Simultaneous removal of phenol and Cu(II) from wastewater by tallow dihydroxyethyl betaine modified bentonite

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Abstract: An organobentonite modified with an amphoteric surfactant, tallow dihydroxyethyl betaine (TDHEB), was used as an adsorbent to simultaneously remove Cu(II) and phenol from wastewater. The characteristic of the organobentonite (named TDHEB-bentonite) was analyzed by X-ray diffraction, Fourier-transform infrared spectra and nitrogen adsorption-desorption isotherm. Batch tests were conducted to evaluate the adsorption capacities of TDHEB-bentonite for the two contaminants. Experiment results demonstrated that the adsorption of both contaminants is highly pH-dependent under acidic conditions. TDHEB-bentonite had about 2.0 and 5.0 times higher adsorption capacity toward Cu(II) and phenol, respectively, relative to the corresponding raw Na-bentonite. Adsorption isotherm data showed that the adsorption processes of both contaminants were well described by Freundlich model. Kinetic experiment demonstrated that both contaminants adsorption processes correlated well with pseudo-second-order model. Cu(II) had a negative impact on phenol adsorption, but not vice versa. Cu(II) was removed mainly through chelating with the organic groups ($-CH_2CH_2OH$ and $-COO-$) of TDHEB. Otherwise, partition into the organic phase derived from the adsorbed surfactant was the primarily mechanism for phenol removal. Overall, TDHEB-bentonite was a promising adsorbent for removing Cu(II) and phenol simultaneously from wastewater.

Introduction

Copper ions (Cu(II)) and phenol are two of the most common pollutants found in waste water discharge from petroleum and petrochemical, leather tanneries, coal conversion and textile industries (Qu et al. 2020, Tri et al. 2020). Many investigations report the concentration of Cu(II) and phenol in various wastewater in the range of tenths to hundreds of mg/L. The US Environmental Protection Agency (USEPA) regulations call for lowering Cu(II) and phenol in the waste water to less than 13 µg/L and 1 mg/L, respectively (Banat et al. 2000, Pal et al. 2014). Both Cu(II) and phenol are harmful to plants, aquatic life and human bodies even at low concentrations. Therefore, the removal of Cu(II) and phenol from wastewater before they are discharged into environment systems is one of the major problems that have to be solved or controlled.

Several methods have been developed to remove Cu(II) and phenol from wastewater, and adsorption method is recognized as one of the most efficient methods on condition that suitable adsorbents are reasonably selected (Cao et al. 2019, Chen et al. 2020, Chu et al. 2020, Lee et al. 2017). Natural Na-bentonite, comprised predominantly of montmorillonite, is widely used as an adsorbent to remove Cu(II) from wastewater because

of its high abundance, low priced, and great cation exchange capacity (CEC) (Bhattacharyya and Gupta, 2008, Veli and Alyüz, 2007). However, its adsorption capacity for phenol is limited because of its hydrophilic mineral surfaces (Andrunik and Bajda 2019, Zhu et al. 2016). To improve the ability to remove phenol, natural Na-bentonite must be modified with cationic surfactants (mainly quaternary ammonium cation). These modification processes, however, can decrease the inherent heavy metal adsorption capacity of natural Na-bentonite (Ma .and Zhu, 2006, Yoo et al. 2004, Yu et al. 2017).

In order to simultaneous remove Cu(II) and phenol from wastewater, a bentonite that can simultaneously adsorb the two contaminants is urgently required. Bentonite amended with an amphoteric surface modifier may be a promising adsorbent. Ma et al (2016) employed an amphoteric modifier, namely hexadecyldimethyl ammonium, to modify bentonite and assessed the adsorption capacity towards to phenol and Cu(II), and found that the adsorption capacity of the amphoteric bentonite for phenol and Cu(II) was improved 5.58 times and 0.95 times, respectively. Ren et al (2020) synthesized a new type of amphoteric bentonite with dodecyl dimethyl betaine (BS-12, an amphoteric surfactant) and evaluated the adsorption capacity of it toward to phenol and Cd(II). They

found that the adsorption capacity of the amphoteric bentonite for phenol and Cd(II) was 10 times and 1.01 times higher than that of unmodified bentonite, respectively. Overall, the amphoteric bentonites reported in the previous studies have a super adsorption capacity toward to phenol; however, the adsorption capacity of them for heavy metals was similar to the unmodified bentonite.

In the present study, an organobentonite modified with an amphoteric surface modifier, namely tallow dihydroxyethyl betaine (TDHEB), was prepared and tested as an adsorbent to simultaneously remove Cu(II) and phenol from wastewater. The reason to selected TDHEB as the amphoteric surface modifier is that it has two hydroxyethyl groups ($-CH_2CH_2OH$), which can increase the surface hydrophilicity of the modified bentonite. Hence, the organobentonite modified with TDHEB may have a greater adsorption capacity toward Cu(II) than that reported in previous studies (Liu et al. 2016; Meng et al. 2008).

Material and methods

Materials
The raw bentonite used for this study was provided by Jilin Liufangzi Bentonite Technology Co. Ltd (Jilin, China). It is a natural and Na-enriched bentonite. The cation exchange capacity (CEC) of the sample was 64.87 meq/100 g. The bentonite sample was air dried, ground and sieved through 1.5 mm sieve. The amphoteric surfactant, namely tallow dihydroxyethyl betaine (TDHEB), was provided by Shanghai Gaoming Chemical Engineering Co. Ltd, having a chemical purity of 40%, and was used without further purification. TDHEB's structure is presented in Fig. 1. Phenol and heavy metal salts were provided by Tianjing Tianli Chemical Reagent Co. Ltd, and both of them are analytical grade. Other chemical materials used in the presented study are also analytical grade. Stock standard solutions of phenol (200 mg/L) and Cu(II) (500 mg/L) were prepared separately by dissolving commercial phenol or $CuSO_4$ in deionized water. The pH of both stock solutions was set at 5.0 by adding of 0.1 M HCl or 0.1 M NaOH solutions.

Synthesis of TDHEB-bentonite
The TDHEB-bentonite was synthesized according to the procedure outlined in Liu et al. (2016). A given amount of TDHEB was poured to 200 mL of distilled water, after which it was stirred at 45±2°C for 1.0 h. Then 10 g Na-bentonite

was mixed into the solution. The amounts of surfactant used were equal to the CEC of the raw Na-bentonite in order to make sure that there was a surfactant molecule for each cation exchangeable site. After that, the bentonite suspensions were stirred at 45±2°C for 6.0 h followed by centrifugation and washing 6 times with deionized water. Last, the collected product was dried at 60 ±2°C.

