Original Article

Removal of reactive blue 19 dyes from textile wastewater by pomegranate seed powder: Isotherm and kinetic studies

Mahboobeh Dehvari, Mohammad Taghi Ghaneian, Asghar Ebrahimi, Behzad Jamshidi[1], Mahboooobeh Mootab

Environmental Sciences and Technology Research Center, Shahid Sadoughi University of Medical Sciences, Yazd, Iran, [1]Faculty Member of Public Health, Department of Environmental Health Engineering, Shahid Sadoughi University of Medical Sciences, Yazd, Iran

Address for correspondence:
Eng. Behzad Jamshidi,
Faculty Member of Public Health, Department of Environmental Health Engineering, Shahid Sadoughi University of Medical Sciences, Yazd, Iran.
E-mail: behzadjamshidi65@yahoo.com

ABSTRACT

Aims: The aim of this study was the evaluation of adsorption kinetics and equilibrium of reactive blue 19 dyes from textile synthetic wastewater by pomegranate seed powder.

Materials and Methods: This study is an experimental research, which was performed in laboratory scale. In this study, the parameters such as adsorbent dose, pH and retention time, initial concentration of dye and agitation rate have been investigated. After washing and boiling of pomegranate seeds for 2 h, they dried, milled and finally pulverized by standard ASTM sieves (40-100 mesh). Maximum adsorption wave length (λ_{max}) by spectrophotometer ultra violet/visible (model SP-3000 Plus) 592 nm was determined. The Langmuir, Freundlich and Temkin isotherm models and the pseudo-first-order and pseudo-second-order kinetic models were analyzed.

Results: According to results, the removal efficiency with adsorbent dose, retention time and agitation rate has a direct relation. Maximum adsorption occurred in the first 60 min. The removal efficiency with initial concentration of dye and pH of solution has indirect relation. The Freundlich isotherm fits the experimental data better than the other isotherms. It was recognized that the adsorption followed by pseudo-second-order model ($R^2 > 0.99$).

Conclusion: Based on the results, pomegranate seeds as a new natural sorbent can be used in removal of dye and other environmental pollutants with desirable absorption capacity.

Key words: Adsorption, isotherms and kinetics, pomegranate seeds, reactive blue 19 dye, textile industry

INTRODUCTION

Due to rapid industrialization, there has been an increase for effluent being disposed to natural water resources. Dyes are one of contaminants found in wastewater.[1,2] Dyes have been used at different industries such as textile, food, paper and etc.[3] Based on the color index, currently more than 10,000 various types of dyes are available in the world.[4] The colored wastewaters produced in textile industries, are very difficult to break down biologically and stable against of sunlight and in environmental conditions.[5,6] The dyes may

Access this article online

Quick Response Code:

Website: www.ijehe.org

DOI: 10.4103/2277-9183.179204

This article may be cited as: Dehvari M, Ghaneian MT, Ebrahimi A, Jamshidi B, Mootab M. Removal of reactive blue 19 dyes from textile wastewater by pomegranate seed powder: Isotherm and kinetic studies. Int J Env Health Eng 2016;5:5.

be have mutagenic and carcinogenic affects and can have severe damage to human beings, such as the reproductive system, brain and central nervous system.[7] Although most commercial dyes are not directly toxic, the discharge of colored wastewaters into receiving streams not only affects the aesthetic nature, but also reduces photosynthetic activity.[8,9] The dye concentration of 1.0 mg/l in drinking water could make it unfit for human consumption; thus, the dyes removal is very important.[10,11] Common technologies applied for treating textile wastewater include various combinations of physical, chemical and biological processes.[12] In spite of the availability of many techniques such as coagulation, chemical oxidation, microbial degradation and membrane separation process for remove of dyes from wastewaters; these methods are not very successful owing to suffering from many restrictions.[11,13,14] All these methods have different color removal capabilities, capital costs and operating rates.[14] Dyes can be effectively removed by adsorption process in terms of initial cost, simplicity of design, easy of operation and insensitivity to toxic substances.[15,16] Activated carbon is the most widely used adsorbent because of high adsorption capacity, but its use is limited due to high-cost; thus, there have been attempts to utilize low-cost and naturally occurring adsorbents.[1,17,18] The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons.[14,17,18] Several wastes and residues have been investigated for the adsorption of dye bearing effluents. However, new economical, easily available and highly effective adsorbents are still needed.[14] So far, adsorbents such as guava,[19] leaf powder,[19,20] Palm ash, apple peel, wheat bran,[20] Eucalyptus bark[21] and corn waste,[22] modified straw[2] and so on used for dye removal.

Reactive dyes have bright color, easy to use technique, low energy consumption and are extensively used in the textile industry.[23] The reactive blue (RB) 19 is very resistant to chemical oxidation due to its aromatic anthraquinone structure highly stabilized by resonance. In particular the RB 19, the relatively low fixation efficiency (75-80%) is due to the competition between the formation of the reactive form and the hydrolysis reactions.[24] Whereas, RB 19 is one of the dyes used in the textile industry of Iran, the objective of this work was the investigation of efficiency of pomegranate seed as a natural adsorbent in the removal of RB 19 dye from textile synthetic wastewater. Pomegranate (*Punica granatum*), a small tree originating in the orient, belongs to the Punicaceae family.[25] Rind and seeds of pomegranate fruits have been demonstrated to be high in antioxidant activity. Pomegranate is native from Iran to northern India and widely cultivated throughout Iran, India, the drier parts of Southeast Asia, Afghanistan and Mediterranean countries, to some extent in the USA and tropical Africa. It is one of the most valuable fruits and is grown on a commercial scale in Iran as well. Pomegranate seed, a by-product obtained during processing of pomegranate juice, is therefore inexpensive.[26] The effect of different parameters such as pH, adsorbent dose, contact time and initial dye concentration were investigated. Finally, the isotherm and kinetics parameter for the adsorption of RB 19 dyes onto the pomegranate seed powder was evaluated. So far only in one study by Amin (2009), efficiency of pomegranate peel in the removal of RB 19 dye from aquatic solutions, has investigated.[14] The aim of this study was the evaluation of adsorption kinetics and equilibrium of RB 19 dye from textile synthetic wastewater by pomegranate seed powder.

