Adsorption of Acid Dyes onto Bentonite and Surfactant-modified Bentonite

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Abstract

Adsorption of Congo red (CR) from water via batch adsorption experiments onto bentonite and CTAB-modified bentonite (CTAB-MBn) was investigated. Studies concerning the factors influencing the adsorption capacities of bentonite and CTAB-MBn, such as initial dye concentration, adsorbent dosage, pH, ionic strength, contact time and temperature were systematically investigated and discussed. The results revealed that CTAB-modified bentonite demonstrated high adsorption capacities toward acid dyes, while bentonite exhibited sorption capacities lower than CTAB-MBn. The kinetic data were analyzed using first order and pseudo-second order models. It was best described by the pseudo-second order model. The isotherm data were investigated according to Langmuir and Freundlich equations. Thermodynamic parameters ΔG°, ΔH° and ΔS° were calculated for the adsorption of CR on bentonite and CTAB-MBn; the value of ΔG° showed the spontaneous nature of adsorption for both sorbents.

Keywords: Adsorption; Congo red; Bentonite; Surfactant

Introduction

Synthetic dyes can be found in the wastewater from various industries like paper, leather, plastics and textiles [1]. Wastewater discharges into rivers and natural streams from the industries that use dyes poses stark environmental problems. Even minor quantities of dyes can color huge water bodies, which influences aesthetic merit and decreases light penetration needed for photosynthesis. Furthermore, many of dyes are toxic or carcinogenic [2,3]. Hence, the elimination of dyes from wastewater accepted environmental importance. Many approaches have been developed for decontamination of water, e.g. precipitation, electrodialysis, adsorption, filtration, coagulation, oxidation and membrane separation. However, adsorption is known to be one of the most effective techniques to eliminate dyes from water. Activated carbon has been familiarized as adsorbent due to its great sorption capacity for the dyes [4]. However the high cost has led us seeking for low-cost sorbents. Recently, low-cost materials such as fly ash [5], natural zeolite [6], red mud [7] and coir pith [8] accepted vital interest for wastewater treatment. Several modified bentonite are also reported to be inexpensive and effective in water decontamination [9-12].

Acid dyes are the most problematic due to their bright colour, acidic and water soluble reactive characteristics. Several studies have been executed on adsorption of basic dyes by clay minerals [13]. However, there is very little works on adsorption of acidic dyes [14]. Generally, the adsorption capacity for anionic dyes is much lower than for cationic dyes, as result of weak attractions between acidic charges on the dyes and the negative surface of clay.

Bentonite comprises of one octahedral alumina sheet lying between two tetrahedral layers of silica. The permanent negative charge of bentonite is attributed to the isomorphous replacement of Al³⁺ for Si⁴⁺ in the tetrahedral layer and Mg²⁺ for Al³⁺ in the octahedral layer. This negative charge is balanced by the presence of replaceable cations (Ca²⁺, Na⁺, etc.) in the lattice structure, which enhance adsorbing cationic pollutants [15-17]. Although, bentonite weakly absorbs acidic contaminants due to repulsion force between the anion and the negative charge on the surface of the bentonite [18,19]. Several authors have informed the use of bentonite modified and organobentonite with a cationic surfactant for acidic dye elimination via high loading quantity of surfactant [20-22]. Preceding studies had shown that the main mechanism of the adsorption interpreted the acidic dye elimination is the anionic exchange between excessive anions and pollutants from the surfactant [23]. Hence, to obtain a high sorption capacity, modifications need surfactants at twice the CEC. Accordingly, the cost increases.

In the present study, bentonite was modified by CTAB resulting in a new adsorbent, CTAB-modified bentonite (CTAB-MBn), to improve the sorption capacity for acidic contaminants. Bentonite and (CTAB-MBn) were characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and Nitrogen adsorption measurements. The capacity of adsorption for the removal Congo red was estimated. The influences of pH, temperature, initial concentration and equilibrium time on the adsorption were also investigated in batch methods.