Characterization methods
X-ray diffraction (XRD) patterns of the raw bentonite and TDHEB-bentonite was recorded on a Rigaku Ultima-IV diffractometer. The Fourier transform-infrared (FTIR) spectra of the raw and modified bentonite were acquired by a Nicolet iS50 FTIR (Thermo Scientific) spectrophotometer with region from 4000 to 400 cm⁻¹. The surface areas and pore size distribution were determined by N_2 adsorption-desorption isotherms using a micrometrics ASAP 2460 volumetric adsorption analyzer.

Adsorption test
Adsorption study in single system
Batch adsorption experiments were used in this study because of their simplicity and time efficiency. A soil-to-solution ratio of 1 to 200 (1:200) by mass was used in all batch adsorption experiments, consisting of 0.1 g of bentonite (dry weight) and 20 mL of aqueous solutions at specified concentrations (5 g/L suspension). The ratio was selected to maximize the change in solute concentration resulted from adsorption, while allowing phase separation and complete mixing. The aqueous solution's pH was adjusted to the required values by adding 0.1 M HCl or 0.1 M NaOH solutions. All bentonite suspensions were placed on a rotary shaker at 35 rpm for a certain time at 25 ± 2°C.

The impact of pH on the adsorption capacity of TDHEB-bentonite was examined by varying solution's pH value (1.0–11.0). In these tests, the initial concentrations for phenol and Cu(II) were set at 100 and 300 mg/L, respectively. The bentonite suspensions were shaken for 6.0 h (sufficient for attaining chemical equilibrium) and were centrifuged at 10,000 rpm for 20 min. After centrifugation, the supernatant aliquots were collected and filtered through a 0.45 μm filter. Then, the Cu(II) and phenol concentrations in the supernatant aliquots were analyzed with atomic adsorption spectrometry and UV-visible spectrometry at λ = 301 nm, respectively.

To examine the impact of contact time on the adsorption capacity of TDHEB-bentonite, the adsorption time was
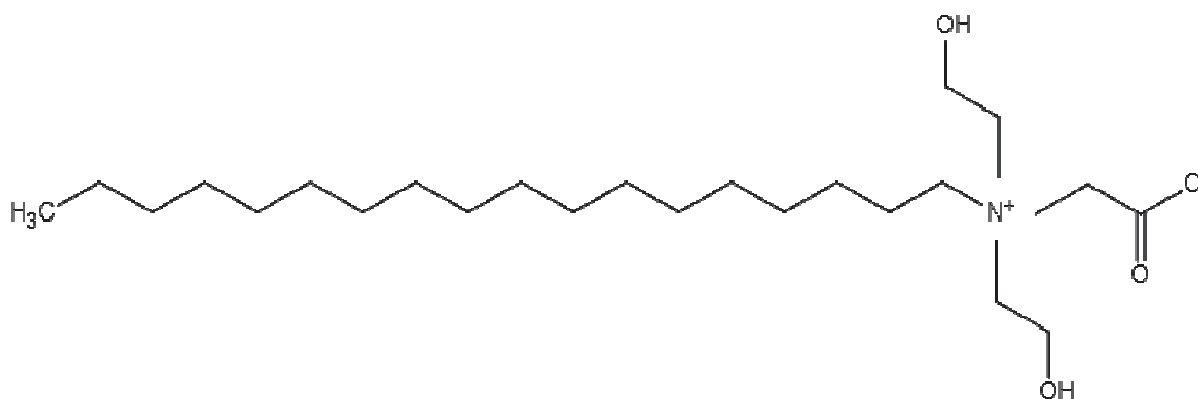

Fig. 1. Molecular structure of tallow dihydroxyethyl betaine (TDHEB)

controlled at 5, 10, 20, 30, 60, 90, 120, 180, 300, 600, and 1,200 min. In these experiments, the initial concentrations of Cu(II) and phenol in the aqueous solutions were fixed at 100 and 300 mg/L, respectively. The initial aqueous solution's pH was set at 5.0. This pH value was chosen to ensure that no Cu(II) precipitation occurred in aqueous solution. After the bentonite suspensions were shaken for an established contact time, they were separated by centrifuging. Then, the concentration of the two contaminants in the supernatant liquid was analyzed.

In the adsorption isotherms experiments, Cu(II) and phenol concentrations in the aqueous solution ranged from 5 to 600 mg/L and from 10 to 200 mg/L, respectively, which cover the typical ranges of Cu(II) and phenol concentration found in wastewater. Similar to the kinetic experiments, the initial pH of the aqueous solution was also fixed at 5.0. Then, the mixture samples were shaken in a rotary shaker for 6.0 h. Afterward, the bentonite suspensions were separated by centrifugation and the concentrations of Cu(II) and phenol in supernatant liquid were determined.

The amount of the two contaminants adsorbed onto bentonites can be calculated by:

$$q_e = \frac{(C_i - C_f)V}{W} \qquad (1)$$

where q_e is the amount of contaminant adsorbed onto bentonite (mg/g); C_i is the initial contaminant concentration before exposure to bentonite (mg/L); C_f is the final contaminant concentration after exposure to bentonite (mg/L); V is the solution volume (i.e. 20 mL); and W is the bentonite mass (i.e. 0.1 g).

Tests using raw bentonite as adsorbent were performed using the same method. A blank test without bentonites was conducted to investigate the possible loss of phenol and heavy metals other than adsorption to the sorbent.

Adsorption study in binary system

In the presented study, the simultaneous adsorption of the binary mixture of Cu(II) and phenol was also investigated because the two types of contaminants are simultaneously present in wastewater. In the binary systems, while evaluating the impact of Cu(II) on phenol adsorption, the concentration of phenol was fixed at 60 mg/L and the concentration of Cu(II) was adjusted from 10 to 300 mg/L. Whereas, in the binary systems, while examining the impact of phenol on Cu(II) adsorption, the Cu(II) concentration was set at 80 mg/L and the concentration of phenol was in the range of 10−150 mg/L. The aqueous solution's pH in the binary system also was fixed at 5.0 to be consistent with those used in the single systems and to prevent the Cu(II) precipitation from formation. All the tests were conducted in triplicate and the average values of the results were submitted for data analysis. All the spent adsorbents were properly stored in a compatible container.

Sorption of models
Kinetic models

In order to elucidate the possible mechanism that was responsible for the adsorption process, pseudo-first-order and pseudo-second-order models were employed to evaluate the uptake behavior of contaminants on bentonites (Nourmoradi et al. 2012). The two models:

$$Q_t = Q_e(1 - e^{-K_1 t}) \qquad (2)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e}t \qquad (3)$$

where Q_t (mg/g) and Q_e (mg/g) are the amount of contaminants adsorbed by bentonite at time t (min) and equilibrium, respectively; K_1 (/min) and K_2 (g/(mg min)) are the related rate constants of pseudo-first-order and pseudo-second-order, respectively.

