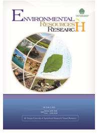

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Removal of Congo red from aqueous solutions using nano-chitosan

A. Razavi[1], H. Rezaei[*2], A. Shahbazi[3]

[1]M.Sc. Student, Department 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

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Abstract

It is now recognized that adsorption using low-cost adsorbents is an effective and economic method for water decontamination. Chitosan is derived by deacetylation of the naturally occurring biopolymer chitin which is the second most abundant polysaccharide in the world after cellulose. In this study, the capacity of the chitosan nanoparticles was studied for the removal of the anionic Congo red from wastewater. The effect of various parameters, such as the initial pH value in the range of 2-4, initial dye concentration (3-50 mg/L), adsorbent dosage (0.1-1.5 g), contact time (5-40 min) and temperature (20-45 °C) on adsorption process was investigated. The results indicated that chitosan nanoparticles under optimal conditions (pH=7, 5 mg/L^{-1} concentration of adsorbent, contact time of 15 minutes and a temperature of 30 °C) are able to remove 99.96% of Congo red from aqueous solutions. Hence, nano-chitosan can be used as an eco-friendly adsorbent for the removal of Congo red from wastewater in terms of lower required time and higher adsorption capacity.

Keywords: Congo red, Adsorption, Wastewater, Chitosan.

[*] Corresponding author; hassanrezaei1979@gmail.com

Introduction

Colors are one of the main classes of the pollutants in wastewaters that are used in various industries in order to paint related products. Hence, a large amount of wastewater is produced. The presence of these colors in water, even in very low concentrations, is highly undesirable (Afkhami *et al.,* 2015). The presence of dye in the body of water increases oxygen demand, which adversely affects metabolic functions of phytoplankton, aquatic flora and fauna by reducing light penetration and thus photosynthesis (Cho *et al.,* 2015).

In general, colors can be divided into three categories of anionic (direct, acidic and reactive dyes), cationic (basic dyes) and nonionic (Disperse Dyes and Vat Dyes). Among these dyes, azo dyes (anionic) due to the presence of nitrogen-nitrogen double bonds (N = N) are considered as the largest class of organic dyes, but their analysis is complicated due to aromatic structures and their poor tendency for decomposition (Zheng *et al.,* 2015). Congo red is a benzidine-based anionic azo dye with a complex chemical structure and high solubility in aqueous solutions, which has major applications in textile, printing, dyeing, paper, rubber and plastic industries (Mahapatra *et al.,* 2013). Metabolized into benzene, Congo red could cause mutagenicity and carcinogenicity in humans. Encountering this dye frequently can cause allergic reactions; hence, removing the remnants of Congo red before mixing with the water source is very important (Chen *et al.,* 2014).

Given the huge damage caused by water pollution, a lot of attention has been paid to water treatment in the past few decades. Among different methods used for water purification, adsorption technique is more commonly used for the removal of dyes from aqueous solutions, due to its simplicity, high efficiency, the availability of a diverse range of absorbent, low cost, high capacity, simple design and reproduction (Vannamudan & Sudhakar, 2015). One of the most effective materials for the adsorption process is theactivated carbon, reproduction of which is costly and expensive. Hence, more recently researchers have focused on the development of adsorbent from polymers such as Chitosan and its derivatives, which have a natural base and present in high quantities in the environment.

Chitosan with the chemical formula of ($C_6H_{11}O_4N$) and by the chemical name (1,4)-2-Amino-2-desoxy- beta-D-glucan is one of the most abundant and cheapest biopolymer in the world. Chitosan is produced from the deacetylation of chitin with sodium hydroxide, from the skeletons of crustaceans such as crabs, lobsters, shrimp and cell walls of fungi and algae (Yilmaz *et al.,* 2015). Chitosan is an adsorbent with a very high adsorption capacity (110-100 $gr.Kg^{-1}$) for the removal of contaminants from water (Haldorai *et al.,* 2015). This high adsorption capacity of chitosan corresponds to the abundance of amine and hydroxyl groups that can bind with the pollutants (Vakili *et al.,* 2014). Chitosan as an abundant, low-cost, non-toxic and biodegradable biopolymer, has wide application in the chemical, pharmaceutical, food, textile, cosmetics, biotechnology, paper, agriculture and wastewater treatment industries to remove ions of heavy metals and dyes from the waste waters (Rasouli Fard *et al.,* 2010).

