

**REMOVAL OF DYE (REACTIVE GREEN 19) From AQUEOUS
MEDIUM USING AMIN MODIFIED RESIN**

**AMİN GRUBU İLE MODİFİYE EDİLMİŞ REÇİNE
KULLANARAK SUCUL ORTAMLARDAN BOYA (REAKTİF
YEŞİL 19) GİDERİMİ**

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ETHICS

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- I did not do any distortion in the data set
- And any part of this thesis has not been presented as another thesis study at this or any other university

08/12/2014

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Abstract

Removal Of Dye (Reactive Green 19) From Aqueous Medium Using Amine Modified Resin

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Systematic batch mode studies of adsorption of reactive green 19 (RG 19) on amine group functionalized poly(GMA-EGDMA) beads were carried out as a function of process of parameters including initial RG 19 concentration, dose of adsorbent, pH, ionic strength and temperature. Amine modified beads, the poly(GMA-EGDMA)-TREN, were found to have excellent adsorption capacity. For RG 19 the Freundlich and Langmuir isotherm models were used to test the equilibrium data. Both the Freundlich and Langmuir models were to be found best fitted isotherm models. The linear regression coefficient R^2 was used to elucidate the best fitting isotherm models. The monolayer (maximum) adsorption capacity (q_m) was found to be 140.84 mg/g beads. The results were fitted to both Freundlich and Langmuir isotherm models. The dimensionless separation factor (R_L) values lie between 0.44 to 0.96 indicated favorable adsorption. The Lagergen pseudo-first order, Lagergen pseudo-second order kinetic models were tested for the kinetic study. Both Lagergen pseudo first and

second order models were as found best fits the kinetics of adsorption ($q_{e(\text{the})} \approx q_{e(\text{exp})}$). Intra particle diffusion model showed boundary layer effect and high linearity of the plots indicated that intra-particle diffusion is the sole rate-limiting step. The results demonstrated that the percentage uptake of RG 19 is highly dependent on the initial concentration of RG 19 and decrease with an increase in dye concentration. Other adsorption parameters (pH, temperature, dose of sorbent and ionic strength) are only affecting the rate of adsorption. In this study it was found that almost 100% of RG 19 was removed from the solution after 1h contact time when concentration of RG 19 is between 10 to 100 mg/L.

Keywords : poly(GMA-EGDMA), TREN, modified resin, RG 19

Özet

Amin Grubu Modifiye Edilmiş Reçine Kullanarak Sucul Ortamdan Boya (Reaktif Yeşil 19) Giderimi

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Bu çalışmada, Reaktif Yeşil 19' un amin grubu modifiye edilmiş poly(GMA-EGDMA) küreleri üzerine adsorplanmasının sistematik kesikli reaktör çalışmaları, başlangıç boya konsantrasyonu, sorbent dozu, pH, iyonik şiddet ve sıcaklık parametrelerinin bir fonksiyonu olarak incelenmiştir. Amin grubu modifiye edilmiş kürelerinin (poly(GMA-EGDMA)), çok yüksek adsorpsiyon kapasitesine sahip oldukları bulunmuştur. Reaktif Yeşil 19 için Freundlich ve Langmuir izoterm modelleri, denge hali verilerinin test edilmesi için uygulanmıştır. Freundlich ve Langmuir modellerinin her ikisi de izoterm modelleri olarak uygun bulunmuştur. Doğrusal regresyon katsayısı R^2 en uygun izoterm modelinin açıklanması için kullanılmıştır. İzoterm çalışmaları sonucunda amin grubu modifiye edilmiş kürelerin maksimum adsorpsiyon kapasitesi 140.84 mg/g küre, bulunmuştur. Sonuçların Freundlich ve Langmuir izoterm modellerin her ikisine de uygun olduğu belirlenmiştir. Birimsiz ayırma faktörü değerleri (R_L) 0,44 – 0,96 aralığında olması uygun adsorpsiyonun gerçekleştiğini göstermiştir. Kinetik çalışma için Lagergen yalancı birinci dereceden, Lagergen yalancı ikinci dereceden kinetik modelleri uygulanmıştır. Kinetik çalışmalar sonucunda Lagergen yalancı birinci ve ikinci dereceden modellerin her ikisi de adsorpsiyon kinetikleri için uygun bulunmuştur ($q_{e(the)} \approx q_{e(exp)}$). İç parçacık difüzyon modeli

sınır tabaka etkisini göstermiş ve grafiklerin yüksek doğrusallığı iç parçacık difüzyonunun tek oran sınırlayıcı aşamasını ifade etmiştir. Çalışma sonuçları RG 19' un yüzde gideriminin aşırı derecede başlangıç boya konsantrasyonuna bağlı olduğunu göstermiş ve bu oran başlangıç boya konsantrasyonu yükseldikçe azalmıştır. Diğer adsorpsiyon parametreleri (pH, sıcaklık, sorbent dozu ve iyonik şiddet) sadece adsorpsiyon hızını etkilemiştir. Bu çalışmanın sonucunda, 1 saat temas süresinden sonra ve RG 19' un başlangıç konsantrasyonu 10-100 mg/L aralığında olduğu zaman, RG 19' un sucul ortamdan 100% giderildiği bulunmuştur.

Anahtar kelimeler: poly(GMA-EGDMA), TREN, modifiye edilmiş reçine, RG 19

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1. INTRODUCTION

1.1. Textile Industry

The textile industry is one of the oldest in the world. The oldest known textiles, which date back to about 5000 B.C., are scraps of linen cloth found in Egyptian caves. The industry was primarily a family and domestic one until the early part of the 1500s when the first factory system was established. It wasn't until the Industrial Revolution in England, in the 18th century, that power machines for spinning and weaving were invented. In the early 17th century of colonial America, textiles were primarily manufactured in New England homes. The twentieth century has seen the development of the first manmade fibers [1].

Natural and synthetic fibers used in textile industry like cotton, wool, silk, nylon, polyester and acrylics. It is a fragmented and heterogeneous sector that is composed of sub-sectors. This sector also varies in scale, from large scale mechanized to small scale traditional units. Generally, textile industry includes the spinning, knitting and weaving of fibers, the finishing of textile and the production of ready made garments [2].

1.1.1. Textile Industry and Environment

The flourishing of industries causes an influx of substances which exerting toxic effects on the biological sphere preventing the activation of biological degradation processes. Therefore, in the last decade, the special attention paid to environmental protection by social, political and legislative international authorities cause the evolution of research activities devoted to environment protection [2].

Textile industries are large industrial consumers of water as well as producers of wastewaters. With the increased demand for textile products, the textile industry and its wastewaters have been increasing proportionally, making it one of the main sources of severe pollution problems worldwide. The diversity in composition of chemical reagents used in textile industries contributes to much of the water pollution. The reagents range from inorganic compounds to polymers and organic

products. Waste water generated by different production steps of a textile mill have high pH, temperature, detergents, oil, suspended and dissolved solids, dispersants, leveling agents, toxic and non-biodegradable matter, color and alkalinity. Important pollutants in textile effluent are mainly recalcitrant organics, color, toxicants and surfactants, chlorinated compounds (AOX).

The textile wastewaters are characterized by extreme fluctuations in many parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, colors and salinity [3].

Also, widespread use of synthetic dyes by textile industries has increased the pollution by wastewater contaminated by dyestuff. Because of complex composition, color depth and high toxicity of dye wastewater which causes severe environmental pollution and human health hazards, it is necessary to treat these wastewater before discharging [4] [5].

1.2. Dye and Dyestuff

By definition Dyes can be said to be colored, ionizing and aromatic organic compounds which shows an affinity towards the substrate to which it is being applied. Dyes are the coloring material that color commodities of our day to day use. Dyes are applied everywhere, from Plastic toys for children to that fabrics we wear, from food to wood; hardly there is any industry where dyes are not used commercially. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. At the very basic level the use of color in identifying individual components of tissue sections can be accomplished primarily with dyes. Dyes also get completely or at least partially soluble in which it is being put to. For example certain kind of dyes can be toxic, carcinogenic or mutagenic and can be hazardous to health.

1.2.1. Dye and Dyestuff Classification

Coloring agents are substances impart color to substrates. Traditionally, coloring agents have been divided into soluble dyes and insoluble pigments. Pigments have stable physical and chemical properties during dyeing, whereas both natural and physical dyes are soluble in water or organic solvents. Dyes are classified according

to their chemical constitution or depending on the methods and field of their application.

Dyes can be classified in several ways, each class has a very unique chemistry, structure and particular way of bonding. Some dyes can react chemically with the substrates forming strong bonds in the process, and others can be held by physical forces. Generally, dyes can be classified by their solubility, dyeing properties and chemical structure.

- Natural / Synthetic
- Organic / Inorganic
- Chemical classification - Based on the nature of their respective chromophores.
- According to practical use
 - Cationic (cotton)
 - Direct (Cellulose)
 - Disperse (Polyamide fibres), etc. [6].

1.2.1.1. Natural and Synthetic Classification of Dyes

Natural dyes are derived from nature through organic and inorganic materials or sources. Logwood is a natural dye obtained from plants. It saturates silk, wool, cellulose acetate, and nylon with a deep black color. Tyrian purple is obtained from animals and Prussian blue is an inorganic dye obtained from naturally occurring minerals.

Synthetic dyes became popular because they were easy-to-use, less expensive and had wider range of colors. Synthetic dyes are obtained by adding chemicals to natural dyes. For example, artificial alizarin is a synthetic dye synthesized from coal tar anthracene. Synthetic dyes are used for modern clothing.

1.2.1.2. Organic and Inorganic Dyes

Organic colorants are made of carbon atoms and carbon-based molecules. Most organic colors are soluble dyes. If an organic soluble dye is to be used as a pigment,

it must be made into particle form. Some dyes are insoluble and must be chemically treated to become soluble. Vegetable-based organic colorants are produced by obtaining certain extracts from the plants.

Inorganic dyes are made up of mineral compounds and these minerals are mainly oxides, sulphides of one or more than one metals.

1.2.1.3. Chemical Classification of Dyes and Pigments

The chemical classification of dyes is primarily based on the presence of the chromophore, a chemical group which determines dyeing power. The principle dyes here are azo, anthraquinone, indigoid, arylmethane and phthalocyanine dyes.

A. Azo Dyes

The azo compound class accounts for 60-70% of all dyes [7]. They all contain an azo group, $-N=N-$, which links two sp^2 hybridized carbon atoms. Often, these carbons are part of aromatic systems, but this is not always the case. Most azo dyes contain only one azo group, but some contain two (*disazo*), three (*trisazo*) or more (*polyazo*).

B. Anthraquinone Dyes

Anthraquinone dyes constitute the second most important class of textile dyes, which have the chromophore groups, $=C=O$ and $=C=C=$, forming an anthraquinone complex. The group is subdivided according to the methods best suited to their application to various fibers [6]. These dyes can be precipitated or adsorbed only in small amounts, while under anaerobic conditions they are cleaved by microorganisms forming potentially carcinogenic aromatic amines [8].

C. Indigoid Dyes

Indigo and indigoid dyes are natural dyes and have been known since Bronze Age. This group of dyes used to dye cellulose and protein fibers as well as for cotton printing. Generally natural indigoid dyes were obtained from woad and the indigo

plant. Moreover, indigo-related pigments were found in historic yarns, textile fibers, printed document, icons and painting [9].

D. Arylmethane Dyes

Arylmethane dyes are so called because they are derived from methane, but in which some of the hydrogen atoms are replaced with aryl rings. Since a synonym for aryl is phenyl, they may also legitimately be called phenylmethane dyes. Aryl rings are often referred to as benzene rings. However, benzene is a specific chemical compound and this usage is technically incorrect, although very common.

E. Phthalocyanine Dyes

Derivatives of tetrabenzotetra azoporphyrine (phthalocyanine) and its complex compounds with metals constitute a group of dyes that called Phthalocyanin dyes. The most widely use phthalocyanin dye is copper phthalocyanine, a blue pigment [10].

1.2.1.4. Classification of Dyes According to Their Practical Use

A. Basic and Cationic Dyes

Basic dyes is one of the most important class of dyes that is on acrylic fibers. Basic dyes dissociate in water to produce coloured cations. This class of dyes characterized by their brilliance and very high tinctorial strength [11]. basic dyes are used for cotton, linen, acetate, nylon, polyesters, acrylics and modacrylics.

B. Direct Dyes

Historically, the direct dyes followed the basic dyes and were widely hailed because they made it unnecessary to use a mordant or binder in dyeing cotton. The colors are not as brilliant as those in the basic dyes but they have better fastness to light and washing, and such fastness can be measurably improved by after treatments (diazotized and developed.) Direct dyes can be used on cotton, linen, rayon, wool,

silk and nylon. These dyes usually have azo linkage $-N=N-$ and high molecular weight [6]. They are water soluble because of sulfonic acid groups.

C. Acid Dyes

This is a very large and important group of dyestuff which is used in an acidic medium. This group of dyes containing azo dyes, anthraquinone dyes and triphenylmethane dyes. This group of dyes exhibit strong chemical strength like other organic dyes [12]. Acid dyes cannot be used for wool tops but are used in dyeing wool piece goods, silk, nylon, and some of the other manmade fibers. The ordinary type of acid dye is reserved largely for apparel fabrics and for knitting and rug yarns. A great deal of it is used on nylon carpeting.

D. Metalized Dyes

This group of dyes that is also known as pre-metallized dyes shows great affinity toward protein fibers. In these dyes one or two molecules are coordinated with metal ion and constitute metal complex. Among the popular metal complex dyes 1:2 metal complex dyes are mostly used for dyeing polyamide fibers. These metal complex dyes are favorable for dyeing wool as well [13].

E. Sulfur Dyes

Sulfur Dyes are insoluble. Sodium sulfide is used for reducing and making these dyes soluble. Dyeing is done at high temperature with large quantities of salt so that the color penetrates into the fiber. The advantages of these dyes are their cheapness and colour fastness [14]. These dyes are fast to light, washing and perspiration and are mostly used for cotton and linen.

