pith or eucalyptus bark.

Good sorption capacities for reactive dyes (60-420 mg.g-1) are found for quaternized organic materials such as cellulose, rice husks and coconut husk. But these materials have not shown been successfully regeneration.

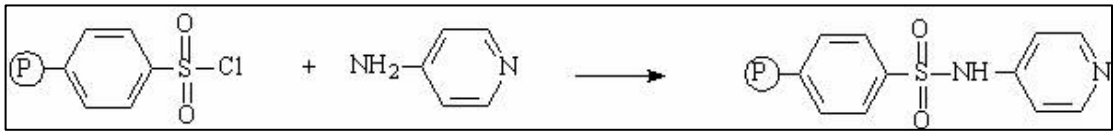
The interaction between polymer and dye leading to polymer–dye complex formation exhibits many interesting and important practical features.

Coulombic, hydrophobic, and steric interactions are major factors governing the thermo chemical and dynamic aspects of complex formation. The interactions of the hydrogels with dyes are of principal interest. Taking into account the environmental requirements, the development of water-based colored polymer materials is one of the modern targets for the chemical industry.

In this study two types cross linked polymers was prepared for removal of dyes from aqueous solutions.

Preparation of sulfonamide resins

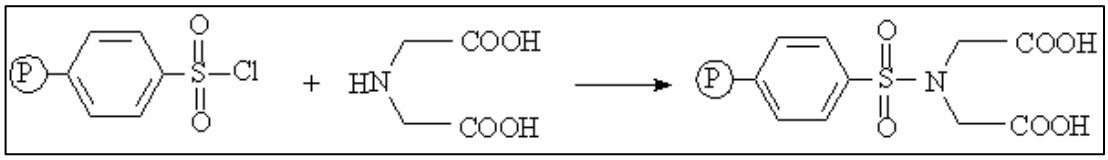
Sulfonamide based resin was prepared starting from Chlorosulfonated polystyrene beads. Resin I was obtained starting from the reaction of chlorosulfonated polystyrene resin and amino pyridine (Scheme 4.1).



Scheme 4.1 : Preparation of Resin I

The resulting Resin I has been shown to be an efficient sorbent for removal of acidic dyes from water. Since tertiary amine groups have a unique reactivity towards acidic dye molecules.

Dicarboxylic acid containing resin (Resin II) has been obtained reaction between Chlorosulfonated polystyrene and Iminodiacetic acid (Scheme 4.2).



Scheme 4.2: Preparation of Resin II

This resin can be used to remove basic dyes from water because of acidic functions.

Extraction of Dyes

Dye extraction experiments were performed simply by contacting wetted polymer samples with aqueous dye solutions (1 g dye/ 50 mL) at room temperature. Capacities were assigned by colorimetrical analysis of residual dye contents. Dye sorptions capacities were given in Table 4.1.

Table 4.1. Dye sorption capacities of the resins

Dye	**Capacity (g dye/g resin)**	**λ_{max} (nm)**
Calcon	0.77	552
Everzol Black	0.17	598
Everzol Blue	0.28	591
Methylene blue	0.43	664

Table 4.2. Maximum dye sorption capacity of the resins depending on pH

Dye	**pH**	**Capacity (g dye / g resin)**
Everzol black	2.0	0.11
	4.0	0.13
	5.0	0.31
	9.0	0.61
Everzol blue	2.0	0.07
	4.0	0.29
	5.0	0.53
	9.0	0.47

It is important to note that the polymers can be used in a wide pH range (Table 4.2). This property is important in utilization of the polymers in industrial applications.

Dye sorption kinetics of the polymers

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 (0.2 g dye / 500 mL water) to investigate the efficiency of the resin in the presence of trace quantities of dyes, Concentration-time plot Figure 4.4. shows that within about 20 min of contact time, the dye concentration falls to zero for methylene blue

Also capacity-time plot of the resin I have been given in Figure 4.3

Regeneration of the loaded polymers

Dye loaded polymers (Resin I) were regenerated by using basic methanol. Regeneration capacity was found 0.26g dye/ g dry resin, for everzol blue. Resin II was regenerated by using 1 M H_2SO_4 and glacial acetic acid.

BOYALARIN GİDERİLMESİ İÇİN PİRİDİN SULFONAMİD VE DİKARBOKSİLİK ASİT İÇEREN REÇİNELERİN HAZIRLANAMASI

ÖZET

Tekstil endüstürisi çok büyük miktardaki atık boyalardan dolayı zorluk yaşamaktadır. Birçok sorbentin içinde aktif karbon,kil,modifiye çitosan ve bazı yüzey modifiye zeolitler atık boyaların giderilmesinde kullanılmaktadır. Aktif karbon organik atıkların ekstraksiyonu için önemli bir sorbent olmasına rağmen düşük kapasitelidir ve büyük ölçekli boya giderimin de rejenerasyonu oldukça pahalıdır.

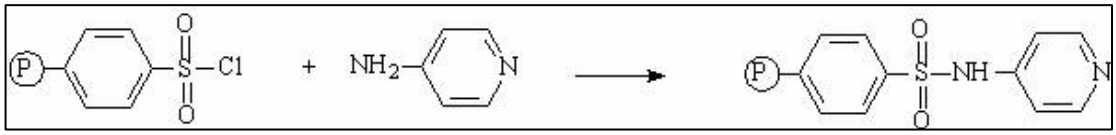
Birçok sorbentler boya giderimi için test edilmektedir. Ancak birçoğu okaliptus yaprağı gibi rejenere edilemez.

Seluloz, pirinç kabuğu , Hindistan cevizi kabuğu gibi birçok kuaternize organik boyalar için iyi birer adsorbant oldukları bulunmuştur. Polimerler ve boyalar arasındaki polimer - boya kompleks oluşumu birçok ilngç ve önemli özellikler sağlar. Elektriksel hidrofobik, sterik etkileşimler kompleks oluşumunun termokimyasal ve dinamik önemli bölümleridir.

Hidrojellerin boyalarla etkileşimleri önemli bir ilgi alanıdır. Çevresel ihtiyaçları dikkate aldığımızda su bazlı renkli polimerik materyallerin gelişmesi kimya endüstrisi için modern hedeflerden biri olmaktadır. (Bu çalışmada sulu çözeltilerden boyaların giderilmesi için iki farklı çapraz bağlı polimer sentezlenmiştir.)

