Research Article

Phenol Red Adsorption from Aqueous Solution on the Modified Bentonite

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Received 26 April 2020; Revised 19 June 2020; Accepted 1 July 2020; Published 28 July 2020

Academic Editor: Pedro M. Mancini

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In the present work, the modified bentonites were prepared by the modification of bentonite with cetyltrimethylammonium bromide (CTAB), both cetyltrimethylammonium bromide and hydroxy-Fe cations and both cetyltrimethylammonium bromide and hydroxy-Al cations. X-ray diffraction (XRD), thermal analysis (TG-DTA), infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and nitrogen adsorption/desorption isotherms were utilized to characterize the resultant modified bentonites. The modified bentonites were employed for the removal of phenol red dye from aqueous solution. Phenol red adsorption agreed well with the pseudo-second-order kinetic model. The equilibrium data were analyzed on the basis of various adsorption isotherm models, namely, Langmuir, Freundlich, and Dubinin–Radushkevich models. The highest monolayer adsorption capacity of phenol red at 30°C derived from the Langmuir equation was 166.7 mg·g⁻¹, 125.0 mg·g⁻¹, and 100.0 mg·g⁻¹ for CTAB–bentonite, Al–CTAB–bentonite, and Fe–CTAB–bentonite, respectively. Different thermodynamic parameters were calculated, and it was concluded that the adsorption was spontaneous ($\Delta G^\circ < 0$) and endothermic ($\Delta H^\circ > 0$), with increased entropy ($\Delta S^\circ > 0$) in all the investigated temperature ranges.

1. Introduction

In recent years, dyes are used widely in many industries such as textiles, paper, printing, and cosmetics. Besides the economic benefits, these industries release a large amount of highly toxic dyes in wastewater every year, most of which have negative effects on human and animal health. Various techniques such as adsorption [1–4], catalysis [5, 6], electrochemical oxidation [7], ozonation [8], membrane filtration [9], biological treatment [10], and enzymes [11] have been used to remove the dye components from polluted wastewater. Phenol red is a fabric dye and if we are exposed to the dye, it will affect the respiratory system and human skin [12]. Therefore, many research studies focus on the preparation of adsorbents or redox agents for the removal of

phenol red. Actually, oxidation and adsorption are the two main methods for the removal of phenol red. In recent reports on the first method, advanced oxidation processes have received the most attention [14–16]. For the second one, Abdullah et al. [13] prepared composite silica-filled ENR/PVC beads for phenol red adsorption. The results showed that the maximal adsorption capacity is 2.67 mg·g⁻¹. Iqbal et al. [14] found that the phenol red adsorption process on activated carbon materials was spontaneous with increasing entropy. The kinetic and thermodynamic studies of the phenol red adsorption on bottom ash and deoiled soya were investigated very specifically by Mittal et al. [12]. The highest monolayer adsorption capacity has been obtained for the phenol red-bottom ash system (2.6×10^{-5} mol·g⁻¹) at 50°C. Recently, many researchers have been using natural

materials like bentonite and modified bentonite for the removal of phenol and other dyes [15–26]. Organo-bentonites have been formed by introducing organic cations into bentonite layers. The purpose of organic bentonite synthesis is to create hydrophobic materials from hydrophilic form, so that they can be used as sorbents for hydrophobic organic compounds. Meanwhile, the inorganic bentonites with hydrophilic surfaces are suitable for adsorbing heavy metals. Thus, simultaneously inserting both metal ions and organic substances into bentonite, a new material is created named inorganic-organic bentonite. Because of the novel properties of the inorganic-organic bentonite, their structural characteristics have drawn great interest in recent years. Intercalation methods, intercalation agents, and bentonite/organic compound/inorganic compound ratios will affect the structures of inorganic-organic bentonite. To date, few studies have clarified the adsorption of the dyes onto organic bentonite and inorganic-organic bentonite.

In the work, the synthesis of CTAB–bentonite, Al–CTAB–bentonite, and Fe–CTAB–bentonite and phenol red adsorption are demonstrated. The kinetics, isotherms, thermodynamics, and the mechanism of phenol red adsorption process on modified bentonite materials are addressed.

2. Experimental

2.1. Materials. Bentonite supplied from TT-Hue Mineral Company, Vietnam, was purified (denoted as B) with chemical composition SiO_2 69.1, Al_2O_3 18.7, Fe_2O_3 4.4, TiO_2 0.37, MgO 4.19, CaO 2.93, K_2O 0.25, and Na_2O 0.07 (mass %). Cetyltrimethylammonium bromide (CTAB) (Merck), phenol red ($\text{C}_{19}\text{H}_{14}\text{O}_5\text{S}$, Merck), aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, Guangzhou, 99%), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Guangzhou, 99%), and silver nitrate (AgNO_3 , Guangzhou) were used in this study.

