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].
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 hours 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 (XPer-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 carried out at 20 °C 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):

\[
q_e = \left( \frac{C_0 - C_e}{V} \right) \times \frac{V}{M}
\]

\[
E = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]

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 \(C_0\) are the equilibrium
Table 1: Basic characteristics of the reactive red 198 dye.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>C_{27}H_{18}C_{l}N_{7}Na_{4}O_{15}S_{5}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial name</td>
<td>Remazol Red 133</td>
</tr>
<tr>
<td>Class</td>
<td>Azo</td>
</tr>
<tr>
<td>C.I. number</td>
<td>18221</td>
</tr>
<tr>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>518</td>
</tr>
<tr>
<td>Molecular structure</td>
<td><img src="image" alt="Molecular structure" /></td>
</tr>
</tbody>
</table>

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\(^{\circ}\). The XRD pattern showed that the cuttlefish bone has a crystallized form. These results agree with the study of \(N\)asr \(e\)t al., (2011), demonstrated the elemental analysis of cuttlefish bone includes 96% pure calcium carbonate with trace quantities of Na\(_2\)O and P\(_2\)O\(_5\) \([17]\).

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 \(E\)lkady \(e\)t 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
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).

\[
\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b} \cdot C_e
\]  
(3)

![Fig. 2: Effect of adsorbent dose on RR198 dye removal.](image)

![Fig. 3: Effect of initial pH on the adsorption capacity of RR198 dye.](image)

![Fig. 4: Effect of contact time on the adsorption capacity of RR198 dye.](image)
Fig. 5: Langmuir isotherm for the adsorption of RR198 dye on cuttlefish bone powder (C₀=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 achieved the same results. According to their results, data followed both Langmuir and Freundlich isotherm models [28]. While, Mahmoodi et al.
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):

\[
\ln \left( q_e - q_t \right) = \ln q_e - \frac{K_1 t}{2.303}
\] (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 \( \ln (q_e - q_t) \) 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):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\] (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 \( (\delta q_t/\delta t) \) 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].

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

<table>
<thead>
<tr>
<th>Initial dye concentration</th>
<th>Pseudo-first-order kinetic</th>
<th>Pseudo-second-order kinetic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_e ) (calc.) (mg/g)</td>
<td>( q_e ) (exp.) (mg/g)</td>
</tr>
<tr>
<td>25 mg/L</td>
<td>0.649</td>
<td>1.081</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 mg/L</td>
<td>0.999</td>
<td>1.817</td>
</tr>
</tbody>
</table>

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.
According to our results, change of pH had no effect on the removal of dye. Regarding 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 absorbent for the removal of industrial dyes and other environmental pollutants.

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