Sülfonamid Reçinenin Hazırlanması

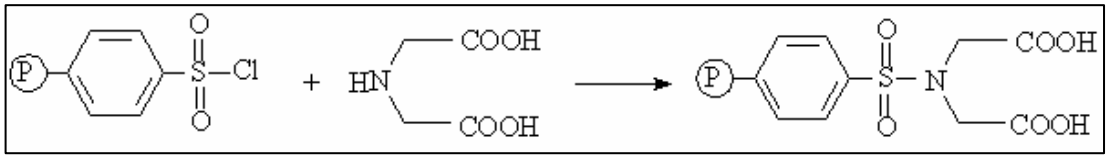
Sülfonamid bazlı reçine klorosülfonlanmış polistiren küreciklerden yola çıkılarak hazırlanmıştır. Reçine 1 klorosülfonlanmış polistren ile amino piridinin reaksiyonundan elde edilmiştir. (Şema 4.1)



Şema 4.1: Reçine 1 in Hazırlanması

Reçine 1'in asidik boyaların sulardan giderilmesi için etkili bir sorbent olduğu gösterilmiştir. Bunun sebebi tersiyer amin gruplarının asidik moleküllere karşı büyük reaktifliğidir.

Dikarboksilik asit içeren reçine (Reçine 2) klorosülfonlanmış ve iminodiasetik asitin reaksiyonundan elde edilmiştir.(Şema 4.2)



Şema 4.2: Reçine 2 nin hazırlanması

Bu reçine asidik fonksiyonlarından dolayı bazik boyaların giderilmesinde kullanılabilir.

Boyaların Ekstraksiyonu

Boya ekstraksiyonu deneyleri ıslatılmış polimer örnekleriyle boya çözeltilerinin (1 g /50 mL) etkileşimi ile oda sıcaklığında gerçekleştirilmiştir. Kapasiteler reçine ile etkileşmeden sonraki kalan boya içeriğinin kolorimetrik analizi ile elde edilmiştir. Boya tutulma kapasiteleri Tablo 4.1 de verilmiştir.

Tablo 4.1: Boya tutulma kapasiteleri

Boya	**Kapasite (g boya /g reçine**	**λ_{max} (nm)**
Kalgon	0.77	552
Everzol Black	0.17	598
Everzol Blue	0.28	591
Metilen Blue	0.43	664

Tablo 4.2: Reçinelerin pH'a bağlı maksimum boya tutma kapasiteleri

Boya	**pH**	**Kapasite (g boya / g reçine)**
Everzol black	2.0	0.11
	4.0	0.13
	5.0	0.31
	9.0	0.61
Everzol blue	2.0	0.07
	4.0	0.29
	5.0	0.53
	9.0	0.47

Belirtilmesi önem arzeden bir konu da polimerlerin geniş bir pH aralığında kullanılabilir olmasıdır.(Tablo 4.2)

Polimerlerin boya tutma kinetikleri

Reçine 2 anyonik boyaların oldukça seyreltik boya çözeltilerinden tamamen giderilmesinde etkili bir malzemedir. Çok düşük miktarlardaki boya çözeltilerinde reçinenin etkinliğini bulabilmek için oldukça seyreltik boya çözeltileriyle kesikli kinetik tutulma deneyleri gerçekleştirilmiştir. Konsantrasyon zaman grafiği Şekil 2 gösterir ki 20 dakikalık bir etkileşim zamanı içinde boya konsantrasyonu sıfıra düşmektedir.

Aynı zamanda Reçine 1 in kapasite zaman grafikleri Şekil 1 de verilmiştir.

Yüklü polimerlerin rejenerasyonu

Boya yüklü polimer reçine (Reçine 1) bazik metanol kullanılarak rejenere edilmiştir. Everzol blue için rejenerasyon kapasitesi 0.26 g boya /g kuru reçine olarak bulunmuştur. Reçine 2 1 M H_2SO_4 ve saf asetik asit kullanılarak rejenere edilmiştir.

1. INTRODUCTION

Most dyestuffs are classified according to their solubility, coloring properties, and chemical structure. After coloring is completed, the waste ought not to be discharged into the environment without purification, because dyestuffs are carcinogenic. These compounds can contaminate underground water in trace amounts by leaking from soil and pose a very great risk to human health over a long period. Consequently, the waste solutions ought to be purified.

One possibility to address reactive dye removal is by sorption onto suitable sorbents in fixed bed filters. Many sorbents have been tested for dye removal. For example, chitosan, monocarboxymethylated chitosan (MCM-chitosan) and rice husk were used as a sorbent for removal of dyes from aqueous solutions.

However, most of them are not regenerable, such as bagasse pith or eucalyptus bark. Good sorption capacities for reactive dyes (60-420 mg.g-1) are found for quaternized organic materials such as cellulose rice husks and coconut husk. However, regeneration of these materials has not been shown successful.

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. Taking into account the environmental requirements, the development of water-based colored polymer materials is one of the modern targets for the chemical industry.

In this study, two different resins have prepared for removal of dyes from aqueous solutions. These resins have been chacterized by using analytical methods. Also, dye removal characteristics of the resins have been investigated.

2. THEORITICAL 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 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 [1]. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [2].

Over 100.000 commercially available dyes exist and more than 7×10^5 tonnes per year are produced annually [3,4]. 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 [5,6]. 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 [7,8].

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 [9]. 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 [10-12]. 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).

2.3. Technologies available for color removal

2.3.1. General considerations

Methods of dye wastewater treatment have been reviewed by Pokhrel and Viraraghavan [13], Slokar and Majcen Le Marechal [14], Dele´e et al. [15] and Cooper [16]. Fungal and bacterial decolorization methods have been reviewed by Aksu [17], Wesenberg et al. [18], Fu and Viraraghavan [19] and Stolz [20].
There are several reported methods for the removal of pollutants from effluents (Table 2. 1).

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

Table 2.1: Principal existing and emerging processes for dye removal

	Technology	Advantages	Disadvantages
Conventional treatment proceses	Coagulation Floccculation	Simple,economically feasible	High sludge production,handling and disposal problems
	Biodegradation	Economically, attractive,publicly acceptable treatment	Slow process,necessary to create an optimal favorable nvironment,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)

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 [21,22]. In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way.

2.3.2. 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 [23]. 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 [8]. In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

2.3.3. 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.

2.3.4. 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 [24]. 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.