MATERIALS AND METHODS

Materials

The RB 19 was purchased from the Dystar (Germany) and used without further purification. All other reagents were analytical grade. The main characteristics of the dye are given in Table 1.[12,15]

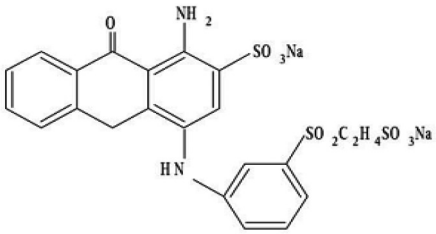
Preparation of the pomegranate seeds

Pomegranate seeds were washed with distilled water and boiled for 2 h and then dried in an oven until a constant weight was reached. It was milled by mixer and pulverized by ASTM standard sieves (40-100 mesh).[14]

Analytical methods

The solutions were prepared with the dye using distilled deionized water. A stock solution (1,000 mg/l) was prepared by dissolving a known quantity of the dye in water and was diluted to the required initial concentrations. To study the effect of important parameters such as the pH, adsorbent dose, contact time and initial dye concentration on the adsorption of RB 19 dyes, batch experiments were conducted. To study the effect of these parameters, initial dye concentration (10, 25, 50, 75 and 100 mg/l), adsorbent dosage (0.1-0.5 g/100 ml), pH (3, 5, 7, 9), contact time of 10, 20, 30, 60, 90, 120, 180 min and 24 h and agitation rate (120-180 rpm), were considered. The pH of solutions

Table 1: Main characteristics of RB19 dye

Characteristics	Value
Chemical structure	
C.I. generic name	C.I. reactive blue 19
Synonym	Remazol brilliant blue R
Production	Dystar, Germany
Molecular formula	$C_{22}H_{16}O_{11}N_2S_3Na_2$
Molecular weight	626.5 g/mol
λ_{max}	592 nm

C.I.: Color index

was adjusted with NaOH and H_3PO_4 (0.1N) using pH meter (Mi 151, Wagtech, England). For each experimental run, 100 mL of dye solutions with concentration of 10, 25 and 50 mg/l, known pH and a known amount of the adsorbent were taken in a 250 mL conical flask. For investigation of the effect of initial dye concentration, solutions with concentration of 10, 25, 50, 75 and 100 were considered. All samples were ultrasonic for 10 min since some adsorbents particles remain suspended and do not settle down easily. The samples were mixed by use of a mechanical shaker (GFL 137; Innova, UK) at a constant speed of 150 rpm. In order to separate the adsorbents from the aqueous solutions, all samples were filtered using a 0.2 µm membrane filter.

The color without filtering or ultrasonic the samples was measured by spectrophotometer. Ultra violet (UV)-visible spectra have been acquired between 200 and 800 nm with a UV-Visible spectrophotometer (Optima SP-3000 Plus model, Japan) as shown in Figure 1. Remaining dye concentration in solutions measured by UV-Visible spectrophotometer at λ_{max} = 592 nm.

The removal efficiency of dye was calculated using the following equation:

$$\%\ Removal = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where C_0 and C_t (mg/l) are the initial dye concentration and concentration at time (t), respectively.[27] The amount of adsorption at equilibrium, q_e, was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

Where q_e is the equilibrium adsorption capacity (mg/g), C_0 and C_e are the liquid-phase concentrations of dye at initial and equilibrium (mg/l), respectively. V (L) is the volume of solution and W (g) is the mass of dry adsorbent used.[2,20,27]

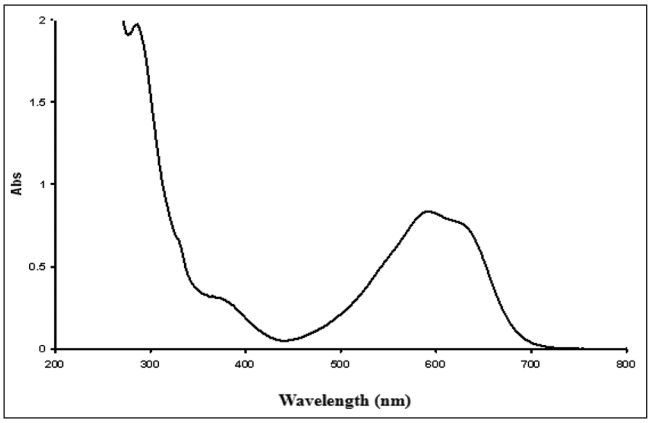


Figure 1: Absorption spectra of the reactive blue 19 dye

Isotherm and kinetic studies

The adsorption isotherm is the relationship between the amount of the dye adsorbed and its concentration in the equilibrium solution.[14,28] The model takes the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

Where q_e (mg/g) is the amount adsorbed, K_L (l/mg) is the Langmuir adsorption constant, q_m (mg/g) is Langmuir constant related to maximum adsorption capacity and C_e (mg/l) is the dye concentration at equilibrium.[14] The constant values (K_L and q_{max}) can be evaluated from the intercept and the slope of the linear plot of experimental data of (C/q) versus C.[29]

In order to describe the adsorption process, the dimensionless separation factor R_L, was calculated. The R_L is defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Where C_0 is the initial dye concentration and K_L is the Langmuir constant. R_L values indicate the type of isotherm to be linear (R_L = 1), irreversible (R_L = 0), favorable (0 < R_L < 1) or unfavorable (R_L > 1).[4,9]

