Dye Pollution Removal from Mining and Industrial Wastewaters using Chitosan Nanoparticles

Hamid Sarkheil, Farshid Noormohammadi, Ahmad Reza Rezaei, Mehrdad Khalili Borujeni

Abstract—Dyes are one of the main pollutants and due to their toxicity, carcinogenesis and irreversible lesions in the environment and humans. Clean, safe and adequate freshwater is crucial to all living organisms and the normal functioning of ecosystems, communities and economies. Adsorption is an economical and commonly used method to uptake of dyes and heavy metals also. In recent years, biopolymers such as chitosan have been used for the separation of dyes from industrial wastewaters. In this study, chitosan and nanochitosan were used for the adsorption of Reactive Blue from water. Size of nano particles in emulsion was determined by particle size analyzer (PSA). The nanochitosan was obtained using a mixture of chitosan and sodium tripolyphosphate. Reactive blue T/Q 150 removal was pH dependent and the optimum adsorption of chitosan and nanochitosan was viewed at pH 6 and 4.6. The experimental data were analyzed using the Langmuir and Freundlich models. The maximum adsorption capacities obtained from the Langmuir model were 153.85, 357.14 mg/g for chitosan and nanochitosan. The kinetics of the adsorption described better with the pseudo-second order model for both adsorbents and maximum adsorption for both absorbents was at about 28°C. From thermodynamic data of both absorbents, it was found that the adsorption process was endothermic and spontaneous.

Keywords—Dye, Pollutant, Wastewater, Environment, Chitosan, Nanoparticles.

I. INTRODUCTION

Water is one of the vital necessities for the survival of human beings. Earth is a planet with 71% of its surface covered by water. Of the total available water on earth 97% is seawater and unavailable for human consumption, only 3% is available as fresh water. Out of this 3%, only a meager 0.06% can be easily accessed as the rest comprises of the frozen polar ice, groundwater and swamp. The water demand doubles globally every 21 years due to the rapid increase in the population and the industrial activities. Compounded with this is the decrease in rainfall in the previous decade. More than 80 countries accounting for 40% of the world's population are facing major water crises. It has been estimated by UN that by 2025, 2.7 billion people will be affected by water deficiency.

Many countries are facing the shortage of clean drinking water and it is estimated that 1.2 billion people are already drinking unclean water. Furthermore, 5-10 million people die annually due to various diseases caused by the consumption of contaminated water. Thus, exploitation of safe water sources to overcome the scarcity of water has been a global challenge for many countries like Australia. The increasing demand of clean water has attracted much of the attention of government organizations and water industries to develop cost-effective technologies for water/wastewater treatment and reclamation. Wastewater reclamation, recycling and reuse are vital to meet the water requirements for irrigation, industry and domestic uses due to increasing population and development in many parts of the world [1]. The term reclamation refers to the treatment of wastewater, which produces water with high quality being reused for agricultural and industrial applications. Wastewater recycling implies reuse of the captured effluent from one user by returning it to the system. The reuse of reclaimed wastewater is essential for sustainable development in the 21st century. The water scarcity is not only a problem of developing countries but also has affected many developed countries as well [2],[3].

Wastewater can be reclaimed from various sources such as industrial effluent, municipal wastewater, agricultural return flows and storm water. Depending upon the physical, chemical and biological constituents, water can be reclaimed by different methods. The selection of wastewater treatment technique is very critical and has to be made considering the contaminants present in wastewater. Mining and Industrial wastewaters largely possess organic and inorganic materials such as dyes (Figure 1), phenolic compounds, aromatic compounds and heavy metals [4]. For example, in copper mining process Acid Mine Drainage (AMD) is one of the major dye pollution in surface and underground waters (Figure 2). Almost all the dyes, even the naturally occurring dyes, used today are now synthesized chemically. Annually, a total of more than 7 x 105 tons of dyes are produced out of which azo dyes account for 60-70%. Over the years, the use of dyes has increased and is immensely used in industries like textile, cosmetics, pulp and paper, paint, pharmaceutical, food, carpet and printing. The discharge from these industries is highly colored as enormous amount of dyes remains unfixed during coloring and washing [5]. Thus, the treatment of this effluent is crucial. The discharge of effluent without proper treatment...
can get mixed with surface and ground waters and eventually can enter the drinking water. Furthermore, dye effluent if discharged untreated affects the photosynthesis of aquatic plants by preventing the light to penetrate through water [6] and [7].

