Adsorption Kinetics and Equilibrium Studies of Reactive Red 198 Dye by Cuttlefish Bone Powder

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ABSTRACT: *In this research, the removal of Reactive Red 198 dye (RR-198) by Cuttlefish bone powder was investigated. The adsorbent was prepared in laboratory conditions and ground by ASTM standard sieves (60-100 mesh). The progress of the process is monitored spectrophotometrically by measuring the absorbance of dye at 518 nm wavelength. In addition, the effects of process parameters such as adsorbent dose, pH, initial dye concentration, and contact time have been investigated. The SEM micrographs and the XRD pattern showed that the cuttlefish bone has the clearly seen pores on its surface and a crystallized form. According to the results, by increasing adsorbent dose and retention time, dye removal efficiency was increased considerably. The adsorption isotherm for initial dye concentration (50 mg/L) was in good concordance with the Langmuir and Freundlich models. The adsorption kinetic studies revealed that the adsorption of RR198 dye was complied with pseudo-second-order kinetic.*

KEYWORDS: *Cuttlefish bone; Reactive red 198 dye; Adsorption kinetic and isotherm.*

INTRODUCTION

Textile industries produce large volumes of colored effluents which are toxic and non-biodegradable. It is estimated that about 15% of dyes is lost during the dyeing unit [1]. The dyes are carcinogen and toxic and their releasing into the environment leading cause some serious environmental and health hazards [2- 5]. Reactive dyes are very important class of textile dyes, whose losses through processing are particularly significant and difficult to treat. The largest class of dyes are azo dyes that is used in textile industry. In general, bacteria are unable to degrade azo dyes. Therefore, to remove azo dyes from wastewater, development of more effective treatment methods is needed [6].

For the treatment of dye-containing wastewater,

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various biological, physical and chemical methods such as microbial biodegradation, membrane filtration, oxidation, ozonation, adsorption, and ultrafiltration are used [7-10]. However, many of these technologies are high costing, especially when applied for treating high volume of waste streams [11]. Comparing to other separation processes, the advantages of adsorption process are simplicity and being cheap in operation [12]. Several types of natural and synthetic adsorbents have been evaluated for the removal of dyes from wastewater [3, 13]. Activated carbon is one of the most widely studied adsorbents for the control of environmental pollution. High costing of production and treatment is the main disadvantage of activated carbon. Thus, many researchers have focused their efforts on optimizing the adsorption and developing novel, alternative adsorbents with high adsorption capacity and low costing [3]. The sorbents include clay materials (bentonite), zeolites, siliceous material, agricultural wastes, industrial waste products and biosorbents have been used as efficient adsorbents in the removal of dyes from wastewaters [14-16].

Cuttlefish bone is rich in calcium and its powder is used in toothpaste preparation. It has been used as an adsorbent for the removal of fluoride too [17]. In another study, fish bones have been used in the removal of Cu (II) ions from water [18]. In this paper, we reported the results of removing reactive red 198 dye from aqueous solutions by cuttlefish bone powder. In addition the adsorption equilibrium time and capacity was determined. Langmuir and Freundlich isotherm models were applied for describing the relationship between the amount of dye solution and adsorbent.

EXPERIMENTAL SECTION

Chemicals and analytical procedure

Azo dye (Reactive Red 198 dye, RR198) was purchased from Dye Star Company and used without further purification. Chemical structure and other characteristics of dye are listed in Table 1 [1, 3]. The pH of the solution was adjusted by using sodium hydroxide or nitric acid solutions (1N). To measure absorbance and pH a model of UV-vis spectrophotometer (Optima SP-3000 Plus model, Japan) with 10 mm quartz cells and Mi-151 pH meter was used, respectively.

A stock solution of the dye (100 mg/L) was prepared by dissolving 100 mg of dye in 1.0 L of distilled water. Other working solutions were prepared by diluting this stoke solution.

Preparation and Characterization of the Cuttlefish bone powder

Cuttlefish bone was rinsed by deionized water. To remove any impurities, it was boiled for 10 minutes and dried at 103–105 ˚C for 24 houres and allowed to cool in a desicator [17]. Then the cuttlefish bone was crushed and pulverized by standard ASTM sieves (with the range of 60 to 100 meshes), into 150-250 µm particles and used as an adsorbent in the following experiments [17]. The X-Ray Diffraction (XRD) patterns of the prepared Cuttlefish bone powder were recorded on a Philips (X'Pert-MPD, Netherland) diffractometer. The morphology of the sample was analyzed by Scanning Electron Microscope (SEM, Philips XL30). The IR spectra were recorded using FT-IR Spectra Bruker Tensor 27 spectrometer (KBr pellets, Nujol mulls, 4000-400 cm^{-1}).