F. Azoic Dyes

Azoic dyes is a large group of dyes used in industry for color printing and textile dyeing. These group of dyes designed to convey high photolytic stability and resistance toward major oxidizing agents [15]. These dyes is manufactured in the

fabric by applying one half of the dye. The other half is then put on and they combined to form the finished color.

G. Vat Dyes

Vat dyes is a class of dyes that involve chromophores such as anthraquinoids and indigoids [16]. They are successfully used on cotton, linen, rayon, wool, silk and sometimes nylon. Vat dyes are also used in the continuous piece of dyeing process sometimes called the pigment application process [17].

H. Disperse Dyes

Disperse dyes are water insoluble. These particles dissolve in the fibers and impart color to them. Disperse dyes is applied for dyeing synthetic fabrics like alcantara, polyester, acetate of cellulose, acrylic and polyamide materials [18].

I. Pigment Dyes

Pigments are insoluble organic and inorganic solid powder colorants. They are extensively used for coloring fabrics like cotton, wool and other manmade fibers due to their excellent light fastness. They do not have any affinity to the fibers and are affixed to the fabric with the help of binders. After dyeing, the fabrics are subjected to high temperatures [19].

J. Mordant Dyes

The mordant or chrome dyes are acidic in character. Sodium or potassium bichromate is used with them in the dye bath or after the process of dyeing is completed. This is done for getting the binding action of the chrome. They are mostly used for wool which gets a good color fastness after treatment with mordant dyes. They are also used for cotton, linen, silk, rayon and nylon but are less effective for them.

K. Reactive Dyes

Dyes that react with the textile fiber to produce both a hydroxyl and an oxygen linkage, the chlorine combining with the hydroxyl to form a strong ether linkage [6]. Reactive dyes molecules form a stable covalent bond with the fibers and gives a bright and stable color to the final product. However, their low degree of fixation on the fiber, approximately between 50% to 90% results in the release of the significant amounts of the dye in the wastewater [7].

Reactive dyeing is now the most important method for the coloration of cellulosic fibres. Reactive dyes can also be applied on wool and nylon; in the latter case they are applied under weakly acidic conditions. In such a condition reactive dyes make covalent bond with fiber that is differ from other kinds of dyes [20]. Reactive dyes have a low utilization degree compared to other types of dyestuff, since the functional group also bonds to water, creating hydrolysis of reactive dyes.

In the case of unwholesome treated this type of dyes, these dyes may have a significant impact on the environment by reduction of sunlight penetration and dissolved oxygen concentration on body of water and detrimental effect on ecosystems [20].

1.3. Reactive Green 19

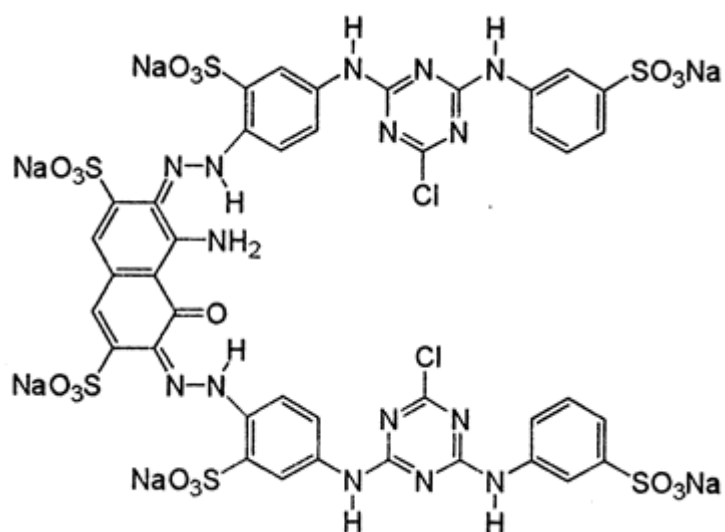
One of the mostly used azo dyes in textile industry because of its cost effectiveness and privileged wash and light fastness properties are Reactive Green 19(RG-19) which is the sulfonated diazo dye with a high molecular weight of $M_w=1418.9 \text{ g mol}^{-1}$ and the chemical structure featured by the presence of two azo groups as the chromophoric moiety and two chlorotriazine groups (Table. 1-1). However, like other azo dyes, RG-19 shows a very low degree of fixation on the fiber, typically between 50% to 90%, which yield to release of serious amount of compound in the dye wastewater. The high aromaticity and low reactivity of RG-19 make this dye highly resident to both microbial and chemical degradation [7].

Moreover, due to RG-19, toxic, carcinogenic and mutagenic effects on environment and organisms (Table. 1-2), it is necessary to treat dye-containing effluents by applying biological sorption, adsorption, membrane, coagulation-flocculation, oxidation-ozonation and advanced oxidation processes.

Table 1-1. Structure and characteristics of RG-19

Name : C.I. Reactive Green 19 (RG19)

Chemical structure :



Chemical Class: Anionic, Diazo

Molecular Formula: C₄₀H₂₃Cl₂N₁₅Na₆O₁₉S₆

Molecular Weight: 1418.94

CAS no. 68110-31-6

λ_{max} (nm) 630

<i>Light Fastness</i>	<i>Oxygen Bleaching</i>		<i>Perspiration Fastness</i>		<i>Soaping</i>	
	<i>fading</i>	<i>stain</i>	<i>fading</i>	<i>stain</i>	<i>fading</i>	<i>stain</i>
4	2- 3(yellow)	4-5	4- 5(yellow) (alkali)	4	4-5(95°C)	4-5

Table 1-2. Particular Risks of RG-19 to Environment and Human Health

-
1. Irritating to eyes
 2. Irritating to respiratory system
 3. Irritating to skin
 4. Danger of very serious irreversible effects
 5. Limited evidence of carcinogenic effects
 6. Risk of serious damage to eye
 7. May cause sensitization by inhalation
 8. May cause sensitization by skin contact
 9. May cause cancer
 10. May cause heritable genetic damage
 11. Danger of serious damage to health by prolonged exposure
 12. May cause cancer by inhalation
 13. Very toxic to aquatic organisms
 14. May cause long term adverse effects in the aquatic environment
 15. Toxic to flora
 16. Toxic to fauna
 17. Toxic to soil organisms
 18. Toxic to bees
 19. Dangerous for ozone layer
 20. May impair fertility
 21. May cause harm to unborn child
 22. May cause harm to breast-fed babies
 23. May cause lung damage if swallowed
 24. Repeated exposure may cause skin dryness or cracking
-

1.4. Dye Removal From Textile Industry Wastewater: Technologies and Methods

During the last three decades, several treatment methods and technology for removing dyes from industrial wastewater effluents have been reported. These technologies divided into three main categories: conventional methods that involved;coagulation/flocculation,precipitation/flocculation,electrocoagulation/electroflotation, biodegradation and adsorption on activated carbon. The second class of technologies named by established recovery methods that involved;

electrochemical treatment, membrane separation, ion-exchange and the third group that named by emerging recovery technologies, involved; advanced oxidation, selective adsorption [21].

I. Coagulation/Flocculation

Coagulation is one of the widely applied processes for removing dyestuff from industrial wastewater streams. Inorganic coagulants such as alum, magnesium, ferrous and vermiculite in forms of carbonate, sulfate and chlorides was investigated in the literature.

Mehrota et.al. (1995), in their investigation in which magnesium carbonate was used as a coagulant, reported the removal of 92% color from vat dye and sulfur dye effluent, and 38% of color from basic dye effluent. In another investigation in which ferrous sulfate used as a coagulant, they reported the minimum 75% removal of color from vat dye effluent. As the use of coagulant for dye removal generate the huge amount of chemical sludge by treatment plants, the amount of sludge, punctual disposal and reuse of waste sludge has become a significant environmental issue [22] [23].

Choi et.al., (1996), investigated the performance of vermiculite extract solution as a coagulant for removing dye from wastewater. As they reported, this process produced less sludge at lower coagulant doses than processes using conventional inorganic coagulants. The alum sludge recycling system that involved the sludge separation, alum solubilization, impurity screening and alum reuse was reported conceivable and cost-effective [23] [24]. However, the operation of alum recovery is complicated. In this regard, as chu (2001), reported, the maximum hydrophobic dye (Dianix Blue) removal of 85% in the optimum pH of 9.13 had achieved with the presence of 100 mg/l of fresh alum concentration and a polymer concentration of 31.25 mg/l. He also reported that, If the RAS sludge is recycled during re-stabilization, negative dye removals will be observed due to the back-diffusion of dye that previously resided in the alum sludge. However, the back-diffusion mechanism can be effectively controlled if fresh alum is added to the recycling system. As his work conclusion, the use of RAS is quite efficient for removing hydrophobic dye from wastewater, but according to the uncontrolled back-diffusion

of pre-resided dye in the RAS, this process is not suitable for hydrophilic dye. Although coagulation by alum is efficient and low-cost, alum is harmful to human and living organisms.

Magnesium chloride in compare with alum is a less commonly used as coagulant in the field of wastewater treatment. In the literature there are lot of investigations that illustrates, if there are enough Mg^{2+} ions was present in the system of lime treatment, the good coagulation could be achieved [25]. Ten et.al. (2000), reported in this study the maximum 97.9% removal of reactive dye (Levax Brill Blue EBRA) in the presence of $MgCl_2$ as a coagulant in the optimum pH of 10.5 and 11.00 and the flocs formed by the $MgCl_2$ treatment are found to give shorter settling time than the alum treatment [25].

Ferric ions are another choice as coagulants to destabilize colloidal and suspended solids like dyestuffs. Ferrous sulfate is an effective coagulant in removing of colors by the percentage of 70-90%. However reactive dyes are difficult to decolorize by inorganic coagulants, and ferric coagulants need a large amount of alkali to resist the pH depression that occurs during coagulation. Therefore, research on alternative coagulants has been active in recent years.

II. Electrocoagulation/Electrofloatation

One of the promising methods for treatment of dyestuff industrial wastewater is electrocoagulation in which the process, coagulation, adsorption, precipitation and flotation occurs by utilization of aluminum and iron anodes to produced aluminum and iron hydroxide flocs by reaction at the anodes followed by hydrolysis. However, it has not been accepted because of high initial cost in compared with other treatment technologies.

The mechanism of the process is to generate flocs by electrical charge and by separation of these flocs we can remove color and turbidity from wastewaters.

Due to this technology' s low-energy consumption, it is very efficient in removal of COD and colors from wastewater.

Generally, three main processes occur serially during electrocoagulation:

- I. electrolytic reactions at electrode surfaces,
- II. formation of coagulants in aqueous phase,
- III. adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or floatation.

Kobyas et al. (2002), reported in an investigation in which, focused on comparison of iron and aluminum electrodes efficiency in removal of COD and turbidity from wastewater in different conditions, that electrocoagulation by using these two electrodes very dependent on pH. According to the results, in acidic medium, pH < 6, COD and turbidity removal efficiencies of aluminum are 98% and 65% respectively, that are higher than those of iron, while in neutral and alkaline medium iron is preferable with the 98-75% and 77-47% removal percentage for turbidity and COD, respectively. As high conductivity favors high process performances, they reported that iron requires less current density than aluminum for the same turbidity or COD removal efficiencies for a operating time of 10 min to reach the same color removal efficiency. Finally they concluded that the energy consumption kWh per kg COD removed is lower with iron, while the electrode consumption per kg COD removed is lower generally with aluminum [26].

Daneshvar et al. (2006), run the same investigation by using sacrificial iron electrodes. As they reported, when pH of the dye solutions was between 5.5 and 8.5, there was maximum color removal efficiency of approximately 95% that is the same as Kobya's reported. In the case of conductivity and energy consumption, both reports indicated the same results. They also reported the optimum electrolysis time of 5 min [27].

Elsewhere, Aleboyeh et al. (2007), run the same investigation in which, iron sacrificial electrodes was used. In the case of effects of pH, optimum current density and time of electrolysis, all the results were the same. As they reported, under optimal value of process parameters, high color removal (>93%) was obtained [28].

III. Biodegradation

One of the alternative approaches for removing colors from wastewater streams is by utilizing microbial biocatalysts. This technology offers potential advantages over physico-chemical processes. Especially, the ability of whole bacterial cells to metabolize azo dyes is the focus of many investigations in recent years. Although under aerobic conditions, azo dyes are not easily metabolized, under anaerobic conditions, many bacteria reduce the highly electrophilic azo bond in the dye molecule, reportedly by the activity of low specificity cytoplasmic azo reductases, to produce colorless aromatic amines. However, these amines are resistant to further anaerobic mineralization and can be toxic and mutagenic to organisms, but once the xenobiotic azo component of the dye molecule has been removed, the remaining amino compounds are good substrates for aerobic biodegradation. That's why many researchers offer mixed aerobic and anaerobic treatment. Moreover, the use of whole cells rather than isolated enzymes is advantageous, because of the high cost of the enzyme purification and the cell can also offer protection from the harsh process environment to the enzymes.

Moreover, degradation is often performed by a number of enzymes working sequentially. Disadvantage of mixed culture is macroscopic view of what's happening in the system and results are not easily reproduced, making thorough, effective interpretation difficult. That's why many researchers have been running their investigations using single bacterial cultures.

As it is obvious in Table. 1-3, although this technology is effective for removing dyestuff from wastewater, long removal time is disadvantage of this technique [29].