![Fig. 1 Industrial wastewaters largely possess organic and inorganic materials such as dyes [8].](image1.jpg)

The reclamation and reuse of the water are essential for the sustainable supply of water in the future to meet the growing demand of freshwater for the increasing industry development and population growth. The prerequisite for the synthesis of dyes is to impart strong color that is stable and does not degrade with time and on exposure to light. Therefore most of the dyes have complex chemical structure and bear an aromatic ring which is hard to break. The dyes are toxic and non-biodegradable, and can lead to increasing pollutants concentrations and environmental risks, if they are discharged into the waterways. Eventually the pollutant concentration will reach high enough levels that will prevent re-establishment of a microbial population as a result water quality will degrade permanently. In humans, toxic dyes can cause dysfunction of kidneys, reproductive system, liver, allergy, dermatitis, skin irritation and cancer [9].

The reclamation of wastewater requires cost effective techniques that can generate high quality water for reuse. The reclamation of wastewater may reduce the demand for freshwater. In recent decade increasing practices for many water industries have focused on using treated and recycled water [10].

Most of the currently available technologies are inadequate for the removal of color-induced toxic pollutants such as dyes from textile wastewater. These technologies mostly transform pollutants from one phase to another and do not completely eliminate them. Even though membrane filtration produces high quality water, it has a major limitation of clogging of micro- or ultra-filtration membranes adding to the operating cost. In a disinfection process by chlorination, chlorine sometimes reacts with organic pollutants and produces disinfection by-products, such as trihalomethanes and haloacetic acid, which are mutagenic and carcinogenic and pose threats to human and aquatic life. Dyes have adverse aesthetic effects and the presence of even 0.005 ppm of dye in water is highly visible. Governments of most countries are imposing stringent legislations for the removal of dyes from industrial effluents and are demanding zero synthetic chemical discharge. These strict rules are compelling industries and scientists to search for novel effective and economical methods of dye removal [11].

Adsorption has been recognized as a potential technology for the removal of dyes from wastewater. In comparison to other physical, chemical and biological methods available for the treatment of textile industry effluent, adsorption is the most preferred technique due to simple and flexible design and easy operation. The adsorption process may generate Utile or no toxic pollutants and involve low initial capital and operating costs. Moreover, it is does not have environment issues as it does not produce any sludge and yields treated water with high quality. Although adsorption is a proven technology for the removal of dye, it has a major limitation to its application due to sparse availability of low-cost adsorbents. Activated carbon is one of the most widely used adsorbents because of its high surface area and excellent adsorption capacity. But the high cost and regeneration difficulties of activated carbon have augmented the need to explore low cost reusable, and biodegradable adsorbents for the removal of dyes. Various low-cost adsorbents that have been successfully implemented for the adsorption of dyes from wastewater are natural and modified clays, spent brewery gram, Modified agricultural by-products, industrial wastes, coir pith, chitosan fly ash, peat, coal, baggase and neem leaves [12]. The pollutant from dyeing industries is highly toxic. The removal of dyes from wastewater before its discharge is a necessary practice for water industry. The significant increase in the use of dyes by various industries is causing severe damage to the environment due to non-biodegradability and high toxicity of these compounds. Adsorption is one of the most effective dye removal techniques. Adsorbents play a vital role in the efficiency of adsorption process. The major cost of the adsorption process is incurred in the adsorbents. Various commonly used adsorbents that provide significant removal of dyes have been discussed. The use of activated carbon is wide spread, though its high cost is creating the need for development of low-cost adsorbents.

