Environmental Resources Research
Vol. 7, No. 2, 2019

GUASNR

Removal of bromocresol green from aqueous solutions using chitin nanofibers

E. Salmalian[1], H. Rezaei[2*], A. Shahbazi[3]
[1]M.Sc. student of Environmental Sciences, Baharan Institute of Higher Education, Gorgan, Iran
[2]Assistant Professor, Department of Environmental Sciences, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran
[3]Instructor, Department of Environmental Sciences, Baharan Institute of Higher Education, Gorgan, Iran

Received: December 2018 ; Accepted: March 2019

Abstract
Dyes in wastewater generate one of the main sources of environmental pollution, and treatment of this pollution is absolutely ncessary for protection of the environment. New economical and environmentally friendly approaches are needed to remove dyes from aqueous solutions. The purpose of this study was to use chitin nanofibers, as a valuable natural material, to remove bromocresol green dye. The effects of effective variables such as pH (2-7), adsorbent dosage (0.25-2.5 gram), initial concentration (0.2-2 $mg.l^{-1}$), temperature (20-45 °C) and contact time (5-30 min) were investigated for color removal. The results showed that color adsorption is pH dependent and pH=6 was selected as the optimal value. Given that at the concentration of 0.4 $mg.l^{-1}$, 92.75% of the color was removed, this concentration was chosen as the optimal case. By taking into account the cost of the absorbent, 1.5 gram was selected as the optimal dosage for bromocresol green. A contact time of 10 minutes at 25°C was considered as the best for these two parameters, which indicates the short duration of this treatment. One way anova and Duncan test in Excel and SPSS software indicated a significant effect of the parameters on removal of dye. The results showed that chitin nanofibers have significant influence on the removal and reduction of bromocresol green from aqueous solutions, and thus wastewaters containing other colors. This process can be replicated in diluted wastewater treatments in textile industry without requiring high pressures and temperatures.

Keywords: Bromocresol green, Chitin nanofibers, Aqueous solution, Dyes, Adsorption.

[*]Corresponding author; hassanrezaei1979@gmail.com

Introduction

Industries consume a significant amount of water and chemical materials during manufacturing of their products for painting purposes, thereby producing large amounts of polluted wastewater (Kondori et al., 2012). Many dyes and their by-products are toxic and carcinogenic for micro-organisms, aquatic life and other organisms, including humans. Most dyes are resistant to light and oxidation because of their complex molecular structure and large sizes (Xu et al., 2015). It is estimated that the industries annually produce 1.6 million tons of dye, 10 to 15 percent of which turns into wastewater. As a result, the dyes are the major water pollutants. Excessive dye accumulation in waters could cause skin irritation and respiratory problems and it might raise the cancer risk in humans (Bing tan et al., 2015). Bromocresol green belongs to the diphenylmethane family. This pH-dependent chemical compound usually serves as a pH indicator and locator of DNA, and take on different colors. Bromocresol green is light brown and dark green respectively in acidic and alkaline ranges. The colors are separated in aqueous solution in the form of single anions (Ghaedi et al., 2012). Bromocresol green has a different molecular structure and functional group, and its dispersion in the environment could cause many problems (Nezamzadeh Ejhieh & Moazzeni, 2013). Decolorization by means of different dye adsorbents has been of interest to many researchers.

Haghighi Fard et al. (2012) used shrimp shell chitin to remove zinc from aqueous solutions and concluded that zinc metal removal rate rises with increase in the amount of adsorbent, and decreases with increasing initial metal zinc concentration. They argued that the absorption process of the zinc element follows a second order kinetic and Freundlich model. Skaran et al. (2015) used chitin nanoparticles to remove methylene blue, bromophenol blue and brilliant blue and came to the conclusion that activated carbon electrical charge and cadmium process is the optimum removal process for the bromocresol green from the aqueous solutions. They also examined pH, contact time, concentration and temperature and found that interparticle distribution functions are not capable of controlling the steps in the removal process, and the maximum decolorization is obtained by following the langmuir model. Harmoudi et al. (2014) applied chitin and chitosan biopolymers to remove dichlorophenoxy acetate, as an insecticide, in aqueous solutions and examined the basic parameters such as initial concentration, pH, contact time and absorbent material. The analysis showed that hydroxyl and amine groups are the sensitive factors in this chemical compound, and hydroxyl groups in chitin and chitosan can determine the molecular compounds, and chemical and kinetics reactions. They also argued that the substitution of poles and stationary bipolarity are the most important factors to achieve maximum absorption.