Table 1-3. Biodegradation of dyes using bacterial cultures: a brief review of studies in the literature

Type of dye	Organisms used	Percentage of removed dye/ run time	Reference
Reactive dyes, diazo dyes, azo dyes, disperse dyes and phthalocyanine dyes	<i>Alcaligenes faecalis</i> , <i>Commomonas acidovorans</i>	100% within 48 h	Nigam P.et.al., 1996
Various azo and diazo reactive dyes	Thermophilic anaerobic bacterial culture	68-84% within 48 h	Banat MI et.al., 1996
Hydrolysed C.I.Reactive Orange 96	Sulphate-reducing bacteria, methane producing bacteria and fermentative bacteria in an anaerobic mixed culture	Sulphate-reducing bacteria can remove 95% within 40 h. Methane producing bacteria take no part in dye removal. Fermentative bacteria can remove 30% within 90 h.	Yoo ES et.al., 2001
C.I.Acid Orange 12	<i>Pseudomonas Cepacia</i> 13NA	90% within 68 h	Ogawa T et.al., 1986
4 reactive azo dyes	<i>Pseudomonas luteola</i>	37-93% within 42 h	Hu TI et.al., 1990
Remazol Black B	<i>Shewanella putrefaciens</i>	85% within 6.5 h	Kamilaki A., 2000
C.I.Reactive Orange 96	<i>Desulfovibrio desulfuricans</i>	95% within 2 h	Yoo ES et.al., 2000
Reactive azo dyes, Direct azo dyes and leather dyes	<i>Pseudomonas luteola</i>	59-99% within 2-6 days	Hu TL, 2001
Reactive red-120	<i>Lentinus sajor-caju</i>	70%	Arica and Bayramoğlu, 2007
Reactive Green 19	<i>Micrococcus glutamicus</i>	100% within 42h	Saratale et.al., 2009

Reactive Blue 172	<i>Exiguobacterium</i> sp.	91.2% within 48h	Dhanve et.al., 2008
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[29] [30] [31] [32].

IV. Adsorption on Activated Carbon

As told further, chemical and biological methods are effective in dye removal from wastewater. However, requirement of specialized equipment and quite energy intensively of these methods and large amount of by-products generated during treatment by these methods make them unwanted [33].

Generally, physical methods which include adsorption, ion exchange, and membrane filtration are effective for removing reactive dyes without producing unwanted by-products.

Studies involving the application of a wide range of adsorbents in the decolourisation of wastewaters are reported in literature, adsorption on activated carbon (AC) being one of the most studied techniques.

Because activated carbons (AC) have a high degree of porosity and an extensive surface area, these materials are effective adsorbents for several organic compounds of concern in the field of water and wastewater treatment. Likewise, the amount and nature of oxygen-containing functional groups in the surface area of the ACs is an important parameter affected the adsorption capacity of these materials [34].

As many authors mentioned in their studies, although ACs are the effective materials in removal of dyes and organic compounds from wastewaters, high cost and non-regenerative features of these materials are disadvantages of application of these materials as sorbents.

Senthilkumar et.al.,2006. Investigated the adsorption of Reactive red dye (RR) onto Coconut tree flower carbon (CFC) and Jute fibre carbon (JFC) from aqueous solution. According to their reports, quantitative removal of dye was found to be at lower pH values. The higher adsorption capacity of RR onto JFC 200 mg/g, compared with that to CFC, 181.9 mg/g suggested JFC a better adsorbent for the removal of Reactive red from aqueous solution at the agitation time of 3h [35].

Elsewhere, Santhy and Selvapathy (2006), carried out another investigation in which activated carbon prepared from coir pith used as sorbent towards three highly used reactive dyes (C.I. Reactive Orange 12; C.I. Reactive Red 2; C.I. Reactive Blue 4) in textile industry. In their study the effect of various parameters such as initial concentration, contact time, pH and adsorbent dose on the adsorption process was investigated. As it obtained, maximum removals of Reactive Orange 12, Reactive Red 2 and Reactive Blue 4 were found to be 82%, 77% and 72%, respectively, at 4 h equilibration time and at 40 mg/L initial concentration and pH range of 1-3 [36].

Navin KA (2008). Investigated the removal of a reactive dye (reactive orange) by three types of activated carbon prepared from bagasse pith, an agricultural solid waste which is locally available and economically viable for wastewater treatment. As he reported, the maximum adsorption of RO dye by bagasse pith occurred at an initial pH of 1.0. Removal efficiency increased with decreasing the dye concentration and increasing dose of adsorbent. Investigation exhibited the maximum removal of RO (approximately 97%) after about 1h of shaking [37].

V. Electrochemical Method

Electrochemistry offers promising approaches for the prevention of pollution problems in the process industry. The potential use of electrochemistry for the treatment of such wastewaters has been differentiated between electrochemical conversion of the contaminant to complete combustion of the organic materials to CO₂ or to a form more attractive to be degraded using other methods. But, both approaches can be carried out using either direct electrolysis at the surface of electrode, or by generating a reactive intermediate that attacks the substrate in a subsequent step. Some papers have reported the use of electrochemical treatment of textile dyes [18] [38]. Carbon electrodes and carbon fiber electrode have been tested [38] and the results indicated an efficient degradation performance comparable with the Fenton's reagent. In addition, the possibility to generate hydroxyl radicals (OH_·) as intermediate species at the anode surface has attracted much attention. A range of anode materials (Ti/PdO-Co₃O₄, Ti/RhO_x-TiO₂, Ti/MnO₂-RuO₂, Ti/Pt-Ir, Ti/SnO₂-Sb₂O₅, Ti/RuO₂-TiO₂ and Ti/Pt, etc.) and photo-

electrochemical methods have been used to the last purpose. Although the electrochemical methods for dye degradation have been successful, the lack of data on the electrochemical properties of anthraquinone dyes has been the main problem in assessing the technique as decolorization source.

VI. Membrane Separation

Several methods for dye removal such as biological treatment, coagulation/flocculation, ozone treatment, chemical oxidation and photocatalytic processes, membrane processes and adsorption are exist.

Nowadays, many of the world's textile manufacturers are equipped with their own wastewater treatment plant, which usually combines an aerobic biological process and a physicochemical process. However, most of these traditional methods were found inadequate due to the large variability of composition of textile wastewater. According to Marmagne and Coste, the coagulation and flocculation process is not an excellent one for reactive dye removal. The poor quality of floc resulted in uneven settlement even after introduction of a flocculant. This treatment method, however, was suitable to be used in sulphur and dispensed dye removal due to the good quality of floc formation. They also revealed their studies on color removal of different types of dyes using an activated carbon treatment. Results indicated that high removal rates (>90%) could only be achieved for acid and cationic dyes. For reactive dyes, a moderate removal (>50%) is considered good. The ozonation process shows a higher reactive dye removal compared to the other treatments, regardless of types of reactive dyes used. It is very effective towards oxidation of dyes and removing color, which is the main disturbing factor for water recycling in the textile industry. Many researchers reported that much better results were obtained using a combined coagulation–precipitation/ ozonation treatment instead of using a single-stage treatment system. However, it may increase the cost of operation or even form toxic by-products from biodegradable substances during the ozonation process. Traditionally, integrated treatment processes such as activated sludge and chemical coagulation had been widely used to deal with textile wastewater. The integrated treatment processes were intended to treat textile wastewater to a level that meets the stringent regulations required by governments.

At present, numerous laboratory-scale experiments have documented the feasibility of various integrated treatment technologies on recovery of rinsed water and chemicals from textile effluent. Mostly, the integrated treatment technologies are promising, but they all still suffer limitations which require further research and development [39].

The need for more efficient treatment processes has attracted the attention of environmental scientists and engineers towards pressure-driven membrane techniques. The application of membrane filtration processes not only enables high removal efficiencies, but also allows reuse of water and some of the valuable waste constituents specifically dyes [40].

Akbari et. al. carried out an investigation in 2001 in which the performance of a polyamide nanofiltration membrane in treating colored textile effluent was investigated. As they reported for anionic dyes (acid red 4, acid orange 10, direct red 80, direct yellow 8, and reactive orange 16), the membrane generally showed acceptable rejection due mainly to its relatively low cut-off and the cationic dyes were more than 95% retained in 1h filtration. But the membrane was not suitable for cationic dye (basic blue 3) removal as they reported [40].

Liu et. al., 2007, used two commercial anion exchange membranes (strong basic SB6407 and weak basic DE81) for removal of two anionic reactive dyes (Cibacron red 3BA and Cibacron blue 3GA). For both membranes more than 95% of both dyes were removed after 2h as they reported. Moreover, more than 75% of dyes were recovered using appropriate desorption conditions [41].

VII. Ion-exchange Technology

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases the term is used to denote the processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic 'ion exchangers'.

Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, and soil humus, etc. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are

also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in *mixed beds* that contain a mixture of anion and cation exchange resins, or passing the treated solution through several different ion exchange materials.

Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure. Typical examples of ions that can bind to ion exchangers are:

- H^+ (proton) and OH^- (hydroxide)
- Single-charged monatomic ions like Na^+ , K^+ , and Cl^-
- Double-charged monatomic ions like Ca^{2+} and Mg^{2+}
- Polyatomic inorganic ions like SO_4^{2-} and PO_4^{3-}
- Organic bases, usually molecules containing the amine functional group $-NR_2H^+$
- Organic acids, often molecules containing $-COO^-$ (carboxylic acid) functional groups
- Biomolecules that can be ionized: amino acids, peptides, proteins, etc.

All of these ions exist in dyes molecular structure and that's the reason many researchers focused on the use of ion-exchangers as an effective sorbents in the field of dye-containing wastewater treatment.

Bayramoglu et. al., carried out an investigation in 2009 in which a functionalized cation exchanger resin (HEMA-g-GMA) is used as a sorbent for removal of two mostly used dyes (Crystal Violet and Basic Fuchsin) in textile industry. As they illustrated cationic sulfonic groups contributed to the adsorption mechanism.

through electrostatic interactions between sulfonic groups of the adsorbent (which are known as strong cation exchangers) and the cationic sites of CV and BF basic dyes. As the investigation indicated more than 97% of both dyes were removed in the contact time of 2h [42].

Karcher et.al., carried out a precious comparative investigation in 2001 by the use of 5 types of reactive azo dyes (RO16, RB 15, RR 120, RR 198 and RB 5) along with, three anion exchangers, S 6328 a, MP 62 and P 2, four polymeric resins without functional groups, OC1064, OC1066, P12 and EP63, two zeolites, DAY-P and DAZ-P and GEH resins, as sorbents.

They derived their experiments at room temperature of 20-25 °C with diluted dye solutions of volume of 100 ml for approximately 72 h to reach equilibrium.

Clearly they were reported, the zeolites and EP 63 removed virtually no dye and OC 1066 only very little, whereas the other sorbents do achieve decoloration. In the case of OC 1064 significant dye removal is obtained only in presence of Ca. zeolites and EP 63 are eventually unsuitable and excluded from further investigations, as they report. In their further screenings in which RO 16 was a very small and RB 15 was a very large dyes using OC 1064, S 6328 and GEH and one more unfunctionalized resin (P 12) and two more anion exchangers (MP 62 and P2) as sorbents, in order to be able to account more clearly for pore size effects. The set of tests with RO 16 shows the anion exchangers MP 62, P 2 and possibly OC 1064 to have the highest removal efficiency of 75%, 90% and 60%, respectively. The picture changes a little when regarding to sorption of large dye(RB 15) in which the OC 1064 shows practically no sorption whereas the GEH perform relatively well with the sorption of approximately, 15 % and 100%, respectively.

As they concluded from the investigation, in the dilute, Ca-free waters which are finding in rinsing steps after dyeing operations where softened water is generally used , OC 1064 is not suitable for all spectrum of dyes as large dyes sorb very poorly.

As conclusion of their research, Zeolites and microporous resins are not suitable for reactive dye sorption. The strongly basic anion exchanger S6328a is not generally suitable for reactive dye removal. In spite of very good sorption characteristics it is not universally applicable because some dyes cannot be desorbed. The non-functionalized resin OC1064 has a relatively low capacity and affinity for the dyes in question. It almost completely fails to sorb large dyes. The weakly basic anion exchange resin MP62, especially in the protonated form, has a

very high capacity and affinity for reactive dyes. MP62 is a promising sorbent for reactive dye removal.

The granulated β -FeOOH GEH has a relatively low maximum capacity for reactive dyes but all tested dyes are removed with comparable efficiency, independent of molecular weight. When comparing loading per volume instead of loading per weight the capacity of GEH looks somewhat better since GEH has a density about twice the one of the other sorbents [43].

Kamboh et.al.,2009, reported in their investigation in which synthesized calix[4]arene based resin ((C4) resin (5)) used as sorbent for removal of three reactive dyes (reactive black 5, reactive red 45 and congo red) that in the optimum pH the maximum removal of 82%, 72% and 60% for RB5, CR and RR45 was obtained, respectively, in the contact time of 1h [44].

Bayramoglu et.al., carried out an investigation upon the removal of RG-19, a sulfonated diazo dye, by amine modified magnetic polymer, in 2012. As they reported the effective pH for removal of RG-19 was pH 3. As its demonstrated from the results of the investigation, the presence of NaCl reduced the dye removal capacity of the amine modified magnetic beads and dye removal capacity of the functionalized beads increased with increasing in temperature. Consequently the maximum capacity of the modified magnetic beads was reported 99% within approximately 4h [45].

As it obvious from the reports ion exchangers and functionalized resins are effective sorbents for dye removal in comparison with other materials.

VIII. Advanced Oxidation

Many chemical treatment processes have been used extensively to treat textile wastewaters. studies, such as chemical precipitation, adsorption by activated carbon and some natural absorbents, photocatalytic oxidation, ozonation focused on color removal. These methods are effective for dealing with treating wastewater containing soluble and in soluble dyes. Each method has its advantages and disadvantages in the case of removal of soluble and insoluble dyes. For example, the ozonation oxidation process can effectively decolorize wastewater containing

soluble dyes, such as reactive dyes. However, ozonation oxidation cannot decolorize insoluble dyes, such as disperse dyes. Insoluble dyes can be effectively decolorized by coagulation, but coagulation is ineffective for soluble dyes [46].

Between these methods advanced oxidation method is one of the most efficient method in decolorizing both soluble and insoluble dyes.

One of the oldest advanced oxidation processes is Fenton Oxidation (FO) in which the process composed at acidic pH yielding hydroxy radicals directly. It is performed in four stages, which are pH adjustment to low acidic values, oxidation reaction, neutralization and coagulation.

Meric et.al. carried out an investigation in 2003, in which the removal of reactive black 5 which is a reactive azo dye is aimed by FO process. As reported in this study, in the optimum pH of 3 and optimum temperature of 40°C and maximum process time of 30 min, the maximum removal of 99% of RB 5 is obtained [47].

Hsueh et.al.(2004), investigated the removal of Red MX-5B using Fenton and Fenton-like systems. As they reported, the optimum pH of the reaction solution for both Fenton and Fenton-like systems were 2.5–3.0. In the optimum pH of 3 and maximum contact time of 480 min, the removal of 99.8% and 99.55 of Red MX-5B is obtained for both Fenton and Fenton-like system, respectively [46].

