Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.934719

56 (2015) 136–145
September

Taylor & Francis
Taylor & Francis Group

Using pistachio shell for Remazol Red removal from aqueous solutions: equilibrium, kinetics and thermodynamics

Bulent Armagan[a,*], Fatih Toprak[b]

[a]*Faculty of Engineering, Environmental Engineering Department, Istanbul University, 34320 Istanbul, Turkey, email: bulent.armagan@istanbul.edu.tr*
[b]*Yenigun Construction Industry and Trade Inc., Ankara, Turkey; email: fthtoprak@gmail.com*

Received 29 July 2013; Accepted 8 June 2014

ABSTRACT

The pistachio shell, an agriculture waste, was studied as a no-cost and readily accessible potential dye adsorbent for the removal of the commercially important reactive azo dye, Remazol Red (C.I. 18221) from its aqueous solution. For this purpose, a series of batch adsorption tests were carried out to assess the effect of various experimental parameters such as adsorbent concentration, mixing time, initial dye concentration, pH and temperature. The experimental results indicated that the maximum dye removal could be attained at pH 2. The equilibrium between the dye and the adsorbent in the solution was established within 10 min. The maximum adsorption capacity of pistachio shell was determined around 108 mg g^{-1} at 20˚C. The pseudo-second-order model provided close fit with the experimental data ($R^2 > 0.99$) for the reactive dye. Equilibrium data also fitted well to the Freundlich isotherm model in the studied concentration range of Remazol Red at 20˚C. The negative values of ΔG indicated that the adsorption process was spontaneous and thermodynamically favorable. Accordingly, the pistachio shell was shown to be a very efficient and low-cost adsorbent, and a promising alternative for eliminating dyes from industrial wastewaters.

Keywords: Pistachio shell; Adsorption; Reactive dye; Kinetics; Thermodynamic

1. Introduction

Synthetic dyes are common water pollutants and they may frequently be found in various quantities in industrial wastewater, e.g. in various branches of the textile industry. Reactive azo dyes are one of the most common synthetic dyes used in the dyeing processes and as much as 40% of these dyes remain in the effluents [1]. They differ from all other classes of dyes in that they bind to the textile fibers such as cotton to form covalent bonds. They have the favorable characteristics of bright color, simple application techniques, and low energy consumption and are used extensively in textile industries [2]. The entire wastewater may contain elements like sulfur, naphthol, vat dyes, nitrates, acetic acid, soaps, and chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all of which collectively make the effluent highly toxic [3,4]. This can lead to acute effects on exposed organisms due to the toxicity of the dyes, abnormal coloration, and reduction in

*Corresponding author.

1944-3994/1944-3986 © 2014 Balaban Desalination Publications. All rights reserved.

photosynthesis because of the absorbance of light that enters the water. It is evident; therefore, that the removal of such colored agents from aqueous solutions is of significant environmental and technical importance [5]. However, wastewater containing dyes is very difficult to treat by traditional methods. Since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat, and oxidizing agents due to their structure and molecular size most of the dyes contain aromatic rings, which make them mutagenic and carcinogenic [6–8].

Many chemical or biological methods have been used either individually or together for the removal of colored and colorless organic pollutants from textile wastewater [9]. Adsorption has been an effective separation process for a wide variety of applications, especially for the removal of non-biodegradable pollutants (including dyes) from wastewater and it is noted to be superior to other techniques for water treatment with regard to cost efficiency, eco-friendliness, simplicity of design, ease of operation, and being insensitive to toxic substances [1,10]. Although activated carbon and polymer resins are widely used as adsorbents for removing chemicals from relatively concentrated wastewaters due to their excellent adsorption abilities, their high price and the necessity of regeneration restrict their usage [3,11]. Therefore, an extensive research has been carried out recently with the goal to find alternative and less expensive materials (sorbents) capable to remove chemical substances from waters. Natural materials and waste materials from industry or agriculture are typically classified as non-conventional sorbents because of their inexpensive production and local availability. In this context, many studies revealed that other alternative adsorbents, such as synthetic calcium phosphates [12], peanut hull [13], wheat straw [14], activated carbon from paper mill sludge [15], cellulose [16], native algae [17], pine cone [18], red mud [19], orange waste gel [20], peanut shells [21], *Agaricus campestris* [22], mesoporous silica [23], cotton seed shell [24], and natural or modified minerals such as montmorillonite [25], clinoptilolite [26,27], sepiolite [2,28,29], bentonite [3,30,31].

The main purpose of the this study is to determine the adsorption abilities of the pistachio shell, as a novel adsorbent, for the elimination of Remozal Red from synthetic aqueous solutions. Because the chemical pre-treatment may increase the cost of the sorbent substantially and thus abolish the main advantage of the non-conventional sorbents, we have focused, in this study, on an application of the pistachio shell. The influence of several parameters such as pH, adsorbent concentration, mixing time, initial dye concentration, and temperature on the pistachio shell under kinetic and equilibrium conditions were investigated. The rate limiting step of the dye onto the adsorbents was determined from the adsorption kinetic results. Adsorption isotherm equations were used to interpret and evaluate the equilibrium data and thermodynamic parameters were calculated.

2. Experimental

2.1. Materials

The pistachio shell was chosen because of its high volatility, low ash content, and reasonable good hardness property. It is grown mainly in Iran, USA, Syria, Turkey, Greece, and Italy. It is one of the most popular nuts in the world with high nutritional values and it has a very unique flavor as a snack and a food ingredient [32]. It contains around 23% protein, 56% fat, 19% carbohydrate, and 5% moisture [33]. Pistachio also contains high amounts of K, P, Ca, Mg, and Fe at different amounts.