There are various methods for decolorization, including physical and chemical methods, such as coagulation and flocculation, flotation, membrane processes, deposition, ozone disinfection, utilization of ultrasound, and adsorption individually or in combination with biological processes as a low cost process (Ghaneian et al., 1391). Therefore, devising new economical and environmentally friendly methods with the purpose of decolorization is a necessity.

Thus, this study seeks to use a new method to remove or reduce the amount of color in aqueous solutions. For this purpose, chitin nanofibers will be used to remove the bromocresol green. Chitin nanofibers are valuable natural material, extracted from the skin of fish, crustaceans and molluscs.

Materials and Methods

Preparation of chitin nanofibers

The chitin nanofibers were acquired from the Nano Novin Polymer knowledge-based company located in Sari, a city in the north of Iran. Chitin nanofiber is a white gel-like material with a diameter of 30 nm, which is obtained from chemo-mechanical processes in a 99% purity. Chitin is obtained from shrimp shells. First, the shrimp skin is cleaned from any impurities to produce chitin particles. Chitin, as a biological compound, is simply decomposed by biological processes.

Identification Instruments

Measurements of pH was carried out by a pH meter (model AZ86552,Taywan); shaker device (RAYMAND.CO) was used for stirring absorption system in different times at a speed of 400 rpm; a centrifuge (UNIVERSAL) with a speed of 4000 rpm was used for 5 minutes to separate the adsorbent particles from the solution; the spectrophotometer (UNIKA USA, UV-2100) was used to measure and evaluate the decolorization at the maximum wavelength of 430 nm; and an incubator fridge (IKAKS 4000ic) was used to maintain the temperature in the range 20-45 °C.

Bromocresol green color assays in a batch system

To investigate the effects of variables pH, time, temperature, initial concentration and adsorbent dosage on the removal of bromocresol green color, 1 gr. of this compound was prepared in a 1000 ml flask, and 1.5 gr. of absorbent was added to each erlenmeyer flask containing 0.3 mg.l^{-1}. After completion of the reaction time, the adsorbent was separated from the solution by centrifugation at around 4000 for 5 minutes. The supernatant was removed and read by spectrophotometer. All adsorption experiments were conducted in a batch system. The impact of each of the parameters was examined at all stages of the experiment by changing the parameters of interest, while maintaining other factors constant. To determine the removal rate of bromocresol green in an equilibrium state by chitin nanofibers, equation ١ was used.

$$R(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \qquad \text{Eq. 1}$$

Where, R is the removal efficiency for bromocresol green (in percent) at any time, C_o is the concentration in milligrams per liter before absorption and C_e is the remaining or not-adsorbed bromocresol green concentration in the solution at equilibrium in terms of mg.g^{-1}.

In order to determine the chitin nanofibers adsorbed dye concentration in equilibrium, equation 2 was used.

$$Qe = \frac{(C_o - C_e)\, V}{M} \qquad \text{Eq. 2}$$

Where, Q_e is the chitin nanoparticle absorption capacity in terms of mg.g^{-1}, C_o is the Congo red initial concentration in the liquid phase in mg.l, C_e represents bromocresol green concentration in the solution at equilibrium after absorption in mg.g^{-1}, V is the solution volume in liters, and M is the chitin nanoparticles weight in grams. All of the tests were carried out with three replications and the averages of the obtained values were used.

Results

Effect of pH

One of the most important parameters in the process of absorption is the initial pH of the solution. By increasing pH, the capacity and performance of the removal process fluctuates, so that at pH 6, the removal percentage and the absorption capacity reached their maximum values respectively at ±90.1% and ±%29 mg/gr. Statistical analysis of one-way ANOVA showed that the effect of pH on the absorption rate is highly significant ($p< 0.05$) and Duncan test results showed that all cases, except the pH means at (4, 6) and (3, 5, 2), were significantly different. The removal efficiency and capacity to absorb color are provided for different pH ranges in Figure 1.