Sorption isotherms models

To test the adsorption capacity of the modified bentonite and elucidate the mechanism controlling the adsorption behavior, the test result was described using Langmuir, Freundlich, Redlich-Peterson and linear isotherm models, as described by Eqs (4), (5), (6) and (7), respectively (Freundlich, 1906, Langmuir, 1918, Redlich and Peterson, 1959). Specifically, Cu(II) adsorption isotherm data was described using the Freundlich, Langmuir, and Redlich-Peterson isotherms; whereas, the experiment result for phenol was described using the Freundlich isotherm and linear model.

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \qquad (4)$$

$$Q_e = K_F C_e^{1/n} \qquad (5)$$

$$Q_e = \frac{K_1 C_e}{1 + K_2 C_e^p} \qquad (6)$$

$$Q_e = K_d C_e \qquad (7)$$

where Q_e=equilibrium adsorbed contaminants concentration, (mg/g); K_L = Langmuir constant, (L/mg); Q_m = maximum adsorbed concentration, mg/g; K_F and n are the constants of the Freundlich adsorption isotherm; K_1 and K_2 are Redlich-Peterson constants; p is the exponent which lies between 1 and 0; K_d=adsorption distribution coefficient (L/g); Q_m, K_F are related to adsorption capacity, and they are generally used to evaluate adsorption performance.

Results

Characterization

The XRD patterns of the raw bentonite and TDHEB-bentonite are shown in Fig 2. As presented in Fig. 2, the raw bentonite has a basal spacing of 1.28 nm, which is a characteristic value of natural Na-bentonite (Park et al. 2013, Wang et al. 2017). After modification with TDHEB, the basal spacing value increased to 2.14 nm. The expansion of basal spacing demonstrates that TDHEB molecules have been intercalated into the bentonite interlayer space and the modification was successful. The electrostatic attraction between positively changed head group of TDHEB molecules and negatively changed sites on bentonite is likely to be the main mechanism response for TDHEB

molecules intercalation (Liu et al. 2016, Meng et al. 2008). XRD measurements show that the raw Na-bentonite is mainly composed of montmorillonite, quartz, potassium feldspar and plagioclase; otherwise, the main mineral composition of the TDHEB-bentonite is montmorillonite, quartz, potassium feldspar and halite. Based on the result, the modification of TDHEB introduces some changes into the mineral composition of bentonite.

The FTIR spectra of raw bentonite and TDHEB-bentonite are illustrated in Fig. 3. Compared with the FTIR spectra of raw bentonite, the TDHEB-bentonite FTIR spectra had some new bands: 3015, 2926, 2857, 1468, 1425, 1380 and 1320 cm^{-1}. The peak near 3015 cm^{-1} may associate with the symmetric stretching of the CH_2-N in the surfactant (Taffarel and Rubio, 2010).

The two bands that appeared at 2926 cm^{-1} and 2857 cm^{-1} could be assigned to the symmetric and asymmetric stretching vibration of $-CH_2$ and $-CH_3$ in the aliphatic chain of the surfactant, respectively. The peak around 1468 cm^{-1} may arise from the symmetric scissoring of $-CH_2$ of the surfactant (Kong et al. 2019). The band at 1425cm^{-1} corresponds to asymmetric and symmetric stretching vibrations of the -COOH. The band around 1380 cm^{-1} is assigned to -OH bending vibration. Regarding the band at 1320 cm^{-1}, it may be the result of the stretching vibration of C-O in the surfactant. These observations (i.e. some new bands appeared) further verify that the surfactant has been interpolated into the Na-bentonite successfully. It is important to notice that these bands' intensities were greatly decreased in the FTIR spectrum of Cu(II) loaded TDHEB--bentonite and phenol loaded TDHEB-bentonite, indicating that the functional groups of the TDHEB-bentonite have been occupied by the two contaminants.

The specific surface areas of Na-bentonite and TDHEB--bentonite were calculated to be 36.05 m^2/g and 2.04 m^2/g, respectively. The average pore diameters of Na-bentonite and TDHEB-bentonite were 28.62 nm and 26.69 nm. The changes in specific surface areas and average pore diameter suggest that the pore structure of TDHEB-bentonite has been blocked by the surfactant molecules. The pH of the raw Na-bentonite and TDHEB-bentonite was 7.98 and 7.13, respectively. The

pH_{zpc} values of two bentonites were determined by plotting the zeta potential values of particulate suspension solutions versus pH (Fig. 4). As shown in Fig. 4, the pH_{zpc} value of TDHEB--bentonite is 5.2; otherwise, the zeta potential values of raw bentonite were constantly negative in the pH range (1.0–11.0) and there was no pH at which the zeta potential is zero.

Adsorption study in single system
Effect of pH on the Cu(II) adsorption

Since the speciation of contaminants, i.e., Cu(II) and phenol, and the surface charge of the TDHEB-bentonite are pH dependent, the sorption of both contaminants onto the modified bentonite vary with pH (Senturk et al. 2009). Fig. 4 shows that the adsorption capacity of the modified bentonite toward Cu(II) increased gradually with increasing pH from 1.0 to 5.0, and a sharp increase occurred when pH increased from 5.0 to 6.0. However, the adsorption capacity almost maintained constant as pH increased from 7.0 to 11.0. Similar results were also reported by Wang et al. (2017), where a dual-cation organomontmorillonite (i.e. modified with cysteamine hydrochloride and octadecyl trimethyl ammonium chloride) was used to adsorb Zn(II) and the adsorption capacity of it increased with increased pH and had a sharp increase when pH changed from 5.0 to 7.0.

The changes in the adsorption capacity of the modified bentonite toward Cu(II) could be a combination of the alteration in H^+ competition ability, the surface charges of modified bentonite, and the existence forms of Cu(II). With increasing pH, the H^+ concentration in the suspension decreased, thereby, the competition ability of H^+ for adsorption sites on the modified bentonite surface dropped (He et al. 2019, Zendelska et al. 2018). Thus, the dropping in H^+ competition ability would favor the modified bentonite adsorb Cu(II). In addition, as pH increased, the zeta potential of the modified bentonite continuously decreased and changed from positive to negative at pH of 5.2 (zero point charge) (Fig. 4).