2.4. 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 [25,26]. In particular, the effectiveness of adsorption on commercial activated carbons (CAC) for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options. Because of their great capacity to adsorb dyes, CAC are the most effective adsorbents. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their

properties. However, activated carbon presents several disadvantages . It is quite expensive, the higher the quality, the greater the cost, non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not 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 [27]. This has led many workers to search for more economic adsorbents.

2.4.1. 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.[28], 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.

2.4.2. 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.

2.4.3. 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 [29-31]. Because of its availability and cheapness, coal is the most commonly used precursor for AC production [32,33]. 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 [34]. Coal based

sorbents have been used by Karaca et al., Venkata Mohan et al. [35,36] and McKay et al. [37] with success 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 [38-42], coir pith [43,44], banana pith [45], date pits [46], sago waste, silk cotton hull, corn cob, maize cob, straw [47], rice husk [48-50], rice hulls, fruit stones [51], nutshells, pinewood [52], sawdust, coconut tree sawdust [53], bamboo [54], cassava peel [55]. There are also several reports on the production of AC from various city wastes and industrial by – products such as waste PET bottles [56], waste tires, refuse derived fuel, wastes generated during lactic acid fermantation from garbage, sewage sludges [57-59], waste newspaper [60], waste carbon slurries [61] and blast furnace slag .

The excellent ability and economic promise of the activated carbons prepared from by-products have been recently presented and described. Juang et al. reported that the adsorption capacities of activated carbons made from corncob had very large values of 1060-790 mg of dye per g of carbon. 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.

2.5. Natural materials

2.5.1. 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 [62]. 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 [63]. Montmorillonite clay has the largest surface area and the highest cation exchange capacity. Its current market price (about US$ 0.04–0.12/kg) is considered to be 20 times cheaper than that of activated carbon .

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. In particular, interactions between dyes and clay particles have been extensively studied [64-85]**.** 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. This means that the sorption capacity can vary strongly with pH. Al-Ghouti et al. showed that the mechanism of adsorption of dye onto diatomite is due to physical adsorption (depending on the

particle size) and the presence of electrostatic interactions (depending on the pH used).

Good removal capability of clay materials to take up dye has been demonstrated. Espantaleon et al. reported that an adsorption capacity of 360.5 mg of dye/g bentonite was achieved. Due to its high surface area, it was suggested that bentonite is a good adsorbent for (basic) dye removal. Similar results have been published by Bagane and Guiza. It was found that 1 g bentonite could adsorb 300 mg of basic blue 9. The adsorption of dyes on kaolinite was also studied. The adsorption to kaolinite was about 20 times greater than to alumina. The removal performances of Fuller's earth and CAC for basic blue 9 were compared by Atun et al. They showed that the They showed that the adsorption capacity is greater on Fuller's earth than on CAC. Moreover, Fuller's earth is an interesting sorbent since its average price is US$ 0.04/kg whereas CAC costs US$ 20/kg. Shawabkeh and Tutunji studied the adsorption of basic blue 9 onto diatomaceous earth (diatomite). They showed that this naturally occurring material could substitute for activated carbon as an adsorbent due to its availability and low cost, and its good sorption properties. The adsorption isotherms revealed that adsorption equilibrium was reached within 10 min. The feasibility of using diatomite for the removal of the problematic reactive dyes was also investigated by Al-Ghouti et al. The sorption of acid blue 9 onto mixed sorbent (activated clay and activated carbon 12:1) has been studied by Ho and Chiang [86].

As with other materials, clay materials can be modified to improve their sorption capacity. Ozdemir et al. investigated modified sepiolite as an adsorbent for a variety of azo-reactive dyes. They showed that the adsorption capacities are substantially improved upon modifying their surfaces with quaternary amines. The adsorption capacity of kaolinite can be improved by purification and by treatment with NaOH solution. The acid-treated bentonite showed a higher adsorption capacity than non-modified bentonite.

2.5.2. 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 [87-90], considering chemical reactivity of their hydrophilic surface, resulting from the

presence of silanol groups. Their porous texture, high surface area and mechanical stability also make them attractive as sorbents for decontamination applications. However, due to their low resistance toward alkaline solutions their usage is limited to media of pH less than 8 [91]. 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. Phan et al. also showed that modified silica beads have a better potential for the removal of acid dyes from colored effluents.

Another sorbent from siliceous materials to adsorb dye is alunite [92-94]. Alunite is one of the minerals of the jarosite group and contains approximately 50% SiO_2. Characteristics of alunite can be found in the review by Dill. 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 [95]. Charred dolomite has a higher equilibrium capacity for reactive dye removal than activated carbon, with a capacity of 950 mg/g of adsorbent for dolomite compared to 650 mg dye adsorbed per g of adsorbent for CAC. However, the mechanism was not clear (probably a combination of precipitation and adsorption). Perlite is a glassy volcanic rock and has a high silica content, usually greater than 70%. It is inexpensive and easily available in many countries. The use of perlite as a low-cost adsorbent for the removal of dyes has been investigated for the first time by Alkan and co-workers [97-99]. 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.

2.5.3. 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. The characteristics and applications of zeolites have been reviewed by Ghobarkar et al. [100]. High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively cheap prices, make zeolites attractive adsorbents. Their price is about US$ 0.03– 0.12/kg, depending on the quality of the mineral. 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 [101-103]. However, raw clinoptilolite was not suitable for the removal of reactive dyes due to extremely low sorption capacities [104]. Similar conclusions have been found by Ozdemir et al. and Benkli et al. [105]. These authors suggested chemical modification with quaternary amines as a means of increasing sorption. In spite of the promising results, the real applicability of these natural materials to purify dye waste waters is still quite unknown. Another problem of zeolites is their low permeability and this requires an artificial support when used in column operations. The sorption mechanism on zeolite particles is complex because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity and other imperfections on the surface [106]. However, it is recognized that, like clay, the adsorption properties of zeolites result mainly from their ion-exchange capabilities.

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.

2.6. 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.

2.6.1. 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, crayfish) primarily because a large amount of the crustacean's exoskeleton is available as a by-product of food processing. The annual worldwide crustacean shells production has been estimated to be $1.2x10^6$ tonnes, and the recovery of chitin and protein from this waste is an additional source of revenue [107]. 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 [108-110]. 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.