Adsorption experiments

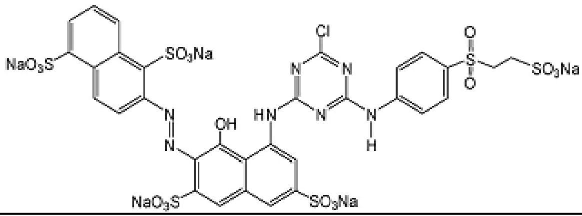
All the adsorption experiments were carriedout at 20 ºC using the batch technique. In all cases, during the experiments, 100 mL of the dye solution with concentrations of 25 and 50 mg/L were taken in a 250 mL Erlenmeyer flask. After adjusting the pH of the solutions, the adsorbent was added into the dye solutions. Then, the solutions were shaken by mechanical shaker (GFL 137 innova, England) at the constant agitation speed (120 rpm) for 24 hours. Subsequently, to separate the adsorbents from the aqueous solutions, all samples were filtered using a 0.45 µm membrane filter. The remaining dye concentration in the solutions was measured by UV-visible spectrophotometer at the wavelength of 518 nm. The amount of dye adsorption capacity (q_e) and dye removal efficiency (E) by using adsorbents was calculated using expressions (1) and (2):

$$q_e = \frac{\left(C_0 - C_e\right) \times V}{M} \tag{1}$$

$$E = \frac{\left(C_0 - C\right)}{C_0} \times 100 \tag{2}$$

Where, q_e is the equilibrium adsorption capacity on adsorbent (mg/g); V is the volume of dye solution (L); M is the mass of adsorbent (g); C_e and C_o are the equilibrium

Table 1: Basic characteristics of the reactive red 198 dye.

Chemical formula	$C_{27}H_{18}ClN_7Na_4O_{15}S_5$
Commercial name	Remazol Red 133
Class	Azo
C.I. number	18221
λ_{max} (nm)	518
Molecular structure	

and initial dye concentrations (mg/L) respectively, as well as, *E* is the removal efficiency [19, 20].

In this study, the Langmuir and Freundlich adsorption isotherms were investigated. To determine the isotherm models, adsorbent doses of 1.0, 1.5, 2.0, and 2.5 g were added to 100 mL of the dye solution (50 mg/L). Adsorption tests were performed for the optimal periods of time and pH. In addition adsorption kinetics study (pseudo-first-order and pseudo-second-order kinetics) was carried out. Two grams of adsorbent was added to 100 mL of dye solution with concentrations of 25 and 50 mg/L. In this experiment temperature and pH value were kept constant. The adsorption kinetics was determined by analyzing the adsorption of the dye from aqueous solution at different time intervals.

RESULTS AND DISCUSSION

Characterization of the Cuttlefish bone powder

The results of Energy Dispersive X-ray (EDX) spectral analysis demonstrated that calcium is the main component of Cuttlefish bone. The SEM micrographs have shown that the cuttlefish bone has the clearly seen pores on its surface (Fig.1 a). To explore the characteristics of the biosorbent FT-IR analysis of cuttlefish bone was performed at the range of 4000-400 cm^{-1} (Fig.1 b). The X-ray diffraction spectrum of the cuttlefish bone powder has been shown in Fig.1 c. The main peak was appeared at $2\theta=26.5^o$. The XRD pattern showed that the cuttlefish bone has a crystallized form. These results agree with the study of *Nasr et al.*, (2011), demonstrated the elemental analysis of cuttlefish bone includes 96% pure calcium carbonate with trace quantities of Na_2O and P_2O_5 [17].

Effect of adsorbent dose

The effect of adsorbent quantity for dye removal was investigated by adding various amounts of adsorbent in the range of 1.0-2.5 g/100 mL into the beaker containing different concentrations of RR198 solutions (25 and 50 mg/L) at pH 9 for all batch experiments. In this step, the shaker speed and reaction time were 120 rpm and 24 h, respectively. The effect of adsorbent dose on RR198 dye removal has been shown in Fig. 2. Based on the results, by increasing of adsorbent dose, the removal efficiency of RR198 dye was increased due to increasing of adsorption sites versus constant rate of dye concentration. These findings are in agreement with other studies like *Elkady et al.* that reported the removal of RR198 dye by using eggshell biocomposite beads increases up to a certain limit and then remains almost constant. In addition, they noted increasing of adsorption with adsorbent dosage was due to increasing of adsorbent surface area and availability of more adsorption sites [3].