This study will provide detailed information and discussion about the release of dyes from dyeing industries and their harmful effects on environment and human health. Furthermore, an insight into the currently available techniques for dye removal will be reviewed. Special attention will be given to current adsorption technologies for dye removal, which is the research focus of this study. Commonly used absorbent and its activation technologies will be detailed.
II. DYES, WATER POLLUTION AND ENVIRONMENT

Dye is an organic compound that imparts color to substances such as textile fiber, leather, hair, plastic materials or wax either as solution or dispersion. Man has long known dyes and in the prehistoric times, they were derived from natural plants, mainly for coloring fabric. At present almost all the dyes are manufactured artificially even the natural dyes. The artificial dyes are thoughtfully delineated to have distinctive characteristics such as; ability to impart specific color to the substance, resistance to fade when exposed to light, chemicals and washing and resistance towards acids and bases [13]. The groups that modify the ability of chromophores to absorb light are called auxochromes (NO2, NHR, NR2, CI and COOH). Dyes can be broadly classified in two ways either based upon chemical composition or application.

Dyes have a wide range of application and are used as a coloring agent for many different substances (table 1). Dyes are widely used to impart color to fabrics and plastics. They are also used in food industry, printing and leather industry [14], [15]. Recently, dyes have gained popularity in another field that is in hair coloring [16].

<table>
<thead>
<tr>
<th>Classification of Dyes Based on their Application</th>
<th>Type of Dye</th>
<th>Example</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid dyes</td>
<td>Methyl orange, Methyl red, Orange I, Orange II, and Congo red</td>
<td>Wool, Silk, Polyurethane fibers, nylon</td>
<td></td>
</tr>
<tr>
<td>Basic dyes</td>
<td>Aniline yellow, Butter yellow, Methylene blue, Malachite green</td>
<td>Reinforced nylon, polyesters</td>
<td></td>
</tr>
<tr>
<td>Direct dyes</td>
<td>Martius yellow and Congo red</td>
<td>Cotton, Rayon, Wool, Silk and Nylon</td>
<td></td>
</tr>
<tr>
<td>Disperse dyes</td>
<td>Celliton fast pink B, Celliton fast blue B</td>
<td>Synthetic polyamide fibers, polyesters, nylon and polycrylonitriles</td>
<td></td>
</tr>
<tr>
<td>Fiber dyes</td>
<td>Procion dye (2, 4, 6-trichloro 1, 3, 5-triazine)</td>
<td>Cotton, Wool and Silk</td>
<td></td>
</tr>
<tr>
<td>Reactive dye</td>
<td>Para red</td>
<td>Cotton (Cellulose), Silk, Nylon, Polyester, Polyurethane and Leather, colouring agent in food</td>
<td></td>
</tr>
<tr>
<td>Ingrain azo dyes</td>
<td>Indigo, Tyrian purple, Benzanthrone</td>
<td>Wool, colouring agent in food</td>
<td></td>
</tr>
<tr>
<td>Mordant</td>
<td>Alizarin</td>
<td>Cotton and wool</td>
<td></td>
</tr>
</tbody>
</table>

Azo dyes are immensely used as commercial dyes. These dyes have been widely applied in virtually all industries, such as textile, cosmetics, pulp and paper, paint, pharmaceutical, carpet and printing, textile, leather and food. Dyes are toxic due to the presence of benzene and aromatic ring in their structure. In humans, the contact with color wastewater may cause serious health problems and hazards-induced diseases, such as allergy, skin diseases, mutation and cancer. They can also harmful for kidneys, liver, brain and central nervous system. The presence of color in water system reduces the penetration of light which affects the photosynthesis of aquatic biota [17], [18] & [19]. The increase in the discharge of coloring effluent has become considerable environmental and health issues. The dye effluent is discharged at several stages. It is estimated that during synthesis of dye 1-2% remains unfixed and is discharged in the effluent. In addition, 1-10% is lost during the process of dyeing of substances in industries. The effluent from dye industries generally constitutes colored solutions, dissolved organics, inorganic solids and suspended solids. However color is highly visible to human eye among all contaminants. Color is the first pollutant to attract attention and presence of even 0.005 ppm can be easily detected by human eye [20], [21].