Various studies on chitin and chitosan have been conducted in recent years [111-124]. These studies demonstrated that chitosan-based biosorbents are efficient materials and have an extremely high affinity for many classes of dyes. They are also versatile materials. This versatility allows the sorbent to be used in different forms, from flake-types to gels, bead-types or fibers. The performance of chitosan as an adsorbent to remove acid dyes has been demonstrated by Wong et al.. They found that the maximum adsorption capacities of chitosan for acid orange 12, acid orange 10, acid red 73 and acid red 18 were 973.3, 922.9, 728.2, and 693.2 mg/g, respectively. Wu et al. also reported the usefulness of chitosan for the removal of reactive dyes. However, the bead type of chitosan gives a higher capacity for dye than the flake type by a factor of 2–4 depending on the source of fishery wastes. For example a comparison of the maximum adsorption capacity for reactive red 222 by chitosan flakes and beads showed 293 mg/g for flakes and 1103 mg/g for beads. This can be explained by the fact that the beads possessed a greater surface area than the flakes.

Both batch contacting and column processes are available for chitosan materials with solution containing dyestuffs [125]. 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.

The interaction between crosslinked chitosan and dyes has been intensively investigated by Chiou et al.. Several crosslinked biomaterials were prepared by using a procedure described by Zeng and Ruckenstein [126]. Chitosan beads were crosslinked with glutaraldehyde (GLA), epichlorohydrin (EPI) or ethylene glycol diglycidyl ether (EGDE). Chiou and Li showed that the chitosan-EPI beads presented a higher adsorption capacity than GLA and EGDE resins. It was found that 1 g chitosan adsorbed 2498 mg of reactive blue 2. Chitosan-based biosorbents have also demonstrated outstanding removal capabilities for direct dyes. In comparison with commercial activated carbon, the beads exhibited excellent performance for adsorption of anionic dyes: The adsorption values were 3–15 times higher at the same pH. Hence chitosan chelation is the procedure of choice for dye removal from aqueous solution. However, it is known that chitosan has a low affinity for cationic (basic) dyes. Chao et al. suggested enzymatic grafting of carboxyl groups onto chitosan as a means to confer the ability to adsorb basic dyes on beads. The presence of new functional groups on the surface of beads results in increases in surface polarity and the density of sorption sites, and this improves the sorption selectivity for the target dye.

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.

Despite the large number of papers dedicated to the removal of dyes by chitosan-based materials, most of them focus on the evaluation of sorption performances and only a few of them aim at gaining a better understanding of sorption mechanisms. This can perhaps be explained by the fact that different kinds of interactions, such as ion-exchange interactions, hydrophobic attraction, physical adsorption, etc., can be acting simultaneously. Wide ranges of chemical structures, pH, salt concentrations and presence of ligands often add to the complication. Wu et al. showed that intraparticle diffusion plays an important role in the sorption mechanism. The uptake of dyes on chitosan may also proceed through ion-exchange mechanisms. The major adsorption site of chitosan is a primary amine group which is easily protonated to form $-NH^{+}_{3}$ in acidic solutions. The strong electrostatic interaction between the $-NH^{+}_{3}$ groups and dye anions can be used to explain the sorption mechanism [100]. The difference in the degree of adsorption may also be attributed to the chemical structure of each dye.

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

2.6.2. 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.

Because of its polar character, peat can effectively remove dyes from solution [127-129]. The use of peat to remove dyes was investigated by Allen et al. [130-132]. It was observed that peat tends to have a high cation exchange capacity, and is an effective sorbent for the removal of dyes. For acid and basic dyes, the removal performance was comparable with that of activated carbon, while for disperse dyes, the performance was much better.

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 [133,134]. Chemical pretreatment and the development of immobilized biomass beads can produce a more robust medium. As with other sorbents, chemical process are also used for improving sorption properties and selectivity. For example, Sun and Yang prepared modified peat-resin by mixing oxidizing peat with polyvinylalcohol and formaldehyde. These materials possess a macroreticular porous structure with enhanced physical characteristics. Their studies demonstrated that modified peat can be used for the removal of a variety of basic dyes. The maximum adsorption capacities for basic violet 14 and basic green 4 were 400 and 350 mg/ g treated peat, respectively.

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 [135]. 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.

2.6.3. Biomass

Decolorization and/or bioadsorption of dye wastewater by (dead or living) biomass, white-rot fungi and other microbial cultures was 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 [136,137]. 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. Biomass has a high potential as a sorbent due to its physico-chemical characteristics. A wide variety of microorganisms including algae, yeasts, bacteria and fungi are capable of decolorizing a wide range of dyes with a high efficiency [138-140]. In fungal decolorization, fungi can be classified into two kinds according to their life state: Living cells to biodegrade and biosorb dyes, and dead cells (fungal biomass) to adsorb dye. Most of the studies concentrated on living fungi for biosorption of the dyes. There are few studies on dye removal using dead fungal biomass, except in recent years. Removal of dyes has recently been studied with strains of Aspergillus niger [141,142] and Rhizopus arrhizus [143,144]. Fu and Viraraghavan [145,146] demonstrated that, compared with commercial activated carbon, dead fungal biomass of Aspergillus niger is a promising biosorbent for dye removal. Aksu and Tezer demonstrated uptake of 588.2 mg of recative black 5 per g using Rhizopus Arrhizus biomass. Waranusantigul et al [147] and Chu and Chen [148,149] also reported the uselfulness of biomass for the removal basic dyes. The biosorption capacity of fungal biomass could be increased by some pretreatment (by autoclaving or by reacting with chemicals). Other types of biomass such as yeasts have been studied for their dye uptake capacities. Yeasts are extensively used in a variety of large-scale industrial fermentation processes and waste biomass from these processes is a source potential for cheap adsorbent material. The performance of yeasts as a low-cost adsorbent to remove dyes has been demonstrated by Aksu and coworkers [150,151]. They found that the maximum adsorption capacities of yeasts for remazol blue and reactive black 5 were 171.1 and 88.5 mg/g, respectively.

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 [152]. 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.

In spite of good sorption properties and high selectivity some problems can occur. The sorption process is slow: In the case of biomass of Aspergillus Niger equilibrium was reached in 42 h. Another problem is that the initial pH of the dye solution strongly influenced the biosorption. Biosorption was also influenced by the functional groups in the fungal biomass and its specific surface properties [153]. Biosorption perfromance depends on some external factors such as salts and ions in solution which may be in competition. Other limitations of the technology include the fact that the method has only been tested for limited practical applications since biomass is not appropriate for the treatment of effluents using column systems, due to the clogging effect. Because of major limitations regarding its efficients utilization in a column reactor, there is a need for it to be immobilized. This step forms a major cost factor of the process.