Recently, nano-materials have attracted much attention due to their large surface area and heat or chemical resistance properties and also high absorption capacity for the removal of contaminants in aquatic environments. One of these nano-materials, is nano-Chitosan which is a natural substance with excellent physico-chemical properties, that is harmless to humans. Hence, this biopolymer has become a more environmentally friendly substance choice (Vakili *et al.,* 2014).

Therefore, this study aimed to investigate the potential of chitosan nanoparticles for the removal of anionic dye of Congo red and the impact of affecting factors to the removal efficiency such as pH, initial dye concentration, adsorbent dosage, contact time and temperature.

Materials and Methods

Materials

Chitosan nanoparticles gel 2.5% with an average size of 40 nm, diacetylation rate of 80-85% and molecular weight of 50000-10000 Da was acquired from the Nano Novin Polymer Knowledge-Based Company, located in the city of Sari.

Congo red with the chemical formula of $C_{32}H_{22}N_6Na_2O_6S_2$ and molecular weight of 696.66 g.mol^{-1} in very high purity, was purchased from Sigma-Aldrich Company and used without further purification. Chemical structure of the Congo redis presented in figure 1.

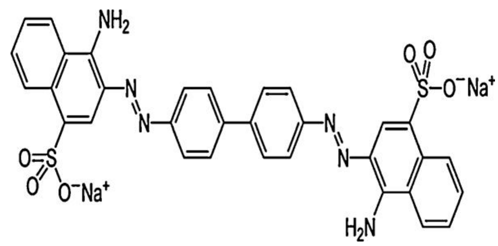

Figure 1. Chemical structure of the Congo red (Afkhami *et al.,* 2015).

Identification tools

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; a spectrophotometer (UV-2100) made in UNIKA USA was used to measure and evaluate the decolorization at the maximum wavelength of 497 nm and an incubator fridge (IKAKS 4000ic) made in Germany was used to maintain the temperature in the range 20-45 °C.

Removal test

First, a 1000 mg.L^{-1} stock solution was prepared from the dye (1gr of the Congo red brought to the volume in a 1000 ml flask) and diluted to form thinner concentrations of 3 to 50 mg.L^{-1}. To investigate the effect of different factors such as pH, time, temperature, adsorbent dosage and the initial concentration, different experiments were designed based on an initial condition in a volume of 100 ml (dye concentration = 5 mg.L^{-1}, consumed adsorbent = 0.5 g temperature = 25 °C, time = 15 min, pH=7). In all experiments, after the addition of absorbent, the solution was placed on the shakers at a speed of 400 rpm for 15 minutes. Afterwards, the centrifuge was set at 4,000 rpm for 5 minutes and the supernatant colored solution was separated from the adsorbent. The dye concentration was measured and then calculated by a spectrophotometer at a wavelength of 497 nm. All tests for the removal of dyes were conducted in a batch system and the influence of each parameter in all stages of the experiment was examined by changing the parameters of interest and maintaining a constant condition for all other variables.

Calculation of the adsorption percentage and capacity of chitosan nanoparticles

The calibration curve of absorbance against concentration was used to calculate the residual concentration of Congo red with a correlation coefficient of 0.9513. To determine the removal rate of Congo red in an equilibrium state by nanochitosan, equation (1) was used (Ghorai *et al.,* 2013; Hou *et al.,* 2012).

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

where, R is the removal efficiency for Congo red (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 Congo red concentration in the solution at equilibrium in terms of mg.g^{-1}. In order to determine the nano-chitosan adsorbed dye concentration in equilibrium, equation (2) was used (Ghorai *et al.,* 2013; Hou *et al.,* 2012).

$$Q_e = \frac{(c_o - c_e)v}{M} \qquad \text{Eq. 2}$$

where Q_e is the chitosan nanoparticle absorption capacity in terms of mg.g^{-1}, C_o is the Congo red initial concentration in the liquid phase in mg.L^{-1}, C_e represents Congo red concentration in the solution at equilibrium after absorption in mg.g^{-1}, V is the solution volume in liters and M is the chitosan nanoparticles weight in grams. It should be noted that all the tests were carried out with three replications and the averages of the obtained values were used.

Results

Effect of pH on the decolorizatin process

The effect of pH of the initial solution on the adsorption of Congo red ions was investigated in the range of 2-7 and for the contact time of 15 minutes. We showed that by increasing pH, efficiency and capacity of adsorption decreases, so that at the pH=4, the removal efficiency and adsorption capacity reaches their minimum values at respectively 98.21% (±0.008) and 982.13 mg.g^{-1} (±0.008). Afterwards, the removal efficiency and adsorption capacity rises for higher pH values, to reach their maximum (i.e. 99.94%) at the pH=7. Thus, Congo red adsorption is pH dependent and removal efficiency and adsorption capacity changes in response to the pH. The results of the examination of the pH effect on the removal of dye are shown in Figure 2. The results of the one-way ANOVA showed that pH significantly affect adsorption ($P<0.05$). The results of the Duncan test also indicated the significant differences between all means.