2.2. Preparation of CTAB-Modified Bentonite and Fe-CTAB-Modified and Al-CTAB-Modified Bentonites. The CTAB bentonite was synthesized as follows: 1.0 g of the purified bentonite (B) in 100 mL distilled water was stirred for 1 h. The 100 mL solution containing 0.8 g of CTAB was dissolved completely by vigorous stirring for 1 h and then was dropped slowly into the bentonite dispersion. The mixture was stirred with a magnetic stirrer for 4 h at 50°C. The obtained mixture was kept at 60°C for 20 h. The modified bentonite was washed many times with deionized water, dried at 100°C for 5 h, and then ground into the powder. The obtained CTAB–bentonite was denoted as CB.

The synthesis of Fe–CTAB–bentonite was carried by the following steps. Firstly, the Fe pillaring solution was prepared from the mixture of 100 mL 0.1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution, and 30 mL 0.1 M NaOH ($\text{OH}^-/\text{Fe}^{3+}$ molar ratio = 0.3). Then, it was stirred for 2 h and kept at room temperature for 24 h. Secondly, the 1% CB suspension was prepared by dispersing 1 g of CB in 1 L of deionized water. Then, the Fe pillaring solution prepared above was dropped

slowly into the CB suspension. The mixture was stirred for 24 h at room temperature. The resultant solid was separated by centrifugation and dried at 100°C for 10 h to obtain the Fe–CTAB–bentonite (denoted as FeCB).

The Al–CTAB–bentonite was synthesized in the same manner, except for the pillaring solution which was prepared by adding drop by drop 200 mL of 0.1 M NaOH solution to 100 mL 0.1 M AlCl_3 solution. This resultant pillaring bentonite suspension was stirred for 7 h at 70°C and then kept at room temperature for 24 h. The Al–CTAB–bentonite solid was separated by centrifugation, dried at 100°C, and denoted as AlCB.

2.3. Characterization. The purified and modified bentonites were studied by X-ray diffraction (XRD, D8-Advance Brucker, Germany with $\lambda_{\text{CuK}\alpha} = 1.5406 \text{ \AA}$). The thermal curves of the products were obtained in a DTG–60H (Shimadzu). Fourier transform infrared spectra (FT-IR) using KBr pressed disk technique were gained on SHIMADZU FT-IR 8010M. Nitrogen adsorption-desorption isotherms were measured on Tri Star 3000. The samples were outgassed for 5 h at 250°C in the degas port of the instrument. The specific surface areas were calculated using the BET model. SEM images were taken by scanning electron microscopy (Hitachi, S–4500). The point of zero charge values (pH_{PZC}) of the samples were calculated by the pH drift method.

2.4. Adsorption Experiments

2.4.1. Effect of pH. The phenol red adsorption of modified bentonites was carried out in a batch system. An exact amount (0.05 g) of modified bentonite was placed into the 100 mL flask containing 50 mL of $100 \text{ mg} \cdot \text{L}^{-1}$ phenol red solution. The pH solution was adjusted from 2 to 10 by adding amounts of 0.01 M NaOH or 0.01 M HCl, and the flasks were stirred by a magnetic stirrer for 6 h at room temperature (30°C) to reach equilibrium. After equilibrium, the supernatant was collected, and the concentration of phenol red was analyzed by UV-Vis method at $\lambda_{\text{max}} = 435 \text{ nm}$.

The adsorption uptake of phenol red by the adsorbent was calculated by using

$$q_t = \frac{C_o - C_t}{m} \cdot V, \quad (1)$$

where q_t is the adsorption uptake of phenol red on the adsorbent at time t , C_o and C_t ($\text{mg} \cdot \text{L}^{-1}$) are the phenol red concentration at the initial time and a certain time, t , respectively, V (L) is the volume of phenol red solution, and m (g) is the mass of the adsorbent.

2.4.2. Adsorption Kinetics and Thermodynamics Studies. A measured amount (0.2 grams) of the adsorbent (B, CB, AlCB, or FeCB) was added to 250 mL of $100 \text{ mg} \cdot \text{L}^{-1}$ phenol red at pH 3.0. The mixture was stirred by a magnetic stirrer at different temperatures (20, 30, 40, and 50°C). This suspension was then centrifuged after a particular time interval,

and the phenol red concentration in the supernatant was measured by UV-Vis spectroscopy.

Kinetic data were applied to pseudo-first/second-order kinetic models [27]. The pseudo-first-order model is given by

$$\ln(q_e - q_t) = \ln(q_e - k_1) \cdot t, \quad (2)$$

where q_e and q_t are the phenol red uptake of adsorbent at equilibrium, and at time t ($\text{mg}\cdot\text{g}^{-1}$), k_1 is the first-order rate constant (min^{-1}).