Zorro and Lavecchia carried out an study in 2013, in which study based on degradation of RG 19 by UV radiation and hydrogen peroxide. On their study, under the best conditions, complete decolorization of the dye solution was achieved in about 20 min [7].

It is obviously obtained from the results of the studies of the evaluation of the advanced oxidation method on the removal of dyes from textile wastewater that this method is one of the effectiveness methods for dye removal.

2. MATERIALS AND METHODS

In this chapter, the procedure of adsorption parameters studies and the adsorbent and dyestuff that was used in the adsorption process and its physical and chemical properties are explained.

2.1. Materials

Reactive Green 19 was supplied by Sigma Chemical Co. (St. Louis, MO, USA) and used as received. Glycidyl methacrylate (GMA) and ethyleneglycol dimethacrylate (EGDMA) were obtained Fluka A.G. (Buchs, Switzerland) and purified by vacuum distillation and stored in a refrigerator until use. Azobisisobutyronitrile (AIBN) and poly(vinyl alcohol) (PVA), were supplied by Sigma Chemical Co. (St. Louis, MO, USA) BDH Chemicals Ltd., Poole, England) and selected as the initiator and the steric stabilizer, respectively. AIBN was recrystallized from methanol. All other chemicals used were reagent grade from Merck A.G. (Darmstadt, Germany) unless otherwise noted. All water used in the adsorption experiments was purified using.

2.2. Preparation of poly(GMA-EGDMA) beads

The suspension polymerization was performed in a magnetic driven, sealed cylindrical reactor (volume: 500 ml) equipped with a temperature control system. A typical procedure applied for the suspension copolymerization of GMA and EGDMA is given below. The monomer phase was comprised of 15 ml GMA, 7.5 mL EGDMA and 5.0% polyvinyl alcohol (20 mL, as stabilizer). Two hundred milligrams of AIBN as initiator was dissolved into the monomer phase. The resulting medium was transferred into the reactor and sonicated for about 5 min at 200 W within an ultrasonic water bath (Bransonic 2200, England) for the complete dissolution of AIBN in the polymerization medium. And the aqueous dispersion phases contained NaCl solution (0.1M, 400 mL) placed in a polymerization reactor. The reactor content was stirred at 500 rpm during the monomer addition completed within about 5 min and the heating was started. Then reactor was purged with bubbling nitrogen for about 5 min. Then, the sealed reactor was placed in a shaking water bath at room temperature. The initial polymerization time was defined when the reactor

temperature was raised to 70 °C. The polymerization was allowed to proceed under nitrogen atmosphere at 70 °C for 2 h and then at 80 °C for 1.0 h (stirring rate: 250 rpm). After completion of the polymerization period, the reactor content was cooled down to room temperature and centrifuged at 5000 rpm for 10 min for the removal of dispersion medium. This reaction led to the formation of white beads. Poly(GMA-EGDMA) beads were redispersed within 10 ml of ethanol and centrifuged again under similar conditions. The ethanol washing (70%; 250 mL) was repeated three times for complete removal of unconverted monomers and other components and then washed with purified water. Finally, poly(GMA-EGDMA) beads were dried in a vacuum oven at 50 °C and stored at room temperature until use.

2.3. Attachment of tris(2-aminoethyl)amine ligand to poly(GMA-EGDMA) beads

The poly(GMA-EGDMA) beads (~ 10.0 g), were washed with phosphate buffer (50 mM, pH 8.0), and then transferred in the same fresh buffer containing tris(2-aminoethyl)amine (TREN) ligand (0.5 M). The reaction was carried out at 65 °C for 12 h while continuous stirring. The beads were collected from the reaction mixture by filtration and then washed with purified water (500 mL) and ethyl alcohol (200 mL). Finally, the beads were dried in a vacuum oven at 50 °C for 6 h. Hereafter the TREN ligand modified bead was referred as poly(GMA-EGDMA)-TREN.

2.4. Characterization of poly(GMA-EGDMA) and poly(GMA-EGDMA)-TREN beads

2.4.1. Size distribution of poly(GMA-EGDMA) beads

The size and size distribution of the poly(GMA-EGDMA) beads were determined by using molecular sieves with different pore size (i.e., 425-300-212-150-75 μm). Polymerization yield was calculated as 67%.

2.4.2. Surface morphology of beads

The morphology and size of the poly(GMA-EGDMA) beads were observed by scanning electron microscopy (ZEISS, Evo 50). Polymer samples were dried at

room temperature and coated with a thin layer of gold (about 100Å) in vacuum and photographed in the electron microscope spectroscopy at Spectroscopy Laboratory of Geology Engineering of Hacettepe University.

2.4.3. Specific surface area of p(GMA-EGDMA) beads

The specific surface area of the silica particles was measured by a surface area apparatus (Leco, CHNS-932, ABD) and calculated using the BET (Brunauer, Emmett, and Teller) method.

2.4.4. FTIR measurements

ATR-FTIR measurements of the bare poly(GMA-EGDMA), modified poly(GMA-EGDMA) and Reactive Green 19 dye adsorbed poly(GMA-EGDMA) bead samples were made in the one-bounce ATR mode in a Spectrum 100 FTIR spectrometer (Perkin-Elmer Inc., Norwalk, CT, USA) equipped with a Universal ATR accessory. Samples were scanned from 4000 to 525 cm^{-1} . The polymer beads were degassed overnight in a vacuum oven maintained at 40 °C before FTIR measurements.

2.4.5. Swelling ratio of beads

The swelling ratio of the poly(GMA-EGDMA) and p(GMA-EGDMA)-TREN modified beads were determined using a volumetric cylinder. The height of the dry resin (H_d) was measured and then purified water was added into the volumetric cylinder and mixed at 50 rpm for 24 h. Then, the height of the swollen beads (H_s) was recorded. The swelling ratio was determined by Equation 1:

$$\text{Equilibrium water swelling ratio} = (H_s/H_d) \quad \text{Equation 1}$$

2.4.6. Epoxy content of the poly(GMA-EGDMA) beads

The amount of available functional epoxy group content of the poly(GMA-EGDMA) beads was determined by pyridine-HCl titration method according to the literature.

0,2 g of the poly(GMA-EGDMA) beads was left in contact with 10 ml of pyridine-HCl solution and refluxed for 1 hour. After filtration, 2 ml of filtrate was taken and epoxy content of the solution was determined by titration with 0.055 M NaOH solution in the presence of phenol-phatalein color indicator.

2.4.7. Amine content of the poly(GMA-EGDMA)-TREN beads

The amount of attached TREN ligand on the resin, poly(GMA-EGDMA)-TREN, was determined via potentiometric titration. The beads about 1.0 g was transferred in a flask containing 0.1 M HCl solution (20 mL). The flask was shaken at room temperature for 12 h. After this period, the beads were removed and washed with 10 mL 0.5 M NaCl solution. The wash solution (10 mL) was combined with reaction mixture and the remaining concentration of HCl in the solution was determined by titration with 0.02 M NaOH.

2.5. Reactive dye removal studies

The adsorption of reactive dye (Reactive Green 19) on the TREN ligand attached poly(GMA-EGDMA) beads was investigated in a batch system. Solutions of the dye, containing 10–400 mg/L, were prepared in purified water. The ranges of concentrations of the dye were prepared from stock solutions (600 mg/mL). Adsorption experiments were performed by agitating magnetically at 150 rpm, at 25 ± 2 °C for 2 h. The volume of the each dye solution was 10 mL in each test. After centrifugation, the amounts of unadsorbed dye in supernatant solutions were analyzed for its dye concentration using a double beam UV–vis spectrophotometer (PG Instrument Ltd., Model T80+; PRC). All measurements were done at 620 nm for Reactive Green 19. The molecular structures of the dye are shown in The amount of adsorbed dye per gram poly(GMA-EGDMA)-TREN beads (mg dye/g dry beads) was obtained by using the following expression in Equation 2:

$$q = (C_0 - C) V / m \quad \text{Equation 2}$$

where C_0 and C are the concentrations of dye in the solution before and after the adsorption in mg/L, respectively. q is the amount of dye sorbed onto a unit dry mass of the beads in mg/g, V is the volume of the dye solution in L, and m is the weight of the dry beads in g.

The values of percentage removal were calculated using relationship shown in Equation 3:

$$\text{Percentage removal} = [(C_i - C_f) / C_i] \times 100 \quad \text{Equation 3}$$

Where, C_i = Initial dye concentration (mg/l), C_f = Final dye concentration (mg/l), m = Mass of adsorbent (g/l).

2.5.1. The effect of pH

The effect of solution pH on the removal efficiency of the resin was investigated in the pH range 2.0–8.0 for Reactive Green-19 (RG-19) at 25°C. The solution pH was adjusted in the range of 2–8 by adding 0.1 N HCl or 0.1 N NaOH solutions according to requirement.

2.5.2. Effect of sorbent dosage

The effect of adsorbent dosage on the removal of selected azo dye was evaluated by varying the dosage of the modified beds, which ranged from 0.01 g to 0.1 g, by keeping constant initial dye concentration at 25.0 mg/L at pH 3.0.

2.5.3. Effect of ionic strength

Sodium chloride (NaCl) was employed as background electrolyte changed between 0.0 and 1.0 M to investigate the influence of ionic strength on the RG 19 removal.

2.5.4. Effect of temperature

The effect of temperature for dye removal was studied at four different temperatures (i.e., 15, 25, 35 and 45 °C) at pH 3.0.

2.5.5. Effect of initial dye concentration

To determine the effect of initial concentrations of the RG 19 on the adsorption rate and capacity on the beads, the initial concentration of reactive dye was varied between 10 and 400 mg/L in the adsorption media at pH 3.0. For each adsorption experiments, the average of three replicates was presented.

2.5.6. Elution and regeneration of the sorbent

To determine the reusability of TREN modified beads consecutive adsorption–desorption cycles were repeated 3 times using the same adsorbent. Desorption of Reactive Green-19 dye was performed using 0.2 M HNO₃ solution. The loaded adsorbent was placed in the desorption medium and stirred at 150 rpm for 2 h at 25 °C. The final dye concentration in the aqueous phase was determined as described above. After each cycle of adsorption–desorption, the beads were washed and transferred into fresh dye solution for adsorption in the succeeding cycle. The desorption ratio was calculated from the amount of dye adsorbed on the resin and the final dye concentration in the adsorption medium.

3. RESULTS AND DISCUSSION

Several techniques has been used for polymerization such as suspension, emulsion and precipitation polymerization [48]. In this work, the p(GMA-EGDMA) beads were synthesized via suspension polymerization. The size and size distrubition of poly(GMA-EGDMA) beads was determined using molecular sieves with different pore size (i.e., 425-300-250-150-75 μm). The yield of polymerization was found as 67%. The particle size fractions of the beads were about 75–150 μm and used for the dye adsorption studies. Scanning electron microscopy (SEM) micrographs at Spectroscopy laboratory of Geology Engineering Department of Hacettepe University (Figure 3-1) shows the surface morphological structure of the poly(GMA-EGDMA) beads. These beads have a spherical form and rough surface due to the pores formed during the polymerization [49]. The specific surface area of the poly(GMA-EGDMA) beads was found as 3.27 m^2/g using BET method.

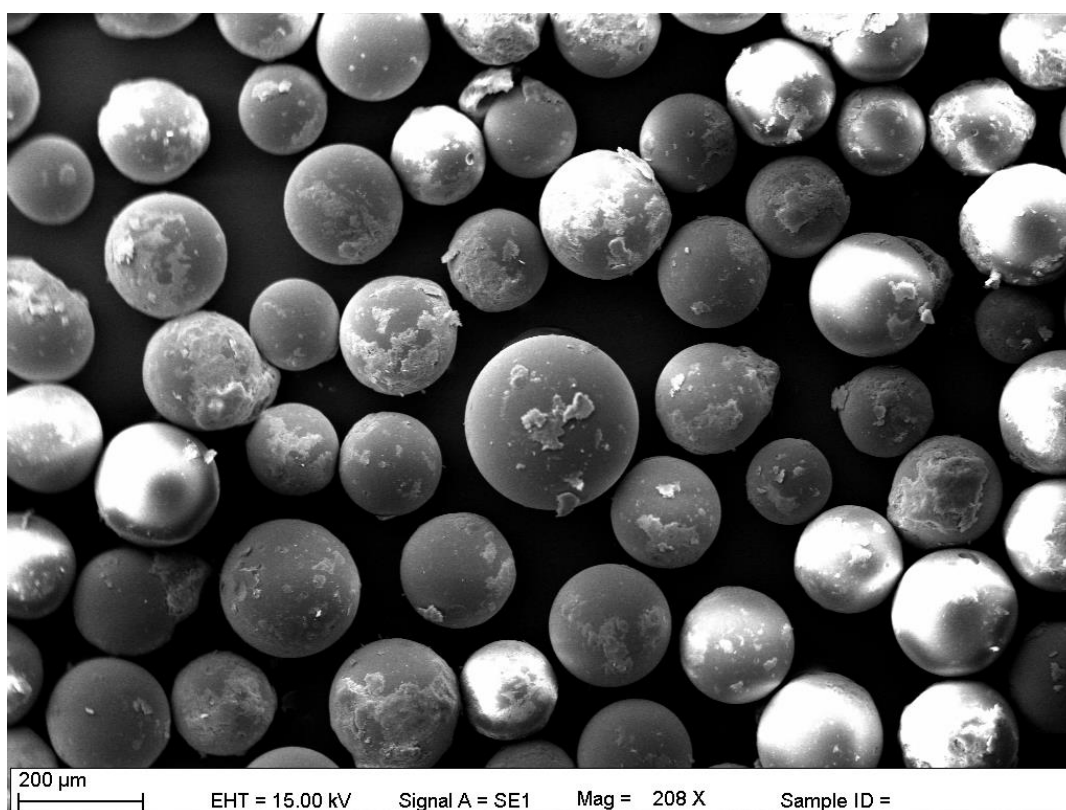


Figure 3-1. SEM micrographs of the beads (Spectroscopy Lab., Geology Engineering Department of Hacettepe University)

The functional epoxy group content of the poly(GMA-EGDMA) beads was determined by the HCl-pyridine method, and was found to be 5.34 mmol g⁻¹ beads. Following TREN ligand attachments, the amino group content of poly(GMA-EGDMA)-TREN beads was determined as 11.2 mmol/g beads. The equilibrium-swelling ratio of the poly(GMA-EGDMA) and modified poly(GMA-EGDMA)-TREN beads was 37.4 and 51.6, respectively. When TREN ligand was introduced on the structure of the beads, the swelling ratio of the grafted beads increased compared plain beads. During the coupling reaction of TREN with epoxy groups of GMA, additional four amine groups and a hydroxyl group were introduced on the polymer backbone, and caused more water uptake.