Freundlich isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.[30] It can be described in the linear form as follows:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (5)$$

Where n and K_F (l/mg) are isotherm constants indicate the intensity and capacity of the adsorption, respectively. The constants K_F and n can be evaluated from the slope and intercept of the linear plot of experimental data of $\log q_e$ versus $\log C_e$ with a slope of $1/n$ and intercept of $\ln K_f$.[4,14,29]

The Temkin isotherm predicts a uniform distribution of binding energies over the population of surface binding adsorption sites.[31] The Temkin isotherm equation is given as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (6)$$

Where $B_1 = R_T/b$, R is the universal gas constant (8.314 J/mol/K), T (K) is the absolute temperature. K_T (l/mg) is the equilibrium binding constant and B_1 is related to the heat of adsorption.[14,32]

In this study, for adsorption isotherms, dye solution concentrations (10, 25 and 50 mg/l) were agitated with known

amount of adsorbent (0.1-0.5 g/100 ml) and in optimum pH until the equilibrium were reached (24 h).

Adsorption kinetics is used to explain the adsorption mechanism and adsorption characteristic.[32] A form of pseudo-first-order model equation was in the form:

$$log(q_s - q_t) = logq_s - \frac{K_f}{2.303}t \quad (7)$$

Where q_e and q_t (mg/g) refer to the amount of dye adsorbed at equilibrium and at time t, respectively. The K_f (min^{-1}) is the pseudo-first-order rate constant.

The pseudo-second-order kinetics expressed in a linear form as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_s^2} + \frac{1}{q_s}t \quad (8)$$

Where the q_e is equilibrium adsorption capacity and the K_2 (g/mg h) second-order constants can be determined from the slope and intercept of plot t/q_t versus t.[20]

In this study, for kinetic studies, 100 ml of the dye solution with concentrations of 10, 25 and 50 mg/l and initial pH 3 were taken in a 250 ml conical flask with a required amount of adsorbent and were agitated in the shaker at 25°C. Samples were withdrawn at different time intervals (10-180 min and 24 h).

RESULTS

Effect of initial pH

The solution pH has a considerable effect on dye removal. The pH of the solution can impact on the surface charge of adsorbent and the speciation degree of adsorbate.[33] The effect of pH was changed to monitor the adsorption behavior of dye in pH range of 3-11. In this stage, dye solutions were prepared with initial concentrations of 10, 25 and 50 mg/l. The adsorbent dose and retention time were 0.5 g/100 ml and 24 h, respectively. The effect of pH on adsorption process is shown in Figure 2. The results revealed that by increasing of pH from 3 to 11, the amount of adsorbed dye (q_e) decreases. This can be related to the surface charge of the adsorbent. The dye remaining concentration (removal efficiency) in dye concentrations of 10, 25 and 50 at pH = 3 were equal with 3.21 mg/l (68%), 4.575 mg/l (81.7%) and 6.8 mg/l (86%), respectively.

Effect of adsorbent dose

The adsorbent dose was one of the important factors in the adsorption process. The effect of adsorbent dose on adsorption rate was investigated at pH = 3, dye concentrations of 10, 25 and 50 mg/l and retention time of 24 h. The dependence of dye sorption on adsorbent dose was studied at room temperature by varying the sorbent amount from 0.1 to 0.5 g/100 ml. Figure 3 shows that the removal efficiency increases with increasing of the adsorbent dose due to the greater availability of the exchangeable sites or surface area.[27] While in adsorbent doses of 0.1 and 0.5 g/100 ml for dye initial concentration of 10 mg/l, removal efficiency was 70% and 77%, respectively. This numbers were for dye concentrations of 25 mg/l, 82.5% and 89.2% and for 50 mg/l, 88.8% and 95.4%, respectively. The increase of adsorption dose led to decrease of adsorption capacity. So that for dye initial concentrations of 10 mg/l, 25 and 50 mg/l with adsorbent