The pseudo-second-order kinetic model is given by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t, \quad (3)$$

where k_2 is the rate constant of the pseudo-second-order kinetic model ($\text{g}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$).

2.4.3. Equilibrium Adsorption Studies. In equilibrium experiments, 0.05 g of adsorbent was added to 50 mL of phenol red solution with different concentrations (20, 40, 50, 60, 70, 80, 90, and 100 $\text{mg}\cdot\text{L}^{-1}$) at initial pH 3.0. The equilibrium adsorption experiments were performed for 24 h at different temperatures of 10°C, 20°C, and 30°C.

Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models were employed to analyze the equilibrium adsorption data. The Langmuir isotherm [27] can be expressed as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \cdot q_m}, \quad (4)$$

where C_e is the equilibrium concentration of adsorbate in the solution ($\text{mg}\cdot\text{g}^{-1}$), q_m is the monolayer maximum adsorption uptake of the adsorbent ($\text{mg}\cdot\text{g}^{-1}$), and K_L is the Langmuir constant ($\text{L}\cdot\text{mg}^{-1}$) which is related to the energy of adsorption, respectively. The other parameters were described above. q_m and K_L can be calculated from the intercept and slope of the linear plot of C_e/q_e versus C_e .

Additionally, the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor (R_L , also called equilibrium parameter) which is defined by the following expression:

$$R_L = \frac{1}{1 + K_L C_0}, \quad (5)$$

where C_0 ($\text{mg}\cdot\text{L}^{-1}$) is the initial dye concentration and K_L ($\text{L}\cdot\text{mg}^{-1}$) is the Langmuir constant.

Freundlich equation [27] is given as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (6)$$

where K_F and n are the Freundlich constants. These constants can be calculated from the slope and intercept of the linear plot of $\ln q_e$ versus $\ln C_e$.

The linear form of the Dubinin–Radushkevich isotherm [28] is given by

$$\ln q_e = \ln q_t - \beta \varepsilon^2, \quad (7)$$

where the constant β is related to the mean free energy E ($\text{kJ}\cdot\text{mol}^{-1}$) of adsorption per molecule of the adsorbate when it is moved to the surface of the solid from the solution ($\text{mol}^2\cdot\text{J}^{-2}$) and ε is the Polanyi potential which can be calculated by

$$\varepsilon = RT \ln \left[1 + \left(\frac{1}{C_e} \right) \right]. \quad (8)$$

The mean free energy can be computed by using the following relation:

$$E = \frac{1}{(2\beta)^{(1/2)}}. \quad (9)$$

The thermodynamic parameters including the standard free-energy changes of Gibbs, ΔG° , standard enthalpy changes, ΔH° , and standard entropy changes, ΔS° , were also studied to better understand the adsorption mechanism. The ΔG° was calculated based on

$$\Delta G^\circ = -RT \ln K_L. \quad (10)$$

$$\ln K_L = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \quad (11)$$

The values of ΔH° and ΔS° can be calculated from the slope and intercept of the linear plot of $\ln K_L$ versus $1/T$.

3. Results and Discussion

3.1. Characterization of the Adsorbents. Basal spacing is one of the most important factors reflecting the structural characteristics of the modified layered clays. XRD was employed to characterize the layer structures of the intercalated bentonite in this study. The XRD patterns of B, CB, AlCB, and FeCB are shown in Figure 1.

The purified bentonite (B) exhibits the characteristic peaks of the montmorillonite according to JCPDS No. 00-003-0014. The changes of basal spacing of the modified bentonite can reflect the intercalations of CTAB, hydroxy-Al, and hydroxy-Fe cations into bentonite interlayer spaces. The bentonite (B) had a basal spacing (d_{001}) of 1.44 nm. For the CB, the (001) reflection was observed at a lower angle, corresponding to a larger basal spacing $d_{001} = 1.81$ nm, which indicated that the CTAB intercalated into bentonite interlayer spaces. As reported by Hu et al. [29], the height of alkyl chain was about from 0.40 to 0.45 nm, and the value of 1.81 nm approximated to the sum of the height of the two alkyl chains and the bentonite thickness (0.96 nm), indicating that the alkyl chains took the arrangement of a bilayer in the interlayer. For AlCB, the peak in the pattern shifted to a smaller value of 2θ , and the corresponding basal spacing was 1.99 nm, which was larger than that of CB. This indicated that hydroxy-Al ($[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, Al_{13}) could be intercalated and expand the interlayers of CB even when the “channels and grooves” between bentonite layers were occupied by CTAB (or CTA^+ cations). For FeCB, there was also change in d_{001} basal spacing ($d_{001} = 1.82$ nm) indicating that polyhydroxy-Fe or polyoxo-Fe cations ($[\text{Fe}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$) intercalated into bentonite