The FTIR spectra of the poly(GMA-EGDMA) beads include the characteristic stretching vibration band of hydrogen-bonded alcohol at 3452 cm⁻¹ (Figure 3-2.a). Among the characteristic vibrations of GMA, and EGDMA are methylene and ester configuration vibrations at 2943 cm⁻¹ and 1729 cm⁻¹. The epoxide group gives the band between at 910 cm⁻¹ (epoxy ring vibrations). The modified beads with TREN ligand show a broad -NH₂ stretching at 3250-3443 cm⁻¹ (Figure 3-2. b). The adsorption band for the TREN modified beads was observed at 1655 cm⁻¹ and 1520 cm⁻¹ and represents N-H bending due to the modification of epoxy groups with TREN ligand. In addition, C-H stretching of methyl groups appears at around 2919 and 1481 cm⁻¹, respectively. These spectral changes confirmed the reaction between the epoxy groups of polymer chains and amine groups of TREN ligand molecules. Thus, the amine groups containing TAEA immobilized on the beads can easily interact with the acidic dye molecules.

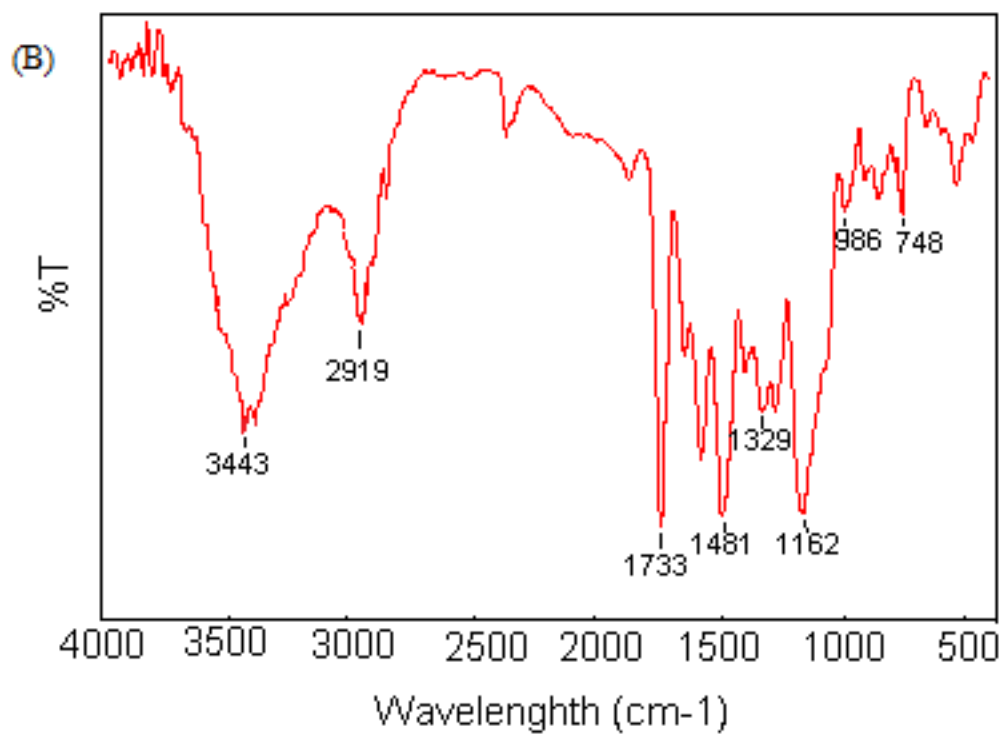
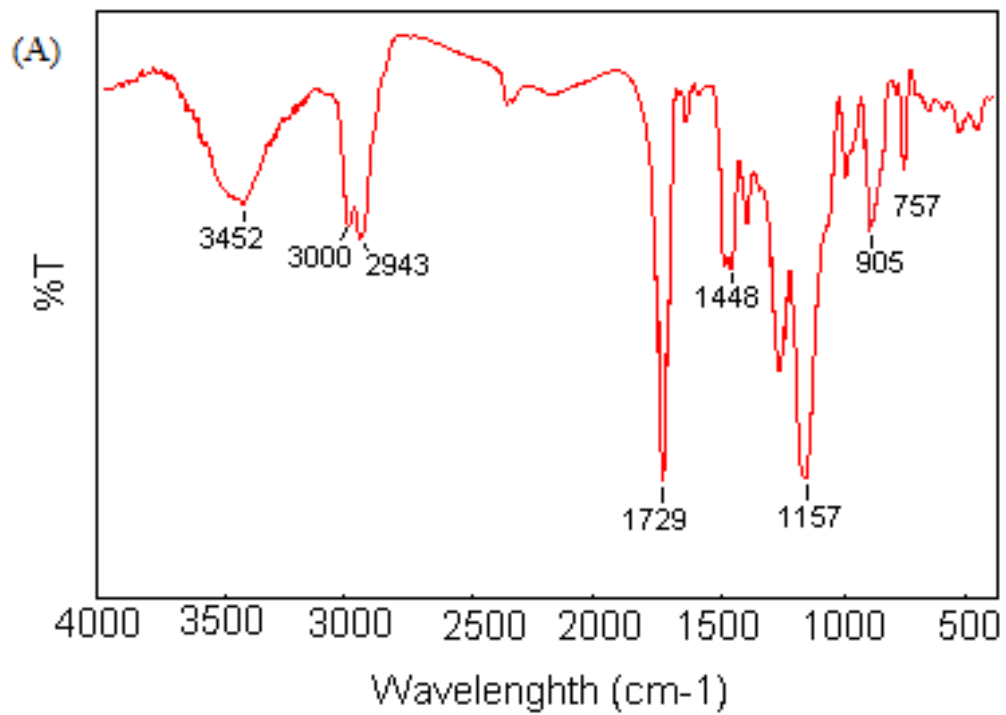


Figure 3-2. The FTIR spectra of (A) the poly(GMA-EGDMA) and (B) the poly(GMA-EGDMA)-TREN beads

3.1. Investigation of Sorption Parameters

Systematic batch mode studies of adsorption of reactive green 19 (RG 19) on amine group functionalized poly(GMA-EGDMA) beads were carried out as a function of process of parameters includes initial RG 19 concentration, dose of adsorbent, pH, ionic strength and temperature.

3.1.1. Effect of pH

Textile wastewaters can have a wide range of pH values and dyeing processes involve adding high concentrations of salts, such as Na_2SO_4 and NaCl , to enhance bath exhaustion, as well as carbonates to adjust pH [43]. That's why the pH is an important factor in controlling the adsorption of dye onto adsorbent. The adsorption of RG 19 from 50 mg/l concentration on the poly(GMA-EGDMA)-TREN beads was studied by varying the pH from 2 to 8. The result reveals that the adsorption of RG 19 decreased from 100% to 81% with increasing in pH of the solution (Figure 3-3). The higher slope of the curves that indicate the pH 2 and pH 3 than other pH curves slope shows better adsorption capacity of the poly(GMA-EGDMA)-TREN beads at low pHs of 2 and 3. At low pH, the carboxyl groups on the surface of the resin responsible for binding with the RG 19 which is the acidic dye are predominantly protonated (-COOH) and hence capable of binding the dye [50]. Therefore, the remaining experiments were carried out at pH 3. The adsorption of this charged dye onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which is in turn influenced by the solution pH.

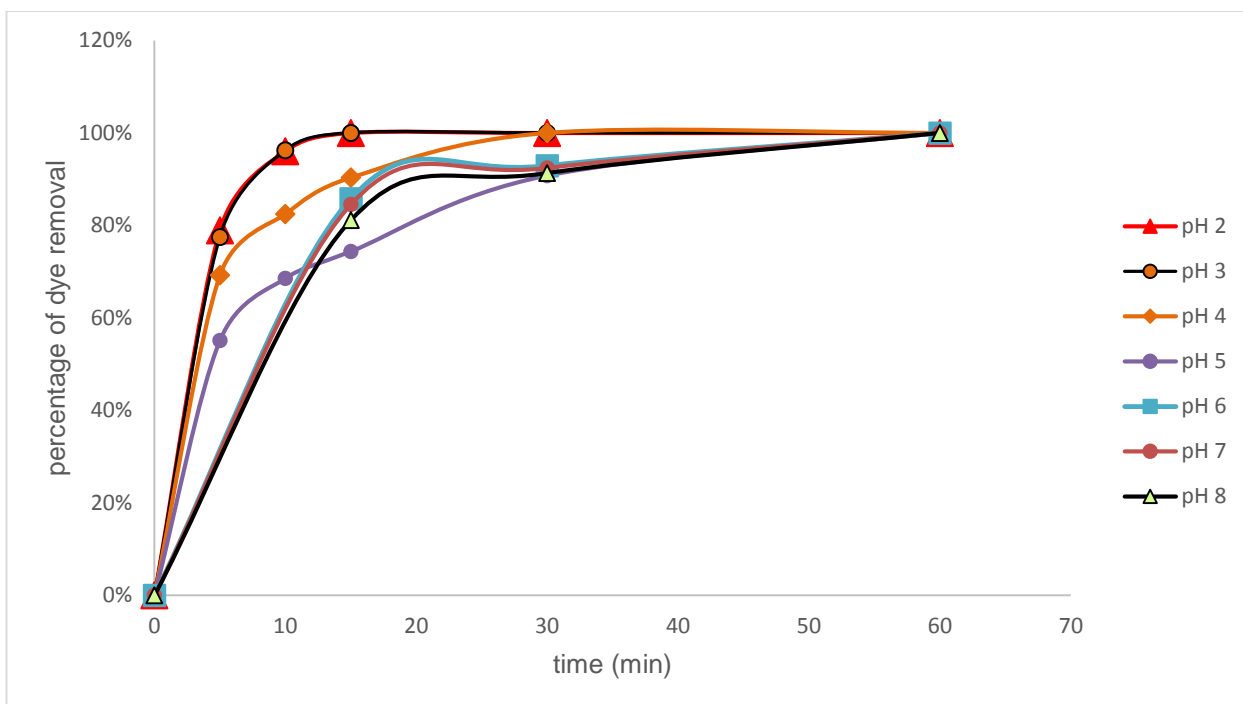


Figure 3-3. Effect of pH and contact time on adsorption of RG 19 onto the poly(GMA-EGDMA)-TREN beads.

(Adsorption conditions- initial concentration of dye : 50 mg/L; solution volume : 10 mL; amount of sorbent : 5 g/L; temperature : 25 °C; varying pH from 2 to 8).

3.1.2. Effect of Initial Dye Concentration

Effect of initial dye concentration with contact time on adsorption of RG 19 is presented in Figure 3-4 Uptake of RG 19 was rapid in the first 5 minutes and after 60 minutes the amount of RG 19 adsorbed did not changed. Therefore, for batch experiments 60 minutes equilibrium time was used (Figure 3-5). Percentage sorption decreased from 100 to 47% (Figure 3-6) but amount of RG 19 adsorbed per unit mass of adsorbent increased from 3.65 to 73.72 mg/ g with increase in RG 19 concentration from 10 to 400 mg/L.

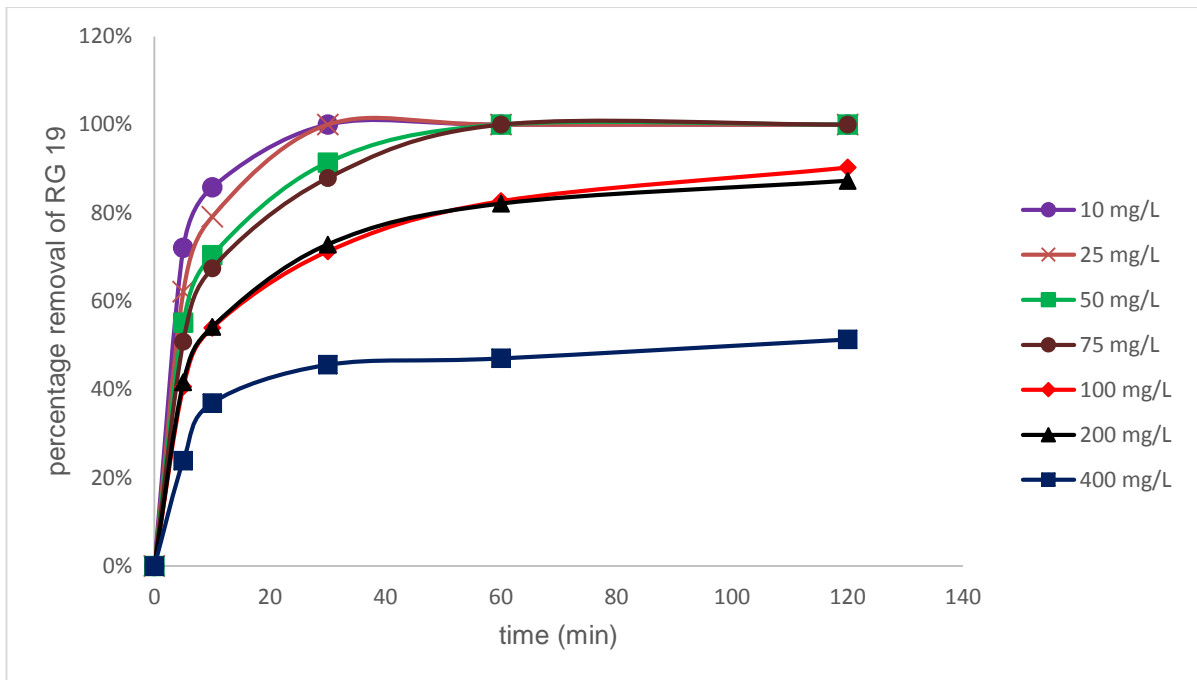


Figure 3-4. Effect of Initial Dye Concentration and Contact Time on adsorption of RG 19 onto the poly(GMA-EGDMA)-TREN beads.