Experimental Procedure

Materials and methods

Bentonite applied in this investigation was obtained from Egypt. The chemical component of the bentonite is illustrated in Table 1 (determined by x-ray fluorescence). Congo red dye was purchased from Sigma Aldrich. Congo red structure of this dye is illustrated in Figure 1.

Synthesis of surfactant-modified Bentonite (CTAB-MBn)

The surfactant-modified bentonite was synthesized by the following steps. For CTAB-B synthesis, 25 g bentonite was put in 250 mL of water

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containing 5 g of CTAB. The reaction components were stirred at 25°C for 12 h. The product was filtered and washed repeatedly with bi-distilled water till no bromide ion was determined by AgNO₃ solution (0.1 M). The CTAB-B was dried at 110°C for 6 h.

Characterization

The specific surface area of the adsorbents was estimated by BET method (Brunauer-Emmet-Teller) using liquid N₂ adsorption at 196°K by means of a conventional volumetric apparatus. This was determined by a McLeod system connected to the apparatus. The morphology of the samples surfaces were investigated using scanning electron microscopy (JEOL, model 6400).

Adsorption studies

The batch sorption was executed on Shaking Water Bath (NE5, Nickel-Electro Ltd., UK) at 200 rpm. To investigate the influence of bentonite and CTAB-MBn on sorption capacities of CR experiments, 0.1 g adsorbent and 50 mL CR solution (initial conc. 1000 mg/L, pH 6.9) were used. The method was operated under shaking at 25°C till adsorption balance was accomplished. The influence of pH on CR elimination was studied via adjusting 50 ml CR solutions (300 mg/L CR) at pH range (5.0-10.0), using 0.01 M NaOH or HCl solution with 0.1 g adsorbent for 360 min at 25°C. The influence of temperature on CR elimination was executed in the 50 mL CR solutions (1000 mg/L, pH 6.9) by adding 0.1 g adsorbent till balance was completed. The influence of sorption time on CR elimination was executed in the 50 mL CR solutions (300 mg/L, pH 6.9), by adding 0.1 g adsorbent at 25°C for determined period of time. The influence of the initial CR concentrations on CR elimination was executed by exciting 50 mL several dye concentrations of CR solution at conditions: pH 6.9; 0.1 g/50 mL; T 25°C; 360 min. Subsequently, the samples were filtered and the adsorbate of residual concentrations was measured. The quantities of CR removed via sorbents qₑ and percent extracted %E can be calculated by the subsequent equations:

$$q_e = \frac{(C_o - C_e)V}{m}$$  \hspace{1cm} (1)

Where qₑ (mg/g) is the equilibrium concentration of CR on the adsorbent, C₀ and Cₑ are the initial and equilibrium liquid-phase concentrations of dye (mg/g), respectively, m (g) is the mass of adsorbent and V (L) is the volume of solution. The concentration of CR in the residual solution was analyzed spectrophotometrically by UV-Vis spectrophotometer at wavelength 498 nm and the amount of adsorption qₑ was calculated according to equation (1).

Results and Discussion

Characterization of bentonite and CTAB-MBn

The surface area and porosity of an adsorbent are significant parameters in determining its adsorption capacity as well as its adsorption performance [24]. The adsorption isotherms so obtained were analyzed via the traditional BET equation. Table 2 lists the surface areas, total pore volumes and mean pore diameters of bentonite and CTAB-MBn. Table 2 reveals that modification of bentonite with (CTAB) was found to be linked with a reduction in the surface area, the mean diameter and total pore volume.