FIGURE 1: XRD patterns of B (bentonite), CB (CTAB-bentonite), AlCB (Al-CTAB bentonite), and FeCB (Al-CTAB bentonite).

interlayer spaces [30], and there was an ion exchange between the intercalated surfactant cations and the polyhydroxy-Fe or polyoxo-Fe cations. It is notable that the (001) reflections of all modified bentonites were more intensive than that of purified bentonite (B), suggesting that these materials had better crystallinity than that of B sample. This might explain that when inserting CTA^+ cations into bentonite, CTAB acted as an ion exchanger with hydrated cation localized in the interlayer spaces of bentonite and promoted the rearrangement of the clay layers (Figure 2), so the material structure obtained was highly orderly, shown in sharp reflection (001) peaks. In other words, CTAB had “assembled” small bentonite particles into larger particles with an orderly structure due to the connection between CTAB particles with negatively charged edges of small bentonite particles.

FT-IR has been widely used for the characterization of the modified bentonite. FT-IR spectra between 4000 and 400 cm^{-1} for B, CB, AlCB, and FeCB are presented in Figure 3.

For B sample, the peak at 3414 cm^{-1} is related to the stretching vibration of the adsorbed water molecules [31], and the peak at 1638 cm^{-1} represented the deformation band ($\delta(\text{O-H})$). The peak at 964 cm^{-1} was due to Si-OH vibration [18], and the peak at 816 cm^{-1} corresponded to Fe-Fe-OH deformation vibration [32]. For organobentonite (CB), the new peaks at 2922 cm^{-1} and 2851 cm^{-1} were attributed to the antisymmetric and symmetric stretching vibrations of $-\text{CH}_2-$, respectively. The corresponding deformation modes of these groups were observed between 1470 and 1418 cm^{-1} [33]. The peak at 1488 cm^{-1} was assigned to the vibration of the quaternary amine functional group [33]. All of these vibration bands confirmed the modification of bentonite with CTAB. With the intercalation of CTAB, H_2O content was reduced with the replacement of the hydrated cations by CTAB, and the surface of bentonite was changed from hydrophilic to hydrophobic. This could be explained by a decrease in the intensity of peak at the 1635 cm^{-1} of the CB

sample. FT-IR spectra of organic-inorganic bentonite samples displayed a doublet at 2922 cm^{-1} and 2851 cm^{-1} with lower intensity compared with that of CB, indicating that some intercalated surfactants were exchanged by hydroxy-Al or hydroxy-Fe. For AlCB, a new peak appeared at 726 cm^{-1} with low intensity, and it corresponded to Al-O vibration in Al-OH, suggesting that Al_{13} cations were intercalated into the layers of bentonite.

TG and DTA curves of the samples are shown in Figure 4. The TG curves of B and modified bentonites samples showed mass loss below 200°C and above 600°C due to the vaporization of adsorbed water or interlayer water in bentonite and the dehydroxylation of the silicate layers, respectively. A mass loss attributed to the decomposition of the organic compounds on the CB was observed between 200 and 600°C (11.9%). The decomposition took place in several steps, which could be seen in the DTA curve (Figure 4(b)). The first strong DTA peak at 289.3°C corresponded to the decomposition of the organic compounds presented in CB, and the second small DTG peak at approximately 510°C was assigned to decompose the residuals of CTAB occluded inside capillaries of bentonite. The TG curves of AlCB and FeCB samples included the stages similar to those of CB. However, the two later mass losses of these samples were larger than those of CB (CB: $\Delta m_2 = 11.9\%$, $\Delta m_3 = 7.5\%$; AlCB: $\Delta m_2 = 29.9\%$, $\Delta m_3 = 9.3\%$; FeCB: $\Delta m_2 = 15.1\%$, $\Delta m_3 = 9.3\%$), suggesting that the stage in the range of the temperatures over 200°C could also be assigned to dehydration of hydroxy-Al or hydroxy-Fe cations.

The SEM micrographs of the materials are presented in Figure 5. The B sample consisted of small-sized clay particles and the particles presented face-face layer aggregations, which were classical arrangements for smectites. The morphology of CB consisted of clay sheets of a few micrometers in diameter, around which were smaller-sized particles, which were not observed in the original bentonite sample. The Fe-CTAB or Al-CTAB modified bentonite samples included sheets of several micrometers in size stacked on top of each other, showing that their layer structures were much clearer than those of the original B sample. In addition, the AlCB and FeCB samples showed less face to edge interactions, increasing the interactions face to face and gave consequently a more ordered morphology. This could be explained by the interaction between CTAB particles and hydroxyl-Al cations or between CTAB particles and hydroxyl-Fe cations inserted into bentonite, between these ions and bentonite layers, leading to the arrangement of the material mainly composed of bentonite layers (face-face).