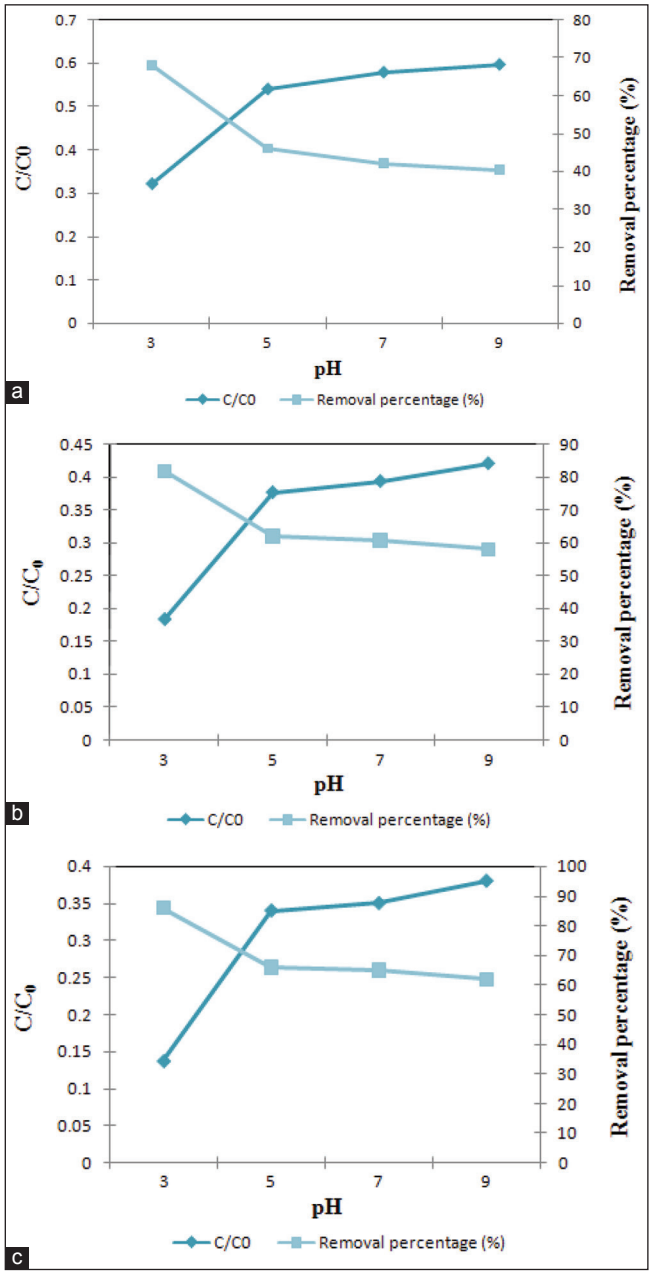


Figure 2: Effect of pH on dye remaining concentration and removal percentage of reactive blue 19 dyes: ((a) C_0 = 10 mg/l, (b) C_0 = 25 mg/l, (c) C_0 = 50 mg/l)

doses of 0.1 and 0.5 g/100 ml, adsorption capacities were 7 and 1.54 mg/g, 20.63 and 4.46 mg/g, 43.4 and 9.54 mg/g, respectively.

Effect of contact time

The effect of contact time on removal of dye is shown in Figure 4. According to results, an increase at contact time led to increase at surface adsorption rate to 60 min and then remains unchanged. Maximum adsorption occurred in the first 60 min. The rapid adsorption at the initial contact time is due to the availability of the positively charged surface of adsorbent.[1] The remaining dye concentration at 10 min for concentrations of 10, 25 and 50 mg/l was 3.55, 5.375 and 7.5 mg/l, respectively. This numbers at 180 min were equal with 2.52, 2.49 and 3 mg/l for concentrations of 10, 25 and 50 mg/l, respectively. According to the results, the adsorption equilibrium was reached at 60 min. The adsorption capacity (q_e), at 10 min and 60 min, for concentration of 10 mg/l was equal to 1.29 and 1.46 mg/g, for concentration of 25 mg/l, 3.925 and 4.445 mg/g and for concentration of 50 mg/l, 8.5 and 9.26 mg/g, respectively.

Effect of initial dye concentration

The removal efficiency of dye is highly depended on the initial dye concentration. The effect of dye different concentrations onto removal percentage was investigated by maintaining biosorbent dose at the rate of 0.5 g/100 ml and pH of 3. Tests was conducted on synthetic wastewater containing concentrations of 10, 25, 50, 75 and 100 mg/l of RB 19 at equilibrium time (t = 60 min). By increasing of the initial dye concentration, the removal efficiency decreases. With the increase in initial dye concentration the active sites required for adsorption of the dye molecules will lack.[11] With increasing of the initial dye concentration from 10 mg/l to 100 mg/l, the efficiency removal (adsorption capacity) was reached from 100% (2 mg/g) to 87.78% (17.556 mg/g). According to results [Figure 5], the most bioadsorption rate observed at a concentration of 10 mg/l.

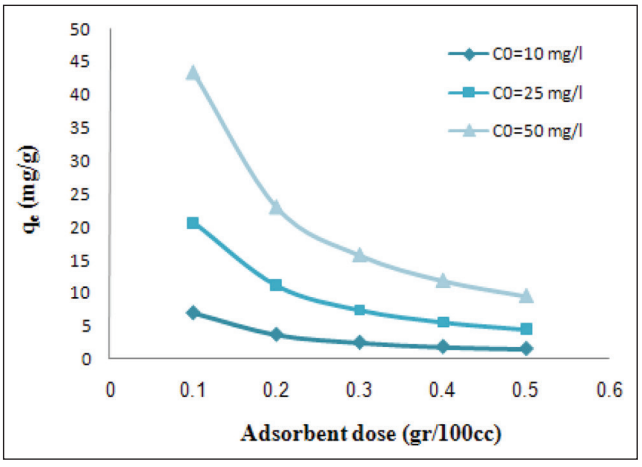


Figure 3: Effect of adsorbent dose on adsorption capacity of reactive blue 19 dyes

Effect of agitation rate

The agitation is a parameter that influences the distribution of the solute in the bulk solution and the formation of the external boundary film.[1,30] The dye removal and the amount of dye adsorbed at equilibrium time increased with agitation rate. However, there was no increase in more than 150 rpm; a little decrease in agitation rate was also observed. The effect of agitation rate on the removal rate of RB 19 was investigated at different agitation rates of 120, 140, 150, 160 and 180 rpm at 60 min contact time. The result of this effect is presented in Figure 6. With the enhancement of the agitation rate, the adsorption increases, reaching a rate-limit over which there