These textural modifications are illustrated when the textural properties of bentonite are compared with those of CTAB-MBn. The evident changes in the textural parameters caused by modifying bentonite by cationic surfactant may be ascribed to the blocking of relatively fine pores via the surfactant molecules leaving behind the comparatively wide pores [25]. To obtain proof for the adsorption of CTAB into bentonite sample, FTIR spectra were shown in Figure 2. Two bands at 2850 and 2925 cm⁻¹, which were observed by the surfactant modified bentonite, could be assigned to the asymmetric and symmetric stretching vibrations of the CH₃ and CH₂ of the aliphatic chain of the CTAB [26]. This band is not observed in the IR spectrum of natural bentonite. Modification of bentonite by CTAB was associated also with evident change in the morphology and particle size. The SEM images of bentonite and CTAB-MBn are shown in Figure 3 and

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Surface area SBET (m²/g)</th>
<th>BET-C constant</th>
<th>Pore volume Vₑ (ml/g)</th>
<th>Aver. pore diam. r (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>32.17</td>
<td>75.29</td>
<td>0.029</td>
<td>1.8</td>
</tr>
<tr>
<td>CTAB-MBn</td>
<td>16.41</td>
<td>37.13</td>
<td>0.015</td>
<td>1.66</td>
</tr>
</tbody>
</table>

Figure 2: FTIR spectra of (a) natural bentonite and (b) DTMA–bentonite.

Figure 3: SEM micrographs of Bentonite.
4, respectively. Obviously, the agglomerates of bentonite contain few numbers of particles compared with those of CTAB-MBn. Several of the particles in bentonite and CTAB-MBn show laminar crystalline habit characteristic of phyllosilicates. However, these certain particles dominate more in CTAB-MBn. Interaction of surfactant molecules in the interlayers may also stand behind the domination of comparatively large laminar crystallites and large agglomerates.

**Effect of pH**

Bentonite and CTAB-MBn have proved to be an effective adsorbent for the removal of acidic dye, CR *via* adsorption from aqueous solution, as can be seen from the data recorded in Figure 5. It can be shown that the influence of the pH on the sorption capacity of CR adsorbed is weak. When the pH increases from pH 5-10, the amount of CR adsorbed at equilibrium (q_e) decrease slowly from 149 to 138 mg/g. The minor decrease in adsorption may be due to the repulsion between acidic dye molecules and the abundance of OH⁻ ions at higher pH values.

**Effect of initial dye concentration**

In general, the sorption of dye was dependent on the initial concentration of the dye [8]. Figure 6 shows the effect of initial CR concentration on the adsorption capacity of Bentonite and CTAB-MBn toward CR. It can be shown that q_e increased sharply from 186.40 to 204.275 mg/g with increasing the initial CR concentration from 400 to 700 mg/L, while that of Bentonite was 15.41 mg/g to 36.78 mg/g from 100 to 400 mg/L. However, the amount of CR adsorbed at equilibrium (q_e) enhanced slightly from 204.275 to 210.10 mg/g with an increase in the initial CR concentration from 700 to 1000 mg/L, while that of Bentonite was 36.78 mg/g to 37.10 mg/g from 400 to 800 mg/L at 25°C. Figure 6 shows higher removal of CR onto CTAB-MBn than that of Bentonite. It appears that an increase in adsorbate concentration results in an increase in the driving force, which leads to an increase in the CR diffusion rate [27,28]. The amounts of CR adsorbed at equilibrium (q_e) increase from 50 to 210.10 mg/g and from 9.145 to 37.10 mg/g, for CTAB-MBn and Bentonite, respectively, and the results indicate that the CTAB-MBn is efficient adsorbent for CR.

**Effect of amount of adsorbent**

The effect of adsorbent dosage on removal of CR by Bentonite and CTAB-MBn is shown in Figure 7. When the sorbent dose increases from 0.025 to 0.2 g, the percent dye removals by Bentonite and CTAB-MBn increase from 8.79% to 13.15% and from 9.32 % to 99.94%, respectively.

It was observed that the adsorption of the CR enhanced rapidly with increasing the amount of adsorbent from 0.025 to 0.075 g and slightly enhanced from 0.1 to 0.25 g. This can be simply attributed to the increased sorbent surface area and availability of more sorption site. However, the amount of CR adsorbed (mg/g) was found to decrease.
with further increase in adsorbent dosage due to the high number of unsaturated adsorption sites.