The nitrogen adsorption and desorption isotherms of the B, CB, AlCB, and FeCB materials are shown in Figure 6. The isotherms were all of type IV in accordance with IUPAC classification. Particularly for the CB sample, it was found that this material hardly adsorbed N_2 molecules, and the adsorption/desorption branches of N_2 sorption isotherm overlapped each other. Table 1 shows that the specific surface area was strongly decreased after intercalating organic cations or both inorganic and organic cations into interlayer spaces of bentonite, from 114.44 (B) to $0.25\text{ m}^2\cdot\text{g}^{-1}$ (CB), $10.07\text{ m}^2\cdot\text{g}^{-1}$ (AlCB), and $16.56\text{ m}^2\cdot\text{g}^{-1}$ (FeCB). This could be

FIGURE 2: The schematic drawing for illustrating the role of CTAB.

FIGURE 3: FT-IR spectra of B, CB, AlCB, and FeCB.

explained that the large size of CTAB particles located in bentonite interlayer spaces or CTAB adsorbed at the outer surface of bentonite blocked the pathway of N_2 molecules. It could be argued that CTAB intercalated into the interlayers of bentonite (filling the micropores of about 5-6 Å) and CTAB could also be located on the outer surface (in the mesopores created between primary bentonite particles), which made the specific surface significantly reduced and the mesopores system wider. Therefore, the outside surface of bentonite would become hydrophobic and could not be able to receive large-sized hydrophobic molecules. Compared with B, the AlCB and FeCB samples had the larger specific surface area, suggesting that a part of the large organic cations was replaced by the inorganic cations of smaller size. In addition, it was found that the organic-inorganic bentonite samples contained no micropores or the windows of micropores were closed, so N_2 molecules could not be able to access these spaces.

3.2. Adsorption Studies

3.2.1. Effect of pH. The pH is one of the most important factors affecting the adsorption capacity of phenol red on modified bentonite surface. The change of pH affects the dissociation of functional groups on the adsorbent and then affects its affinity to adsorbate. The pH effect on the adsorption of phenol red on the modified bentonites is shown in Figure 7.

As shown in Figure 7, the phenol red absorption on the CB sample was generally less affected by pH than that on the AlCB and FeCB samples. The amount of the adsorbed phenol red increased slightly in the range of pH from 2.0 to 3.0 and then decreased slightly from 3.0 to 9.0. For AlCB and FeCB samples, the red phenol absorption had a similar trend: a maximum absorption at pH 3.0 and a remarkable decrease of adsorption capacity were observed when increasing pH from 3.0 to 9.0. This could be explained by electrostatic interactions between phenol red and adsorbents. In aqueous solution, phenol red exists in different forms of $H_2^+PS^-$, HPS^- , and PS^{2-} depending on the pH of the solution (Scheme 1).

Thus, in any environment, the red phenol also contains a group of sulfate with a negative charge. The pH_{PZC} of CB, AlCB, and FeCB samples determined by the pH drift method was found to be 7.1, 6.3, and 5.8, respectively, so at $pH < pH_{PZC}$, the modified bentonite surface was positively charged which was favorable for the adsorption of phenol red by electrostatic interaction. However, at a $pH > pH_{PZC}$, the modified clay surface was negatively charged, causing a repulsion force between bentonite surface and the phenol red as well as OH^- anion (hydroxyl ions and phenol red could compete for adsorption at high pH), resulting in the decrease of the adsorption capacity when pH increased. In addition, due to the presence of CTAB in bentonite, phenol red adsorption on modified bentonite was also conducted by ligand exchange, but this process did not involve a change

FIGURE 4: TG and DTA curves of (a) B, (b) CB, (c) AlCB, and (d) FeCB.

in pH (this was verified experimentally): $\text{CTA}^+ - \text{Br}^- + \text{HPS}^- \longrightarrow \text{CTA}^+ - \text{HPS}^- + \text{Br}^-$

In short, the reduction of phenol red adsorption over the pH range could be related to two possible mechanisms: electrostatic interaction and chemical reaction between modified bentonites and phenol red. From this result, the optimum pH 3.0 for red phenol adsorption on modified bentonite samples was chosen for further studies.

3.2.2. Adsorption Kinetics. The kinetics data obtained at different temperatures using the *pseudo*-first and *pseudo*-second kinetic models are presented in Figures 8–10.

Parameters of the *pseudo*-first-order and *pseudo*-second-order kinetic model are listed in Table 2.