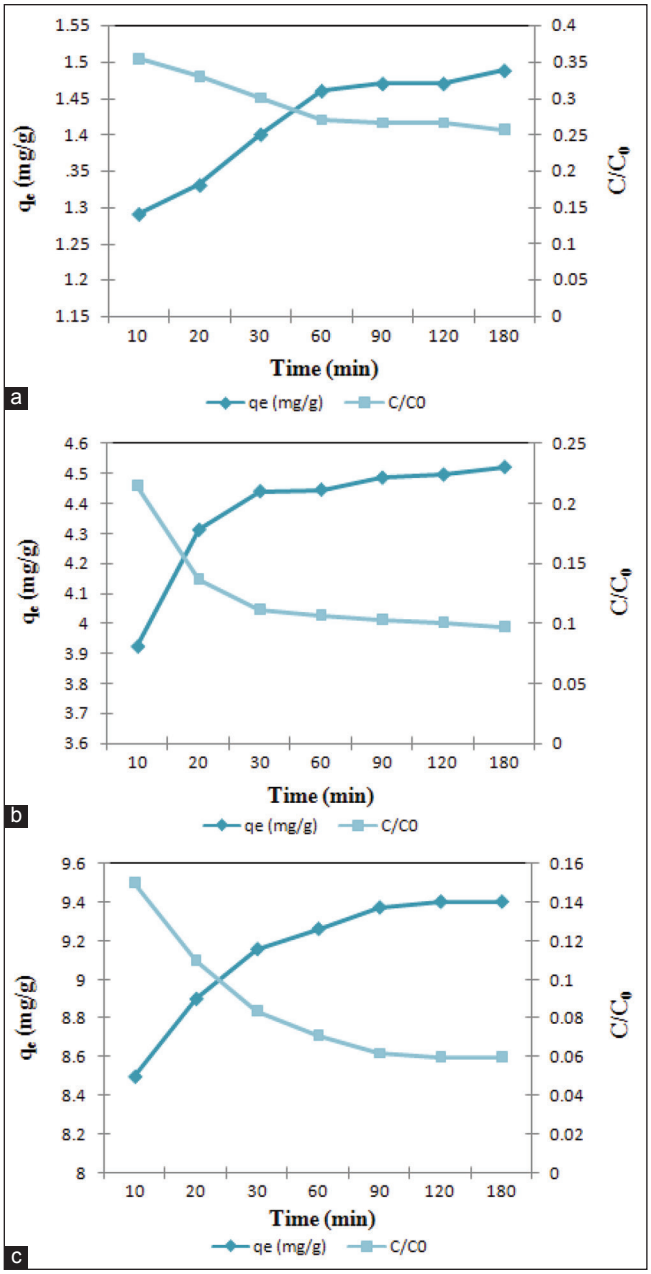


Figure 4: Effect of contact time on removal percentage and adsorption capacity of reactive blue 19 dyes. ((a) C_0 = 10 mg/L, (b) C_0 = 25 mg/L, (c) C_0 = 50 mg/L)

is no significant change. The q_e rates for agitation rate of 120 rpm in concentrations of 10, 25 and 50 mg/l were equal with 1.46, 4.3 and 9.44 mg/g. This numbers for agitation rate of 150 rpm were 1.678, 4.7 and 9.95 mg/g.

Adsorption isotherms

In this study, the Langmuir, Freundlich, Temkin isotherm equations were investigated. Isotherm parameters are presented in Table 2. Values of the correlation coefficient (R^2) are regarded as a measure of the goodness-of-fit of experimental data on the isotherm's model. The R^2 values for the Freundlich and Temkin isotherms were higher than 0.9, but R^2 values for Freundlich isotherm are higher ($R^2 = 0.981, 0.939, 984$) indicating a very good fit. According to the results, 1/n value is less of 1 ($1/n = 0.168$, 0.354 and 0.623), which confirms adsorption of RB 19 dye by pomegranate seed powder is favorable and suggests that the process was controlled by order chemisorptions [Figure 7].

Adsorption kinetics

In this study, pseudo-first and pseudo-second-order adsorption models, was analyzed. Constants of relation to each model are calculated and presented in Table 3. The correlation coefficient (R^2) values of the pseudo-second-order equation for initial dye concentrations were close to 1. The values of the R^2 for concentrations 10, 25 and 50 mg/l in the pseudo-second-order model are equal to 1, 1 and 0.999, respectively. Thus, pseudo second-order model provides a good correlation for adsorption of RB 19 [Figure 8].

DISCUSSION

The obtained results showed that with the increase of pH, removal efficiency and mount of dye adsorbed per mass unit of adsorbent (q_e) decreased. This shows the presence of hydroxyl group and its relationship with pH of reaction environmental. The target adsorbent has negatively charged adsorption sites, but it is positively charged at low pH values. With increasing of pH due to the abundance of OH^-, the negative charge of dye and also the positive charge of adsorbent surface, removal efficiency decreases. These findings are agreed with results of Li *et al*. (2010). They studied the adsorption of acid dyes onto cationic polymer-loaded bentonite. In their study, was observed that with the increase of pH from 1 to 13, the removal efficiencies decreased.[33] Ciçek *et al*. (2007) were investigated the removal of reactive dyes using wheat bran. When the pH of aqueous solution increased from 1 to 4, q_e decreased.[8]

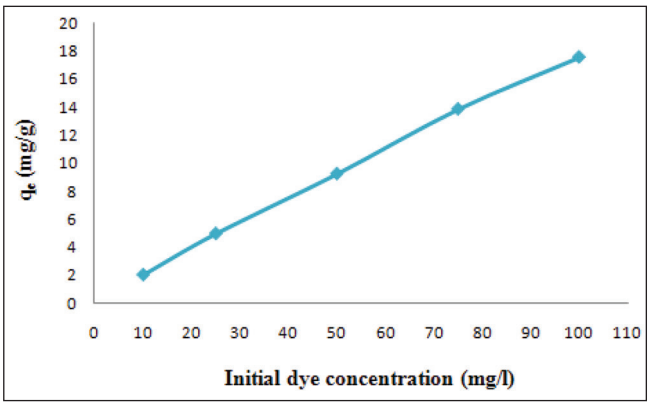


Figure 5: Effect of initial dye concentration on adsorption capacity of reactive blue 19 dyes