The pistachio shell is a low-cost agricultural waste as well as a profoundly accessible potential dye adsorbent in the SE part of Turkey. The samples used in the experiments were obtained commercially from Sanliurfa, Turkey. The pistachio shell consists of internal and external shells. In this study, internal pistachio shell samples were used. They were washed several times with distilled water to remove surface impurities and then dried at 110°C in an oven for 12 h to reduce the moisture content. The pistachio shell was crushed, grounded, and sieved to obtain a particle size in the range of 250–2,000 μm with a coffee grinder (waring commercial) to increase the surface area.

The textile reactive azo dye, Remazol Red (C.I. 18221) was provided from Bursa, Turkey and used in all the adsorption experiments without further purification. The chemical structure of Remazol Red is illustrated in Fig. 1. It contains anionic sulfonate groups to various degrees.

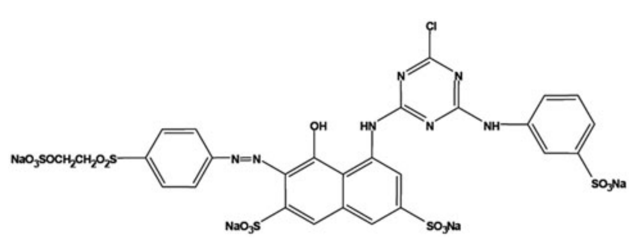

Fig. 1. The general chemical structure of Remazol Red (C.I. 18221).

2.2. Apparatus and laboratory equipment

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. It is useful for determining the particle shape, porosity, and appropriate size distribution of the adsorbent. The Fourier transform infrared (FTIR) spectroscopic measurement was carried out with KBr pellets (2 mg/300 mg KBr) on a spectrometer (Model 580, Perkin-Elmer) with a resolution of 4.00 cm^{-1}. All the absorbance measurements of Remazol Red were made with a UV–vis spectrophotometer (Shimadzu T70) at the $\lambda_{max} = 520$ nm.

2.3. Methods

Adsorption kinetic experiments for pistachio shell were carried out by a batch equilibrium technique by placing a known quantity of the adsorbent in a glass bottle containing 40 mg/L of an aqueous solution of pistachio shell with a predetermined concentration. After the solution was prepared, the bottles were placed on an orbital shaker at 150 rpm at room temperature for 4 h, and then samples were centrifuged at 4,000 rpm for 10 min. In order to observe the effects of experimental deviations/personal error on the dye removal, each experiment was repeated twice under the same working conditions. The reproducibility of the data varied in the range of ±1.5%.

2.4. Adsorption isotherms

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. Adsorption equilibrium is established when the amount of solute being adsorbed on to the adsorbent is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. By plotting solid phase concentration against liquid phase concentration graphically, it is possible to depict the equilibrium adsorption density [34]. The adsorption density, q_e(mg/g), was calculated using the following relationships (Eq. (1)).

$$q_e = \frac{(C_i - C_e) \times V}{1000 \times m} \tag{1}$$

where q_e = amount of dye adsorbed per gram of adsorbent in mg/g, C_i = initial dye concentration in mg/l, C_e = equilibrium (residual) dye concentration in mg/l, V = the volume of the solution in ml, and m = mass of adsorbent (g).

Adsorption isotherm data of the Remazol Red was investigated to fit the models of Langmuir and Freundlich. For the non-linear method, a trial and error procedure, which is applicable to computer operation, was developed to determine the isotherm parameters by minimizing the respective coefficient of determination between experimental data and isotherms using the solver add-in with Microsoft's spread-sheet. In first instance, the Langmuir model assumes that adsorption occurs in a monolayer where the actives sites are identical and energetically equivalent. This isotherm is given by (Eq. (2)):

$$q_e = \frac{q_{\max} K C_e}{1 + K C_e} \tag{2}$$

where $q_{\max}$ is the maximum adsorption capacity (mg/g) and K (L/mg) represents the Langmuir equilibrium constant, respectively. Both $q_{\max}$ and K are obtained from data correlation. Alternatively, the Freundlich model is an empirical expression used to describe a heterogeneous system, which is defined as (Eq. (3)):

$$q_e = K_f C_e{}^{(1/n)} \tag{3}$$

where K_f and n are Freundlich constants as indicators of adsorption capacity and adsorption intensity, respectively. Linear regression was frequently used to determine the most fitted isotherm. The linear least-squares method to the linearly transformed isotherm equations was widely applied to confirm the experimental data and isotherms using coefficient of determination [35]. However, several studies have shown that the transformation of non-linear adsorption models to linear forms usually results in parameter estimation errors and uncertainties [36]. Thus, in this study, a non-linear regression approach employing a stochastic global optimization method was used to determine the model parameters of isotherm equations.

To analyze the kinetics of adsorption of different concentrations of Remazol Red onto the pistachio shell, the pseudo-first- and second-order-kinetic model were applied for the interpretation of experimental data [37]. The linearized form of the pseudo-first-order model is given by (Eq. (4)):

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \tag{4}$$

where q_t is the amount of dye sorbed (mg/g) at time t (min); q_e is the amount of dye sorbed at equilibrium (mg/g), and k_1 is the equilibrium rate constant of pseudo-first-order adsorption ($\min^{-1}$). The slopes and intercepts of plots of log ($q_e - q_t$) vs. time were used to determine the first-order rate constant k_1. The second-order kinetic model [36] is linearized as (Eq. (5)):

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 \times {q_{e2}}^2}\right) + \left(\frac{1}{q_{e2}}\right)t \tag{5}$$

where k_2 is the rate constant of pseudo-second-order adsorption. The slope and intercepts of plot of t/q_t vs. t was used to calculate the second-order rate constant k_2 and q_{e2}.