Based on the value of R^2 and the difference of q_e calculated by two models compared with the empirical q_e , it was found that *pseudo*-second-order model showed better goodness of fit to the experimental data than the *pseudo*-first-order model. Similar results were reported for the phenol red on bottom ash and deoiled soya [12]. From Table 2, it can be seen that the k_2 value increased with the

temperature for all three samples (CB: $0.778 \cdot 10^{-3}$ – $1.524 \cdot 10^{-3} \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$, AlCB: $0.73 \cdot 10^{-3}$ – $2.53 \cdot 10^{-3} \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$, FeCB: $4.1 \cdot 10^{-3}$ – $6.53 \cdot 10^{-3} \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). Under the same conditions, the phenol red adsorption rate on FeCB sample was faster than that on other samples. The interesting result of the simultaneous insertion of organic and inorganic species into bentonite was that the adsorption capacity of phenol red was reduced, but the adsorption rate increased compared to those of bentonite intercalated by organic cations. The phenol red has a molecular size of about 15 Å, so the phenol red adsorption had to occur in the mesopores of materials (~several hundred Å) and could not occur between the smectite layers (~5–10 Å). The values of k_2 of all modified bentonite samples were the same order (10^{-3}), which suggested that the phenol red adsorbed mainly at the outer surface and in the capillaries created between the primary particles.

The values of rate constants from the *pseudo*-second-order model can be used to calculate the activation energy of the sorption process by the Arrhenius equation. Figure 11 depicts the Arrhenius plots of phenol red adsorption onto CB, AlCB, and FeCB.

FIGURE 5: SEM micrographs of B (a), CB (b), AlCB (c), and FeCB (d).

FIGURE 6: N₂ adsorption-desorption isotherms of B, CB, AlCB, and FeCB.

TABLE 1: Textural parameters of B, CB, AlCB, and FeCB samples.				
Sample	S_{BET} (m ² ·g ⁻¹)	S_{micro} (m ² ·g ⁻¹)	S_{ext} (m ² ·g ⁻¹)	V_{total} (cm ³ ·g ⁻¹)
B	114.44	44.72	69.72	0.187
CB	0.25	0.22	0.03	0.002
AlCB	10.07	—	—	0.110
FeCB	16.56	—	—	0.072

FIGURE 7: Effect of pH on the adsorption uptake of phenol red onto CB, AlCB, and FeCB samples (C_o (phenol red) = 100 mg L^{-1} , $T = 303$, $K m = 0.05 \text{ g t} = 6 \text{ h}$).

SCHEME 1: Different forms of phenol red.

FIGURE 8: (a) The pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model of phenol red adsorption by CB at different temperatures (C_o (phenol red) = 100 mg L^{-1} , pH 3.0, $m = 0.2 \text{ g}$).

FIGURE 9: (a) The *pseudo*-first-order kinetic model and (b) *pseudo*-second-order kinetic model of phenol red adsorption by AlCB at different temperatures ($C_{o(\text{phenol red})} = 100 \text{ mg L}^{-1}$, pH 3.0, $m = 0.2 \text{ g}$).

FIGURE 10: (a) The *pseudo*-first-order kinetic model and (b) *pseudo*-second-order kinetic model of phenol red adsorption by FeCB at different temperatures ($C_{o(\text{phenol red})} = 100 \text{ mg L}^{-1}$, pH 3.0, $m = 0.2 \text{ g}$).

The values of the activation energy were found to be $17.82 \text{ kJ}\cdot\text{mol}^{-1}$, $33.87 \text{ kJ}\cdot\text{mol}^{-1}$, and $17.52 \text{ kJ}\cdot\text{mol}^{-1}$ for the phenol red adsorption onto CB, AlCB, and FeCB, respectively. The magnitude of activation energy can give information if the adsorption process is physical or chemical. The value of E_a was not large, indicating that phenol red adsorption on the three investigated materials was mainly physical adsorption (due to electrostatic interaction) as analyzed above. Comparing the E_a values of phenol red adsorption on the three materials, the E_a value of AlCB material was the highest. This suggested that phenol red

adsorption on CB and FeCB materials was more advantageous in terms of energy than that on AlCB material.

3.2.3. Adsorption Isotherms. The mechanism of adsorption reactions could be determined by evaluating the equilibrium data obtained from the experiments. The experimental data plotted with the Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models are shown in Figures 12–14. The estimated adsorption constants with the correlation coefficient obtained from the isotherms are listed in Table 3.

TABLE 2: Parameters of pseudo-first-order and pseudo-second-order kinetic model of phenol red adsorption by CB, AlCB, and FeCB at different temperatures.