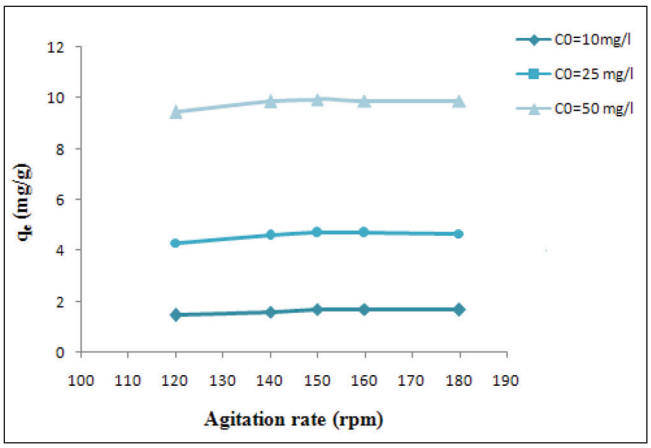


Figure 6: Effect of agitation rate on adsorption capacity of reactive blue19 dyes

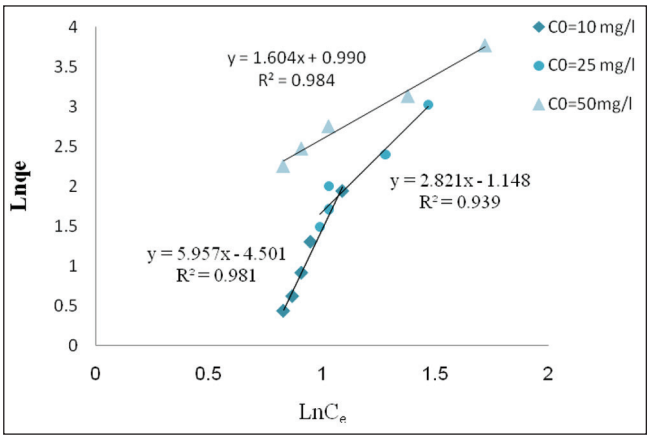


Figure 7: Freundlich isotherm plots for adsorption of reactive blue 19 dye

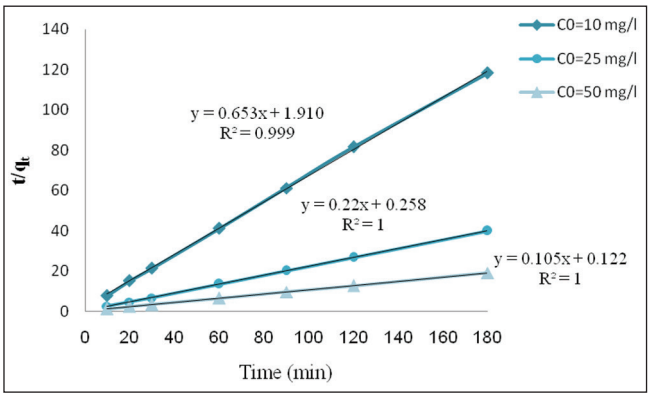


Figure 8: Pseudo-second-order kinetics plots for adsorption of reactive blue 19 dyes

Table 2: Characteristics of adsorption isotherms

Dye concentration (mg/L)	Langmuir isotherm		Freundlich isotherm		Temkin isotherm	
10	B (l/mg)	3.236	K (mg/g).(l/mg)$^{1/n}$	0.011	K_t (l/mg)	21.97
	q_{max} (mg/g)	0.212	$1/n$	0.168	B_T (J/mol)	17.11
	R^2	0.768	R^2	0.981	R^2	0.981
	R_L	0.03				
25	B (l/mg)	5.78	K (mg/g).(l/mg)$^{1/n}$	0.317	K_t (l/mg)	30.50
	q_{max} (mg/g)	1.044	$1/n$	0.354	B_T (J/mol)	25.55
	R^2	0.856	R^2	0.939	R^2	0.927
	R_L	0.007				
50	B (l/mg)	11.49	K (mg/g).(l/mg)$^{1/n}$	2.69	K_t (L/mg)	35.95
	q_{max} (mg/g)	3.61	$1/n$	0.623	B_T (J/mol)	21.50
	R^2	0.934	R^2	0.984	R^2	0.949
	R_L	0.002				

Table 3: Kinetics constants of RB 19 adsorption onto pomegranate seed powder

Dye concentration (mg/L)	Pseudo-first-order		Pseudo-second-order	
10	q_e (calc.) (mg/g)	0.297	q_e (mg/g)	1.531
	q_e (exp.) (mg/g)	1.62	K_2	0.223
	K_1 (min^{-1})	0.006	R^2	1
	R^2	0.877		
25	q_e (calc.) (mg/g)	0.371	q_e (mg/g)	4.545
	q_e (exp.)(mg/g)	4.62	K_2	0.187
	K_1 (min^{-1})	0.008	R^2	1
	R^2	0.658		
50	q_e (calc.)(mg/g)	0.762	q_e (mg/g)	9.524
	q_e (exp.) (mg/g)	9.62	K_2	0.09
	K_1 (min^{-1})	0.008	R^2	0.999
	R^2	0.75		

RB: Reactive blue

One of studied parameters in this research was adsorbent dose. Increasing of adsorbent dose led to decrease of the mount of dye adsorbed per mass unit of adsorbent (q_e). This phenomenon is because of increase of sorption active sites at the adsorbent surface.[3] Elkady *et al*. (2011) in their study were reached to same results. They reported that the Remozal Red 198 removal by eggshell bio-composite beads increases up to a certain limit and then it remains almost constant. They reported that the increase of adsorption with adsorbent dosage attributes to increase in adsorbent surface area and the greater availability of the exchangeable sites or surface area.[4] Similar data also obtained by El Ashtoukhy *et al*. (2009)[27] and Dawood *et al*. (2012).[34]