For 2.0 and 2.5 grams of adsorbent dose at the initial concentration of 25 mg/L, the dye removal efficiency were determined as 85% and 86% as well as for 50 mg/L initial dye concentration, the removal efficiency were 73% and 77%, respectively. Regard to the results of this study, by increasing cuttlefish bone dose from 1.0 to 2.5 g, for the initial adsorbate concentration of 25 mg/L and 50 mg/L, the q_e (mg/g) decreased from 1.581 mg/g

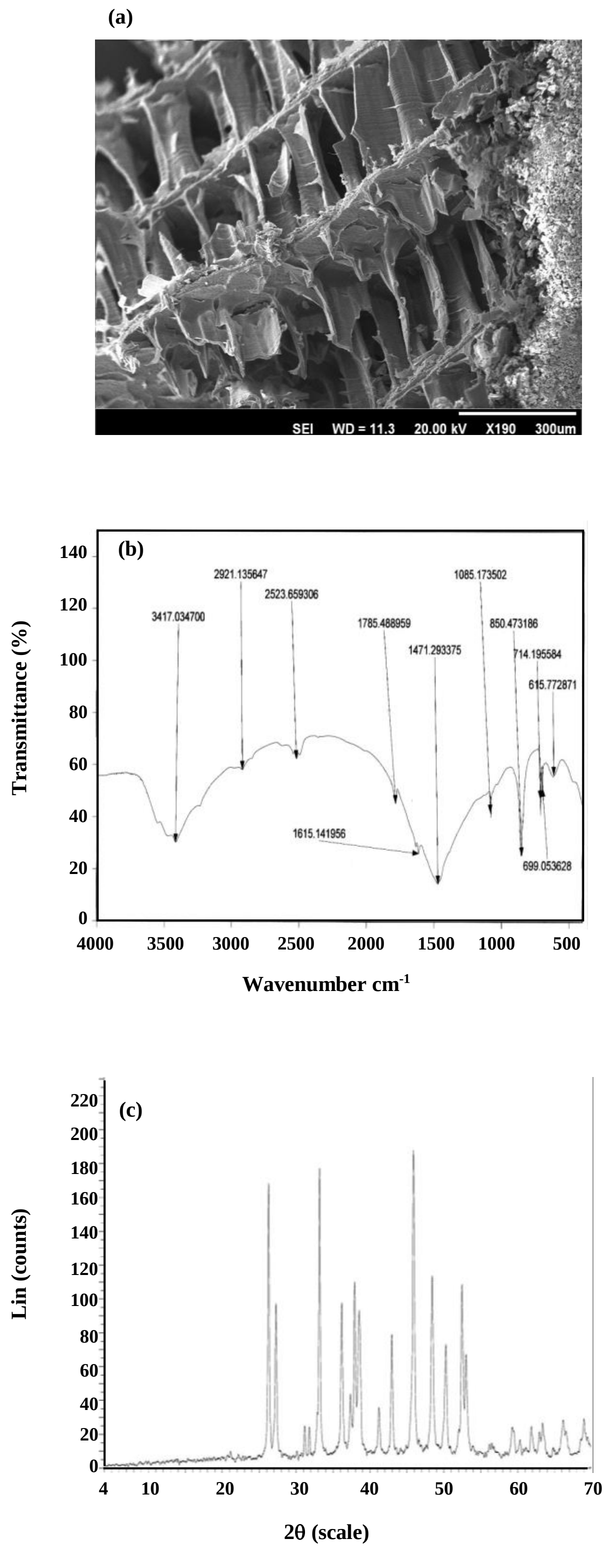


Fig. 1: Characterization of the Cuttlefish bone powder ((a): Scanning Electron Microscope (SEM) micrograph, (b): FT-IR spectrum, (c): XRD spectrum).

to 0.842 mg/g and from 2.295 mg/g to 1.492 mg/g, respectively. It can be interpreted that although increasing of adsorbent dose led to increasing of dye removal, the amount of adsorbed dye per mass unit of adsorbent (q_e) is declined; this phenomenon can be related to increasing of adsorbent surface area. Similar types of observations were also reported in previous studies. *Ghaneian et al.* studied the removal of reactive red 198 dye by pomegranate seed powder and reported that increasing the amount of adsorbent led to increasing the efficiency of dye removal [21].

According to the present results, the optimal and effective adsorbent concentration was detected to be 2 g/100 mL.

Effect of pH

pH is an important parameter in the adsorption process, which affects the degree of dye ionization as well as the surface properties of biosorbent. In this study, by considering different values of pH (4, 7 and 10) in dye solutions of 25 and 50 mg/L as well as the presence of 2.0 g/100 mL adsorbent dose, the effect of initial solution of pH on the dye adsorption into cuttlefish bone powder was assessed. After 24 hours of contact time, the remaining dye concentration was determined spectrophotometrically. The effects of the initial pH on the removal of RR198 dye by sorption on cuttlefish bone powder are illustrated in Fig. 3.