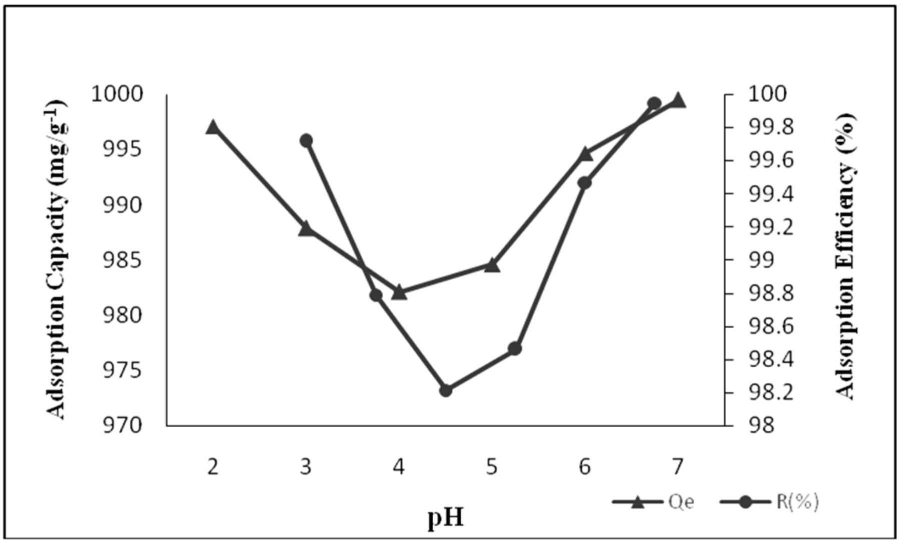

Figure 2. Effect of pH on the removal of Congo red dye using nano-chitosan.

Effect of initial concentration on decolorization process

Removal efficiency and adsorption capacity of the color ions using nano-chitosan were investigated for the concentrations of 3-50 mg.L^{-1}, pH=7 and adsorbent dosage of 0.5 g.L^{-1}. As can be seen in Figure 3, the highest removal efficiency and adsorption capacity occurs at 5997.66 mg.g^{-1} (±0.003) and 99.96% (±0.003) for the concentration of 30 mg.L^{-1}. The effects of the initial concentration on the removal efficiency and adsorption capacity of the Congo red dye using nano-chitosan are presented in Figure 3. The results of the one-way ANOVA showed that the initial concentration significantly affected adsorption ($P<0.05$). The results of the Duncan test also indicated significant differences between all means, except for the concentration of 50 mg.L^{-1}.

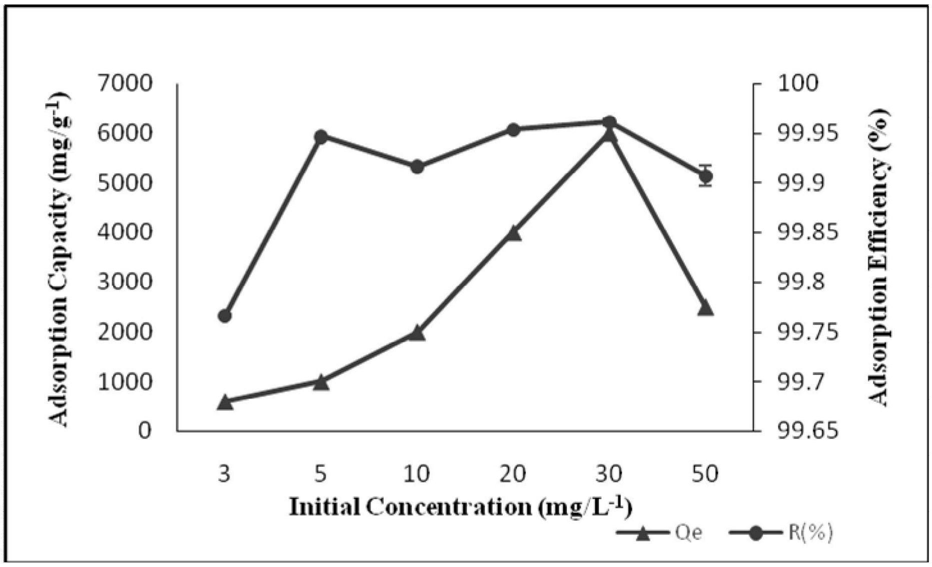

Figure 3. Effect of initial concentration on the removal of Congo red dye using nano-chitosan.