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 [154]. 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 [155]. 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 [156]. However, these technologies are still being developed and much more work is required.

2.7. Miscellaneous sorbents

Other materials have been studied as low-cost sorbents, such as starch [157-159] and cyclodextrins [160-165]. 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 [166]. 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. A review of cyclodextrin- based materials can be found in a recent review by Crini and Morcellet.

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.

In spite of varied characteristics and properties, a limited number of dye adsorption studies have been carried out on starch-based derivatives. Crini et al. demonstrated that efficient extraction of dyes is achieved using crosslinked cyclodextrin gels. The presence of CD molecules in the polymer network permits an increase in its sorption properties. Delval et al. proposed crosslinked starch polymers containing amine groups. The polymers were prepared by crosslinking an agroalimentary by-product. The sorption results showed that the adsorption rate was high and the sorption capacities were significant. Several hundred ppm of dyes could be removed from water effectively in a few minutes using column experiments. The control of the crosslinking reaction allows control of the sorption properties of the material. However, due to the protonation of the amine groups on the surface of the sorbent, its adsorption behavior is strongly influenced by the pH values. Another interesting idea is to combine the properties of two biopolymers. Attempts were made to prepare adsorbents by coupling chitosan and cyclodextrin (CD) via several spacer arms without affecting the selectivity of the two polymers. The novel biosorbents containing both cyclodextrin and chitosan are in general more hydrophilic than commercial synthetic resins. Decontamination of water containing textile dyes was carried out with these sorbents. The results showed excellent sorption properties toward different classes of dyes. The chitosan beads containing CD are also characterized by a rate of sorption and a efficiency superior to that of the parent chitosan bead without CD and of the crosslinking cyclodextrinepichlorohydrin gels. The maximum adsorption capacities of starch-based material, crosslinked cyclodextrin and chitosan/cyclodextrin mixed sorbents for acid blue 25 were 249, 88 and 77.4 mg/g, respectively. There are several disadvantages of using starch-based

materials for dye removal. The efficiency of adsorption depends strongly on the control or particle size and the expansion of the polymer network. Performance is also dependent on the type of material used. Another problem with these materials is that they are nonporous and possess low surface area. Adsorption by starch-based materials occurs by physical adsorption, complexation and ion-exchange interactions.

Other materials used to adsorb dyes are cotton waste [167,168] and alumina [169]. Cotton is the most abundant of all naturally occurring organic substrates and is widely used. This material characteristically exhibits excellent physical and chemical properties in terms of stability, water absorbency and dye removal ability. The performance of treated cotton in a continuous system has been demonstrated by Bouzaida and Rammah. They found that the adsorption capacities of cotton for acid blue 25, acid yellow 99 and reactive yellow 23 were 589, 448 and 302 mg/g, respectively. McKay et al. also evaluated the performance of cotton waste for dye removal. It was found that this waste had the potential to adsorb 875 and 277 mg of basic red 2 and basic blue 9/g, respectively.

Polymeric sorbents are effective for dye removal and also they can be regenerated easily

3. EXPERIMENTAL

3.1 Materials and Instruments

Material

Amino pyrridine (SIGMA -ALDRICH), Iminodiacetic acid (SIGMA -ALDRICH), Divinyl benzene (DVB, 55%) of which is a mixture of meta and para isomers), Methylene blue (E.Merck), Calcon (E.Merck), Everzol Blue, Everzol black were supplied from EVERLIGHT COMPANY, TAIWAN

Chloroacetic acid (E.Merck), chlrosulfonic acid (Fluka), styrene (Fluka), and all the other chemicals used were analytical grade commercial products.

Instruments

UV-Vis Spectrophotometer (Perkin-Elmer Lamda 25)

3.2 Preparation of polymeric sorbents

Two types of polymeric sorbents were prepared according following procedures.

3.2.1 Crosslinked Poly (styrene-divinyl benzene) beads

Beads were prepared by the suspension polymerization of a mixtured styrene (54 ml, 0.48 mol) and DVB (55 % grade, 10 ml, 0.038 mol) in toluene (60 ml), using gum-Arabic as stabilizer, according to a previously described procedure. The beads were sieved and the 420-590 μm size fractions were used for further reactions.

3.2.2 Chlorosulfonation of the beaded polymer

The beaded polymer was chlorosulfonated using excess of chlorosulfonic acid at room temperature for 24 h. Than, reaction mixture was filtrated and was poured ice-water to remove chlorosulfonic acid. Chlorosulfonated resin was filtrated and washed with cold water and acetone respectively. The degree of chlorosulfonation was determined by analysis of the liberation of chloride ions. For these purpose, a

polymer (0.2 g.) sample was added to 10% NaOH (20 ml) and boiled for 4 h. After filtration and neutralization with HNO_3 (5 M), the chlorine content was determined by the mercuric-thiocyanate method. This gave a final chlorosulfonation degree of 4 mmol. g^{-1}.

3.3 Preparation of pyridine sulfonamide resin (Resin I)

Chlorosulfonated resin (10 g.) was added portion wise to a stirred of aminopyrridine 5 g (0.02 mol) in 2-methyl pyrrolidone (NMP) 30 ml at 0 ^oC. The mixture was shaken with a continuous shaker for 24 at room temperature. 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 11.2 g.

3.3.1 Determination of amine content of the Resin I

The amine content of the resin 1 was determined by Kjeldahl nitrogen analysis as follows. The polymer sample (0.2 g) was put into 20 mL H_2SO_4 (80%) and refluxed for 8 h. After cooling the mixture was diluted caustiously to 50 mL and filtered. The filtrate was used the Kjeldahl analysis the consumption of 7.5 mL 1 M HCl for the neutralization of the evolved ammonia indicated 3.75 mmol as the total nitrogen content.

3.4 Preparation of Dicarboxylic acid containing sulfonamide based resin (Resin II)

The chlorosulfonated polymer (8 g.) was added portion wise to a stirred solution of iminodiacetic acid (6 g, 0.045 mol) in 2-methyl pyrrolidone (25 ml) at 0 ^oC. The mixture was shaken with a continuous shaker for 12 h at room temperature. The reaction content was poured into water (500 ml), filtered and washed with excess water. The product was dried under vacuum at 40 ^oC for 24 h. The yield was 10.8 g.