According to the results, increasing the initial pH from 4 to 10 had no significant effect on the adsorption efficiency and the final pH changed to 9.0-9.5 due to releasing of carbonated compounds to aqueous solution. Cuttlefish bone, when is added to water, produce some species like HCO_3^-, CO_3^{2-}, Ca^{2+}, $CaHCO_3^+$ and $CaOH^+$ in aqueous solution [17]. By increasing the initial pH from 4 to 10, the dye removal was decreased from 87% to 85% for 25 mg/L dye concentration as well as it decreased from 75% to 73% for 50 mg/L initial dye concentration.

Effect of contact time

To reach equilibrium, the most important design parameter in the wastewater treatment is contact time that affects the performance of adsorption processes. Therefore, adsorption processes were carried out in different contact times of 10, 30, 60, 120, 180, and 240 min. For each experiment, 2g/100mL adsorbent was added into the dye solutions with the initial concentrations 25 and 50 mg/L at pH 9.00 and then remaining dye measured.

Consistently with previous literature [22, 23], by increasing of contact time, the removal efficacy of RR198 dye have been increased, as well as by increasing the initial dye concentration, the possibility of encounter and contact between adsorbent and adsorbate is increased (Fig. 4).

As represented in Fig. 4, the optimum contact time for adsorption of dye was considered 120 min so that by increasing of contact time from 120 to 240 min, the removal efficiency for 25 mg/L initial dye concentration changed from 74% to 84% and for 50 mg/L it is increased from 56% to 64%, respectively.

The results of this study demonstrated that by increasing of RR198 dye concentration q_e (mg/g) was increased. These results show that the removal of RR198 dye with cuttlefish bone powder depends on the dye concentration and may be related to driving forces to overcome the resistance of pollutant migration from aqueous solutions to the biosorbent surface [19]. Samarghandi et al. investigated the removal of Acid Red 14 dye by Pumice stone. They reported that by increasing of contact time, the dye removal efficiency was increased and the equilibrium time was before 390 min [24].

Adsorption isotherms

In order to optimize the use of cuttlefish bone powder as an adsorbent, it is important to establish the most appropriate adsorption isotherm. Thus, the correlation of equilibrium data with either theoretical or empirical models is essential for practical operation [25]. In this study, Langmuir and Freundlich equations were used to analyze the experimental data of cuttlefish bone powder to remove RR198 dye.

The Langmuir isotherm theory assumes the monolayer coverage of adsorbate over a homogeneous adsorbent surface, equally available for adsorption and with equal energies of adsorption. Therefore, at equilibrium condition, a saturation point is reached where no further adsorption can take place at the site. The generalized linear form of the Langmuir isotherm model is expressed by equation (3).

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \qquad (3)$$

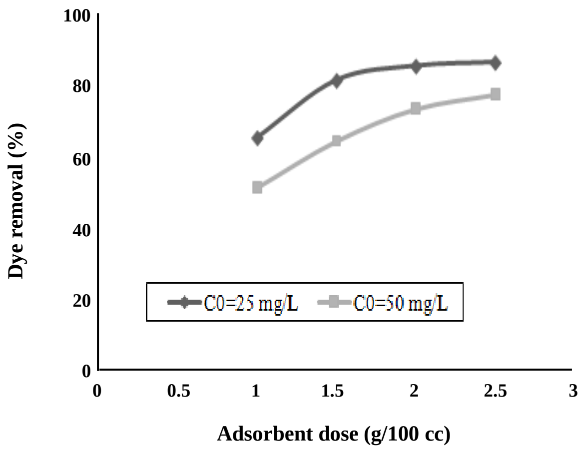


Fig. 2: Effect of adsorbent dose on RR198 dye removal.

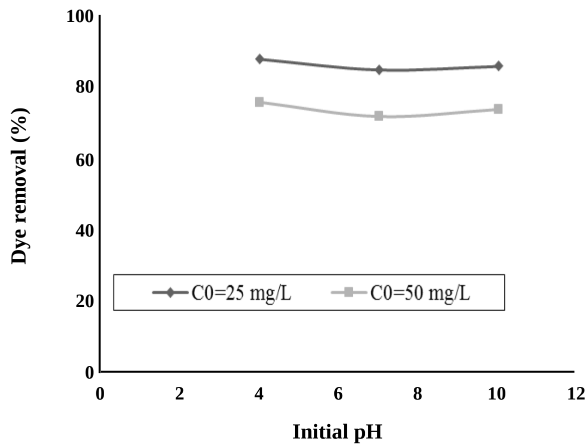


Fig. 3: Effect of initial pH on the adsorption capacity of RR198 dye.