Thus, as pH became greater than 5.2, there was an electrostatic attraction between the modified bentonite and Cu(II). This was why a higher Cu(II) adsorption capacity was observed as pH was higher than 5.2. The formation of
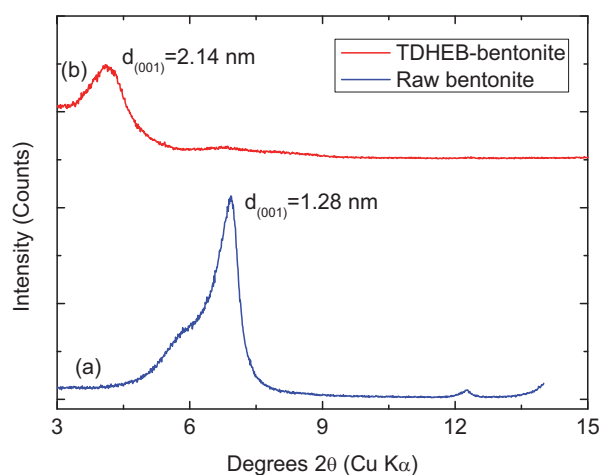

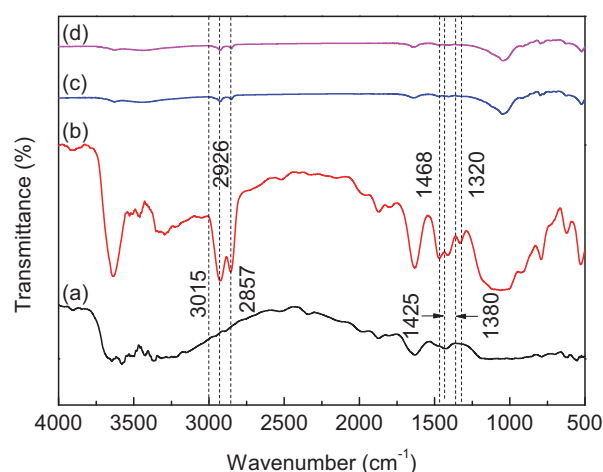
Fig. 2. XRD of (a) raw and (b) TDHEB-bentonite

Fig. 3. FTIR spectra of (a) raw bentonite, (b) TDHEB-bentonite, (c) Cu(II) loaded TDHEB−bentonite and (d) phenol loaded TDHEB−bentonite

hydroxyl complexes of Cu(II), such as $Cu_2(OH)_2^{2+}$, $Cu_2(OH)^{3+}$, $Cu_3(OH)_4^{2+}$, and $Cu(OH)^+$, may be responsible for the large increases in the adsorption capacity over the pH range of 5.0−6.0 (Fig. 5).

Fig. 6 shows the speciation of copper obtained using Visual MINTEQ (v. 3.0, maintained by Jon Petter Gustafsson at KTH, Sweden). The figure shows that when the solution pH was greater than 5.2, the fraction of hydroxyl complexes of Cu(II) increased with pH, whereas, the free Cu(II) ion concentration decreased. Similarly, Griffin and Shimp (1976) noted that the adsorption capacity of a natural montmorillonite for Pb(II) increased significantly when pH was higher than a certain value (i.e. pH = 6.0), and they proposed that the formation of hydroxyl Pb(II) species was the primary mechanism for the improvement of Pb(II) adsorption.

Effect of pH on the phenol adsorption

The impact of pH on the adsorption of phenol on the modified bentonite is illustrated in Fig. 7. The Fig. 7 shows that when pH ranged from 1.0 to 5.0, the adsorption capacity increased gradually as pH increased. The gradual increase in adsorption

capacity could be mainly related to the progressive decrease in the concentration of H+ with increased pH. As the H+ concentration decreased, the competition between H+ and surfactant decreased, which increased the surfactant density on the bentonite surface and the hydrophobicity of the bentonite. Thus, the adsorption capacity for the phenol increased.

Fig. 7 shows that there are no apparent changes in the adsorption capacity with increasing pH from 5.0 to 11.0. This result seems to contradict the results of Ma et al. (2016) and Senturk et al. (2009), where the organobentonite (or montmorillonite) had lower phenol adsorption capacity under alkaline condition (pH >9.96) than under acidic condition. The authors proposed that the drop in adsorption capacity may be the result of deprotonation of phenol (the *pKa* is 9.96 for phenol) and electrostatic repulsive force between the anionic forms of phenol and the increased negative charge of the modified bentonite. The uncommon adsorption behavior of the modified bentonite in the present study (i.e. the adsorption capacity for phenol did not decrease as the mixture pH became higher than 9.96) may be mostly attributed to the special structure of TDHEB, i.e., having two $-CH_2CH_2OH$ groups. Specifically, while the phenol
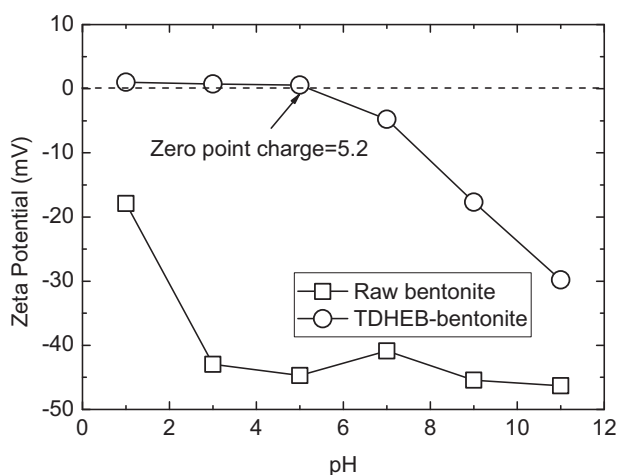

Fig. 4. Impact of pH on raw and TDHEB-bentonite zeta potential

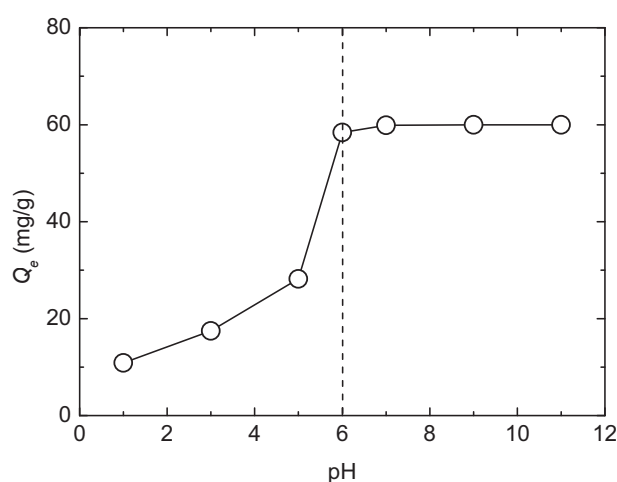**Fig. 5.** Impact of pH on the Cu(II) up take onto TDHEB-bentonite (C_{Cu}=300 mg/L, TDHEB-bentonite=5 g/L, *T*=25± 2°C)
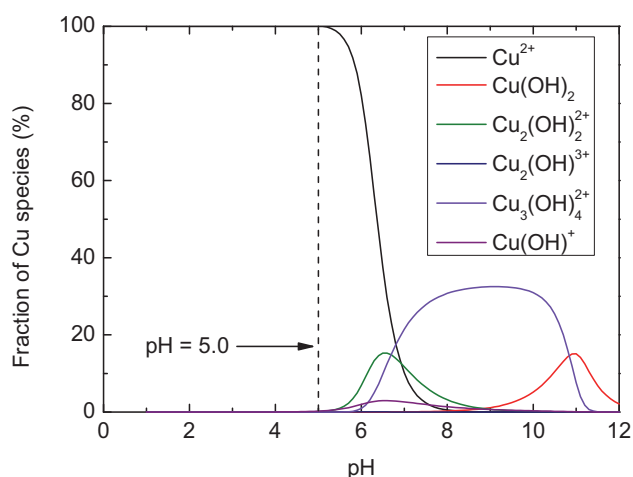