2.5. Thermodynamics of adsorption

In order to understand the effect of temperature on the adsorption process thermodynamic parameters including change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), were determined by using the following equations (Eqs. (6–8)) [20,23].

$$K_c = \left(\frac{C_{Ae}}{C_e}\right) \tag{6}$$

$$\Delta G = -RT \ln K_c \tag{7}$$

$$\ln K_c = ((\Delta S)/R) - ((\Delta H)/RT) \tag{8}$$

where K_c is the equilibrium constant, C_{Ae} is the amount of dye (g) adsorbed on the adsorbent per L of the solution at equilibrium, C_e is the equilibrium concentration (g/L) of the dye in the solution, T is the solution temperature in Kelvin (K) and R is the gas constant and is equal to 8.314 J/mol K^{-1}.

3. Results and discussion

3.1. The efficiency of the pistachio shell for Remazol Red adsorption

The chemical analysis of the pistachio shell was performed by using an energy dispersive X-ray spectrometer (Zeiss) attached to a scanning electron microscope. This photomicrograph shows the fibrous structure of the pistachio shell. Scanning electron micrographs of raw and adsorbed pistachio shells with Remazol Red were shown in Fig. 2. It is clear from the figure that, the pistachio shells have considerable numbers of pores where, there was a good possibility for dye to be trapped and adsorbed into these pores. The SEM picture of the pistachio shells showed very distinguished dark spots which can be taken as a sign for the effective adsorption of dye molecules in the cavities and pores of this adsorbent. After adsorption, the pores were packed with dyes.

In order to investigate the surface characteristics of the pistachio shell, FTIR (Perkin–Elmer Spectrophotometer Spectrum One) in the range of 450–4,400 cm^{-1} was studied (Fig. 3). The FTIR spectroscopic measurement was carried out with KBr pellets (2 mg/300 mg KBr) on a spectrometer (Model 580, Perkin–Elmer) with a resolution of 4.00 cm^{-1}. Infrared spectra were recorded in the 450–4,400 cm^{-1} range. The FTIR spectrum of the pistachio shell showed that the peak positions are at 3,409.77, 2,925.33, 2,855.20, 1,640.97, 1,631.20, 1,547.15, 1,427.27, 1,378.55, 1,329.80, and 1,163.03 cm^{-1}. The band at 3,409.77 cm^{-1} is due to O–H and N–H stretching. The bands at 2,925.33 and 2,855.20 cm^{-1} correspond to unsymmetrical and symmetrical aliphatic C–H stretching, respectively. While the bands at 1,600–1,400 cm^{-1} reflect carbonyl group stretching (amide) and N–H bending, respectively, the bands at 1,300–1,100 cm^{-1} corresponding to C–O bending and indicate the presence of phenolic groups [38–40].

3.2. The effect of solution pH

In order to determine the pH effect on the adsorption capacity of the pistachio shell for Remazol Red, dye solutions were prepared at different pH levels in the range of 2–10, after introducing adsorbent at 25°C and initial dye concentration of 40 mg/L. The results showed that the amount of adsorbed dye on the pistachio shell decreased as the pH increased from 2 to 10 as seen in Fig. 4. The percentage of removal increased to 94% at pH 2 and to 83% at pH 4. Consequently, it is clear that the optimum pH is 2 and was kept constant during each batch experiment. The variation in adsorption capacity in this pH range was largely due to the structural changes being effected in the dye molecules and the surface adsorption characteristics of the pistachio shell indicating that the adsorption capacities of the adsorbents were pH dependent. Similar observations were reported by other colleagues for adsorption of dyes indicating that the adsorbent had a net positive charge on its surface [11,16].

3.3. The effect of temperature

The adsorption studies were carried out at four different temperatures 20, 30, 40, and 50°C. Compared to the 30°C, the adsorption of Remazol Red onto the pistachio shell increased at 40°C. It was observed from the figure that the maximum adsorption capacity of the dye increased from 6.06 to 6.10 mg/g for the pistachio shell.