Effect of adsorbent dosage on dye decolorization process

As given, the removal of dye increases initially in response to the addition of adsorbent dosage, so that removal efficiency reaches its maximum (i.e. 99.94% (±0.002)) at the dosage of 0.5 $g.L^{-1}$. After that, there exists a sharp drop in terms of removal efficiency against adsorbent dosage. Effects of initial concentration on the removal capacity of Congo red against adsorbent dosage is illustrated in Figure 4. The results of the one-way ANOVA showed that the adsorbent dosage significantly affected adsorption ($P<0.05$). The results of the Duncan test also indicated significant differences between all means, except for the (0.1,0.3,0.5,0.7) and (0.7,1,1.5).

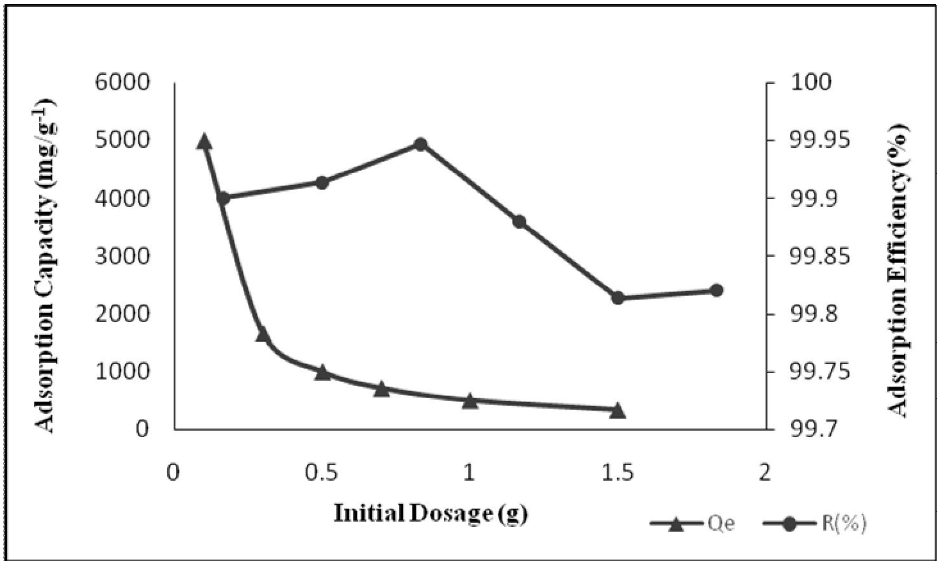

Figure 4. Effect of adsorbent dosage on the removal of Congo red dye using nano-chitosan.

Effect of temperature on dye decolorization process

The effect of temperature on the removal and adsorption of dye in different temperatures is illustrated in Figure 5. As given, with the increase in temperature to 30 °C, the effective collisions between the sorbent and dye molecules rises. At this temperature, the solubility of the dye is higher which results in much higher efficiency in the removal of the dye. Yet, at higher temperatures than 35 °C, removal reduces due to the destruction of the bonds between the nanoparticles and dye molecules. The results of the one-way ANOVA showed that temperature affected adsorption non significantly ($p>0.05$). The results of the Duncan test also indicated significant differences between all means.