Fig. 6. I Impact of pH on the speciation of Cu(II) (calculated usingVisual Minteq)

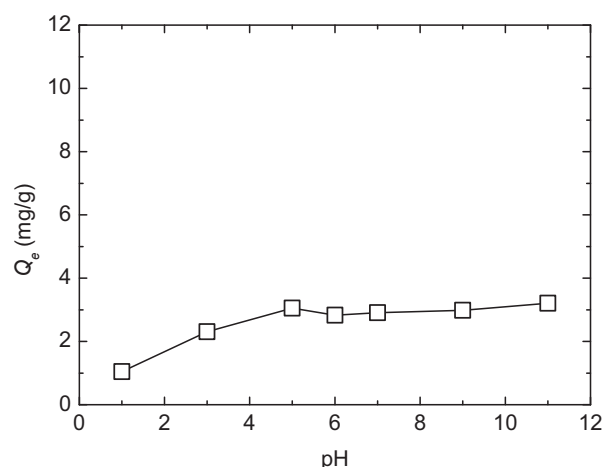**Fig. 7.** Impact of pH on the phenol adsorption onto TDHEB-bentonite (C_{phenol}=100.0 mg/L, bentonite=5.0 g/L, *T*=25± 2°C)

would deprotonate and exist as an anion ($C_6H_5O^-$) when pH was greater than 9.96, the $C_6H_5O^-$ ions would not go into solution (i.e. the concentration of it did not increase), because they would interact with the -CH_2CH_2OH groups through hydrogen bonding and then be adsorbed on the surface of the modified bentonite. As a result, no decrease in phenol adsorption was found under alkaline conditions in this study.

Effect of contact time on Cu(II) adsorption

The time course for Cu(II) adsorption on raw and TDHEB modified bentonites is presented in Fig. 8. As can be seen in Fig.8, the adsorption capacity of the TDHEB-bentonite for Cu(II) increased dramatically within 60 min, whereas, only a slight fluctuation was observed during the next time periods and equilibrium was obtained within 300 min. Similarly, the uptake of Cu(II) on raw bentonite was also completed during the same time range. This result shows that modification with TDHEB does not produce a negative impact on the adsorption rate of Cu(II). Moreover, according to the results presented in Fig. 8, the TDHEB-bentonite has a greater adsorption capacity relative to the corresponding raw bentonite. As the equilibrium can be completed in 300 min, to ensure equilibrium was achieved, 360 min was chosen as the optimum reaction time for subsequent batch tests in this study.

To understand the mechanism of Cu(II) adsorption, the transient behavior of Cu(II) was fitted to two well-known kinetic models: pseudo-first-order and pseudo-second-order models, as described by Eqs (2) and (3). The corresponding models fitting parameters are summarized in Table 1. From Table 1, it can be found that the pseudo-second-order model had a higher

correlation coefficients (R^2) compared to the pseudo-first--order model, which suggests that the former model was more suitable for describing the Cu(II)adsorption. The applicability of the pseudo-second-order model demonstrated that the Cu(II) adsorption on TDHEB-bentonite was predominated by chemical adsorption.

Effect of contact time on phenol adsorption

The adsorption of phenol on the two bentonites as function of time is presented in Fig. 9. For TDHEB-bentonite, the adsorption capacity increased significantly within 30 min and reached equilibrium within 300 min. Otherwise, with regard to raw bentonite, the fast sorption process lasted for about 90 min and got equilibrium during 300 min. This result shows that the modification with the surfactant improved the adsorption rate of the bentonite for phenol. The increase in adsorption rate could be attributed to the organic medium derived from the surfactant adsorbed on the modified bentonite. Since the equilibrium could be completed within 300 min, the optimum equilibrium time for phenol adsorbed on bentonites was set as 360 min for subsequent experiments.

To clarify the possible mechanisms for phenol uptake, the kinetic experimental data were fitted to the pseudo-first--order model and pseudo-second-order model. The relevant parameters are given in Table 1. Having greater correlation coefficients (R^2) (Table 1), the pseudo-second-order model seems to be more suitable to describe the phenol uptake on modified bentonite. This implies that chemical adsorption is the controlling factor in the phenol uptake process. Similarly, Senturk et al. (2009) found that the adsorption
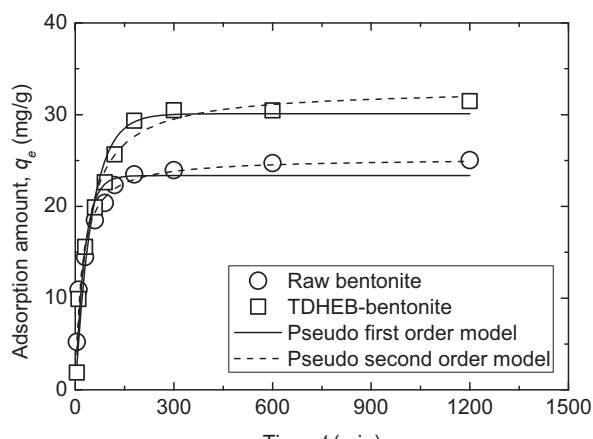
Fig. 8. Impactof contact time on Cu(II) adsorption on raw and TDHEB-bentonite (C_{cu}=300.0 mg/L, bentonite=5.0 g/L, pH=5.0, T=25± 2°C)

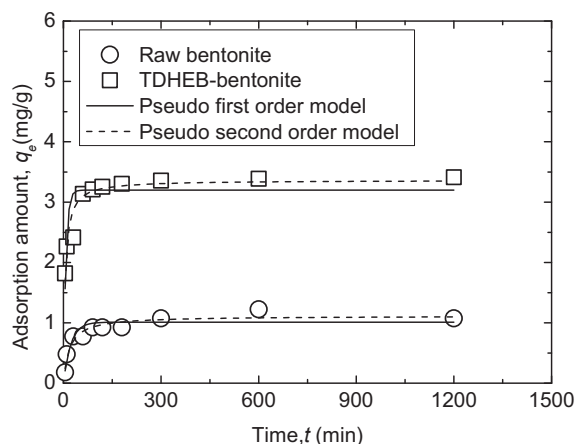**Fig. 9.** Impact of contact time on phenol adsorption on raw and TDHEB-bentonite (C_{phenol}=100.0 mg/L, bentonite=5.0 g/L, pH=5.0, T=25± 2°C)