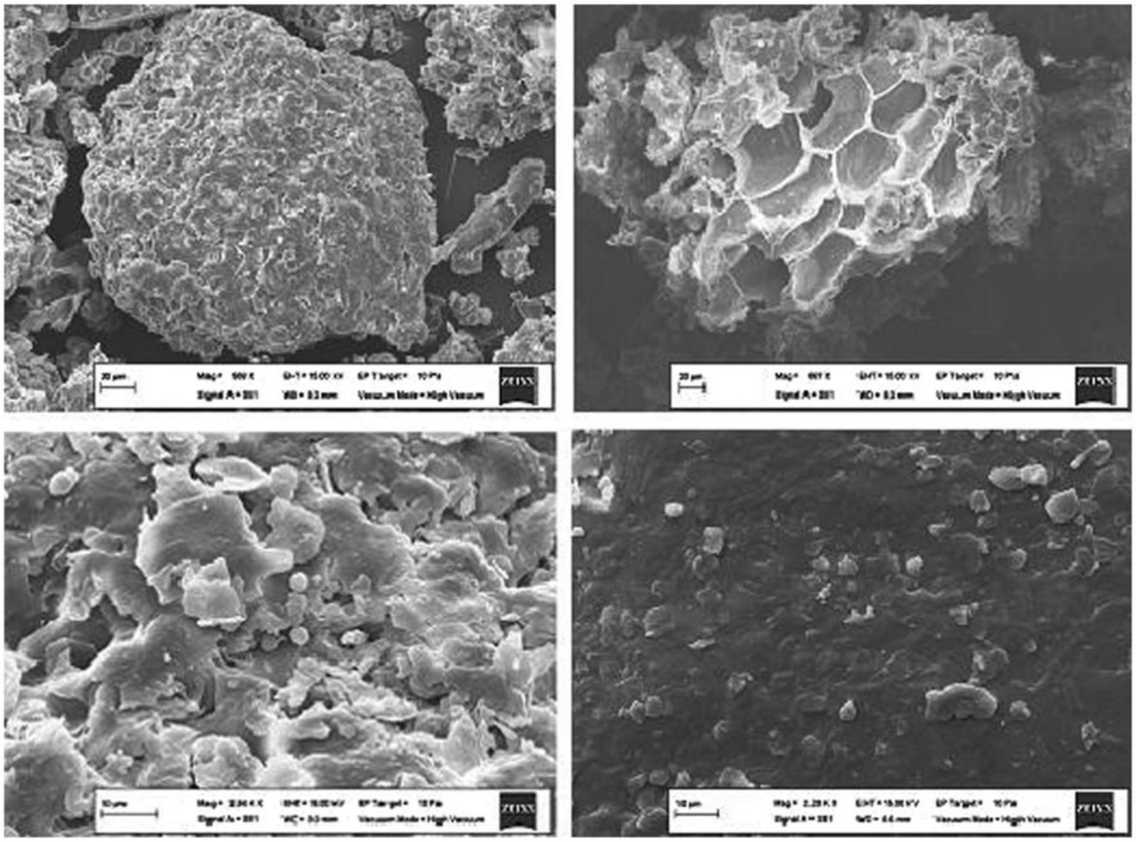

Fig. 2. SEM images of raw and Remazol Red dye adsorbed onto the pistachio shells.

The adsorption density increased with the increasing temperature, indicating that the adsorption was an endothermic process. The increase in dye adsorption with an increasing temperature has been widely observed in many studies [20,22]. Thermodynamic constraints, ΔH and ΔS were calculated from the slope and intercept of the van't Hoff plot of $\ln K_c$ against $1/T$ (Fig. 5). The results were given in Table 1. When the temperature was increased from 20 to 50°C, the magnitude of free energy change shifted to a high negative value (from 5.60 to 6.39 kJ/mol) suggesting that the adsorption of Remazol Red dye adsorption onto the pistachio shell was spontaneous and thermodynamically favorable. Besides, the change in free energy for physisorption is between 20 and 0 kJ/mol; chemisorption has a range of 80–400 kJ/mol [34]. The calculated ΔG value was obtained to be 5.60 kJ/mol for the Remazol Red dye and this could be considered as physisorption.

3.4. The effect of mixing time

The distribution of adsorbate between adsorbent and solution is influenced by mixing time. The adsorption capacity of the pistachio shell vs. the mixing time (from 10 to 240 min.) is shown in Fig. 6. The figure revealed that the adsorption capacity increased with the mixing time up to 10 min. The adsorption of Remazol Red onto the pistachio shell reached equilibrium at 10 min. Therefore, the optimum mixing time, to be used in other studies for further testing, was chosen as 10 min [13,16].

3.5. The effect of adsorbent concentration

In order to determine the effect of adsorbent concentration, the adsorbent amount used in the experiments varied from 0.01 to 1 g/L. As the adsorbent amount was increased from 0.01 to 1 g/L, the percentage of dye adsorption was also increased, but the uptake capacity of the adsorbent decreased. This may be attributed to the availability of more sorption sites due to higher amount of the sorbent. At higher adsorbent to solute ratios, there is a very fast sorption onto the sorbent surface that produces a lower solute concentration in the solution as compared to a lower sorbent to solute concentration ratio (Fig. 7). The initial concentration of the dye is a key driving force for mass diffusion and transfer between the aqueous and