Adsorbents	T (K)	q_e (experimental) (mg·g ⁻¹)	First-order kinetic model			Second-order kinetic model		
			k_1 (min ⁻¹)	q_e (cal) (mg·g ⁻¹)	R^2	k_2 (g·mg ⁻¹ ·min ⁻¹)	q_e (cal) (mg·g ⁻¹)	R^2
CB	293	112.53	0.062	112.62	0.994	$0.778 \cdot 10^{-3}$	132.86	0.999
	303	114.38	0.082	136.32	0.987	$0.925 \cdot 10^{-3}$	140.86	0.997
	313	114.65	0.073	67.97	0.945	$1.043 \cdot 10^{-3}$	142.86	0.997
	323	115.54	0.045	52.61	0.940	$1.524 \cdot 10^{-3}$	125.00	0.999
AlCB	293	105.39	0.035	67.83	0.996	$0.730 \cdot 10^{-3}$	125.00	0.998
	303	105.65	0.034	61.19	0.964	$1.09 \cdot 10^{-3}$	110.12	0.997
	313	105.69	0.033	37.98	0.907	$1.93 \cdot 10^{-3}$	111.10	0.999
	323	107.34	0.047	39.69	0.844	$2.53 \cdot 10^{-3}$	111.50	0.999
FeCB	293	66.20	0.029	17.01	0.968	$4.10 \cdot 10^{-3}$	70.20	0.998
	303	66.79	0.033	16.44	0.954	$5.00 \cdot 10^{-3}$	71.23	0.999
	313	67.61	0.035	14.56	0.882	$6.53 \cdot 10^{-3}$	71.43	0.998

FIGURE 11: Arrhenius plots of phenol red adsorption onto CB, AlCB, and FeCB.

FIGURE 12: (a) Plots of Langmuir, (b) Freundlich, and (c) Dubinin-Radushkevich isotherms in linear form for the adsorption of phenol red onto CB at different temperatures.

FIGURE 13: (a) Plots of Langmuir, (b) Freundlich, and (c) Dubinin–Radushkevich isotherms in linear form for the adsorption of phenol red onto AlCB at different temperatures.

FIGURE 14: (a) Plots of Langmuir, (b) Freundlich, and (c) Dubinin–Radushkevich isotherms in linear form for the adsorption of phenol red onto FeCB at different temperatures.

In terms of the correlation coefficient R^2 values, the experimental data could be well fitted to the Langmuir isotherm model rather than the Freundlich and D-R models at all investigated temperatures, indicating that the adsorption process occurred on the surface of modified bentonites. The calculated values of R_L were found to be between 0 and 1, indicating that the adsorption of phenol red onto CB, AlCB, and FeCB samples was favorable. At the same conditions, the value of $q_{\max}$ calculated from the Langmuir equation of all samples decreases in the order of CB, AlCB, and FeCB in the temperature range 20–40°C. The maximum phenol red adsorption capacities ($q_{\max}$) at 30°C (room temperature) are 166.7 mg·g⁻¹ for CB, 125.0 mg·g⁻¹ for AlCB, and 100 mg·g⁻¹ for FeCB. It is known that the specific surface area of CB was smaller but its adsorption capacity is

higher than that of other two materials. This suggested that the presence of hydroxy–Al and hydroxy–Fe cations in CTAB-bentonite reduced the phenol red adsorption capacity of this material. In addition, the K_L value at the same temperature on three investigated materials was different illustrating that active sites on these three materials were different. In comparison with previous studies [25, 26], the phenol adsorption capacity of organobentonite was higher than phenol red adsorption capacity of CTAB-bentonite in this study; this could be explained by the fact that the size of phenol was smaller than that of phenol red, so it was more easily diffused into the capillary than phenol red. However, it is notable that the present adsorbents exhibit much higher adsorption capacity compared with those of adsorbents for phenol red reported previously, suggesting that modified

TABLE 3: The parameters of isotherm models in linear form for the adsorption of phenol red onto the modified bentonite.

CB									
T (K)	Langmuir model			Freundlich model				D-R model	
	q_m (mg·g ⁻¹)	K_L (L·mg ⁻¹)	R^2	R_L	K_F (mg·g ⁻¹)	n	R^2	E (kJ·mol ⁻¹)	R^2
293	156.3	0.185	0.964	0.211–0.752	49.95	3.01	0.808	13.95	0.932
303	166.7	0.278	0.983	0.167–0.782	93.04	8.19	0.784	15.97	0.952
313	169.4	0.625	0.998	0.098–0.535	80.16	4.22	0.897	17.86	0.913
AlCB									
T (K)	Langmuir model			Freundlich model				D-R model	
	q_m (mg·g ⁻¹)	K_L (L·mg ⁻¹)	R^2	R_L	K_F (mg·g ⁻¹)	n	R^2	E (kJ·mol ⁻¹)	R^2
293	71.4	0.23	0.979	0.316–0.725	30.60	1.93	0.969	11.46	0.974
303	125.0	0.62	0.959	0.017–0.040	46.99	2.58	0.787	14.11	0.943
313	142.9	0.82	0.956	0.111–0.373	35.91	4.59	0.701	18.74	0.695
FeCB									
T (K)	Langmuir model			Freundlich model				D-R model	
	q_m (mg·g ⁻¹)	K_L (L·mg ⁻¹)	R^2	R_L	K_F (mg·g ⁻¹)	n	R^2	E (kJ·mol ⁻¹)	R^2
293	90.9	0.77	0.996	0.073–0.191	55.31	6.45	0.885	21.83	0.969
303	100.0	0.61	0.987	0.028–0.313	31.12	2.90	0.856	13.62	0.868
313	110.1	0.56	0.993	0.040–0.400	51.42	5.46	0.810	21.71	0.998