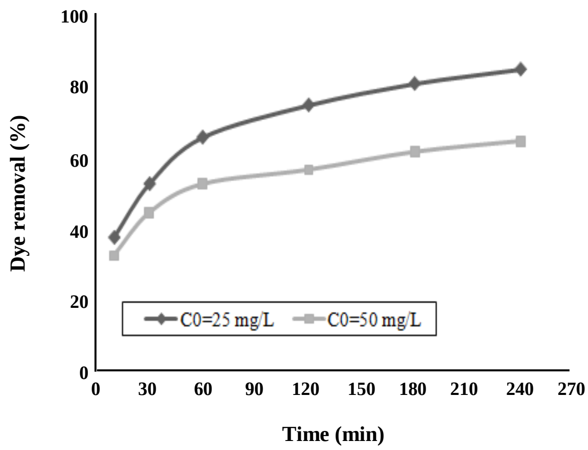


Fig. 4: Effect of contact time on the adsorption capacity of RR198 dye.

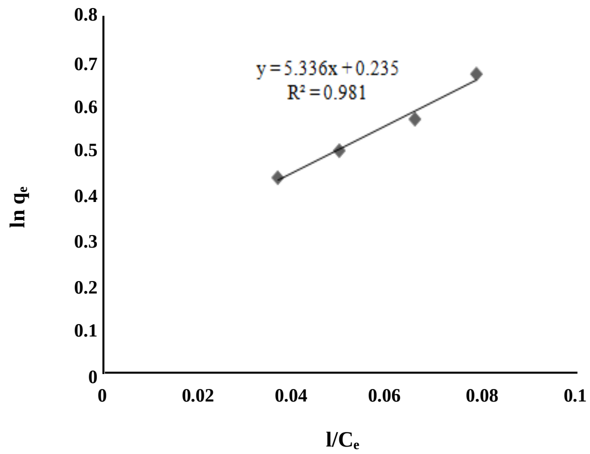


Fig. 5: Langmuir isotherm for the adsorption of RR198 dye on cuttlefish bone powder (C_0=50 mg/L).

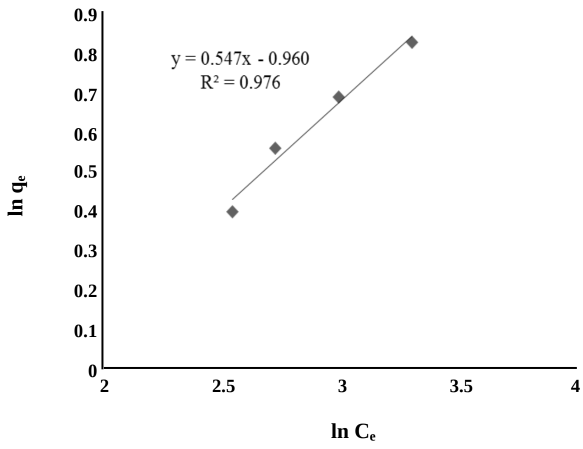


Fig. 6: Freundlich isotherm of the adsorption of RR198 dye on cuttlefish bone powder (C_0=50 mg/L).

Where q_e is equilibrium adsorption capacity (mg/g), C_e is the equilibrium dye concentration (mg/L), q_m and b are Langmuir constants related to maximum adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. These constants can be determined from the linear plot of C_e/q_m versus C_e, which has a slope of $1/q_m$ and an intercept of $1/kq_m$. The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called separation factor (R_L) and is calculated by equation (4):

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

Where b is the Langmuir constant and C_0 is the initial dye concentration. The value of separation factor indicates the nature of adsorption process. R_L values indicate the adsorption process to be irreversible (R_L=0), favorable (0<R_L<1), linear (R_L=1), or unfavorable (R_L>1) [3, 15, 26, 27].

Fig. 5 shows the Langmuir isotherm for 50 mg/L dye concentration. Based on the dimensionless separation factor (R_L) in the Langmuir model, the value of this parameter for the adsorption of RR198 dye on cuttlefish bone powder is less than 1 (R_L=0.0009) that confirms the adsorption of RR198 dye on this adsorbent is favorable under the conditions of this study.

In Freundlich adsorption isotherm model, a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface is assumed. Eq. (5) suggests that the places of solidarity are not the same or independent. The Freundlich adsorption isotherm model can be expressed by Eq. (5):

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \quad (5)$$

Where q_e is the equilibrium adsorption capacity of the adsorbent (mg/g), C_e is the equilibrium concentration of the dye (mg/L), k_f and n are Freundlich constant, related to the adsorption capacity and intensity, respectively. The Freundlich constants, n and k_f, were obtained from the plot of $\ln q_e$ versus $\ln C_e$ that should give a straight line with a slope of 1/n and the intercept of $\ln k_f$ [3].The 1/n values indicate the adsorption process to be irreversible (1/n=0), favorable (0<1/n<1), and unfavorable (1/n>1) [25].