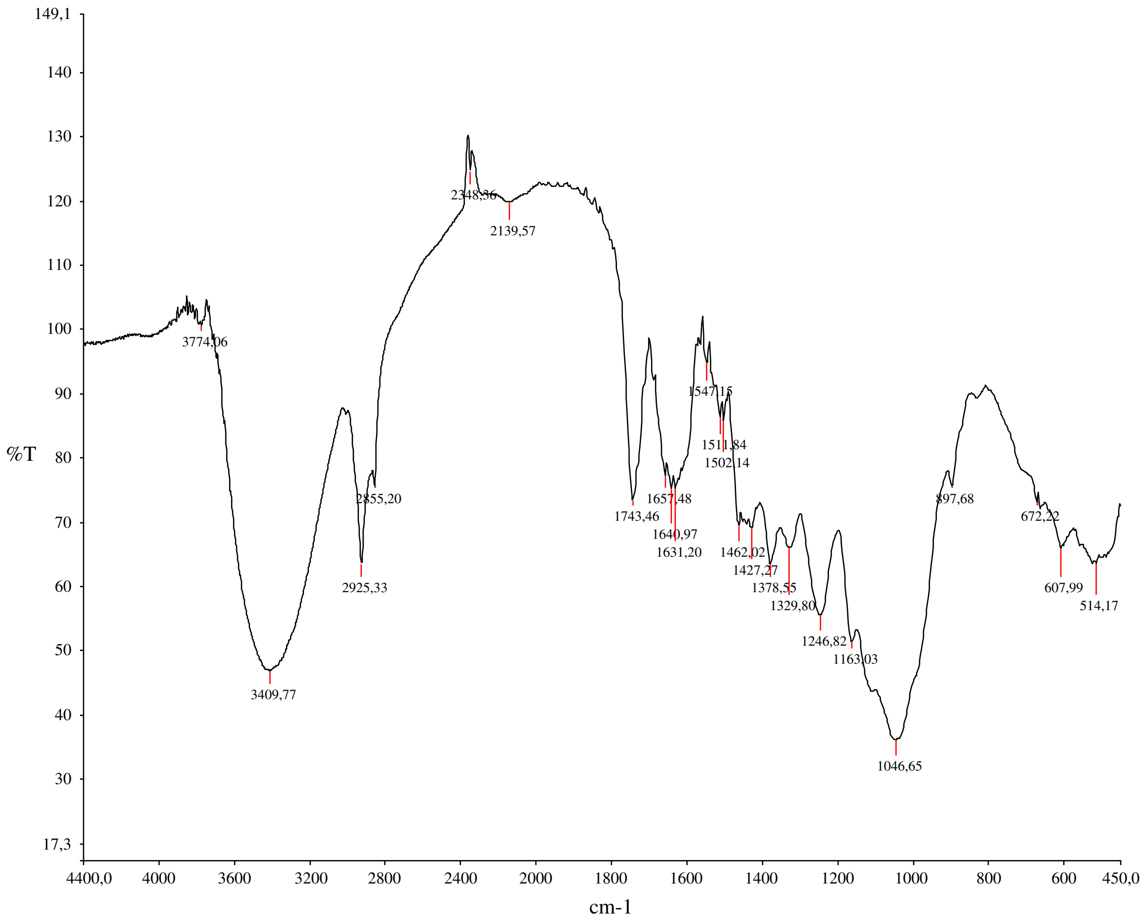

Fig. 3. FTIR spectrum of the pistachio shell.

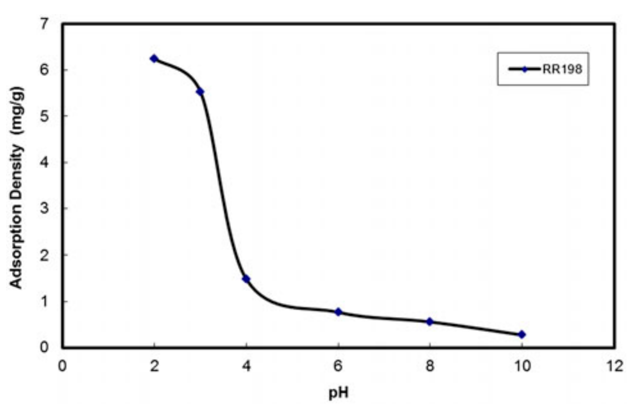

Fig. 4. The effect of solution pH on the adsorption of Remazol Red by the pistachio shell.

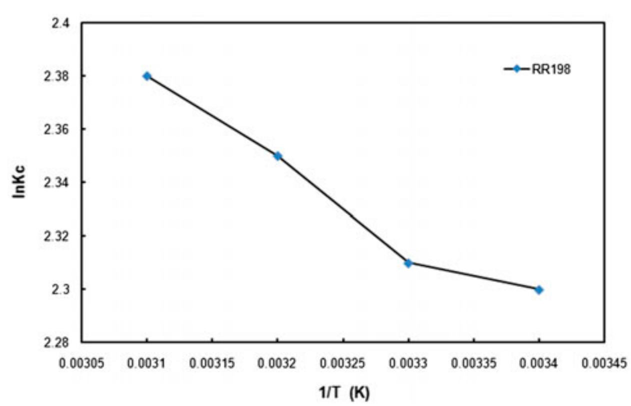

Fig. 5. A plot of $\ln K_c$ against $1/T$ for the adsorption of Remazol Red onto the pistachio shell.

solid phases. The increase trend indicates that the absorbing sites of the absorbent were not saturated [4].

3.6. The effect of initial dye concentration

The effect of initial dye concentration on the adsorption capacity of pistachio shells was also studied in the initial concentration range of 50–1,000 mg/L.

Table 1
The thermodynamic parameters of Remazol Red adsorption onto the pistachio shell

T (K)	K_c	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (JK^{-1}/mol)
293	9.97	–5.60	0.03	19.21
303	10.15	–5.82		
313	10.51	–6.11		
323	9.81	–6.39		

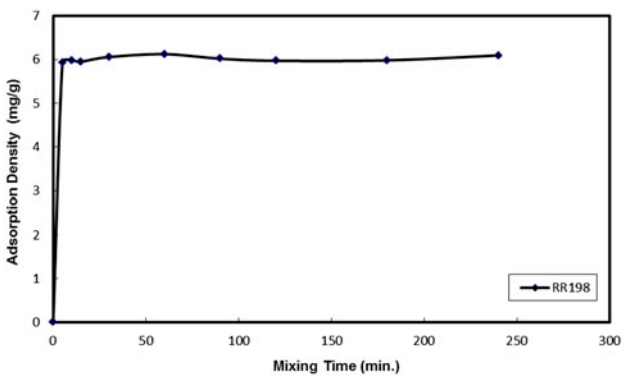

Fig. 6. The effect of mixing time on the adsorption of Remazol Red by the pistachio shell.

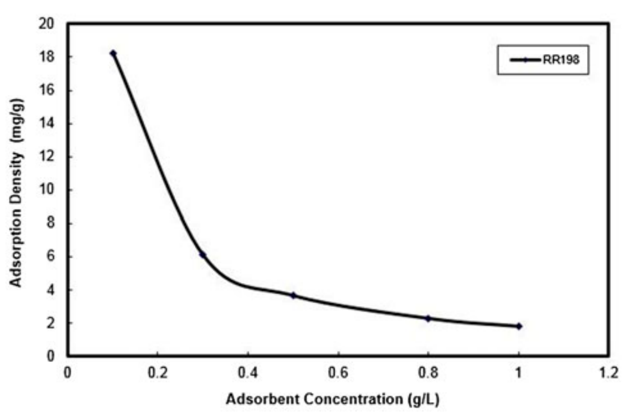

Fig. 7. The effect of adsorbent concentration on the adsorption of Remazol Red by the pistachio shell.