TABLE 4: Comparison of the adsorption capacity for various adsorbents in phenol red removal that confirm their applicability and suggest their attractive candidates for dye removal.

Adsorbents	Maximum monolayer adsorption uptakes (mg·g ⁻¹)	Ref.
Bottom ash	7.4	[12]
Deoiled soya	5.3	[12]
Silica-filled ENR/PVC beads	2.6	[13]
Activated charcoal	0.04	[14]
Barley husk-derived activated carbon	6.76	[34]
TiO ₂ -NPs-ACWR	55.6	[35]
PAC	43.9	[36]
ZnS: Cu-NPs-PAC	196.0	[36]
CB	166.7	This work
AlCB	125.0	This work
FeCB	100.0	This work

FIGURE 15: Plot of $\ln K_L$ versus $1/T$.

TABLE 5: Thermodynamic parameters for the phenol red adsorption onto CB, AlCB, and FeCB.

T (K)	CB			AlCB			FeCB		
	ΔG° (kJ·mol ⁻¹)	ΔH° (kJ·mol ⁻¹)	ΔS° (kJ·mol ⁻¹ ·K ⁻¹)	ΔG° (kJ·mol ⁻¹)	ΔH° (kJ·mol ⁻¹)	ΔS° (kJ·mol ⁻¹ ·K ⁻¹)	ΔG° (kJ·mol ⁻¹)	ΔH° (kJ·mol ⁻¹)	ΔS° (kJ·mol ⁻¹ ·K ⁻¹)
293	-27.02	26.21	0.249	-27.58	48.36	0.261	-29.70	12.34	0.144
303	-28.97			-30.97			-30.95		
313	-32.03			-32.75			-32.57		

bentonite materials are attractive candidates for dye removal. Table 4 presents the absorption capacities based on the Langmuir model of some adsorbents.

3.2.4. Thermodynamics Studies. The plot of $\ln K_L$ versus $1/T$ for the determination of thermodynamic parameters is depicted in Figure 15 and the thermodynamic parameters are listed in Table 5.

The negative values of ΔG° at different temperatures indicated the feasibility of the process and the spontaneous nature of the adsorption. The positive ΔH° values indicated that the adsorption of phenol red onto CTAB-bentonite and Fe- or Al-CTAB bentonites was endothermic. Furthermore, a higher positive ΔS° of phenol red adsorption process clearly stated that the randomness increased the modified bentonite-solution interface during adsorption. This result suggested that the phenol red adsorption onto three investigated materials was promoted by entropy than by enthalpy.

4. Conclusions

The synthesis of CTAB-bentonite, Al-CTAB-bentonite, and Fe-CTAB-bentonite by ion exchange was demonstrated. It was found that the CTAB, hydroxy-Al, and hydroxy-Fe cations were intercalated into the interlayer spaces of bentonite leading to an increase in the basal spacing d_{001} . Among the investigated materials, CTAB-bentonite exhibited the highest monolayer adsorption capacity at the temperature of 30°C (166.7 mg·g⁻¹), followed by Al-CTAB-bentonite (125.0 mg·g⁻¹) and Fe-CTAB-bentonite (100 mg·g⁻¹). Introduction of hydroxy-Al and hydroxy-Fe cations into CTAB-bentonite clearly reduced the phenol red adsorption capacity of this material. Phenol red adsorption agreed well with the *pseudo*-second-order kinetic model in all the investigated temperature ranges. The results of activation energy calculation showed that phenol red adsorption on CTAB-bentonite and Fe-CTAB-bentonite materials was more advantageous in terms of energy than that on Al-CTAB-bentonite. The negative values of ΔG° indicated that the adsorption was spontaneous whereas the positive values of ΔH° and ΔS° indicated the endothermic nature and increase in randomness of the adsorption, respectively. From these studies, organic and organic-inorganic bentonite materials could be used as an effective adsorbent for the removal of dyes from aqueous solution.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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