Fig. 6 shows the Freundlich isotherm for 50 mg/L dye concentration. According to our results, 1/n value is less than 1 (1/n=0.547), therefore it is confirmed that the adsorption of the RR198 dye on cuttlefish bone powder is favorable.

Values of correlation coefficient (R^2) are regarded as the measures of the goodness-of-fit of experimental data on the isotherm models. The adsorption isotherm for 50 mg/L dye concentration was in good concordance with Langmuir and Freundlich models with R^2>0.95. These findings are agree with those by Kamal Amin, demonstrated that the adsorption of reactive orange dye onto activated carbons prepared from sugarcane bagasse pith can be well described by both Langmuir and Freundlich isotherms [26]. *Ishaq et al.* also investigated the removal of xylenol orange from aqueous solution onto the coal ash and achived the same results. According to their results, data followed both Langmuir and Freundlich isotherm models [28]. While, *Mahmoodi et al.*

Table 2: Kinetics constants of RR 198 adsorption on cuttlefish bone powder.

Initial dye concentration	Pseudo-first-order kinetic		Pseudo-second-order kinetic	
25 mg/L	q_e(calc.)(mg/g)	0.649	q_e(mg/g)	1.10
	q_e(exp.)(mg/g)	1.081	k_2	0.039
	K_1(min^{-1})	0.01	R^2	0.997
	R^2	0.991		
50 mg/L	q_e(calc.)(mg/g)	0.999	q_e(mg/g)	1.616
	q_e(exp.)(mg/g)	1.817	k_2	0.033
	k_1(min^{-1})	0.005	R^2	0.997
	R^2	0.945		

investigated the kinetics and equilibrium characteristics of textile dye adsorption on the pine cone. Their results showed that Acid Black 26 (AB26) and Acid Green 25 (AG25) followed the Langmuir isotherm and Acid Blue 7 (AB7) followed Freundlich isotherm [25].

Adsorption Kinetics

Several models can be used to express the mechanism of dye adsorption onto a natural biosorbent. To assess the reaction kinetics, in this study, we used pseudo-first-order and pseudo-second-order models.

Pseudo-first-order adsorption model is generally expressed by equation (6):

$$\ln\left(q_e - q_t\right) = \ln q_e - \frac{K_1 t}{2.303} \tag{6}$$

Where q_e and q_t are the amount of adsorbed dye per unit weight of the adsorbent (mg/g) at equilibrium time and time t, respectively; k_1 is the rate constant and t is time (min). The first-order-rate constant (k_1), can be obtained from the slope of the plot ln (q_e– q) versus time. According to Table 2, an increase at initial dye concentration led to decrease at pseudo-first-order rate constant k_1. The estimated values of q_e were calculated from the Eq. (6), where q_e differs substantially from those measured experimentally, which confirms that the RR198 dye adsorption using pseudo-second-order equation is successfully used to describe the reaction kinetics of pollutants on adsorbent. Pseudo-second-order kinetics may be expressed by equation (7):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

Where q_e is equilibrium adsorption capacity (mg/g), q_t is the amount of adsorbed dye at time t (mg/g) and k_2 is the rate constant of adsorption (g/mg.min). During the present study the equilibrium adsorption capacity (q_e) and the rate constant (k_2) were determined by plot of (t/q_t) versus time, [3, 19, 29].

In pseudo-second-order equation, the calculated q_e values were closer to the experimental q_e ones [30]. This showed that adsorption of RR198 on cuttlefish bone powder follows pseudo-second-order.

Compared to pseudo-first-order equation, the R^2 values of pseudo-second-order equation were closer to unity for both of the initial dye concentrations (Table 2). The values of the correlation coefficient (R^2) for 25 and 50 mg/L of dye concentrations in pseudo-second-order model were found 0.997. Thus, pseudo-second-order model provides a good concordance with the adsorption of RR198 dye on cuttlefish bone powder (Fig. 7). Jamshidi et al., studied the adsorption kinetics of reactive blue 19 on olive kernel ash and reported that the adsorption of RB19 onto olive kernel ash complies with pseudo-second-order kinetics equation [31]. In another research, the kinetic data obtained from Cu (II) adsorption experiments, using pretreated fish bones, have shown a good compliance with pseudo-second-order kinetic and correlation coefficient, for the linear plots were higher than 0.99 for all experimental data [18].

CONCLUSIONS

The present study showed that the increase in adsorption dose and time contact led to increase in the dye removal efficiency. While, increasing of initial dye concentration led to decreasing the same parameter.