3.4.1 Determination of the carboxylic acid content of the resin II

To 15 mL of 1 M NaOH solution 0.21 g of the resin II was added and left to stand overnight. The mixture was filtred and titrated with 1 M HCl the resulting 1.5 mL of the titrant indicates 7.3 $mmol.g^{-1}$ carboxyl content.

3.5 Extraction of the Acidic Dyes by Resin I

Dye capacities of the resin were determined by mixing weighed amount of polymer sample (0.2 g) with 10 mL aqueous dye solution (1.0 g dye /50 mL water -0.555 g /50 mL (ethanol 50%-water 50 %) (for calcon). In these experiments everzol blue, everzol black, and calcon were used as acidic dyes. The mixture was stirred for 24 h and then filtered.

Capacities were assigned by colorimetrical analysis of residual dye contents. Dye sorption capacities were found as 0.77 g per gram for calcon.

Also different concentrations of dyes were used to determine adsorption parameters of the resin I.

3.5.1 Kinetics of the dye sorption

In order to estimate the efficiency of the resin for trace dye, batch kinetic experiments were performed using highly diluted dye solutions ($1x10^{-3}$ g dye / L-$0.22x10^{-3}$ g/L water). For this purpose, resin (0.14 g.) was wetted with distilled water (1.5 ml) and added to a solution of dye (90 ml). The mixtures were stirred with a magnetic stirring bar and aliquots of the solution (5 ml) were taken at appropriate time intervals for the analysis of the residual dye contents by the method as described above.

3.5.2 Regeneration of the Resin I

This process was performed by using 5% KOH in ethanol-water mixture. 0.1 g dye loaded resin was placed into 20 mL of KOH solution. This mixture was stirred for 24 h at room temperature and refluxed for 3 h. Regeneration capacity was found as 0.26 g per gram polymer.

3.6 Extraction of the Basic Dye by Resin II

For this purpose, carboxylic acid containing polystyrene resin II (0.23 g) was used and sorption experiments were performed by using methylene blue (0.4 g/ 50 mL). Capacity of the resin was determined according to the above.

3.6.1 Kinetics of the dye sorption

Batch kinetic experiment was studied by using highly diluted dye solution ($8x10^{-3}$ g dye /L water). For this purpose, resin (0.2 g.) was wetted with distilled water (1.5 ml) and added to a solution of dye (90 ml). The mixtures were stirred with a magnetic stirring bar and aliquots of the solution (5 ml) were taken at appropriate time intervals for the analysis of the residual dye contents by the method as described above.

3.6.2. Regeneration of the Resin II

For this purpose, dye loaded was connected with 1 M H_2SO_4 and glacial acetic acid for 24 h at room temperature.

Regeneration capacity of the resin II was found 0.26 g / g resin for 1 M H_2SO_4 and 0.05 g / g resin for glacial acetic acid.

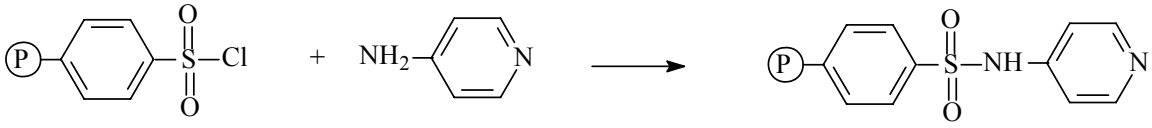
4. RESULTS AND DISCUSSION

In this study, two different sulfonamide resins were prepared removal of acidic and basic dyes from water.

Sulfonamide based resins were synthesized starting from crosslinked polystyrene-DVB (10%). Polystyrene beads were reacted with excess of chlorosulfonic acid to obtain chlorosulfonated polystyrene resin. Chlorosulfonation degree was found as 4.0 $mmol.g^{-1}$ (~70%).

4.1. Preparation of Resin I

Resin I was obtained starting from the reaction of chlorosulfonated polystyrene resin and amino pyridine (Scheme 4.1).



Scheme 4.1 : Preparation of Resin I

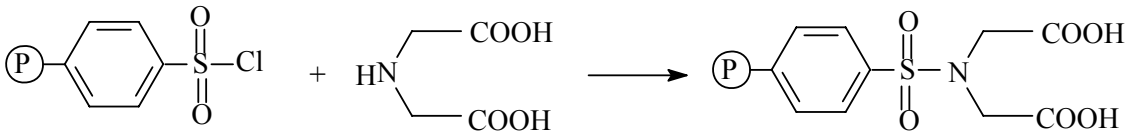
The resin was characterized by using Kjeldehal nitrogen analysis and FT-IR spectrophotometer.

Nitrogen content of the resin was calculated as about 3.75 $mmol.g^{-1}$.

Resin I was characterized by FT-IR spectroscopy. In the sulfonamide resin, S=O streching vibration occurs at 1362 cm^{-1} and 1159 cm^{-1}. The out of plane CH deformation vibrations in the pyridine ring are observed 1030-820 cm^{-1} .

4.1.1. Preparation of the Resin II

Dicarboxylic acid containing resin was prepared reaction with crosslinked chlorosulfonated polystyrene resin and iminodiacetic acid (Scheme 4.2).



Scheme 4.2: Preparation of the Resin II

This resin was characterized by using determination of carboxylic acid content and FT-IR spectrophotometer.

Carboxylic acid content was calculated as 7.3 mmol.g^{-1}.

Also, resin II was characterized by using FT-IR spectroscopy. S=O vibration in sulfonamide group is observed at 1362 cm^{-1} and 1156 cm^{-1}. The C=O stretching vibrations are observed in the range 1730-1600 cm^{-1} .

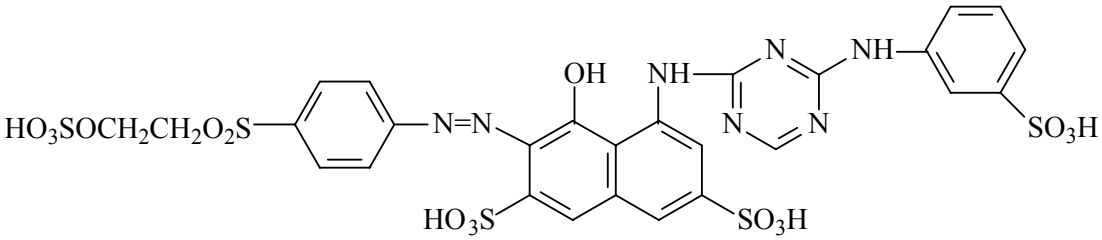
4.1.2. Extraction of Dyes

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.