Effect of Concentration

The effects of changing the initial concentration of bromocresol green on removal efficiency and adsorption capacity by chitin nanofibers are shown in Figure 2. As can be seen, in concentrations of 0.3 and 0.4 mg.l^{-1} the adsorption efficiency of bromocresol green increases, and adsorption capacity falls towards higher concentrations. Initial adsorption in initial concentrations is higher, because the adsorption resistance or color uptake reduces as a result of the mass transfer force.

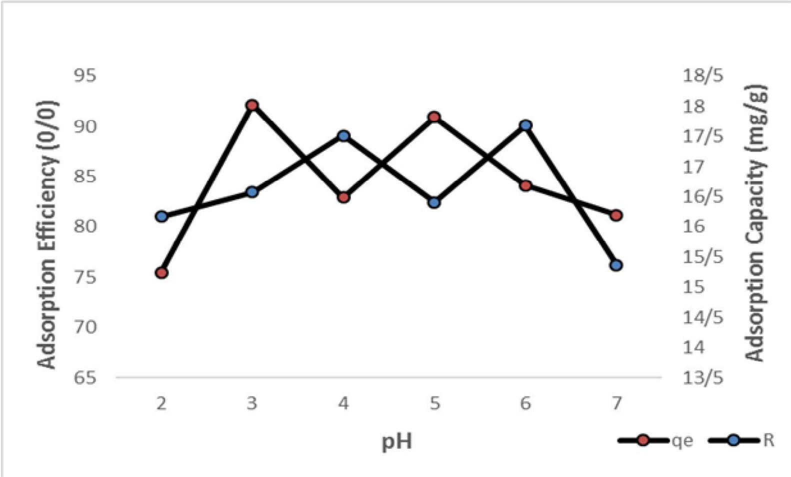


Figure 1. Effects of pH on adsorption of bromocresol green by chitin nanofibers

Higher initial concentration leads to a considerable driving force which overcomes the mass transfer resistance. This also results from the interaction between the adsorbent and the color (Ghani Zadeh and Asgari, 2009). The results of one-way ANOVA showed that the impact of the concentration effect on the absorption rate is highly significant ($p < 0.05$). Duncan test results also indicated significant differences in all cases, with the exception of the average concentrations at 0.2 and 0.3 $mg.l^{-1}$.

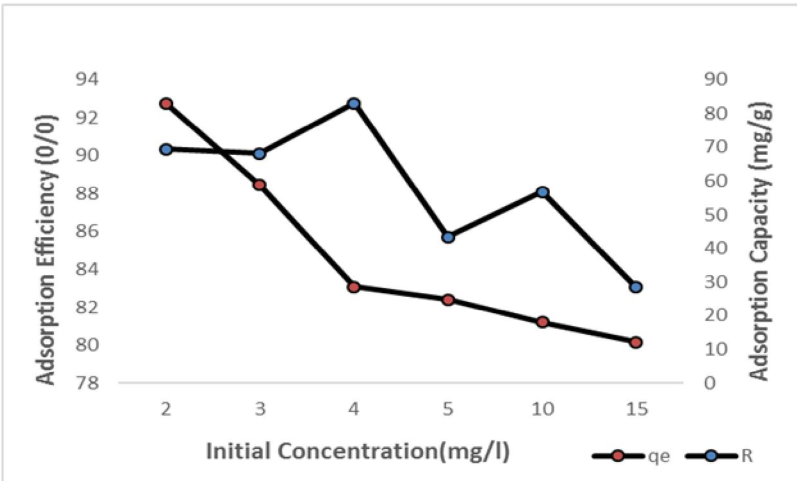


Figure 2. Effect of initial concentration on adsorption of bromocresol using chitin nanofibers

Effect of adsorbent dosage

Efficiency and adsorption capacity of bromocresol green by varying the dose of the adsorbent is provided in Figure 3. As can be seen, with an increase of the adsorbent dosage from 0.25 to 1 gr, adsorption fluctuates. At the dosage of 1.5 gr., adsorption reaches ±90.11, while dropping for higher concentrations. The results of one-way ANOVA showed that the adsorbent dosage significantly changes the adsorption ($p<0.05$). The results of the Duncan test also indicated significant differences in all cases, with an exception for the averages at (1.5,2), (0.5,2), and (0.5,0.25,1).