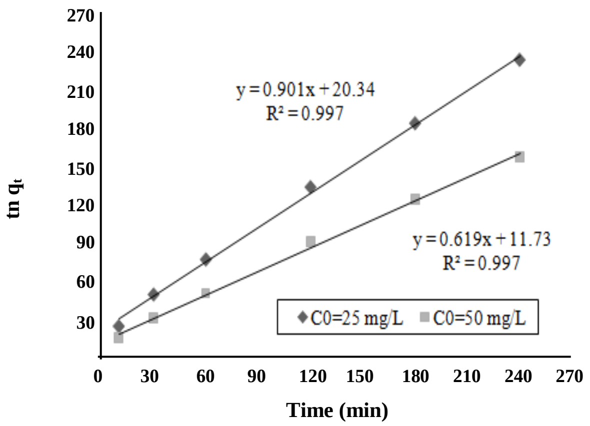


Fig. 7: Pseudo-second-order kinetics for RR198 dye adsorption on cuttlefish bone powder.

According to our results, change of pH had no effect on the removal of dye. Regard to the high cost of synthetics adsorbents, it is important to introduce an easily available, low-cost, and natural adsorbent.

Based on the results, the cuttlefish bone can be used as a cheap adsorbent for the removal of industrial dyes and other environmental pollutants.

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REFERENCES

[1] Moussavi G.H., Mahmoudi M., Removal of Azo and Anthraquinone Reactive Dyes from Industrial Wastewaters Using MgO Nanoparticles, *Journal of Hazardous Materials*, **168** (2-3):806-812 (2009).

[2] Rezaee A., Ghaneian M.T., Hashemian J., Mossavi Gh., Hajizadeh E., Enhanced Decolorization of Reactive Blue 19 Dye from Synthetic Textile Wastewater through UV Photolysis in Alkaline Conditions, *Environmental Engineering and Management Journa.*, **7**(2):119-123 (2008).

[3] Elkady M.F., Ibrahim A.M., Abd El-Latif M.M., Assessment of the Adsorption Kinetics, Equilibrium and Thermodynamic for the Potential Removal of Reactive Red Dye Using Eggshell Biocomposite Beads, *Desalination*, **278**(1-3): 412-423 (2011).

[4] Rezaee A., Ghaneian M.T., Khavanin A., Hashemian S.J., Moussavi G., Ghanizadeh G.H., Hajizadeh E., Photochemical Oxidation of Reactive Blue 19 Dye (RB19) in Textile Wastewater by UV/$K_2S_2O_8$ Process, *Iranian. Journal of Environmental Health Science & Engineering*, **5** (2): 95-100 (2008).

[5] Han R., Ding D., Xu Y., Zou W., Wang Y., Li Y., Zou L., Use of Rice Husk for the Adsorption of Congo Red from Aqueous Solution in Column Mode, *Bioresource Technology*, **99** (8):2938-2946 (2008).

[6] Puzyn T., Mostrag-Szlichtyng A., "Organic Pollutants Ten Years after the Stockholm Convention - Environmental and Analytical Update". 482 pages. IN TECH WEB.ORG. (2012).

[7] Ncibi M.C., Mahjoub B., Seffen M., Adsorptive Removal of Textile Reactive Dye Using Posidoniaoceanica (L.) Fibrous Biomass, *International Journal of Environmental Science & Technology*, **4**(4):433-440 (2007).

[8] Forgacs E., Cserhatia T., Oros G., Removal of Synthetic Dyes from Wastewaters, *Environment International*, **30**(7): 953-971 (2004).

[9] Gharbani O., Tabatabaii S.M., Mehrizad A., Removal of Congo Red from Textile Wastewater by Ozonation, *International Journal of Environmental Science & Technology*, **5**(4): 495-500 (2008).

[10] Ghasemi F., Tabandeh, F., Bambai, B., SambasivaRao, K.R.S., Decolorization of Different Azo Dyes by Phanerochaetechrysosporium, RP78 under Optimal Condition, *International Journal of Environmental Science & Technology*, **7**(3): 457-464 (2010).

[11] Igbinosa E.O., Okoh A.I., Impact of Discharge Wastewater Effluents on the Physico-Chemical Qualities of a Receiving Watershed in a Typical Rural Community, *International Journal of Environmental Science & Technology*, **6**(2):175-182 (2009).

[12] Crini G., Non-conventional Low-Cost Adsorbents for Dye Removal: a Review, *Bioresource Technology*, **97**(9):1061–1085(2006).

[13] Aksu Z., Application of Biosorption for the Removal of Organic Pollutants: a Review, *Process Biochemistry*, **40**(3-4):997–1026 (2005).

[14] Golob V., Vinder A., Simonic M., Efficiency of the Coagulation/FLocculation Method for the Treatment of Dyebath Effluents, *Dyes and Pigments*, **67**(2): 93–97 (2005).