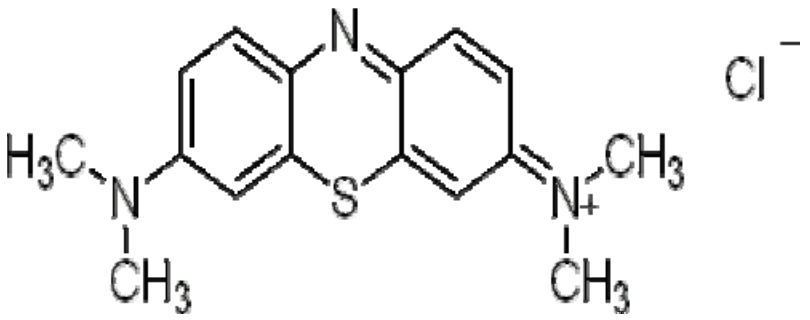
It has been reported that the basic mechanism in dyeing protein fibers with acid dyes is salt formation with amino groups as follows [170]:

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

Scheme 4.3: Salt formation of dyes with amino groups



Everzol Red RBN (Reactive Red)



Methylene Blue

Scheme 4.4: Molecular formula of everzol red and methylene blue

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 [171].

Table 4.1. Sorption capacities of the resins

Dye	**Capacity (g dye/g resin)**	**λ_{max} (nm)**
Calcon	0.77	552
Everzol Black	0.17	598
Everzol Blue	0.28	591
Methylene Blue	0.43	664

Table 4.2. Maximum dye sorption capacity of the resins depending on pH

Dye	pH	Capacity (g dye / g resin)
Everzol Black	2.0	0.11
	4.0	0.13
	5.0	0.31
	9.0	0.61
Everzol Blue	2.0	0.07
	4.0	0.29
	5.0	0.53
	9.0	0.47
Methylene Blue	2.0	0.3
	4.0	0.32
	5.0	0.24
	9.0	-

The resin shows reasonably high dye sorptions. It is important to note that the resin can be used in a wide pH range (Table 4.2). 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 [172,173].

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 [174]:

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

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

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

4.1.3. Dye sorption kinetics of the Resin II

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 (0.04 g dye / L water) to investigate the efficiency of the resin in the presence of trace quantities of dyes. The concentration–time plot in Figure 4 shows that within about 20 min of contact time, the dye concentration falls to zero for methylene blue.

5. CONCLUSION

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

Characterizations of the sorbents were performed by using analytical determination metods according to the literature.

Resin I has tertiary amine groups therefore it can sorb reactive (acidic) dyes .According to the experimental results resin I can remove reactive dyes successfully. Regeneration of the resin I was performed by KOH solution.

Resin II can sorb basic dyes because of acidic character of the resulting resin. There are two carboxylic acid groups in the resin therefore dye sorption kinetics of the resin is very rapid. Trace quantity of the dyes can be removed within about 20 minute. Regeneration of the resin was carried out by 1 M H_2SO_4 succesfully.