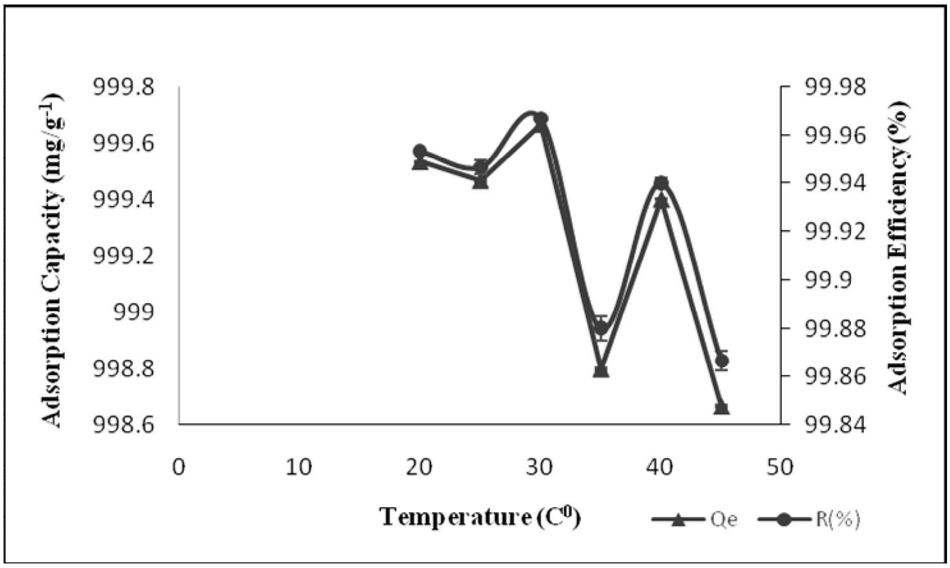

Figure 5. Effect of temperature on the removal of Congo red dye using nano-chitosan.

Effect of time on decolorization process

Figure 6 provides an illustration of the effect of time on the removal and adsorption of Congo red. The tests were performed in a time range of 5 to 40 minutes. As can be detected, at the initial times, higher adsorptions occur, so that during the first 15 minutes of the experiment, the highest removal occurred as 99.94% (±0.002) and the figure reduced to 99.80% (±0.0005) at 20 minutes. The results of the one-way ANOVA showed that time does not significantly affect adsorption ($P>0.05$). The results of the Duncan test also indicated significant differences between all means, except for the time of 15 minutes.

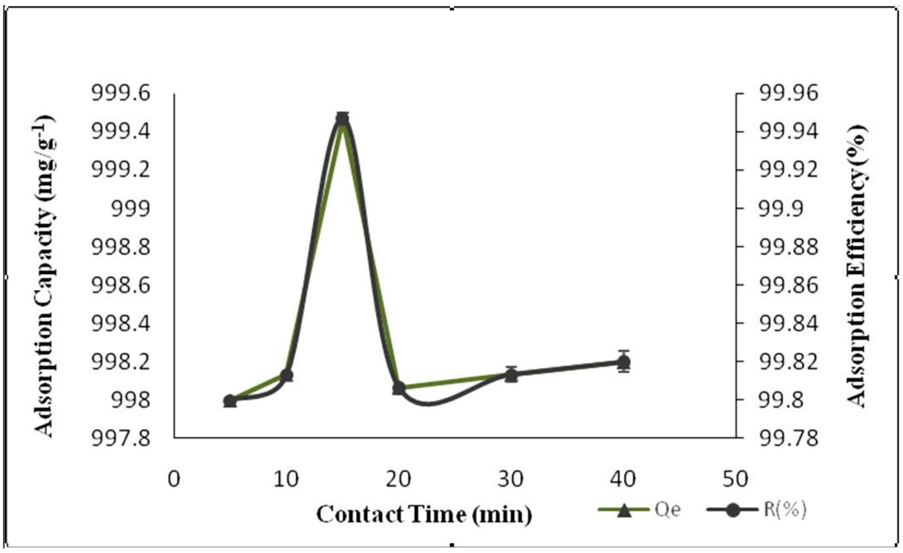

Figure 6. Effect of time on the removal of Congo red dye using nano-chitosan.

Discussion

Contaminated solutions' pH plays a significant role in the adsorption process, especially in determining the adsorption capacity of the chemical compounds. It not only affects the surface electrical charge of an adsorbent, but also changes the ionization rate of the compounds of the solution, dissociation of functional groups on the active terminal of the adsorbent and the chemical properties of the dye (Salehi *et al.,* 2010). The adsorption process is an electrostatic bond between the anionic azo dyes and the amino groups of the chitosan (the dye and the adsorption surface) (Huang *et al.,* 2011). In aqueous solutions, Congo red dye is ionized into anionic dyes with sulfonate groups. The removal of the Congo red with chitosan, is mainly due to the electrostatic reactions between the amino groups of the chitosan (NH^{3+}) and the sulfonate group (SO^{3-}) of the anionic dye (Li *et al.,* 2014). At the basic pH, the reduction of the adsorption capacity takes place because of: 1. reduction of the amino groups and thus adsorption terminals of the chitosan and 2. increase in electrostatic driving force between the locations with the negative charge on the adsorbent and the anionic dye (Chatterjee *et al.,* 2009). The results suggest that any increase in pH, would lead to a consequent augmentation of the removal efficiency and adsorption capacity, so that a pH=7, could result in the maximum values for the latter parameters, which could be attributed to the increased electrostatic reactions between the dye and the surface of the adsorbent.