However, the equilibrium removal rate were similar for 10 mg/L, 25 mg/L, 50 mg/L, 75 mg/L and for 100 mg/L and 200 mg/L initial dye concentration.

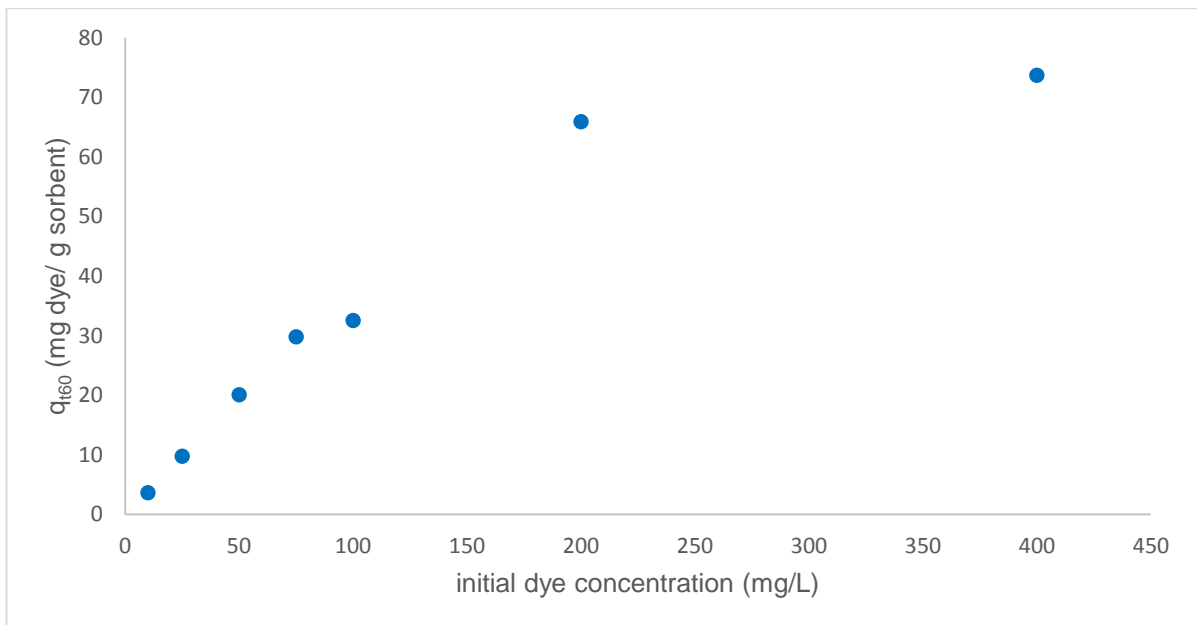


Figure 3-5. Effect of initial dye concentration on the removal capacity of the poly(GMA-EGDMA)-TREN beads.

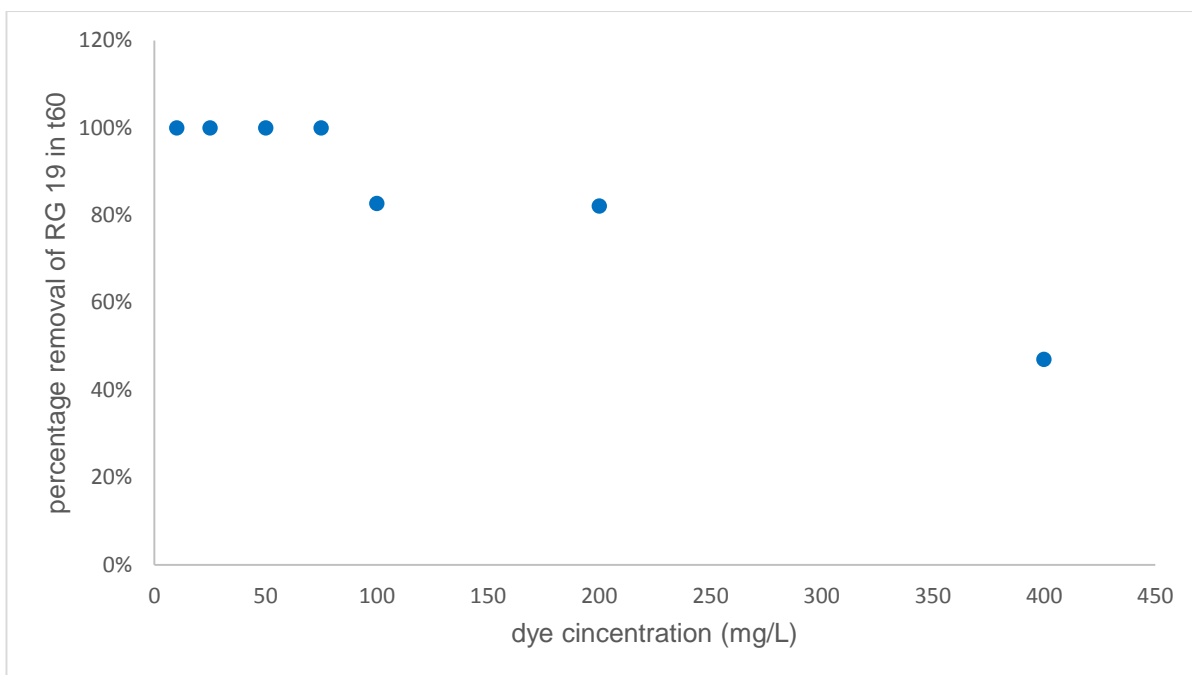


Figure 3-6. Effect of initial dye concentration on percentage removal capacity of the poly(GMA-EGDMA)-TREN beads.

(Adsorption conditions- solution volume : 10 mL; pH 3.0; temperature : 25 °C; adsorbent dosage from 2.5 g/L).

3.1.3. Effect of Adsorbent Dosage

The dependence of dye adsorption on adsorbent dosage was studied by varying the amount of adsorbents in the medium from 1 to 10 g/L while keeping other parameters constant such as initial concentration of dye (25 mg/L), pH 3.0, temperature 25 °C and contact time 2 h. As shown in Figure 3-7, the removal efficiency of the adsorbent improved with increasing in dosage of adsorbent. This is expected due to the fact that the higher dose of adsorbents in the adsorption medium, the greater the availability of exchangeable sites for the ions. The adsorption capacity of RG 19 onto the POLY(GMA-EGDMA)-TREN BEADS is 100 % after 1h contact time. Increasing the adsorbent dosage from 1 to 10 g/l increase the adsorption rate. As the adsorbent dose increases, surface area and available sites for the dye molecules also increase, and consequently better adsorption takes place [51]. As conclusion, the adsorption rate of RG 19 increased with the increase in the adsorbent dosage and reached faster to an equilibrium value around 10.0 g/L of adsorbent dosage .

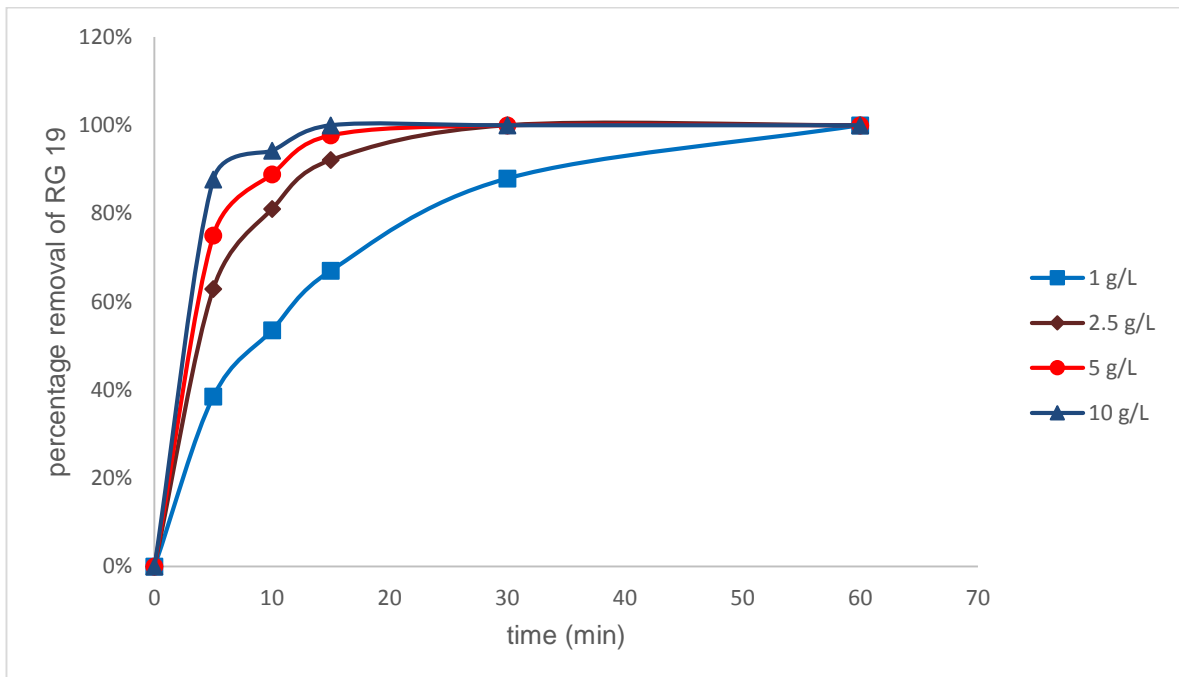


Figure 3-7. Effect of the poly(GMA-EGDMA)-TREN beads dosage and contact time on removal of RG 19.

(Adsorption conditions- initial concentration of dye : 25 mg/L; solution volume : 10 mL; pH 3.0; temperature : 25 ° C; varying the poly(GMA-EGDMA)-TREN beads dosage from 1 to 10 g/L).

3.1.4. Effect of Ionic Strength

Sodium chloride is currently used in textile dyeing processes as it promotes the adsorption of the dyes by the textile fibers. Figure 3-8 shows, the influence of the presence of NaCl on the adsorption of RG 19 onto the the poly(GMA-EGDMA)-TREN beads. Addition of NaCl produced an important decrease of the performance of the poly(GMA-EGDMA)-TREN beads for RG 19. As can be seen in this figure, the sorption capacity of the adsorbent depended on the ionic strength of the solution. When the ionic strength was increased, the electrical double layer surrounding the adsorbent surface was compressed [52] and correspondingly resulted in a decrease in RG 19 adsorption on to the poly(GMA-EGDMA)-TREN beads.

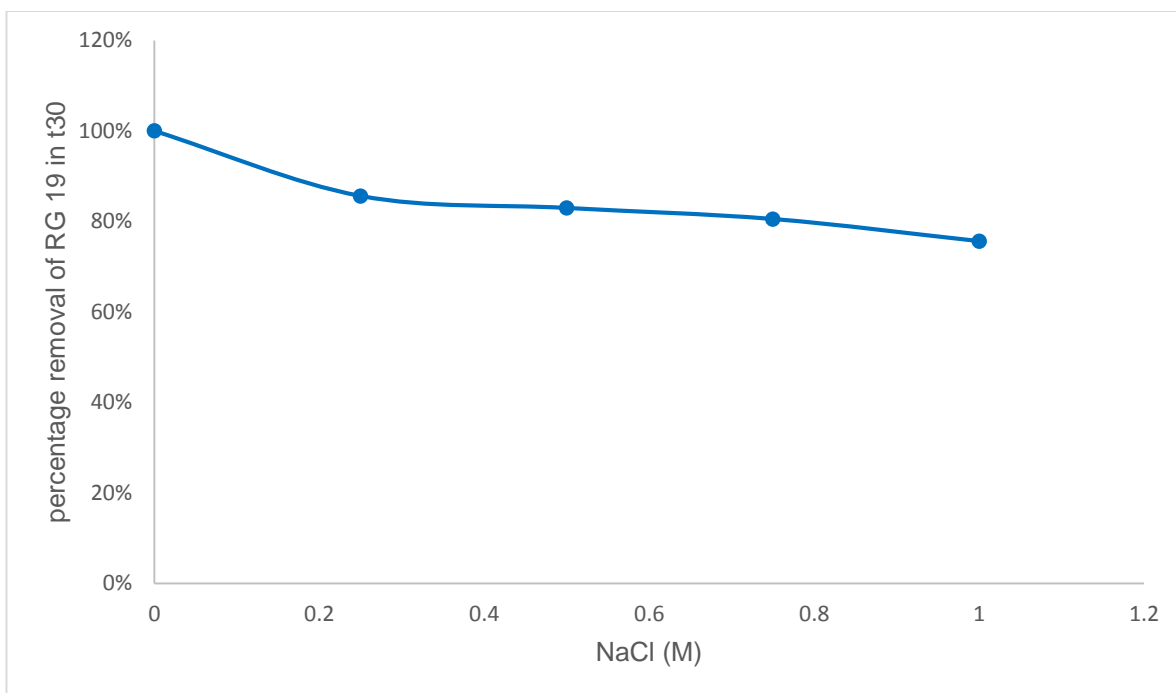


Figure 3-8. Effect of NaCl concentration on the adsorption capacity of the poly(GMA-EGDMA)-TREN beads

(Adsorption conditions- initial concentration of dye : 25 mg/L; solution volume : 10 mL; pH 3.0; temperature : 25 °C; adsorbent dosage from 2.5 g/L).