[15] Annadurai G., Ling L.Y., Lee J.F., Adsorption of Reactive Dye from an Aqueous Solution by Chitosan: Isotherm, Kinetic and Thermodynamic Analysis, *Journal of Hazardous Materials*, **152**(1): 337–346 (2008).

[16] Dizge N., Aydiner C., Demirbas E., Kobya M., Kara S., Adsorption of Reactive Dyes from Aqueous Solutions by Fly Ash: Kinetic and Equilibrium Studies, *Journal of Hazardous Materials*, **150**(3):737–746 (2008).

[17] Ben Nasr A., Walha K., Charcosset C., Ben Amar R., Removal of FLuoride Ions using Cuttlefish Bones, *Journal of Fluorine Chemistry*, **132**(1): 57-62 (2011).

[18] Kizilkaya B., Tekinay A.A., Dilgin Y., Adsorption and Removal of Cu (II) Ions from Aqueous Solution Using Pretreated Fish Bones, *Desalination*, **264**(1-2): 37–47 (2010).

[19] Ehrampoush M.H., Ghanizadeh G.H., Ghaneian M.T., Equilibrium and Kinetics study of Reactive Red 123 dye Removal from Aqueous Solution by Adsorption on Eggshell, *Iranian Journal of Environmental Health Science & Engineering*, **8**(2): 101-108 (2011).

[20] GhanizadehGh., Ehrampoush M.H., Ghaneian M.T., Aplication of Iron Impregnated Activated Carbon for Removal of Arsenic from Water, *Iranian Journal of Environmental Health Science & Engineering*, **7**(2): 145-156 (2010).

[21] Ghaneian M.T., Jamshidi B., Dehvari M., Amrollahi M., Pomegranate Seed Powder as a New Biosorbent of Reactive Red 198 Dye from Aqueous Solutions: Adsorption Equilibrium and Kinetic Studies, *Research on Chemical Intermediates*, **41** (5):3223-3234 (2015).

[22] Mahmoodi N.M., Hayati B., Arami M., Lan Ch., Adsorption of Textile Dyes on Pine Cone from Colored Wastewater: Kinetic, Equilibrium and Thermodynamic Studies, *Desalination*, **268**(1-3): 117–125 (2011).

[23] Kamal Amin N., Removal of Reactive Dye from Aqueous Solutions by Adsorption onto Activated Carbons Prepared from Sugarcane Bagasse Pith, *Desalination*, **223**(1-3):152-161 (2008).

[24] Samarghandi M.R., Zarrabi M., NooriSepehr M., Panahi R., Foroghi M., Removal of Acid Red 14 by Pumice Stone as a Low Cost Adsorbent: Kinetic "and Equilibrium Study, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **31**(3): 19-27(2012).

[25] Sivasamy A., Nethaji S., JosminLalliNisha L.L., Equilibrium, Kinetic and Thermodynamic Studies on the Biosorption of Reactive Acid Dye on Enteromorphaflexuosa and Gracilariacorticata, *Environmental Science and Pollution Research*, **19**, 1687–1695 (2012).

[26] Yu J.X., Li B.h., Sun X.m., Jun Y., Chi R.a., Adsorption of Methylene Blue and Rhodamine Bon Baker's Yeast and Photocatalytic Regeneration of the Biosorbent, *Biochemical Engineering Journal*, **45**(2): 145-151 (2009).

[27] Ghaneian M.T., Ehrampoush M.H., MoslehArany A., Jamshidi B., Dehvari M., Equilibrium and Kinetic Studies of Cr (VI) Removal from Synthetic Wastewater by Acroptilonrepense Flower Powder, *Polish Journal of Chemical Technology*, **15**(2): 40-47 (2013).

[28] Ishaq M., SaeedKh., Ahmad I., Sultan S., AkhtarSohail., Coal Ash as a Low Cost Adsorbent for the Removal of Xylenol Orange from Aqueous Solution, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **33** (1): 53-8 (2014).

[29] Kumar E., Bhatnagar A., Kumar U., Sillanpaa M., Defluoridation from Aqueous Solutions by Nano-Alumina: Characterization and Sorption Studies, *Journal of Hazardous Materials*, **186**(2-3):1042-1049 (2010).

[30] Moussavi G., Mahmoudi M., Degradation and biodegradability Improvement of the Reactive red 198 azo Dye Using Catalytic Ozonation with MgOnanocrystals, *Chemical Engineering Journal*, **152**(1): 1–7 (2009).

[31] Jamshidi B., Ehrampoush M.H., Dehvari M., Utilization of Olive Kernel Ash in Removal of RB19 from Synthetic Textile Wastewater, *Journal of Environmental Treatment Techniques*, **1**(3):151-7 (2013).