Table 1. Kinetic parameters for the adsorption of Cu(II) and phenol onto raw and TDHEB-bentonite (C_o=100 mg/L for phenol; 300 mg/L for Cu(II); pH=5.0, T=25±2°C)

Contaminants	Adsorbent	C_o (mg/L)	Pseudo-first-order model			Pseudo-second-order model		
			q_e(mg/g)	k_1(1/min)	R^2	q_e(mg/g)	k_2(g/mgmin)	R^2
Cu(II)	TDHEB-bentonite	300	30.100	0.020	0.953	32.870	0.001	0.977
	Raw bentonite	300	23.359	0.036	0.910	25.283	0.002	0.980
Phenol	TDHEB-bentonite	100	3.198	0.135	0.720	3.363	0.058	0.904
	Raw bentonite	100	1.011	0.045	0.851	1.114	0.051	0.929

process of phenol on organobentonite (i.e. preparedwith cetyl trimethylammonium bromide) also was primarily controlled by chemical adsorption.

In addition, it can be found that the pseudo-second order rate constant values, k_2 (g/mg min), for phenol on TDHEB-bentonite is higher than that for Cu(II) (Table 1). This may be attributed to the hydrophilicity of two pollutants. Because of lower hydrophilicity, phenol has a higher tendency to the TDHEB-bentonite surface than Cu(II).

Sorption isotherm for Cu(II)

The experimental isotherm data for Cu(II) adsorption on TDHEB-bentonite and raw bentonite are presented in Fig. 10. The isotherm was fitted to the Langmuir, Freundlich and Redlich-Person isotherm models described by Eqs (4), (5) and (6). The isotherm parameter of the modeling and their correlation coefficient (R^2) are given in Table 2. As shown in Table 2, the maximum adsorption capacity (Q_{max}) of the modified bentonite reached 45.063 mg/g, which was about 2.0 times greater compared to that of the corresponding unmodified bentonite. This result shows that the modification with TDHEB improved the adsorption capacity of bentonite toward Cu(II). This increased Cu(II) adsorption capacity can be primarily related to the -COO$^-$ and -CH$_2$CH$_2$OH functional groups of the adsorbed surfactant on the modified bentonite. These two kinds of organic functional groups can chelate strongly with the Cu(II) separately or together. Liu et al. (2016) also proposed that chelating with organic groups was the primary reason why amphoteric modified bentonite had a greater heavy metals adsorption capacity compared to corresponding unmodified one.

The n_f calculated by Freundlich model is larger than unity (Table 2), implying that the adsorpion of Cu(II) is favorable in this study. From Fig. 10 and Table 2, it can be found that the adsorption pattern of Cu(II) onto bentonites was well fitted with both Freundlich and Redlich-Peterson isotherm models, evidenced by the higher correlation coefficients. This suggests that the adsorption of Cu(II) on bentonites surface was mainly controlled by both heterogeneous multilayer and homogeneous monolayer adsorption.

Sorption isotherm for phenol

Fig. 11 shows the adsorption isotherm for phenol on the modified and raw bentonite. The test results were described using the Freundlich, Redlich-Peterson and linear isotherm models, as depicted by Eqs (5), (6) and (7). The isotherm parameters and their associated correlation coefficient (R^2) are shown in Table 2. According to the K_d value presented in Table 2, the modified bentonite had about 5.0 times higher adsorption capacity for phenol than the corresponding raw bentonite. The increase in adsorption capacity could primarily be attributed to the organic medium derived from the adsorbed surfactant on the bentonite surface. The organic medium had -CH$_2$CH$_2$OH and -COO$^-$ groups, which can adsorb phenol via hydrogen bonding. Furthermore, the organic phase improved the bentonite hydrophobic property and favored partition of phenol.

Table 2 shows that the Freundlich model had higher correlation coefficients (R^2) relative to linear model. This implied that the adsorption of phenol was more suitable to be described by the Freundlich isotherm model and was nonlinear. This result appears to be different from those

Table 2. Isotherm parameters for the adsorption of phenol and Cu(II)on raw and TDHEB-bentonite

Contaminants	Adsorbent	Langmuir model			Freundlich model			Redlich-Peterson				Linear model	
		K_L (L/mg)	Q_m (mg/g)	R^2	K_F (L/g)	n_f	R^2	K_1	K_2	p	R^2	K_d (L/g)	R^2
Cu(II)	TDHEB-bentonite	0.020	45.063	0.942	4.927	2.729	0.986	103.957	21.316	0.628	0.981	–	–
	Raw bentonite	0.052	26.075	0.933	5.582	3.841	0.948	19.306	3.090	0.767	0.937	–	–
Phenol	TDHEB-bentonite	–	–	–	0.007	0.683	0.977	–	–	–	–	0.069	0.941
	Raw bentonite	–	–	–	0.003	0.791	0.953	–	–	–	–	0.013	0.936

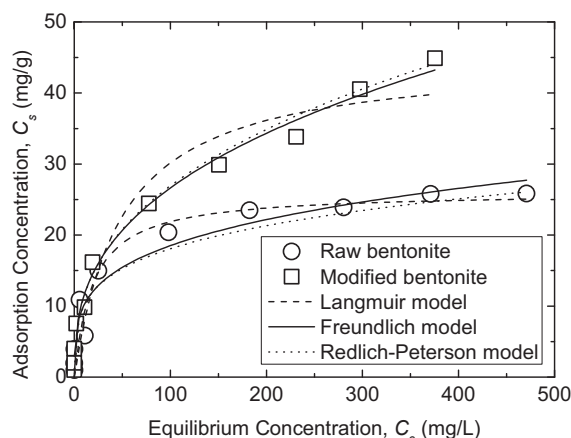**Fig. 10.** Adsorption isotherms of Cu(II) on raw and TDHEB-bentonite in single system. (C_{cu}=5.0−600.0 mg/L, bentonite =5.0 g/L, pH=5.0, T=25± 2°C)

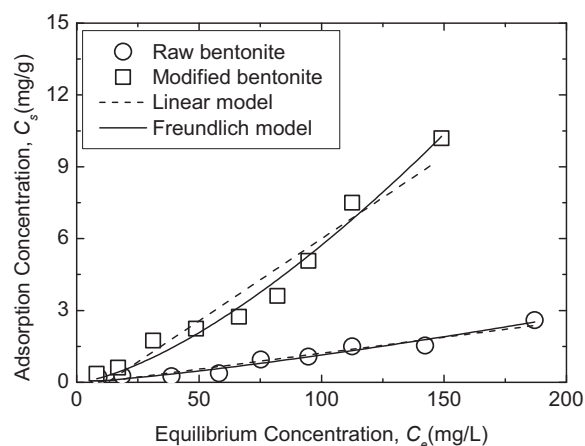**Fig. 11.** Adsorption isotherms for phenol on raw and TDHEB-bentonite in single system. (C_{phenol}=10.0–200.0 mg/L, bentonite =5.0 g/L, pH=5.0, T=25± 2°C)

obtained by Ma et al. (2016), where the adsorption of phenol on organically modified bentonite was linear and partition into an organic phase was the primarily important mechanism responsible for the phenol removal. There is little doubt that partition into the organic phase was the dominant mechanism responsible for phenol adsorption in this study. As for the nonlinear sorption behavior, the most likely explanation was that other mechanisms (i.e. hole-filling) also contributed to the adsorption of phenol on the modified bentonite. In other words, the nonlinear sorption of phenol by the modified bentonite may be the result of a combination of partition and hole-filling. Chen et al. (2004) reported that hole-filling involved in the adsorption of ionizable organic compounds on hexadecyltrimethyl ammonium-modified loess and made the adsorption isotherm became nonlinear.