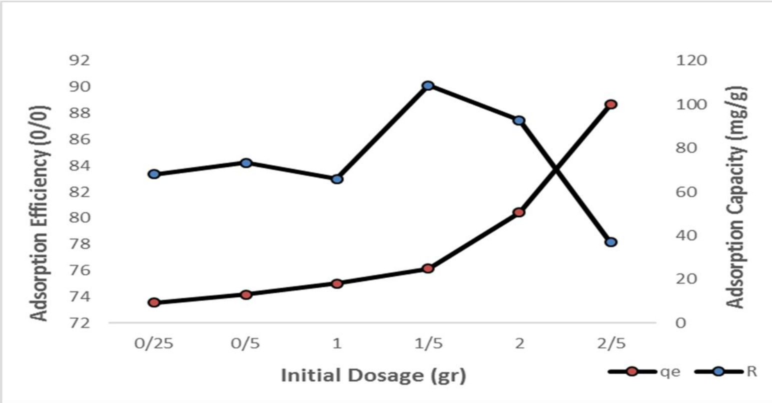


Figure 3. Changes in the chitin nanofibers dosage and adsorption of bromocresol green

Effect of contact time

Efficiency and adsorption capacity of bromocresol green by changing the contact time is provided in Figure 4. As is seen, adsorption efficiency and capacity is directly proportional to the contact time. The highest removal efficiency and capacity occur at ± 92.55% and ± 18.51 $mg.gr^{-1}$ for a contact time of 25 min.

The results of one-way ANOVA indicated a significant effect for the contact time on the adsorption ($p<0.05$). The Duncan test also indicated significant differences in all cases except for the contact time of 5 min.

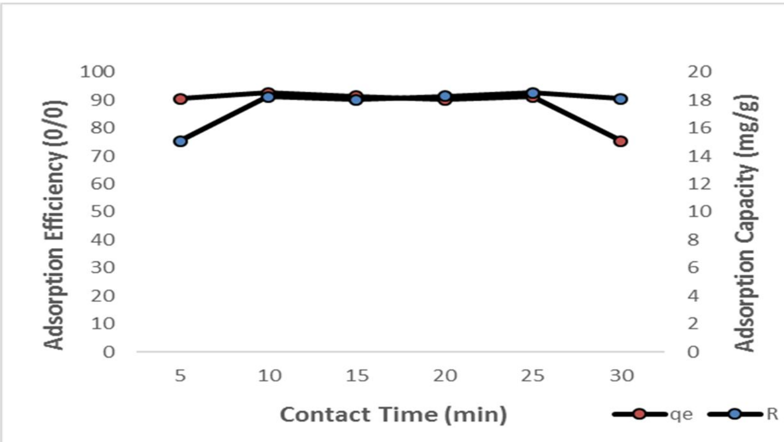
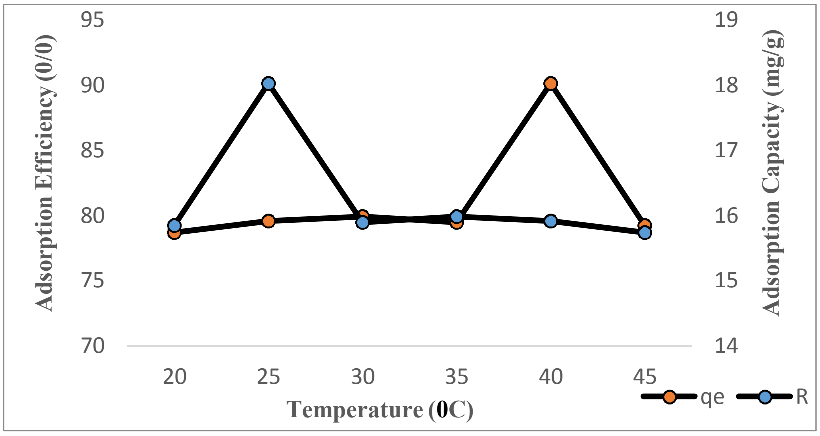