The contact time is of significant importance in the wastewater treatment by adsorption.[34] It was found that the increase in retention time resulted in increase of adsorbed dye amount. The highest uptake was in the first 60 min. This phenomenon attributed to the availability of the positively charged surface of adsorbent, which led to fast electrostatic adsorption of the RB 19 from the solution. The slow rate of dye adsorption is probably causes of the electrostatic repulsion between the adsorbed negatively charged and the available a sorbate species in solution.[1,35] Similar result was found for the adsorption kinetics of RB 221 on kaolinite. The adsorbed amount of dye increased with the increase in time and then reached equilibrium at 60 min. The most removal of dye occurred in the first 5 min.[1] In Gok *et al*. (2010) study revealed that the adsorption capacity increased with the contact time up to 60 min when the maximum adsorption is reached; therefore the optimum contact time was chosen as 60 min.[35]

The results showed that the amount of dye adsorbed (q_e) increases with the increase in the dye initial concentration. This increase is due to the decrease in resistance to the uptake of dye from solution.[14] These results accord well with the findings of other investigators such as Amin (2009) who was studied removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel. As the initial concentration provides an important driving force to overcome the mass transfer resistance of dye between the aqueous and solid phases.[14] Ergene *et al*. (2009) reported that uptake of RB 19 dye by the immobilized active and heat inactivated S. quadricauda, increased with increasing the initial dye concentration due to the saturation at higher dye concentrations.[31] By increasing of the initial dye concentration, the removal efficiency decreases, which this may be due to increase in the loading capacity of the adsorbent and the saturation of adsorption sites on the adsorbent surface; in other words, with the increase in initial dye concentration the active sites required for adsorption of the dye molecules will lack.[11,32] El Ashtoukhy el (2009) reported same results.[27]

With stirring rate, uptake increased. The difference of the adsorption rate was insignificant as the agitation rates increased. In low agitation rates, the dyes can hard find

the possible active sites on the adsorbent. The chemical structures of dyes also influenced this agitation behavior. The rate of agitation reduced the boundary-layer resistance and increased the mobility of the system. The increase of agitation lowers the external mass transfer.[30] Similar phenomenon was observed in Karaoglu *et al*. study (2010) about adsorption of RB 221 on kaolinite.[1] Kyzas *et al*. (2012) also reached to same results.[28]

Equilibrium data are basic requirements for the design of adsorption systems that commonly known as adsorption isotherms.[32] 1/*n* constant used to verify types of adsorption. If 1/*n* is below unity indicates that adsorption is a chemical process.[35] Results of this study showed that equilibrium data fitted better by Freundlich model due to the higher R^2 value. In Freundlich isotherm, 1/*n* values were less of 1. In Amin (2009) study on the removal of direct blue-106 dye using new activated carbons developed from pomegranate peel, each three isotherms were in good concordance with data ($R^2 > 0.9$) and Freundlich model has higher agreement with the experimental data.[14] Dawood *et al*. (2012) studied about removal of anionic dye Congo red from aqueous solution using raw pine and acid-treated pine cone powder. In their study, Freundlich isotherm fitted well with the equilibrium data.[34]

In order to investigate the adsorption mechanisms, kinetic models were used to fit the experimental data. In the present study, data was in accordance with pseudo-second-order kinetic for three initial dye concentrations. It indicated that the rate controlling mechanism for adsorption was chemisorptions.[2] In Amin study (2009), on the removal of direct blue-106 dye using new activated carbons developed from pomegranate peel, he found that adsorption kinetics to follow pseudo-second-order rate kinetic model, with a good correlation ($R^2 > 0.99$).[14] Similar results were also reported by Zhang *et al*. (2012), who were investigated adsorption of anionic dyes by chemically modified straw.[2]

CONCLUSION

According to obtained results, increasing of adsorption dose, time contact and agitation rate led to increase the rate of adsorption and increasing of pH and initial concentration dye led to decrease of removal efficiency. Results showed that removal of RB 19 by pomegranate seed powder follows Freundlich isotherm. In studies of adsorption kinetic was determined that kinetics of RB 19, follows the pseudo-second-order kinetic model. According to the high cost of synthetics adsorbents, importance of development and application of cheap and natural adsorbents is essential. Based on the results, Pomegranate seed as a new natural adsorbent can be used in removal of dye and other environmental pollutants.

Financial support and sponsorship
Nil.

Conflicts of interest
There are no conflicts of interest.