III. CURRENT DYE REMOVAL TECHNIQUES

Chitin and chitosan are natural aminopolysaccharides. Although chitosan exists in fungal biomass and insect cuticle but the main sources of chitosan are crabs and shrimp shells and other crustaceans. Chitosan is obtained by the alkaline deacetylation of chitin, one of the most abundant biopolymers in nature. It is showed in figure 3. The principal parameters that can be used for the characterization of chitosan are the degree of deacetylation, the polymer weight and the crystallinity. The presence of acetylglucosamine and glucosamine units causes to the existence of heterogeneities in the polymer. Amine groups are reactive with metal ions strongly [22]. Nitrogen atoms hold free electron doublets that can react with metal cations. Amine groups are thus responsible for the uptake of metal cations by a chelation mechanism.

The degree of deacetylation can be employed to differentiate between chitin and chitosan because it determines the content of free amino groups in the polysaccharides. In fact there are two advantages of chitosan over chitin. In order to dissolve chitin, highly toxic solvents such as lithium chloride and dimethyl acetamide are used whereas chitosan is readily dissolved in diluted acetic acid. The second advantage is that chitosan possesses free amine groups which are an
active site in many chemical reactions. The degree of deacetylation of chitosan ranges from 56% to 99% with an average of 80%, depending on the crustacean species and the preparation methods. Chitin with a degree of deacetylation of 75% or above is generally known as chitosan.

While chitin is insoluble in most organic solvents, chitosan is readily soluble in dilute acidic solutions below pH 6.0. Organic acids such as acetic, formic, and lactic acids are used for dissolving chitosan. The most commonly used is 1% acetic acid solution at about pH 4.0 as a reference. Chitosan is also soluble in 1% hydrochloric acid but insoluble in sulfuric and phosphoric acids. Solubility of chitosan in inorganic acids is quite limited.

The good adsorption behavior of polysaccharides is mainly attributed to: high hydrophobicity of the polymer due to hydroxyl groups of glucose units; presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups); high chemical reactivity of these groups; flexible structure of the polymer chain. Against these advantages, chitosan is soluble in acidic media and therefore cannot be used as an insoluble adsorbent under these conditions, except after physical and chemical modifications.

IV. MATERIALS & EXPERIMENTAL METHODS

A. Materials

Sodium tripolyphosphate (STPP), Sodium chloride (NaCl), Acetic acid (CH₃COOH), Hydrochloric acid (HCl) and Sodium hydroxide (NaOH) were procured from Merck (Germany), Chitosan with degree of deacetylation of the Chitosan was more than 90% and viscosity of less than 200 mPa.s was purchased from Zhejiang Aoxing Biotechnology Co., Ltd (China).

The anionic dye, Reactive Blue T/Q 150, used in the study was obtained from Dye Cose China and was used as received without any purification. The chemical formula of Reactive Blue T/Q 150 is C₅₂H₃₂Cl₂N₁₆Na₆O₂₄S₆ with Color Index 51307. The molecular weight of Reactive Blue T/Q 150 is 51307gmol⁻¹. The chemical structure of Reactive Blue T/Q 150 is shown in figure 4.

B. Instruments

In adsorption experiments, solutions were stirred by HS 260 basic shaker (IKA Co. Germany) and RH basic hot plate magnet mixer (IKA Co. Germany). pH meter Jenway 3510 measured pH of solutions and the centrifuge model EBA 8 used for separating solid and liquid phases. Residual concentration of Reactive Blue T/Q 150 was determined using an UV-vis spectrophotometer (model γ, helios, UK).

To investigate particle size of nanochitosan using the dynamic light scattering the device a zeta plus from (Brookhaven Co., USA) and Qudix particle size analyzer (South Korea) were used. The surface size and morphology of chitosan nano particles characterized by field emission scanning electron microscopy (FESEM) HIT 4160 02. Temperature was fixed by means of KS 4000 ic control incubator (USA).