Figure 4. Changes in the contact time for adsorption of bromocresol green by chitin nanofibers



Figue 5. Changes in temperature and bromocresol adsorption using chitin nanofibers

Effect of time

Efficiency and adsorption capacity of bromocresol green by changing temperature is provided in Figure 5. As can be seen, by increasing the temperature from 20 to 25 ^{0}C, color adsorption changes from ±79.22 to±90.11% and adsorption capacity changes from 15.84 to 18.02 mg.gr^{-1}. The results of the one-way ANOVA indicated a significant effect of temperature on the adsorption ($p<0.05$). The Duncan test also indicated significant differences in all cases except for the temperature at 25 ^{0}C.

Discussion

We saw that pH affects the properties of absorbent. As is clear from the results, pH 6 has been selected as an optimal pH. An increase in pH causes the positively charged amino groups in the chitin to decrease in quantitative terms and turn carboxyl groups into a more active state, to form an electrostatic bond with the positively charged dye molecules, thus increasing the amount of decolorization (Sadeghi Kiakhani and Arami, 2012). The solution’s pH plays an important role in the whole process and determines the adsorption capacity. It not only affects the adsorbent surface charge, but also changes the degree of ionization and dissociation of functional groups in the active locations of the adsorbent and solution chemistry.

At a certain concentration of adsorbent, with increasing concentration, the amount of material adsorbed increases while adsorption percentage decreases. In other words, the residual concentrations of color molecules are higher at the initial concentrations. At lower concentrations, the initial number of color molecules is less than the available space, therefore, the amount of adsorption occurs independent of the initial concentration. At higher concentrations, the number of available locations reduces. As a result, the amount of dye removal depends on the initial concentration (Mahmudy, 2013).

Adsorbent quantity is an important factor because it determines the amount of the color that is removed. Increasing the amount of absorbent causes an increase in the available adsorption locations, thus increasing adsorption. However, the amount of adsorption per unit mass of adsorbent decreases (Mahmudy, 2013).

According to a survey conducted (Rasouli Fard et al., 2009), the removal efficiency of bromocresol green rises by increasing retention time in a stable condition. After 10 minutes, absorption reaches an equilibrium state and by increasing the contact time, due to increased chance of collisions of the color molecules with the adsorbent surface, the rate of adsorption increases, mainly due to chemical structures and functional groups and high rate of the absorption in the initial times (Rasouli Fard et al., 2009).

Increasing temperature could not only affect the solubility of the dye in the solution, but also the chemical potential of the sorbent. Thus, increasing temperature provides higher numbers of adsorption terminals on the polymeric chain, which are capable of controlling the adsorption process (Momenzadeh et al., 2011).

Conclusion

Based on the results chitin nanofibers have very high capability for the removal of bromocresol green from aqueous solutions. Parameters like pH, adsorbent dosage, initial concentration, temperature, and contact time have the largest influence on the removal efficiency and adsorption capacity. The results indicate that the adsorption of the bromocresol green depends on pH, and the best figure is achievable at the pH=6. This chemical compound is highly capable of adsorbing anionic dyes such as bromocresol green, and this capability augmented linearly in response to the initial concentration of the dye, with the maximum removal rate and adsorption capacity realizing at 0.4mg.l^{-1} ±%92.75. Rising temperature to 25 °C could increase the chance of collisions between the dye molecules and the dye, leading to an improved decolorization. As a result, this temperature was selected as the optimum value. Likewise, by considering the cost of adsorbent preparation, the concentration of 1.5 grams was selected as the optimum case for the removal of bromocresol green. The best contact time was estimated at 10 minutes, which indicates the short duration of the treatment. Data analysis in Excel and SPSS softwere indicated a significant effect of considered parameters in the one way anova test. The speed and capacity of adsorption by the adsorbent is high due to the small size, high surface area, existence of a unique network order and thus high reactivity of the nano absorbent. The results of this research can be used to manage the removal of bromocresol green color from the environment, particularly aquatic environments, to protect humans, plants, animals, and especially aquatic mammals whose life depend on water environments.