From Fig. 8, it can be seen that the adsorption capacity of pistachio shells increases with the increase of the initial dye concentration. While the adsorption capacity of Remazol Red on pistachio shells for 10 min with the initial dye concentration at 150 mg/L is 19.16 mg/g, this is due to the increase in the concentration gradient which acts as a increasing driving force to overcome all mass transfer resistances of the dye molecules between the aqueous and solid phase, leading to an

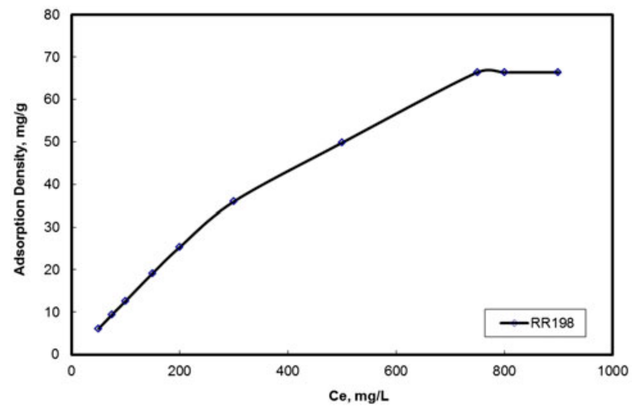

Fig. 8. The effect of initial dye concentration on the adsorption of Remazol Red by the pistachio shell.

increasing equilibrium adsorption until adsorbent saturation is achieved [34]. The adsorption density increases to 750 mg/L with increasing equilibrium concentration until 66 mg/g above which the adsorption density remains nearly constant.

3.7. Kinetic studies

To analyze the kinetics of adsorption of different concentrations of Remazol Red onto the pistachio nut shell, the pseudo-first- and second-order-kinetic model were applied for the interpretation of experimental data [38]. The models were applied to the adsorption of Remazol Rot by the pistachio nut shell. In order to quantify the applicability of the model, the correlation coefficient, R^2, was calculated from these plots. The models were applied to the adsorption of Remazol Rot by the pistachio shell and the result was presented in Fig. 9. The fitted linear regression plots showed that the experimental data had its best fit with the pseudo-second-order model with higher determination coefficients ($R^2 > 0.99$) than those of the pseudo-first-order model. Besides, the q_{e2} and k_2 values of the second-order model are 6.057 mg/g and 0.303 L/g, respectively.

However, the q_e value of the pseudo-first-order model was found negative and showed desorption. From the results, it is also seen that the equilibrium adsorption from the pseudo-second-order model are much close to the experimental data. The calculated adsorption capacity, q_{e2}, increases with the increase in the initial dye concentration but there is no linear relationship with pH and temperature. This suggests that the pseudo-second-order kinetic model can be applied to predict the amount of dye adsorbed at different experimental conditions.

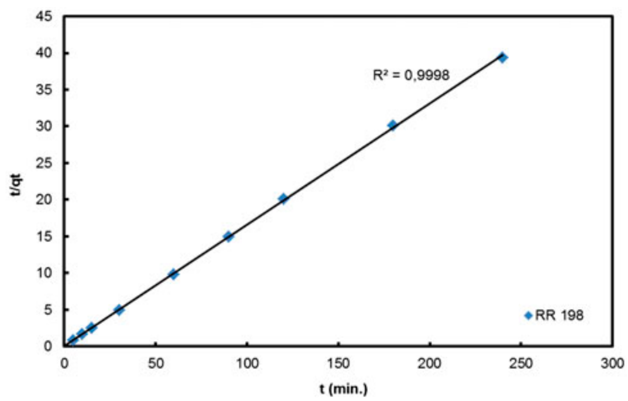

Fig. 9. The pseudo-second-order kinetic plots for the adsorption of Remazol Red onto the pistachio shell.

3.8. Adsorption isotherms

Adsorption isotherm data of Remazol Red was investigated to fit the models of Langmuir and Freundlich. Figs. 10 and 11 show experimental data and the predicted equilibrium curve using the non-linear method for the two-equilibrium isotherm Freundlich and Langmuir at 20˚C, respectively. The calculated isotherm constants by the non-linear method were shown in Table 2. The Freundlich model appears to fit the experimental data better than the Langmuir model as reflected with the correlation coefficients in the range of 0.98 (Table 2). The maximum adsorption capacity of the pistachio shell was determined as 108.15 mg g^{-1}at 20˚C. In the literature, the maximum adsorption capacity of Remazol Red on eggshell was found to be 46.9 mg g^{-1} at 22˚C [35]. Similar trends were also observed by Gulnaz et al. [9].

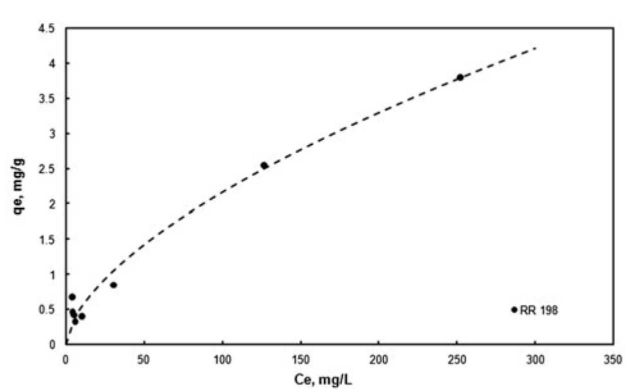

Fig. 10. Freundlich plots for the adsorption of Remazol Red dye onto the pistachio shell.