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APPENDIX

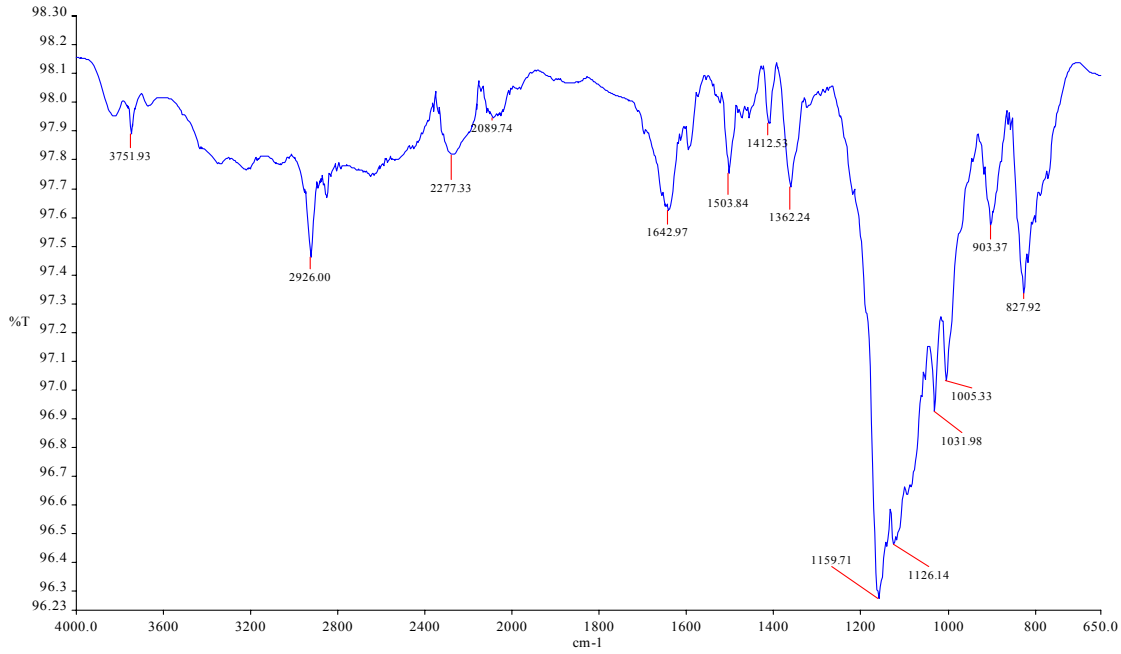


Figure 4.1: FT-IR spectrum of Resin I

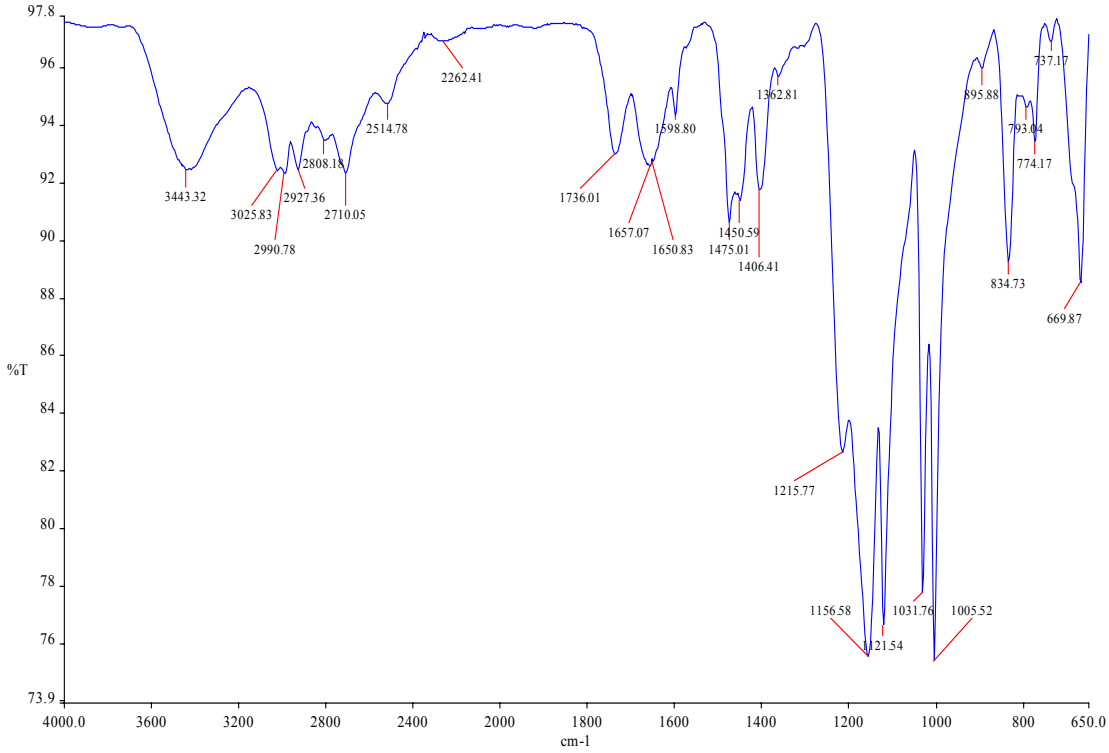


Figure 4.2: FT-IR spectrum of Resin II

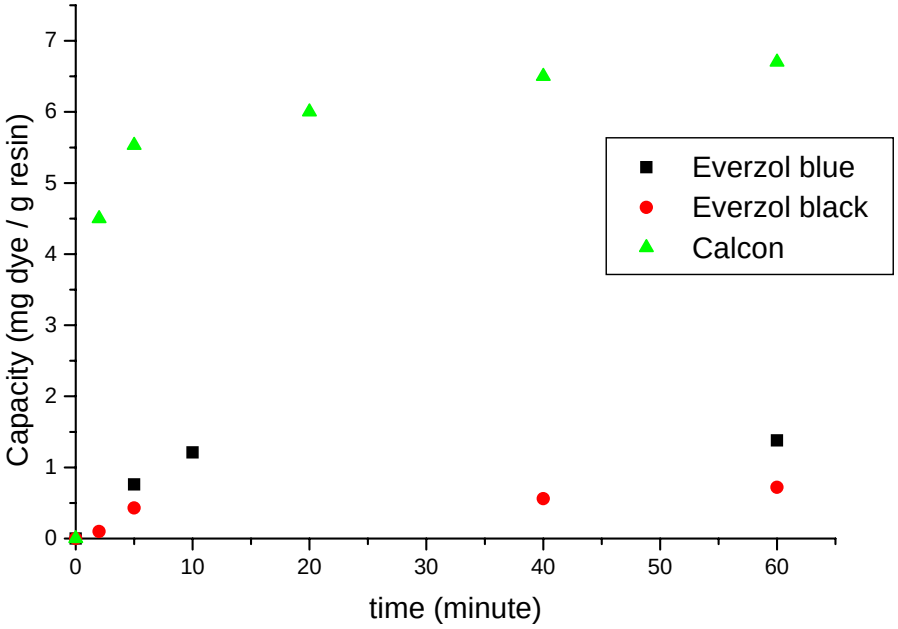


Figure 4.3: Dye sorption kinetics of the hydrogel from diluted aqueous solutions

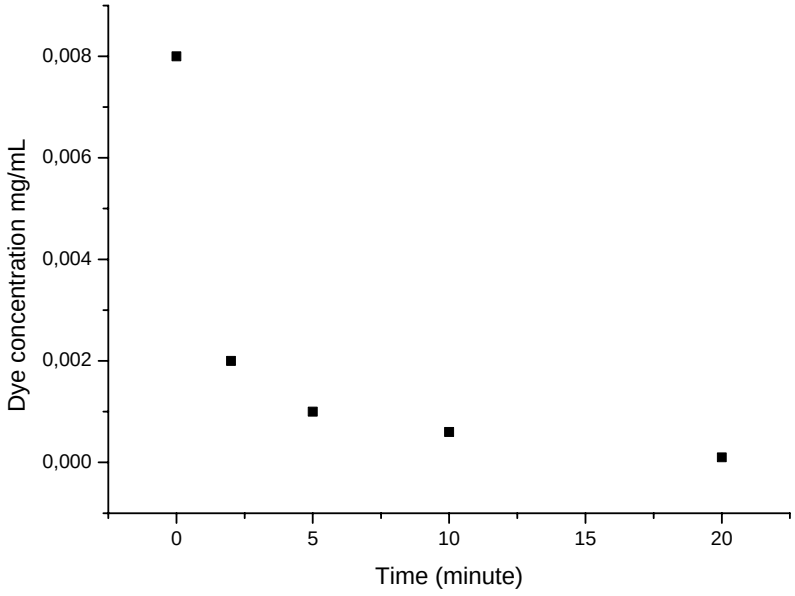


Figure 4.4 Sorption kinetic of methylene blue

AUTOBIOGRAPFY

He was born in 1976 in İstanbul . He graduated Antalya High School and attended to the Atatürk Univesity,Faculty of Engineering, Department of Chemistry.In 2003, he began as a master student in İstanbul Technical University, Polymer Science and Technology. Currently, he has been working in General Directorate of İstanbul Water and Sewerage Administration, Department of Water Quality Control since 2003.