REFERENCES

1. Karaoğlu MH, Dogan M, Alkan M. Kinetic analysis of reactive blue 221 adsorption on kaolinite. Desalination 2010;256:154-65.
2. Zhang W, Li H, Kan X, Dong L, Yan H, Jiang Z, *et al*. Adsorption of anionic dyes from aqueous solutions using chemically modified straw. Bioresour Technol 2012;117:40-7.
3. Mahmoodi NM, Hayati B, Arami M, Lan Ch. Adsorption of textile dye son pine cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies. Desalination 2011;268:117-25.
4. Elkady MF, Ibrahim A, Abd-El-Latif MM. Assessment of the adsorption kinetics, equilibrium and thermodynamic for the potential removal of reactive red dye using eggshell biocomposite beads. Desalination 2011;278:412-23.
5. Dinçer AR, Güneş Y, Karakaya N. Coal-based bottom ash (CBBA) waste material as adsorbent for removal of textile dyestuffs from aqueous solution. J Hazard Mater 2007;141:529-35.
6. Ledakowicz S, Solecka M, Zylla R. Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes. J Biotechnol 2001;89:175-84.
7. Sivaraj R, Namasivayam C, Kadirvelu K. Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions. Waste Manag 2001;21:105-10.
8. Çiçek F, Ozer D, Ozer A, Ozer A. Low cost removal of reactive dyes using wheat bran. J Hazard Mater 2007;146:408-16.
9. Ehrampoush MH, Ghanizadeh GH, Ghaneian MT. Equilibrium and kinetics study of reactive red 123 dye removal from aqueous solution by adsorption on eggshell. J Environ Health Sci Eng 2011;2: 101-8.
10. Dizge N, Aydiner C, Demirbas E, Kobya M, Kara S. Adsorption of reactive dyes from aqueous solutions by fly ash: Kinetic and equilibrium studies. J Hazard Mater 2008;150:737-46.
11. MohdSalleh MA, Mahmoud K, Abdul-Karim AA, Idris A. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. Desalination 2011;280:1-13.
12. Chen TY, Kao CM, Hong A, Lin CE, Liang SH. Application of ozone on the decolorization of reactive dyes — Orange-13 and blue-19. Desalination 2009;249:1238-42.
13. Sulak MT, Demirbas E, Kobya M. Removal of astrazon yellow 7GL from aqueous solutions by adsorption onto wheat bran. Bioresour Technol 2007;98:2590-8.
14. Amin NK. Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics. J Hazard Mater 2009;165:52-6.
15. Hasan M, Ahmad AL, Hameed BH. Adsorption of reactive dye onto cross-linked chitosan/oil palm ash composite beads. Chem Eng J 2008;136:164-72.
16. Slokar YM, LeMarechal AM. Methods of decoloration of textile wastewaters. Dyes Pigm 1997;37:335-56.
17. Rezaee A, Ghaneian MT, Khavanin A, Hashemian SJ, Moussavi GH, Ghanizadeh GH. Photochemical oxidation of reactive blue 19 (RB19) dye from wastewater by UV/$K_2S_2O_8$ process. Iranian J Environ Health Sci Eng 2008;5:95-100.
18. Schubert SY, Lansky EP, Neeman I. Antioxidant and eicosanoid enzyme inhibition properties of pomegranate seed oil and fermented juice flavonoids. J Ethnopharmacol 1999;66:11-7.
19. Ponnusami V, Vikram S, Srivastava SN. Guava (*Psidium guajava*) leaf powder: Novel adsorbent for removal of methylene blue from aqueous solutions. J Hazard Mater 2008;152:276-86.
20. Hameed BH, Mahmoud DK, Ahmad AL. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost

adsorbent: Coconut (*Cocos nucifera*) bunch waste. J Hazard Mater 2008;158:65-72.
21. D´avila-Jim´enez MM, Elizalde-Gonz´alez MP, Pel´aez-Cid AA. Adsorption interaction between natural adsorbents and textile dyes in aqueous solution. Colloids Surf A Physicochem Eng Asp 2005;254:107-14.
22. Elizalde-González M, Geyer W, Guevara-Villa MRG, Mattusch J, Peláez-Cid AA, Wennrich R. Characterization of an adsorbent prepared from maize waste and adsorption of three classes of textile dyes. Colloids Surf A Physicochem Eng Aspects 2006;278:89-97.
23. Andrade LS, Ruotolo LA, Rocha-Filho RC, Bocchi N, Biaggio SR, Iniesta J, *et al*. On the performance of Fe and Fe,F doped Ti-Pt/PbO2 electrodes in the electrooxidation of the blue reactive 19 dye in simulated textile wastewater. Chemosphere 2007;66:2035-43.
24. Lizama C, Frrer J, Baeza J, Mansilla H. Optimized photodegradation of reactive blue 19 on TiO_2 and ZnO suspensions. Catal Today2002;76:235-46.
25. Devatkal SK, Naveena BM. Effect of salt, kinnow and pomegranate fruit by-product powders on color and oxidative stability of raw ground goat meat during refrigerated storage. Meat Sci 2010;85:306-11.
26. Miguel MG, Neves MA, Antunes MD. Pomegranate (*Punica granatum* L.): A medicinal plant with myriad biological properties-A short review. J Med Plants Res 2010;4:2836-47.
27. El Ashtoukhy el SZ. Loofa egyptiaca as a novel adsorbent for removal of direct blue dye from aqueous solution. J Environ Manage 2009;90:2755-61.
28. Kyzas G, Lazaridis N, Mitropoulos ACh. Removal of dyes from aqueous solutions with untreated coffee residues as low-cost adsorbents: Equilibrium, reuse and thermodynamic approach potential. Chem Eng J 2012;189-90:148-59.
29. Khalid Mahmoud D, Amran Mohd Salleh M, Wan Abdul Karim WA, Idris A, Zainal Abidin Z. Batch adsorption of basic dye using acid treated kenaf fibre char: Equilibrium, and thermodynamic studies kinetic. Chem Eng J 2012; 181-2:449-57.
30. Nemr AE, Abdelwahab O, El-Sikaily A, Khaled A. Removal of direct blue-86 from aqueous solution by new activated carbon developed from orange peel. J Hazard Mater 2009;161:102-10.
31. Ergene A, Ada K, Tan S, Katircioglu H. Removal of remazol brilliant blue r dye from aqueous solutions by adsorption onto immobilized scenedesmus quadricauda: Equilibrium and kinetic modeling studies. Desalination 2009;249:1308-14.
32. Tanyildizi MS. Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull. Chem Eng J 2011;168:1234-40.
33. Li Q, Yue QY, Su Y, Gao BY, Li J. Two-step kinetic study on the adsorption and desorption of reactive dyes at cationic polymer/bentonite. J Hazard Mater 2009;165:1170-8.
34. Dawood S, Sen TK. Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: Equilibrium, thermodynamic, kinetics, mechanism and process design. Water Res 2012;46:1933-46.
35. Gok O, Ozcan AS, Ozcan A. Adsorption behavior of a textile dye of reactive blue 19 from aqueous solutions on to modified bentonite. Appl Surf Sci 2010;256:5439-43.