Comparison with other organically modified bentonite or montmorillonite

The adsorption capacity of TDHEB-bentonite for Cu(II) and phenol was compared with that of other organoclay modified with other surfactants (Tables 3 and 4). The adsorption capacity toward Cu(II) was measured by the maximum adsorption capacity, i.e., Q_m, obtained from the Langmuir isotherm model, whereas the magnitude of the adsorption capacity for phenol was quantified by the distribution coefficient, i.e., K_d, provided by the linear isotherm model. The adsorption amount for Cu(II) was of 45.06 mg/g, which was higher relative to that of the organobentonites studied in the literature. Whereas, the adsorption capacity (represented by K_d) of TDHEB-

-bentonite for phenol was comparable to that of most of the reported organobentonites except for the ones modified with hexadecyldimethyl (3-sulphonatopropyl) ammonium and cetyltrimethylammonium bromide. Accordingly, TDHEB-bentonite may be a hopeful sorbent to simultaneously get rid of Cu(II) and phenol from wastewater.

Adsorption study in the binary system

To determine the possible interantagonistic effect between Cu(II) and phenol, the adsorption tests were conducted using a solution containing phenol and Cu(II) simultaneously. The test results are displayed in Fig. 12(a) and (b). The Fig. 12(a) shows that as the Cu(II) concentration increased from 10 to 200 mg/L, the adsorbed phenol decreased, suggesting that the presence of Cu(II) interfered with phenol adsorption. Similar result was also reported by Meng et al. (2008), where Cd(II) inhibited phenol adsorbed on an organobentonite modified by an amphoteric modifier (i.e. duodalkyl betaine). The dropped in phenol adsorption capacity could be related to the competition of Cu(II) for the adsorption site (i.e. -CH$_2$CH$_2$OH and -COO$^-$ groups of the adsorbed surfactant) on the modified bentonite. The two aforementioned organic groups can adsorb phenol through hydrogen bonding and Cu(II) by chelating, respectively. Therefore, when the Cu(II) was added into the solution, it would compete for the adsorption sites originally available for phenol, decreasing the phenol adsorption capacity.

The data presented in Fig. 12(b) show that the adsorption amount of Cu(II) almost kept constant as phenol concentration increased from 10 to 150 mg/L. These observations agree

Table 3. Adsorption capacity of the TDHEB−bentonite and other modified clays toward Cu(II)

Soil type	Surfactant name	Adsorption condition			Adsorption capacity (mg/g)[a]	Reference
		pH	Soil:Water	Temperature		
Montmorillonite	Hexadecyltrimethylammonium bromide	5.0	1:200	25°C	2.940	(Ma et al., 2016)
Montmorillonite	Hexadecyldimethyl (3-sulphonatopropyl) ammonium	5.0	1:200	25°C	14.150	(Ma et al., 2016)
Montmorillonite	Dodecylsulfo betaine	5.0	1:1000	18−35°C	10.200	(Fan et al., 2014)
Montmorillonite	Sodium dodecylsulfate	3.0	1:400	25°C	16.070	(Lin & Juang, 2002)
Bentonite	Tallow dihydroxyethyl betaine	5.0	1:200	25±2°C	45.063	This study

Note,[a] The maximum obtained from Langmuir model (Q_M).

Table 4. Adsorption capacity of the TDHEB−bentonite and other modified clays toward phenol

Soil type	Surfactant name	Adsorption condition			K_d(L/g) [a]	Reference
		pH	Soil:Water	Temperature		
Montmorillonite	Hexadecyltrimethylammonium bromide	5.0	1:200	25°C	0.072	(Ma et al., 2016)
Montmorillonite	Hexadecyldimethyl(3-sulphonatopropyl) ammonium	5.0	1:200	25°C	0.136	(Ma et al., 2016)
Bentonite	Cetyltrimethylammonium bromide	–	1:100	25±1°C	0.200	(Ma & Zhu, 2007)
Bentonite	Hexadecyltrimethylammonium bromide	6.0	1:100	25°C	0.059	(Díaz-Nava et al., 2012)
Bentonite	Bencylhexadecyldimethylammonium chloride	6.0	1:100	25°C	0.074	(Díaz-Nava et al., 2012)
Bentonite	Tallow dihydroxyethyl betaine	5.0	1:200	25± 2°C	0.069	This study

Note, [a] the distribution coefficient obtained from linear model (K_d).

with the studies conducted by Yan et al. (2007) and Wang et al (2020) and imply that the presence of phenol did not produce a suppressed impact on Cu(II) adsorption. The dominant reason for this behavior is that Cu(II) has a higher affinity toward the modified bentonite compared to phenol. Specifically, the chelating bonds between Cu(II) and modified bentonite (i.e. mainly the surfactant on bentonite) was stronger than the hydrogen bonds between phenol and the modified bentonite (i.e. mainly the surfactant on bentonite). Thus, phenol could not replace the Cu(II) originally adsorbed on the modified bentonite. This is why the adsorption capacity of modified bentonite toward Cu(II) kept constant as the phenol concentration increased.

Mechanisms of Cu(II) and phenol adsorption on TDHEB-bentonite

There are several possible mechanisms involved in the adsorption of Cu(II) on the modified bentonite (Fig. 13). First, the chelating interaction with -CH_2CH_2OH and -COO^- of the surfactant (i.e. TDHEB) separately or together might be the predominant mechanism for Cu(II) adsorption by the modified bentonite (Fig. 13 ① and ②). Meng et al. (2008), Liu et al.