**Effect of volume of Congo red**

Volume of CR solution is one of the factors that influence the effective capacity of the adsorption for CR. Various CR volumes (0.025-0.25 L) with 0.1 g sorbent were applied at pH 6.9, 25°C, and CR 300 mg/L. Figure 8 shows higher removal of CR onto CTAB-MBn than that of Bentonite. CR removal decreased slightly from 99.95% to 51.56% (CTAB-MBn), and from 23.32% to 9.10% (Bentonite) with increasing CR volume from 0.025 to 0.25 L.

**Effect of contact time**

Figure 9 showed the influence of contact time on the sorption capacity of Bentonite and CTAB-MBn for dye solution when concentration 300 ppm. It is evident that the sorption capacity of Bentonite and CTAB-MBn enhance rapidly by the increase of contact time from 0 to 90 min, and more than 92% of the equilibrium sorption capacity for CR executed at 90 min. In the next 120 min, the sorption capacity became constant and the adsorption accomplished equilibrium. Consequently, 120 min was chosen as the contact time for the sorption of CR onto the aggregates under our study conditions.

**Effect of ionic strength**

The availability of salt in water leads to high ionic strength may be more effective on the efficiency of the adsorption process [29]. As can be shown in Figure 10, the variation of salts concentration (NaCl, KCl, and CaCl2) makes a major effect on the range of acidic dyes adsorption. The current study indicates that the sorption of negatively charged CR, on negatively charged Bentonite and positively charged CTAB-MBn enhanced with the addition in the order: NaCl<KCl<CaCl2. The escalates of ionic strength in aqueous solution may result in the compression of the diffuse double layer on the adsorbent. This eases the electrostatic attraction and participates in the adsorption consequently [30-32].

**Effect of temperature**

The influence of temperature on sorption was investigated at 25, 35 and 45°C, and the consequences are shown in Table 3. It could be clearly seen that, the amount adsorbed at equilibrium increases with increasing temperature. When the temperature increased from 25°C to 45°C, the maximum amounts of CR removed by Bentonite and CTAB-MBn are found to be increased from 37.050 to 45.596 mg/g and 210.10 to 224.361 mg/g, respectively. It is found that higher temperature eased the sorption of CR on CTAB-MBn. It is common that increasing temperature may create a swelling influence inside the adsorbent structure, penetrative the additional big dye molecule [33].

**Adsorption kinetics**

The value constant of adsorption is specified from the first-order rate expression given by Lagergren [34] can be expressed as Eq. (3):

\[
\log \left( \frac{q_t}{q_e} \right) = \log q_e - \frac{Kl}{2.303} \tag{3}
\]
Where \( q_e \) and \( q_t \) (mg/g) are the amounts of CR adsorbed at equilibrium and at time \( t \), respectively, and \( k_e \) is the equilibrium constant (min\(^{-1}\)), which were obtained from the slopes of the linear plots of \( \ln(q_e-q_t) \) versus \( t \), as shown in Figure 11a.

The pseudo-second-order model is depended on the supposition of chemisorption of the adsorbate on the adsorbents. This model [35] can be expressed as Eq. (4):

\[
\frac{t}{q_t} = \frac{1}{q_e} + \frac{t}{k_e q_e}
\]

(4)

Where \( k_e \) (g/mg.min) is the equilibrium rate constant for the pseudo second-order adsorption and \( q_e \) can be obtained from the plot of \( t/q_t \) against \( t \), as shown in Figure 11b. A comparison of the results with the correlation coefficients for the first-order kinetic and second-order kinetic models is shown in Table 4. For Bentonite CTAB-MBn: the second order model is the best fit model for experimental kinetic data, this because of the value of the calculated \( q_e \) approve very well with the experimental data and \( r^2 \) is greater than 0.986 for all adsorbents. These results also indicated that the applicability of this kinetic equation and the second-order nature of the adsorption process of CR on clays [36].