References

Bing Tan, K., Vakili, M.T., Amini Horri, B., Eong Poh, P., Zuhairi Abdullah, A., and Salamatinia, B. 2015. Adsorption of dyes by nanomaterials: Recent developments and adsorption mechanisms.separation and purification Technology. 150, 229-242.

Dhananasekaran, S., Palanivel, R.Sh., and Pappu, S. 2015. Adsorption of Methylene Blue, Bromo phenol Blue and Coomassie Brilliant Blue by a-chitin nanoparticles. Journal of Advanced Research. 7, 113-124.

Ghani Zadeh, Gh., and Asgari, Gh. 2009. Methylene blue dye removal from wastewater using bone char. Journal of Health and Environment. 2, 113-104.

Ghaneian, T., Dehvardi, M., Yazdi, J.N., Motab, M., and Jamshidi, B. 2012. Evaluation of the efficiency of Acroptilon powder in the removal of Reactive Blue 19 from wastewater. Journal of the University of Medical Sciences. 10: 831-842.

Ghaedi, M.R., Nejati Biyareh, M., Nasiri Kokhdan, S., Shamsaldini, Sh., Sahraei, R., Danesh far, A., and Shahriyar, S. 2012. Comparison of the efficiency of palladium and silver nanoparticles loaded on activated carbon and zinc oxide nanorods loaded on activated carbon as new adsorbents for removal of Congo red from aqueous solution: Kinetic and isotherm study. Materials Science and Engineering. 32, 725-734.

Harmoudi, H., El Gaini, L., Daoudi, E., Rhazi, M., Boughaleb, Y., El Mhammedi, M.A., Migalska-Zalas, A., and Bakasse, M. 2014. Removal of 2,4-D from aqueous solutions by adsorption processes using two biopolymers: chitin and chitosan and their optical properties. Optical Materials. 36, 1471-1477.

Jafar Zadeh Haghighi Fard, A.N., Mangoli Zadeh, A.N., and Hormozi Nejad, M. 2012. The use of shrimp shell chitin for biosorption of zinc from aqueous solution. Water and Wastewater. 1, 53-62.

Kondori, F.A.F., Badiei, Kh., and Masoumi, M.A. 2012. Assessing the removal of organic dyes from industrial wastewater by the nano-sorbents. Extension Journal of the studies in the world of color. 1, 33-42.

Mahmoudi, M.N. 2013. Removal of basic dyes from aqueous solutions with a nickel-zinc ferrite magnetic nanoparticles. Textile Science and Technology. 1, 36-29.

Momen Zadeh, H., Khosravi, R.A., Tehrani Bagha, R.A., and Gharanjig, A.K. 2010. Fac tors affecting the removal of reactive dye from solutions using an emulsion containing chitosan nanoparticles. Journal of Science and Technology of Color. 5, 1-1.

Nezamzadeh-Ejhieh, A.R., and Moazzeni, N. 2013. Sunlight photodecolorization of a mixture of Methyl Orange and Bromocresol Green by CuS incorporated in a clinoptilolite zeolite as a heterogeneous catalyst. Journal of Industrial and Engineering Chemistry. 19, 1433-1442.

Rasouli Fard, H.M., Taheri Ghazvini, N., Farhang Nia, A., Heidari, A., and Doust Mohammadi, M.M.S. 2009. Removal of anionic organic direct yellow 9 and orange reactive 122 direct from the contaminated water using bio-polymer chitosan adsorbent. Journal of Science and Technology, 4, 23-17.

Sadeghi Kiakhani, M., and Arami, M. 2012. Removal of the basic purple 16 dye from textile manufactory wastewater using bio-adsorbents of chitosan Ethyl acrylate polymer. Journal of advanced materials and new coatings, Scientific Society of the Iranian Paint industry, 1, 15-26.