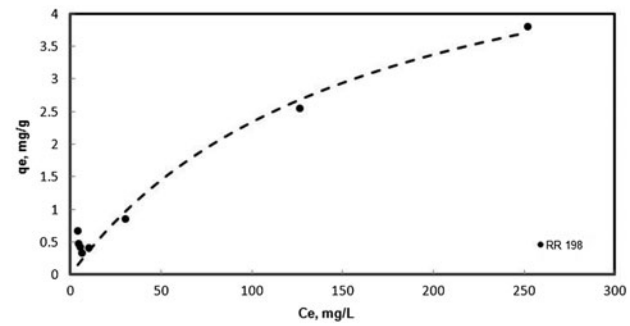

Fig. 11. Langmuir plots for the adsorption of Remazol Red onto the pistachio shell.

Table 2
The parameters of the Freundlich and Langmuir isotherms*

	Freundlich			Langmuir		
Adsorbent	K_F (mg g^{-1})	n	R^2	$q_{\max}$ (mg g^{-1})	K_L	R^2
Pistachio shell	0.1328	1.65	0.98	108.15	0.006319	0.96

*T = 20˚C, contact time = 10 min, adsorbent particle size = 0.025 < X < 0.5, C_i = 50 ppm.

4. Conclusions

In this study, kinetic and equilibrium of Remazol Red (C.I. 18221) dye adsorption onto the pistachio shell were carried out as a series of batch adsorption tests. The characteristics of adsorbent were confirmed by using FTIR and SEM analysis. The amount of dye adsorbed was found to depend on the adsorbent concentration, mixing time, initial dye concentration, pH and temperature. The adsorbent was most effective at pH 2 and 20˚C. The equilibrium between the dye and the adsorbent in the solution was established within 10 min. The pseudo-second-order model provided close fit with the experimental data (R^2 > 0.99) for the reactive dye. Equilibrium data were also fitted well to the Freundlich isotherm model. The maximum adsorption capacity of the pistachio shell was determined as 108.15 mg g^{-1} at 20˚C. The negative values of free energy changes ΔG indicate that the adsorption of the Remazol Red dye adsorption onto the pistachio shell was spontaneous and thermodynamically favorable. Results showed that the pistachio shell was an effective adsorbent for the removal of Remazol Red dye from aqueous solution.

References

[1] Ö. Gök, A.S. Özcan, A. Özcan, Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite, Appl. Surf. Sci. 256 (2010) 5439–5443.

[2] E. Demirbas, M.Z. Nas, Batch kinetic and equilibrium studies of adsorption of Reactive Blue 21 by fly ash and sepiolite, Desalination 243 (2009) 8–21.

[3] X. Zhang, A. Li, Z. Jiang, Q. Zhang, Adsorption of dyes and phenol from water on resin adsorbents: Effect of adsorbate size and pore size distribution, J. Hazard. Mater. 137 (2006) 1115–1122.

[4] Y. Safa, H.N. Bhatti, Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk, Desalination 272 (2011) 313–322.

[5] G.L. Gutto, L.A.A. Pinto, Adsorption of food dyes onto chitosan: Optimization process and kinetic, Carbohydr. Polym. 84 (2011) 231–238.

[6] M.A. Ashraf, M. Hussain, K. Mahmood, A. Wajid, Removal of acid yellow-17 dye from aqueous solution using eco-friendly biosorbent, Desalin. Water Treat. 51 (2013) 4530–4545.

[7] A. Mittal, J. Mittal, A. Malviya, D. Kaur, V.K. Gupta, Adsorption of hazardous dye crystal violet from wastewater by waste materials, J. Colloid Interface Sci. 343 (2010) 463–473.

[8] J. Singh, S. Banerjee, D. Gusain, Y.C. Sharma, Equilibrium modelling and thermodynamics of removal of orange g from its aqueous solutions, J. Appl. Sci. Environ. Sanit. 6 (2011) 317–326.

[9] O. Gulnaz, A. Sahmurova, S. Kama, Removal of Reactive Red 198 from aqueous solution by *Potamogeton crispus*, Chem. Eng. J. 174 (2011) 579–585.

[10] I.A. Aguayo-Villarreal, A. Bonilla-Petriciolet, V. Hernández-Montoya, M.A. Montes-Morán, H.E. Reynel-Avila, Batch and column studies of Zn^{2+} removal from aqueous solution using chicken feathers as sorbents, Chem. Eng. J. 167 (2011) 67–76.

[11] G. Moussavi, R. Khosravi, The removal of cationic dyes from aqueous solutions by adsorption onto pistachio hull waste, Chem. Eng. Res. Des. 89 (2011) 2182–2189.

[12] H. El Boujaady, A. El Rhilassi, M. Bennani-Ziatni, R. El Hamri, A. Taitai, J.L. Lacout, Removal of a textile dye by adsorption on synthetic calcium phosphates, Desalination 275 (2011) 10–16.

[13] M.S. Tanyildizi, Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull, Chem. Eng. J. 168 (2011) 1234–1240.

[14] X. Ren, X. Zhang, L. Zhang, R. Han, Biosorption of methylene blue by natural and chemical modified wheat straw in fixed-bed column, Desalin. Water Treat. 51 (2013) 4514–4523.

[15] W. Li, Q. Yue, P. Tu, Z. Ma, B. Gao, J. Li, X. Xu, Adsorption characteristics of dyes in columns of activated carbon prepared from paper mill sewage sludge, Chem. Eng. J. 178 (2011) 197–203.