C. Preparation of Chitosan Nanoparticles

Two grams of chitosan was dissolved in 0.5% (volume percent) aqueous acetic acid; 3g of NaCl was added to new solution gently. Then 5 ml of STPP 2gL was added into the chitosan solution drop-wise under magnetic stirring at room temperature. After 5 min stirring with a speed of 1000 rpm, a milky dispersion with a pH of 4.6 was obtained.

D. Particle Size Analysis

Base of nanochitosan dispersion preparation is an ionic gelation interaction between positively charged chitosan and negatively-charged tripolyphosphate. Figure 5 shows FESEM image of a part of selective nanochitosan particle and figure 6 shows morphology of this adsorbent.

To investigate particle size of nanochitosan dispersion using the dynamic light scattering technique and quadix technique. Figure 7 shows result of samples. According to particle size distribution of nanochitosan dispersion, the average particle size of nanochitosan was measured 34.6 nm.
**E. Adsorption Results**

Effect of pH on Reactive Blue T/Q Adsorption:

Reactive Blue T/Q 150 uptake is depended on pH value as it can be seen in figure 8 to 10. The chitosan pH range investigated was 4-10, however for nanochitosan the studied pH range was 3-10.

At low pH, hydronium ions have high concentration and hydronium ions compel with Reactive Blue T/Q 150 ions for adsorption that causes decreasing adsorption. Increasing pH maid hydronium ions concentration to decrease and increases Reactive Blue T/Q 150 adsorption.

The optimum pH for Reactive Blue T/Q 150 removal by chitosan appeared at pH 6. The adsorption increased extremely above pH=6, because as this pH Reactive Blue T/Q 150 hydroxide was produced.

As was shown in figure 6, increasing the pH increases gently the adsorption of Reactive Blue T/Q 150 due to reducing the hydronium ions. The optimum pH for nanochitosan was around 4.6 and increasing the pH is resulted a slight decrease in adsorption. At pH higher than 4.6 the nanochitosan solution gently removed from nano dispersion and at pH=7 adsorption of nanochitosan is consistent with chitosan.

**Adsorption Isotherm:**

Equilibrium data known as adsorption isotherms, describe how Reactive Blue Q/T 150 interact with adsorbents. Equilibrium adsorption experiments were performed for chitosan and nanochitosan particle sizes at controlled pH. The data from all sizes were modeled by Longmuir (figure 8 and 9) and Freundlich (figure 11 and 12) for macro and nano chitosan sizes.

![Fig. 8 pH effect on adsorption of Reactive Blue T/Q 150 on chitosan macro size particle, initial concentration of 1000 ppm, shaking rate of 300 rpm, temperature of 25°C](image)

![Fig. 9 pH effect on adsorption of pb2+ on chitosan nano particles, initial concentration of 1000 ppm, shaking rate of 300 rpm, temperature of 25°C](image)

![Fig. 10 Longmuir isotherm model fitting for adsorption of chitosan macro size particles, shaking rate of 300 rpm, temperature of 25°C, pH = 6](image)
Effects of contact time:

Figure 13 shows the concentrations of Reactive Blue T/Q 150 adsorbed onto chitosan as a function of time, at controlled initial pH. In nanochitosan, the rate of adsorption was faster than chitosan in the initial stages of the adsorption process, but gradually decreased later on the way toward equilibrium. The experimental results indicate that the particle size has a principal influence on the rate of Reactive Blue T/Q 150 uptake. Equilibrium time for the nanochitosan was around 45 min and that of chitosan was approximately 130 min.

The values of the isotherm parameters for Reactive Blue T/Q 150 are shown in Table 2 and 3. According to results, for both adsorbents the Langmuir model is fitted the experimental data of adsorption equilibrium better than other models. Therefore adsorption can be represented more appropriate by a monolayer adsorption. According to the Langmuir model maximum amounts of Reactive Blue T/Q 150 adsorption were 154 (mg/g) and 357 (mg/g) for chitosan and nanochitosan, respectively.