(2016), Long et al. (2013) and Ren et al. (2020) also proposed that chelating with the carboxyl group and the amidocyanogen group of organic surfactant is an important mechanism for heavy metals being adsorbed by organobentonites used in their studies. The second possible mechanism for Cu(II) adsorption was the cation exchange between the Cu(II) with the Na^+ originally existing in the bentonite (Fig. 13 ③). The third possible mechanism for Cu(II) adsorption was the formation of inn-sphere complexes through hydroxyl groups (i.e. Si-OH and Al-OH) at the bentonite edges (Matthes et al. 1999) (Fig. 13 ④). Moreover, Cu(II) could chelate with phenol and produce a Cu(II)-phenol complex, which can be adsorbed on the modified bentonite via partition into the organic phase derived from surfactant (Fig. 13 ⑤) (Yang et al. 2015). As for phenol, partition into the organic phase derived from adsorbed surfactant on the modified bentonite surface may be the primary removal mechanism (Fig. 13 ⑥). In addition, hydrogen bond may be formed between phenol and the -CH_2CH_2OH or -COO^- of adsorbed surfactant and contribute to the adsorption of phenol (Fig. 13 ⑦). Furthermore, hole-filling might also occur in the phenol adsorption process and make the isotherm became nonlinear (i.e. followed the Freundlich model).
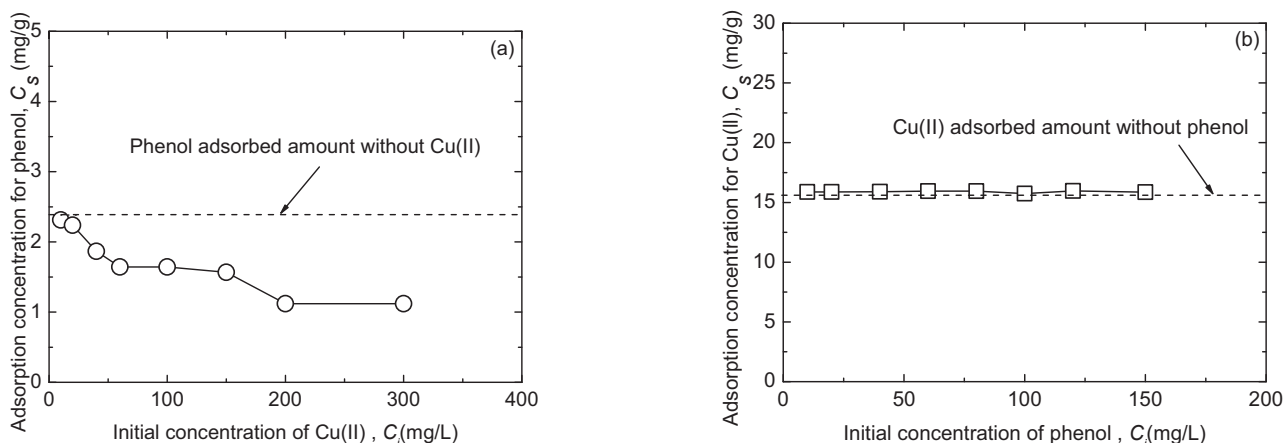

Fig. 12. Impact of Cu(II) or phenol on the uptake of phenol or Cu(II) on the TDHEB-bentonite(bentonite = 5.0 g/L, pH=5.0, T=25± 2°C)
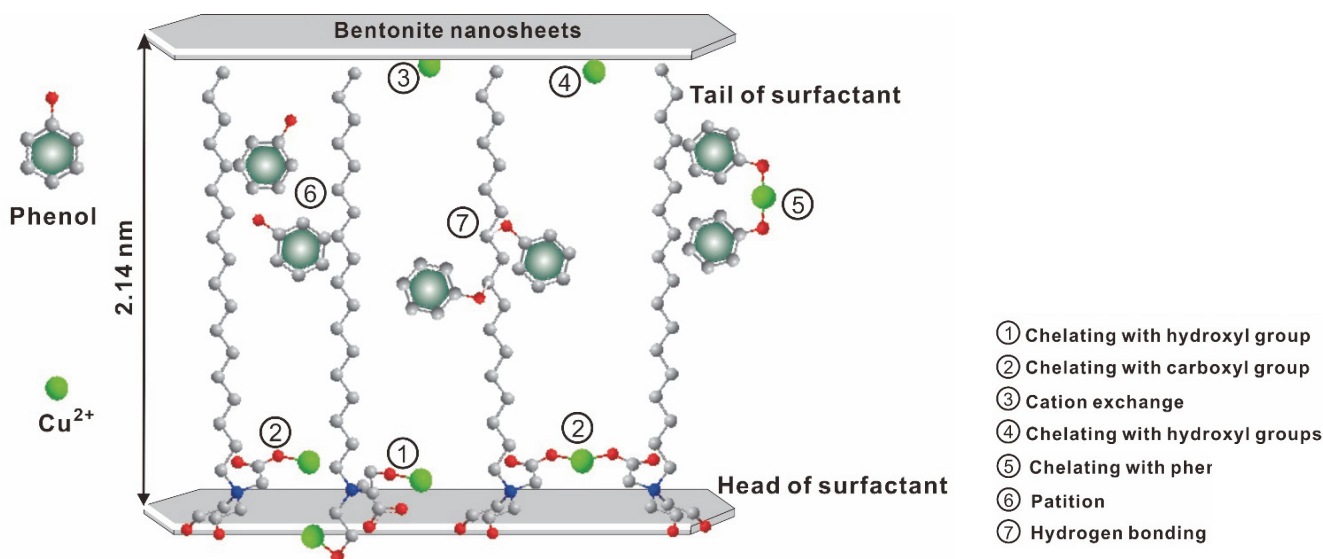

Fig. 13. Possible mechanism for Cu(II) and phenol adsorption on TDHEB−bentonite

Conclusion

In the presented study, an organobentonite modified with an amphoteric surface modifier, namely tallow dihydroxyethyl betaine (TDHEB), was developed to simultaneously get rid of Cu(II) and phenol from wastewater. Bath tests were conducted to determine the impact of pH, contact time, and initial concentration of contaminants on the adsorption capacity of modified bentonite toward Cu(II) and phenol. The mechanisms involved in adsorption process also were examined. The following conclusions can be drawn:

- The adsorption capacity of TDHEB−bentonite for Cu(II) and phenol was about 2.0 and 5.0 times greater compared to that of the unmodified one, respectively.
- The Cu(II) and phenol adsorption on TDHEB-bentonite can be described by the pseudo-second-order mode.
- The Freundlich isotherm was more suitable to fit the adsorption of Cu(II) and phenol on TDHEB-bentonite.
- Cu(II) inhibited phenol adsorption on TDHEB--bentonite, but not vice versa.
- Cu(II) was removed mainly by chelating with the -CH_2CH_2OH and -COO^- of the surfactant on the modified bentonite, whereas phenol was eliminated primarily by partition and formatting hydrogen bonding with the two aforementioned organic functional groups.
- Overall, the bentonite modified with TDHEB is a hopeful adsorbent to get rid of Cu(II) and phenol simultaneously from waste water.

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