[16] L. Wang, J. Li, Adsorption of C.I. Reactive Red 228 dye from aqueous solution by modified cellulose from flax shive: Kinetics, equilibrium, and thermodynamics, Ind. Crops Prod. 42 (2013) 153–158.

[17] A.H. Sulaymon, A.A. Mohammed, T.J. Al-Musawi, Removal of lead, cadmium, copper, and arsenic ions using biosorption: Equilibrium and kinetic studies, Desalin. Water Treat. 51(22–24) (2013) 4424–4434.

[18] F. Deniz, Color removal from aqueous solutions of metal-containing dye using pine cone, Desalin. Water Treat. 51(22–24) (2013) 4573–4581.

[19] A. Bhatnagar, V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, A review of the use of Red Mud as adsorbent for the removal of toxic pollutants from water and wastewater, Environ. Technol. 32 (2011) 231–249.

[20] B. Pangeni, H. Paudyal, K. Inoue, H. Kawakita, K. Ohto, H. Harada, B.K. Biswas, S. Alam, Optimization of an adsorption process for tetrafluoroborate removal by zirconium (IV)-loaded orange waste gel from aqueous solution, Environ. Technol. 33 (2012) 845–850.

[21] J.X. Zhang, L.L. Ou, Kinetic, isotherm and thermodynamic studies of the adsorption of crystal violet by activated carbon from peanut shells, Water Sci. Technol. 67(4) (2013) 737–744.

[22] Ü. Danış, Kinetic and thermodynamic studies of the biosorption of Cu(II) by *Agaricus campestris*, Environ. Prog. Sustain. Energy 30(2) (2011) 177–186.

[23] D.D. Asouhidou, K.S. Triantafyllidis, N.K. Lazaridis, K.A. Matis, Adsorption of Remazol Red 3BS from aqueous solutions using APTES- and cyclodextrin-modified HMS-type mesoporous silicas, Colloids Surf., A 346 (2009) 83–90.

[24] D. Ucar, B. Armagan, The removal of Reactive Black 5 from aqueous solution by cotton seed shell, Water Environ. Res. 84(4) (2012) 323–327.

[25] F.M. Mohammed-Azizi, S. Dib, M. Boufatit, Algerian montmorillonite clay as adsorbent for the removal of aniline from the aqueous system, Desalin. Water Treat. 30 (2011) 74–79.

[26] J. Torres-Pérez, M. Solache-Ríos, M.T. Olguín, Sorption of azo dyes onto a mexican surfactant-modified clinoptilolite-rich tuff, Sep. Sci. Technol. 42 (2007) 299–318.

[27] J. Kluczka, T. Korolewicz, M. Zolotajkin, W. Simka, M. Raczek, A new adsorbent for boron removal from aqueous solutions, Environ. Technol. 34 (2013) 1369–1376.

[28] S.C.R. Santos, R.A.R. Boaventura, Adsorption modelling of textile dyes by sepiolite, Appl. Clay Sci. 42(1–2) (2008) 137–145.

[29] B. Armagan, O. Ozdemir, M. Turan, M.S. Çelik, Adsorption of negatively charged azo dyes onto surfactant-modified sepiolite, J. Environ. Eng. 129 (2003) 709–715.

[30] Q. Li, Q.Y. Yue, Y. Su, B.Y. Gao, H.J. Sun, Equilibrium, thermodynamics and process design to minimize adsorbent amount for the adsorption of acid dyes onto cationic polymer-loaded bentonite, Chem. Eng. J. 158 (2010) 489–497.

[31] F.M. Mohammed-Azizi, S. Dib, M. Boufatit, Removal of heavy metals from aqueous solutions by Algerian bentonite, Desalin. Water Treat. 51 (2013) 4447–4458.

[32] E. Kucukoner, B. Yurt, Some chemical characteristics of *Pistacia vera* varieties produced in Turkey, Eur. Food Res. Technol. 217(4) (2003) 308–310.

[33] M. Pala, F. Ackurt, M. Loker, The composition of pistachio paste produced in Turkey, Food Technol. Rev. 6(19) (1994) 405–409.

[34] H. Patel, R.T. Vashi, Adsorption of crystal violet dye onto tamarind seed powder, J. Chem. 7 (2010) 975–984.

[35] M.F. Elkady, A.M. Ibrahim, M.M.A. El-Latif, Assessment of the adsorption kinetics, equilibrium and thermodynamic for the potential removal of Reactive Red dye using eggshell biocomposite beads, Desalination 278 (2011) 412–423.

[36] S. Wang, H. Li, Dye adsorption on unburned carbon: Kinetics and equilibrium, J. Hazard. Mater. 126 (2005) 71–77.

[37] Q.H. Hu, S.Z. Qiao, F. Haghseresht, M.A. Wilson, G.Q. Lu, Adsorption study for removal of Basic Red dye using bentonite, Ind. Eng. Chem. Res. 45 (2006) 733–738.

[38] C. Long, Z. Lu, A. Li, W. Liu, Z. Jiang, J. Chen, Q. Zhang, Adsorption of reactive dyes onto polymeric adsorbents: Effect of pore structure and surface chemistry group of adsorbent on adsorptive properties, Sep. Purif. Technol. 44 (2005) 91–96.

[39] J. He, W. Ma, J. He, J. Zhao, J.C. Yu, Photooxidation of azo dye in aqueous dispersions of H_2O_2/α-FeOOH, Appl. Catal., B 39 (2002) 211–220.

[40] D.I. Pavia, G.M. Lampman, G.S. Kaiz, Introduction to Spectroscopy: A Guide for Students of Organic Chemistry, W.B. Saunders Company, 1987.