### Table II

<table>
<thead>
<tr>
<th>Table Head</th>
<th>Longmuir Isotherm</th>
<th>Freundlich Isotherm</th>
</tr>
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<tbody>
<tr>
<td>Adsorption parameter</td>
<td>$Q_{max}$ (mg/g)</td>
<td>$a_L$</td>
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<tr>
<td>Macro size chitosan particles</td>
<td>100</td>
<td>0.043</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.9654</td>
</tr>
<tr>
<td></td>
<td>$K_F$</td>
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<tr>
<td></td>
<td>$b_f$</td>
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<td></td>
<td>$R^2$</td>
<td>0.9431</td>
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### Table III

<table>
<thead>
<tr>
<th>Table Head</th>
<th>Longmuir Isotherm</th>
<th>Freundlich Isotherm</th>
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<tr>
<td>Adsorption parameter</td>
<td>$q_{max}$ (mg/g)</td>
<td>$a_L$</td>
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<tr>
<td>Chitosan nano particle</td>
<td>263.15</td>
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<td></td>
<td>$R^2$</td>
<td>0.9889</td>
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<td></td>
<td>$K_f$</td>
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<tr>
<td></td>
<td>$b_f$</td>
<td>0.5741</td>
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<td></td>
<td>$R^2$</td>
<td>0.9849</td>
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</table>

### Table IV

<table>
<thead>
<tr>
<th>Table Head</th>
<th>Lagergren’s Pseudo First Order Kinetics</th>
<th>Ho Pseudo Second Order Kinetic</th>
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<tr>
<td>Adsorption parameter</td>
<td>$q_t$ (mg/g)</td>
<td>$K_t$</td>
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<tr>
<td>Macro size chitosan particles</td>
<td>98.15</td>
<td>0.0355</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9949</td>
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<tr>
<td>Chitosan nano particles</td>
<td>258.29</td>
<td>0.0725</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9783</td>
</tr>
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</table>

The kinetics parameters for Reactive Blue T/Q 150 adsorption by chitosan and nanochitosan are shown in Table 4. When limiting step in the adsorption mechanism is mass transfer first order kinetic model is adapted to the adsorption kinetics. If the limiting step in the adsorption mechanism is adsorption reaction then second order kinetics model is adopted to the adsorption kinetics. When intra-particle diffusion was dominance, adsorption is controlled by an external film resistance and/or mass transfer.
V. CONCLUSIONS

Results showed that chitosan can be effectively used as a biosorbent for the removal of anionic dyes. Nano dispersion of chitosan in dilute acetic acid media with STPP as agent was produced. Parameters affecting the size of chitosan nanoparticles were investigated. The best procedure obtained is as follows: 5 mL STPP (2g/L) + 70 mL chitosan (2g/L in 1% acetic acid + 210 mg NaCl) under magnetic stirring (750rpm), at 25°C. The size of particles was about 90nm while pH after production by this procedure was about 4.6.

Freundlich model is the best model fitted to equilibrium data in this study to describe Reactive Blue T/Q 150 & chitosan adsorption system.

Results show that pH 6.0 is the optimal pH for adsorption of Reactive Blue T/Q 150 onto micro size chitosan. The optimum pH for Nano particles for Reactive Blue T/Q 150 adsorption is around 5 and the best adsorbent size in this study is 90nm and it can be concluded that the surface area of chitosan is very important in the adsorption process.

Maximum capacity of chitosan for adsorbing Reactive Blue T/Q 150 at the best condition in experiments was obtained 580 (mg dye/g chitosan) for micro size and 1036 (mg dye/g chitosan) for Nano size which is comparable with the results of other published researches.

In addition, the chitosan nanoparticles showed much higher adsorption capacity and faster adsorption kinetics than micro size chitosan. The adsorption kinetics followed the pseudo-second-order equation for all systems studied and the adsorbent initial concentration investigation shows if the initial concentration is lower, the removal efficiency will be higher. Dye pollutions, refers to this method can be removed from harmful and waste materials and make a safe environment for human life and natural ecosystems.

ACKNOWLEDGMENT

The authors would like to acknowledge the technical support provided by Petroleum University of Technology specially Abadan Faculty of petroleum engineering (Shahid Tondgouyan), especially Dr. Naghi Jadidi and Dr. Alireza Alizadeh Attar.

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