Several researchers have attempted to study the effect of the dye's surface chemical properties on the removal capacity of the chitosan even though the molecular size and the number of sulfonate groups in the chemical structure of the dye influence the adsorption process. However, no significant relationship could be established between the number of the latter parameters and the adsorption capacity of the chitosan. It appears that other variables (hydrophobic property, substituent groups of the dye, etc.) might influence the adsorption capacity. It has been reported that the dye compounds with smaller sizes are capable of deeply thrusting into the perforated structure of the chitosan (Crini and Badot, 2008). Therefore, the concentration of 30 $mg.L^{-1}$ was selected as the optimum case owing to the highest obtained removal percentages.

Access to sufficient adsorbent is one of the major factors for decolorization, because this factor determines the free adsorption terminal according to the initial concentration of dye (Mahmoudian *et al.,* 2015). In this research, higher adsorption concentrations resulted in higher decolorization performance, which gives indication of a linear relationship between the adsorbent dosage and the removal of dye. This could be explained by the increased adsorption surfaces and simpler access to adsorption terminals. Moreoever, by increasing adsorption concentration, adsorption values reduce, given the interferences of the adsorption terminals for the dye molecules (Li *et al.,* 2014). The reduction in the adsorption capacity might be explained by the particle size distribution and large amounts of adsorbent. This distribution could lead to less adsorption surface and longer diffusion paths (Sheshmani *et al.,* 2014). In practical situations, the least effective amount of adsorbent has to be decided upon. Therefore, a concentration of 0.5 $g. L^{-1}$ was selected as the optimum case, to be applied in further studies.

Temperature is one of the main parameters that affects adsorption. Generally, any increase in temperature, due to higher penetration rate of the dye molecules into the adsorbent, would results in a significantly higher adsorption rates. This increase could not only influence the solubility of the dye in the solution, but also the chemical properties of the adsorbent compounds. Thus, higher temperature would facilitate the formation of much higher numbers of adsorption terminals on the polymeric chain, which could regulate the whole adsorption process (Crini and Badot, 2008). The results of this research suggested that temperature increase could positively affect the removal of the Congo red dye, reaching its maximum (i.e. 99.96% (±0.0005)) at 30 °C.

In general, by increasing contact time, the chance of the collisions of the dye molecules with the adsorbent surface grows and so does the adsorption level. The chemical structure and the existence of cationic functional groups in chitosan and high adsorption rations, probably results into the maximum adsorption during the first 15 minutes of the test. Furthermore, the reduction in adsorption at 20 minutes of the test forward, despite escalated removal efficiency and adsorption capacity, might be explained by the blockage of the adsorption terminals. It has to be noted that a 99.94% (±0.002) removal rate during the first 15 minutes of the test, testifies to the high efficiency of this experiment. With regards to the economic terms and for time saving purposes, 15 minutes was selected as the optimum time for further similar trials. Table 1 shows the comparison of the optimum time of Congo red with other absorbents.

Table 1. Comparison of the optimum time of Congo red with other absorbents.

Adsorbent	Time (min)	References
Magnetic nickel zinc ferrite nanocomposite	30	[1]
hydroxyapatite/chitosan composite	180	[12]
polypyrrole–polyaniline nanofibers	120	[3]
$CoTiO_3$	60	[11]
$CuTiO_3$	30	[11]
Roots of Eichhornia crassipes	90	[22]
Sawdust Modified by Polianilin	60	[2]
nano-chitosan	15	This Work

Conclusion

The results of current research suggest that nano-chitosan, for its high surface area and inclusion of amino and carboxyl groups, could effectively remove the Congo red ions. 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 Congo red depends on pH and the best figure is achievable at pH=7. This chemical compound is highly capable of adsorbing anionic dyes such as Congo red and this capability augmented linearly in response to the initial concentration of the dye, with the maximum removal rate and adsorption capacity being realized at 30 $mg.L^{-1}$. Rising temperature to 30 °C could increase the chance of collisions between the dye molecules and the dye and thus led 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 0.5 $g.L^{-1}$ was selected as the optimum case for the removal of Congo red. The best contact time was estimated at 15 minutes, which indicates the short duration of the treatment. Comparison of characteristic performances of the proposed method with some previous CR removal reports shows the superiority and applicability of this new adsorbent in terms of lower optimum time and higher adsorption capacity.

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