3.1.5. Effect of Temperature

Temperature has important effects on adsorption process. Thermodynamic parameters like heat of adsorption and energy of activation play an important role in predicting the adsorption behavior and both are strongly dependent on temperature. Adsorption of RG 19 at four different temperatures (15 °C, 25 °C, 35 °C, 45 °C) onto the poly(GMA-EGDMA)-TREN beads was studied for 25 mg/L initial RG 19 concentrations. It was observed that as the experimental temperature increased from 15 °C to 45 °C, the dye adsorption rate also increased (Figure 3-9). As the temperature increase, rate of diffusion of adsorbate molecules across external boundary layer and internal pores of adsorbent particle increases [45]. Changing the temperature will change the equilibrium capacity of the adsorbent for particular adsorbate and the removal rate were higher at 45 °C, 35 °C, 25 °C than 15 °C.

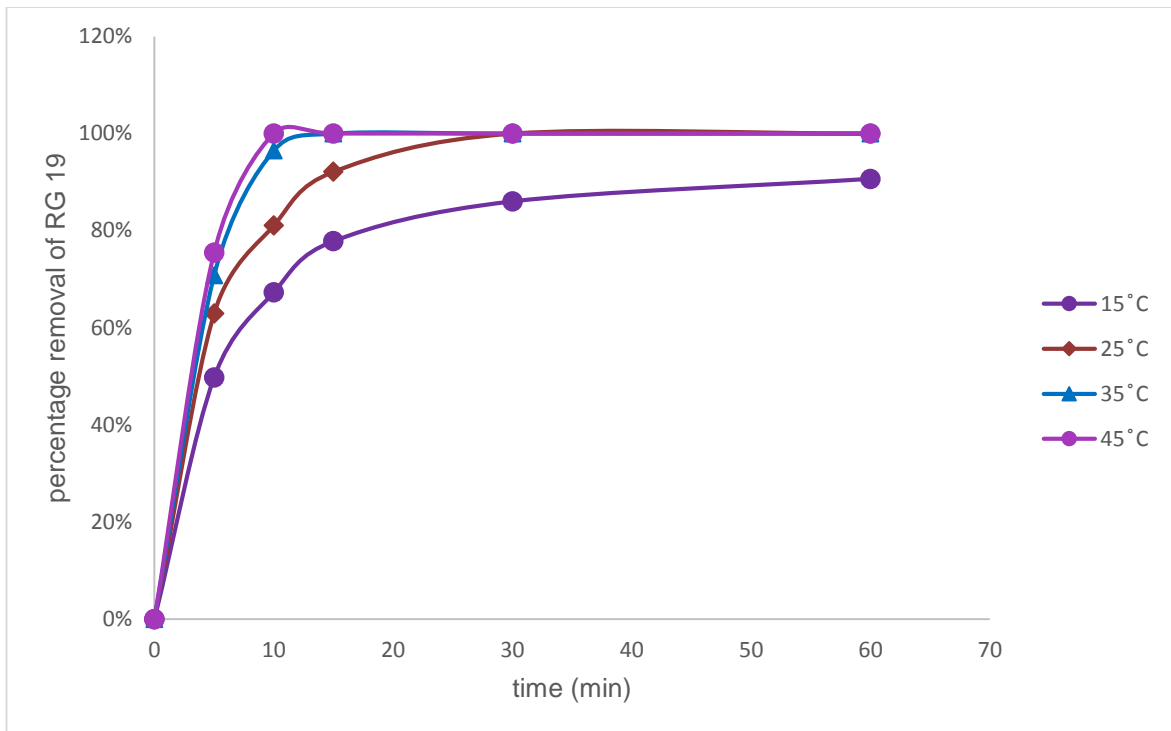


Figure 3-9. Effect of temperature on adsorption of RG 19 onto the poly(GMA-EGDMA)-TREN beads.

(Adsorption conditions- initial concentration of dye : 25 mg/L; solution volume : 10 mL; pH 3.0; adsorbent dosage from 2.5 g/L).

3.2. Adsorption Kinetics

The kinetics of adsorption is important from the point of view that it controls the process efficiency. In order to examine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, kinetic models were used to test the experimental data. The kinetics of dye adsorption on the poly(GMA-EGDMA)-TREN beads was determined with three different kinetic models, i.e., the first- and second-order and the intra-particle diffusion model. The first-order rate equation of Lagergren [53] is one of the most widely used equations for the sorption of solute from a liquid solution. For this model, the Equation 4 was used for the variation of adsorbed concentration with respect to time.

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303) t \quad \text{Equation 4}$$

where k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and q_{eq} and q_t denote the amounts of adsorption at equilibrium and at time t (mg/g), respectively. The slopes and intercepts of plots of $\log (q_{eq} - q_t)$ versus t were used to determine

the pseudo-first order rate constant k_1 and q_e (Figure 3-10). $q_e(\text{the})$ were compared with the $q_e(\text{exp})$ values in Table 3.1. $q_e(\text{exp})$ values were not different from the corresponding $q_e(\text{the})$ values at low dye concentrations of 10-25 mg/L and also correlation coefficient values (R^2) values were high for these dye concentrations.

Although the results showed that pseudo first order equation of Langergen does fit well in low dye concentrations of 10-25 mg/L in this study, at high dye concentrations the deviation of the plots from the origin and significant differences between $q_e(\text{the})$ and $q_e(\text{exp})$ values indicated that pseudo first order model does not fit well at high dye concentrations of 50 to 400 mg/L.

In addition, a pseudo-second-order equation (Equation 5) based on sorption equilibrium capacity may be expressed in the form [53]:

$$t/q_t = 1/(k_2 * q_e^2) + t/q_e \quad \text{Equation 5}$$

where k_2 (g/(mg min)) is the rate constant of pseudo-second-order adsorption. The rate constant (k_2) and adsorption at equilibrium (q_{eq}) can be obtained from the intercept and slope, respectively (Figure 3-11). the experimental results obtained for the adsorption of RG 19 on the poly(GMA-EGDMA)-TREN beads at optimum conditions of pH, contact time and dose of adsorbent were found to obey the second-order kinetic.

In order to assess the nature of the diffusion process reasonable for the adsorption of dyes onto the resin attempts were made to calculate the pore diffusion coefficients. When the water sample is shaken, the dye molecules are transported to the solid phase by the intra-particle transport phenomenon. The intra-particle transport is supposed to be the rate-controlling step. The rate of particle transport through this mechanism is slower than adsorption on the exterior surface site of the adsorbent. The amount of adsorbed species can lead varies proportionately with a function of retention time [42]. The intra-particle diffusion model was proposed by Weber and Morris shown in Equation 6, the initial rate of intra-particle diffusion is calculated by linearization of the curve $q = f(t^{0.5})$:

$$q = K_i t^{0.5} \quad \text{Equation 6}$$

where q (mg/g) is the amount of adsorbed dye on the resin at time t (s), and K_i is the diffusion coefficient in the solid (mg/g min^{0.5}). K_i has been determined by a plot $q = f(t^{0.5})$ taking account only of the initial period [53].

As can be seen in Figure 3-12, all the plots have the similar general features, initial linear portion followed by a plateau. The initial linear portion was attributed to the intraparticle diffusion. However, such a deviation of the straight line from the origin could likely be due to the difference in the rate of boundary layer diffusion in the initial stage of adsorption. Generally, the intercept of the plot of qt versus time 0.5 gives an idea about boundary layer thickness, the larger the value of the intercept, the greater the boundary layer diffusion effect is. The values of intraparticle diffusion rate constant, K_i , are shown in Table 3-1. If the regression of q versus $t^{0.5}$ is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step. The deviation of straight lines from the origin indicates that intra-particle transport is not the rate-limiting step.

Table 3-1. The first- and second-order kinetics and intra-particle diffusion models for adsorption of RG 19 on the poly(GMA-EGDMA)-TREN beads.

Dye conc. (mg/L)	Pseudo first order model			Pseudo second order model				Intra particle diffusion model	
	q _e (exp) (mg/g)	K ₁ (1/min)	q _e (the) (mg/g)	q _e (exp) (mg/g)	K ₂ g/(mgmin)	q _e (the) (mg/g)	R ²	K _i (mg/g/min ^{1/2})	R ²
10	3.656	0.193	3.28	3.656	0.313	3.73	0.998	0.661	0.850
25	9.792	0.156	9.12	9.792	0.184	10.11	0.996	1.782	0.918
50	20.112	0.076	15.33	20.112	0.147	20.85	0.993	2.486	0.870
75	29.816	0.065	22.84	29.816	0.119	31.01	0.990	3.702	0.899
100	32.544	0.060	25.20	32.544	0.120	33.92	0.989	4.049	0.914
200	65.932	0.067	51.77	65.932	0.055	68.78	0.99	8.234	0.905
400	73.724	0.113	62.39	73.724	0.034	76.87	0.994	9.357	0.837

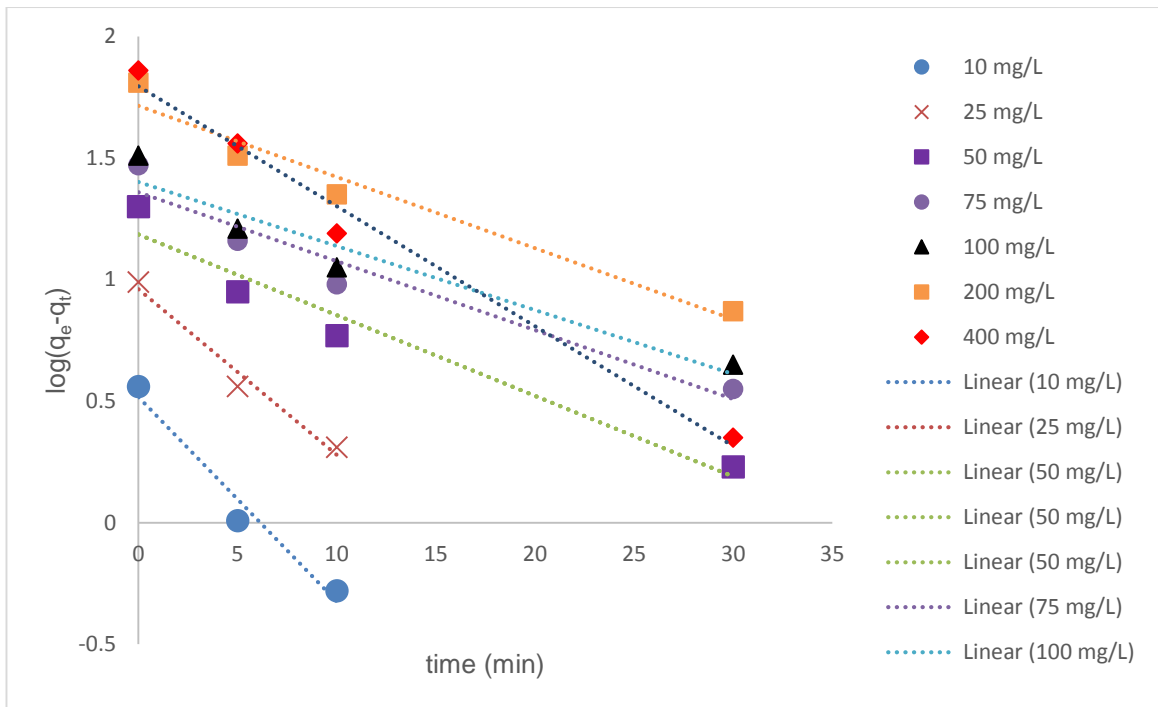


Figure 3-10. pseudo first order plot of effect of dye concentration on adsorption of RG 19 onto the poly(GMA-EGDMA)-TREN beads.

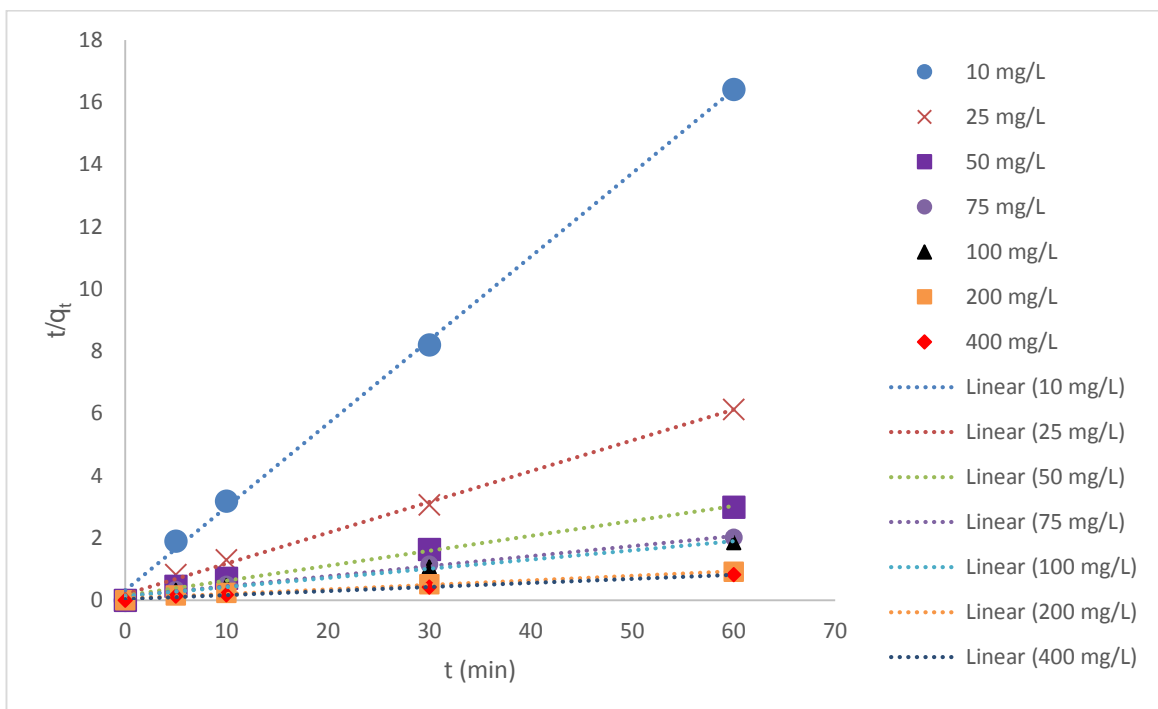


Figure 3-11. pseudo second order plot of effect of dye concentration on adsorption of RG 19 onto the poly(GMA-EGDMA)-TREN beads.