**Adsorption isotherms**

The equilibrium adsorption isotherms were explained using Langmuir and Freundlich isotherm equations [37,38], respectively:

\[
\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}
\]

(5)

\[
q_e = K_f C_e^n
\]

(6)

Where, \( b \) is Langmuir equilibrium constant (L mg\(^{-1}\)), and \( q_m \) (mg g\(^{-1}\)) is the monolayer adsorption capacity; \( n \) and \( K_f \) (mg g\(^{-1}\)) are the Freundlich’s constants. The Freundlich parameters can be obtained by the following linearized equation:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

By linear plotting \( \ln q_e \) as the function of \( \ln C_e \), the values of \( K_f \) and \( n \) can be obtained from the intercept and the slope of the plot (Figure 12). The isotherm parameters for the adsorption of CR onto Bentonite and CTAB-MBn are given in Table 5. Langmuir adsorption model provides
Table 6: Thermodynamic parameters for adsorption of CR by Bentonite and CTAB-MBn at different temperatures.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>$\Delta H^\circ$ (KJ/mol)</th>
<th>$\Delta S^\circ$ (KJ/mol K)</th>
<th>$\Delta G^\circ$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>12.37991</td>
<td>0.112323</td>
<td>298 K 308 K 318 K</td>
</tr>
<tr>
<td>CTAB-MBn</td>
<td>12.71387</td>
<td>0.133851</td>
<td>-21.104 -22.191 -23.352</td>
</tr>
</tbody>
</table>

the best fit with experimentally obtained data for Bentonite and CTAB-MBn with (r²>0.986). However, the Freundlich adsorption can be used also for modeling the equilibrium data for the three sorbents (r²>0.9.3.6 for all cases). This shows the surface of CTAB-MBn was enveloped by the monolayer of Congo red molecules.

**Thermodynamic studies**

Thermodynamic parameters were calculated from the difference of the thermodynamic distribution coefficient, $k_c$, with change in temperature. The standard free energy change, $\Delta G^\circ$, was calculated using the expression:

$$\Delta G^\circ = -RT \ln k_c$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

Where, R is gas constant (8.314 J/mol/K), T is the standard temperature in K and K is the Langmuir constant. Standard enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) of adsorption could be estimated from Van't Hoff equation:

$$\ln k_c = \frac{\Delta S^\circ}{RT} - \frac{\Delta H^\circ}{RT}$$

The thermodynamic parameters are offered in Table 6. It is evident from the table that the values of $\Delta G^\circ$ are negative for Bentonite and CTAB-MBn. The negative values of $\Delta G^\circ$ for all adsorbents at various temperatures indicate the process to be feasible and spontaneous. Actually that the values of $\Delta G^\circ$ decrease with increasing temperature shows the increase of spontaneous influence. For all the sorbents, the positive value of $\Delta H^\circ$ suggested the endothermic nature of the adsorption process. Moreover, the positive value of $\Delta S^\circ$ also indicates the increased randomness during sorption process.

**Conclusion**

The result of the present study reveals that Bentonite and CTAB-MBn can be a frequently valuable adsorbent for application in the treatment of industrial wastewater and water polluted with dyes. The amount of CR adsorbed was found to increase in order CTAB-MBn (210.10 mg/g)>Bentonite (37.10 mg/g). Results show that the adsorption capacity increases with the increase of initial CR concentration, adsorbent dosage, temperature and pH in the range of 5-9, where ionization surface area. The adsorption of CR onto the CTAB-Mn reached equilibrium within about 120 min. The results could be well described by Langmuir isotherm model. The adsorption kinetics followed a pseudo-second order kinetic model was involved in the adsorption process. Thermodynamic studies indicated that the adsorption process was endothermic and spontaneous in nature.

**References**