Xu, Z.J., Li, W., Xiong, Z.D., Fanga, J., Li, Y., Wang, Q., and Zeng, Q.F. 2015. Removal of anionic dyes from aqueous solution by adsorption onto amino-functionalized magnetic nanoadsorbent. www.deswater.com. 1-1 Bing Tan, K., Vakili, M.T., Amini Horri, B., Eong Poh, P., Zuhairi Abdullah, A., and Salamatinia, B. 2015. Adsorption of dyes by nanomaterials: Recent developments and adsorption mechanisms.Separation and purification Technology, 150, 229-242.

Dhananasekaran, S., Palanivel, R.Sh., and Pappu, S. 2015. Adsorption of Methylene Blue, Bromo phenol Blue and Coomassie Brilliant Blue by a-chitin nanoparticles. Journal of Advanced Research, 7, 113-124.

Ghani Zadeh, Gh., and Asgari, Gh. 2009. Methylene blue dye removal from wastewater using bone char. Journal of Health and Environment, 2, 113-104.

Ghaneian, T., Dehvardi, M., Yazdi, J.N., Motab, M., and Jamshidi, B. 2012. Evaluation of the efficiency of Acroptilon powder in the removal of Reactive Blue 19 from wastewater. Journal of the University of Medical Sciences, 10, 831-842.

Ghaedi, M.R., Nejati Biyareh, M., Nasiri Kokhdan, S., Shamsaldini, Sh., Sahraei, R., Danesh far, A., and Shahriyar, S. 2012. Comparison of the efficiency of palladium and silver nanoparticles loaded on activated carbon and zinc oxide nanorods loaded on activated carbon as new adsorbents for removal of Congo red from aqueous solution: Kinetic and isotherm study. Materials Science and Engineering, 32, 725-734.

Harmoudi, H., El Gaini, L., Daoudi, E., Rhazi, M., Boughaleb, Y., El Mhammedi, M.A., Migalska-Zalas, A., and Bakasse, M. 2014. Removal of 2,4-D from aqueous solutions by adsorption processes using two biopolymers: chitin and chitosan and their optical properties. Optical Materials, 36, 1471-1477.

Jafar Zadeh Haghighi Fard, A.N., Mangoli Zadeh, A.N., and Hormozi Nejad, M. 2012. The use of shrimp shell chitin for biosorption of zinc from aqueous solution. Water and Wastewater. 1, 53-62.

Kondori, F.A.F., Badiei, Kh., and Masoumi, M.A. 2012. Assessing the removal of organic dyes from industrial wastewater by the nano-sorbents. Extension Journal of the studies in the world of color, 1, 33-42.

Mahmoudi, M.N. 2013. Removal of basic dyes from aqueous solutions with a nickel-zinc ferrite magnetic nanoparticles. Textile Science and Technology, 1, 36-29.

Momen Zadeh, H., Khosravi, R.A., Tehrani Bagha, R.A., and Gharanjig, A.K. 2010. Fac tors affecting the removal of reactive dye from solutions using an emulsion containing chitosan nanoparticles. Journal of Science and Technology of Color, 5, 1-1.

Nezamzadeh-Ejhieh, A.R., and Moazzeni, N. 2013. Sunlight photodecolorization of a mixture of Methyl Orange and Bromocresol Green by CuS incorporated in a clinoptilolite zeolite as a heterogeneous catalyst. Journal of Industrial and Engineering Chemistry, 19, 1433-1442.

Rasouli Fard, H.M., Taheri Ghazvini, N., Farhang Nia, A., Heidari, A., and Doust Mohammadi, M.M.S. 2009. Removal of anionic organic direct yellow 9 and orange reactive 122 direct from the contaminated water using bio-polymer chitosan adsorbent. Journal of Science and Technology, 4, 23-17.

Sadeghi Kiakhani, M., and Arami, M. 2012. Removal of the basic purple 16 dye from textile manufactory wastewater using bio-adsorbents of chitosan Ethyl acrylate polymer. Journal of advanced materials and new coatings, Scientific Society of the Iranian Paint industry, 1, 15-26.

Xu, Z.J., Li, W., Xiong, Z.D., Fanga, J., Li, Y., Wang, Q., and Zeng, Q.F. 2015. Removal of anionic dyes from aqueous solution by adsorption onto amino-functionalized magnetic nanoadsorbent. www.deswater.com. 1-12.