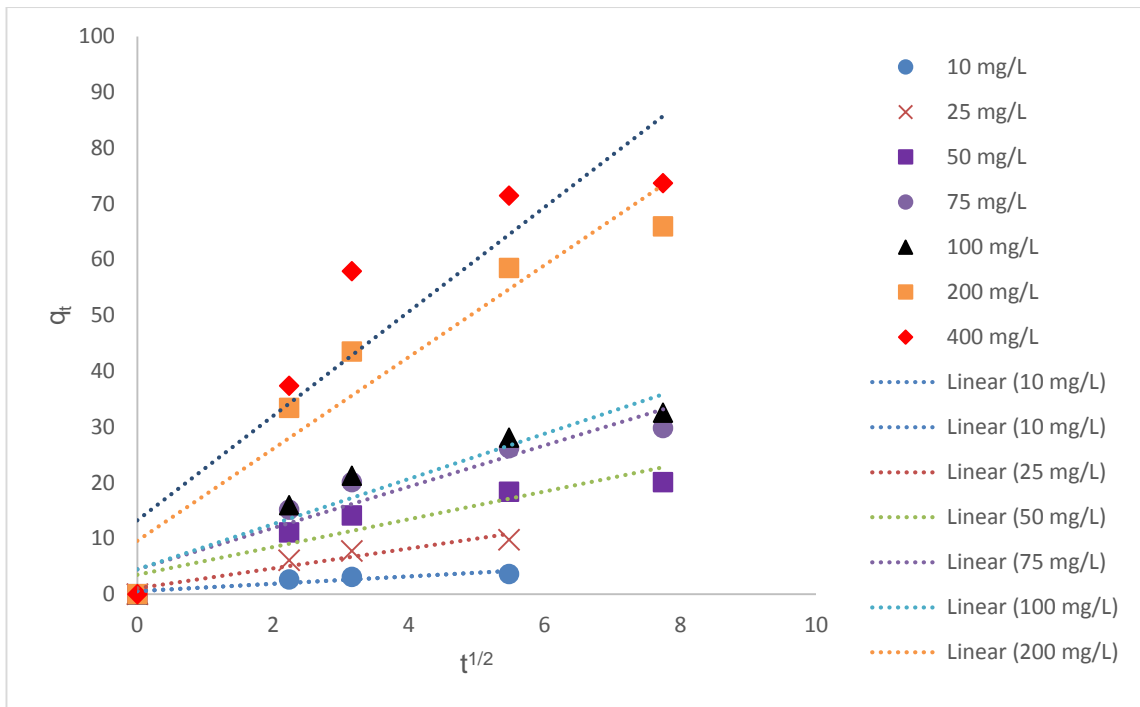


Figure 3-12. Intra particle diffusion plot of effect of temperature on adsorption of RG 19 onto the poly(GMA-EGDMA)-TREN beads.

3.3. Adsorption Isotherms

Equilibrium data, commonly known as adsorption isotherms, are the basic requirements for the design of adsorption systems. Obtaining equilibrium data for a specific adsorbate/adsorbent system can be performed experimentally, with a time-consuming procedure that is incompatible with the growing need for sorption systems design. Analysis of equilibrium data is important for developing an equation that can be used to compare different sorbents under different operational conditions and to design and optimize an operating procedure [42].

The equilibrium removal of dyes was mathematically expressed in terms of adsorption isotherms. Some isotherm equations have been tested in the present study, namely the Langmuir and Freundlich isotherm models.

The Freundlich equation was employed for the adsorption of RG 19 onto the adsorbent. The isotherm was represented by Equation 7.

$$\log q_e = \log K_f + 1/n \log C_e \quad \text{Equation 7}$$

Where q_e is amount of RG 19 adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of RG 19 in solution (mg/L), K_f and n are constant incorporating factors affecting the adsorption capacity and intensity of adsorption respectively.

The plots of $\log q_e$ against $\log C_e$ showed good linearity ($R^2 = 0.972$) indicating the adsorption of RG 19 obeys the Freundlich adsorption isotherm (Figure 3-13). The value of K_f and n given in the Table 3-2, Value of n between 2 to 3 indicates an effective adsorption [54] while higher values of K_f represents an easy uptake of adsorbate from the solution [55].

The Langmuir isotherm was represented by Equation 8.

$$C_e / q_e = 1 / (q_m * b) + C_e / q_m \quad \text{Equation 8}$$

Where q_m is monolayer (maximum) adsorption capacity (mg/g) and b is Langmuir constant related to energy of adsorption (1/mg). A linear plot of C_e / q_e against C_e (Figure 3-14) suggest the applicability of the Langmuir isotherms ($R^2= 0.877$). The value of q_m and b were determined slop and intercept of the plot, Table 3-2. The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_L , which is defined by Equation 9 given by Hall, et al., 1966

$$R_L = 1 / (1+bC_o) \quad \text{Equation 9}$$

Where C_o is initial RG 19 concentration (mg/l).

The nature of adsorption if,

$R_L > 1$ = Unfavorable, $R_L = 1$ Linear, $R_L = 0$ Irreversible , $0 < R_L < 1$ Favorable .

In the present study, R_L values lies between 0.44 to 0.96 for the poly(GMA-EGDMA)-TREN beads indicates favorable adsorption (Table 3-3).

Table 3-2. Isotherm models constants and correlation coefficients for adsorption of RG 19 from aqueous solution.

Freundlich isotherm parameters			Langmuir isotherm parameters		
k_f	n	R^2	q_m	b	R^2
0.59	1.14	0.972	140.84	0.0031	0.877

Table 3-3. The dimensionless separation factor (R_L) values

Dye concentration	R_L
10	0.96
25	0.92
50	0.86
75	0.81
100	0.76
200	0.61
400	0.44

Although results were fitted to both Freundlich and Langmuir isotherm models, the higher R^2 value of Freundlich isotherm model indicated that the adsorption of RG 19 obey this model more than Langmuir isotherm model.

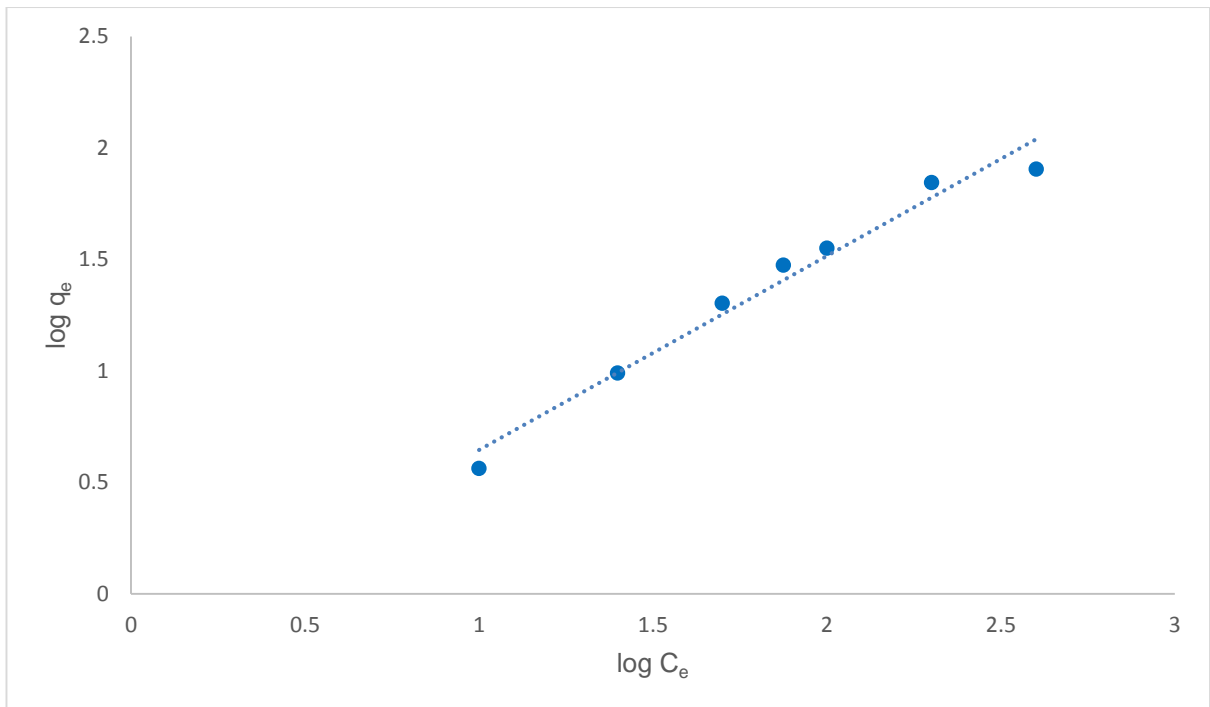


Figure 3-13. Freundlich isotherm plot of effect of initial dye concentration on adsorption of RG 19 onto the poly(GMA-EGDMA)-TREN beads

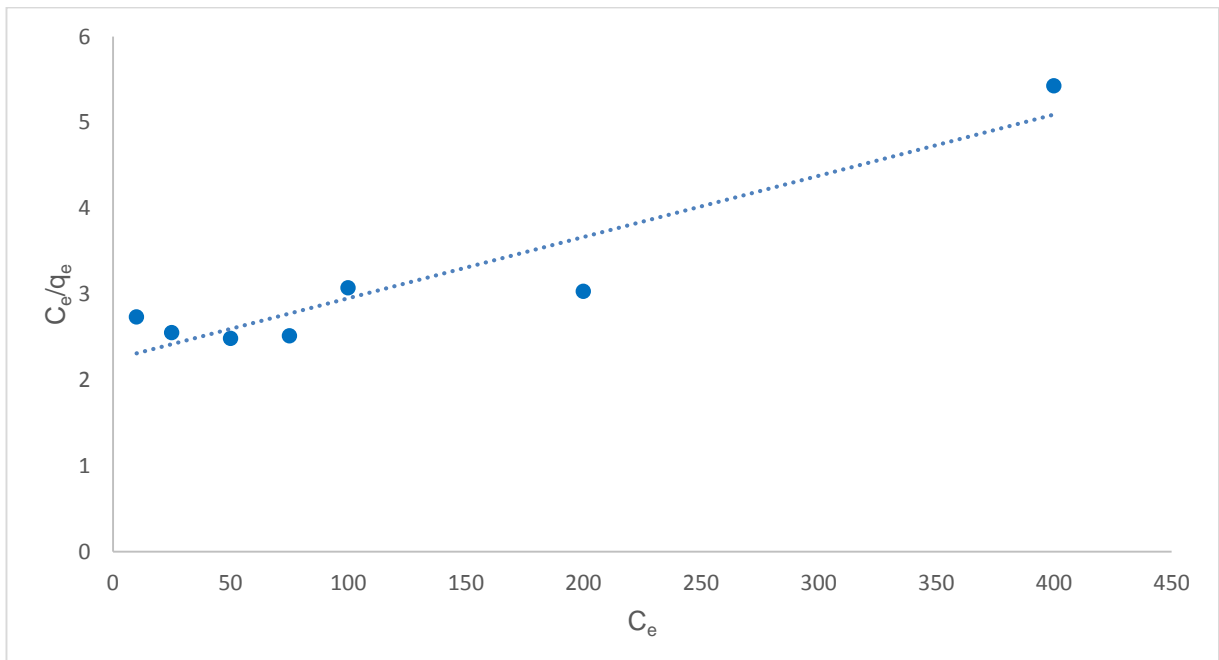


Figure 3-14. Langmuir isotherm plot of effect of initial dye concentration on adsorption of RG 19 onto the poly(GMA-EGDMA)-TREN beads.

3.4. Desorption and Reusability Studies

The use of an adsorbent in wastewater treatment depends not only on the adsorptive capacity but also on how well the adsorbent can be regenerated and reused. For repeated use, adsorbed pollutants should be easily desorbed under suitable conditions, so desorption of adsorbed RG 19 dye was studied in a batch system with 0.2 M HNO₃ for 2 h. Under these conditions, up to 97% of the adsorbed RG 19 was released. To show the reusability, the adsorption–desorption cycle was repeated three times with the same sample of adsorbent. The adsorption capacity of the resin did not significantly change for the RG 19.

4. CONCLUSION

Adsorption process was shown to be highly efficient for color removal from wastewaters due to its sludge-free clean operation, simplicity and flexibility of design and complete removal of dyes even from dilute solutions. In the field of adsorption technology for dye removal from wastewater streams the surface modification of adsorbents is very helpful in the improvement of adsorption capacity and selectivity of adsorbents by taking advantage of specific interactions between the adsorbents and the target molecules. The adsorbents surface area is another prominent factor for improving the adsorption capacity of the adsorbents as well.

This study has demonstrated that cationic sulfonic groups contributed to the adsorption mechanism through electrostatic interactions between sulfonic groups of the adsorbent and the cationic sites of RG 19.

The results demonstrated that the percentage uptake of RG 19 is highly dependent to the initial concentration of RG 19 and decreasing with an increase in dye concentration. Adsorbent dosage is another factor that affecting the adsorption capacity and as its demonstrated from the results that the removal efficiency of the adsorbent improved with increasing in dosage of adsorbent. Also increasing in temperature was shown to be improved the rate of adsorption.

Consequently, according to the results obtained from adsorption studies, maximum removal rate of RG 19 onto poly(GMA-EGDMA)-TREN beads were obtained at pH 2 and pH 3, sorbent dosage of 10 g/L, and in the solution without additional NaCl at 45°C.

Moreover the values amount of RG 19 adsorbed per unit mass of the poly(GMA-EGDMA)-TREN beads obtained by pseudo second order model, $q_e(\text{the})$ were in consistent with the experimental values, $q_e(\text{exp})$. Intra particle diffusion model showed boundary layer effect and high linearity of the plots indicated that intra-particle diffusion is the sole rate-limiting step.

The equilibrium adsorption behavior of RG 19 onto the poly(GMA-EGDMA)-TREN beads followed by both Freundlich and Langmuir isotherms with the maximum adsorption capacity of 140.84 mg/g resin. The adsorption of RG 19 onto the amine

modified resin was found to be mainly based on ion-exchange interactions, and these were confirmed by the results of adsorption isotherms.

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