Research Article

Adsorptive Removal of Copper by Using Surfactant Modified Laterite Soil

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Removal of copper ion (Cu^{2+}) by using surfactant modified laterite (SML) was investigated in the present study. Characterizations of laterite were examined by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), inductively coupled plasma mass spectrometry (ICP-MS), and total carbon analysis. The optimum conditions for removal of Cu^{2+} by adsorption using SML were systematically studied and found as pH 6, contact time 90 min, adsorbent dosage 5 mg/mL, and ionic strength 10 mM NaCl. The equilibrium concentration of copper ions was measured by flame atomic absorption spectrometry (F-AAS). Surface modification of laterite by anionic surfactant sodium dodecyl sulfate (SDS) induced a significant increase of the removal efficiency of Cu^{2+} . The surface modifications of laterite by preadsorption of SDS and sequential adsorption of Cu^{2+} were also evaluated by XRD and FT-IR. The adsorption of Cu^{2+} onto SML increases with increasing NaCl concentration from 1 to 10 mM, but at high salt concentration this trend is reversed because desorption of SDS from laterite surface was enhanced by increasing salt concentration. Experimental results of Cu^{2+} /SML adsorption isotherms at different ionic strengths can be represented well by a two-step adsorption model. Based on adsorption isotherms, surface charge effects, and surface modification, we suggest that the adsorption mechanism of Cu^{2+} onto SML was induced by electrostatic attraction between Cu^{2+} and the negatively charged SML surface and nonelectrostatic interactions between Cu^{2+} and organic substances in the laterite.

1. Introduction

Removal of heavy metal ion from aqueous solution is important in environmental concern because heavy metal can induce serious problems to human health through the water resources. Therefore, so many projects focus on the removal of heavy metal ion to protect water resources [1–7]. Numerous treatment techniques have been used for heavy metal ion removal from the aquatic environment such as adsorption, ion exchange, coagulation/flocculation, chemical precipitation, photodegradation, and electrochemical oxidation [8–11]. Among these techniques, adsorption is one of the most common technologies for removing heavy metal ions [8, 10, 12–15]. Although activated carbon and activated metal oxides are effective adsorbent for the removal of heavy metal ions [2, 4, 14–17], a big challenge is costly. Thus, cheap

adsorbents or/and natural adsorbents or modified cheap adsorbents are preferable in developing countries [5, 8, 12, 18]. To increase the removal efficiency of heavy metal ion by natural minerals, a modification of adsorbent surfaces is needed because the surface of such materials is nonactive. The modified solid adsorbents to remove metal ion was successfully investigated by many researches and, in these cases, not only adsorption capacity but also the adsorptive selectivity was significantly enhanced [19–21].

Copper, which is well-known heavy metal, is toxic and nonbiodegradable to aquatic ecosystems and living organisms [22]. Therefore, copper can accumulate in sediments and tissues of living organisms, and separation of copper ions is essential to discharge wastewater into environment. Recently, many studies investigated the removal of copper ion, Cu(II) , by adsorption techniques using novel adsorbent

[3, 16, 22–25]. Adsorptive removal of Cu(II) by chemically modified adsorbent was investigated in previous studies [3, 26].

Laterite is a common soil in tropical countries. Laterite is also easily collected in Vietnam, meaning that laterite is very low cost. Basically, laterite has positive charge in the acid and neutral media so it has been widely used for the removal of many toxic anionic ions including anionic heavy metal [5, 27, 28]. Nevertheless, the removal of cations is rather hard due to the strong electrostatic repulsive force. Thus, in order to increase the removal efficiency of the heavy metal cations by adsorption technique, surface modification of laterite is necessary. Anionic surfactant such as sodium dodecyl sulfate (SDS) is an ecofriendly chemical that can be used in environmental remediation to remove both inorganic and organic pollutants [29]. However, SDS modified laterite to remove Cu^{2+} has not been studied [5].

Adsorption is normally conducted under isothermal condition so that adsorption isotherms fitted by theoretical models are useful to better understand adsorption mechanisms and to explain the interactions between the laterite and copper ion. As for describing adsorption characteristics of heavy metal ions, Langmuir and Freundlich isotherm models are often discussed [30, 31]. However, Langmuir and Freundlich models cannot be applied for adsorption isotherms of surfactants. Thus, adsorption of inorganic pollutants onto surfactant modified laterite could not be fitted by Langmuir and Freundlich models. Fortunately, a two-step model presented by Zhu and Gu [32] with a general adsorption isotherm equation was successfully applied to various types of surfactants, polymers, and dyes adsorption isotherms for numerous systems [32–37]. Adsorptive removal of both organic and inorganic pollutants by using surfactant modified alumina was thoroughly studied by Pal and coworkers [2, 16, 38–41], indicating that surfactant modified solid adsorbent is a novel adsorbent. Nevertheless, the authors have not studied adsorption of Cu(II) on surfactant modified laterite.

In this study, we investigate adsorptive removal copper ion using surfactant modified laterite (SML). To the best of our knowledge, this is the first systematic study on the adsorption of copper ion from aqueous solution on SML. Characterizations of laterite and SML were determined by X-ray diffraction (XRD), inductively coupled plasma mass spectrometry (ICP-MS), Fourier transform infrared spectroscopy (FT-IR), and total carbon analysis. The optimum parameters for adsorptive removal copper ion by using SML are systematically studied. The surface modification before and after adsorption is also investigated by XRD and FT-IR. The adsorption mechanism is also proposed on the basis of adsorption isotherms and surface modification.

2. Experimental

2.1. Materials. Raw laterite was collected from a local place of Thach That, Hanoi, Vietnam. The laterite was treated before measurements as follows: the laterite was washed various times by ultrapure water to reach neutral pH and then dried at 110°C. The treated laterite was cooled in a desiccator at room

temperature and stored in a polyethylene container. The dried laterite was sieved in order to collect the particles with the size lower than 0.1 mm. The laterite which was modified with 0.01 M SDS (solid/liquid ratio 200 mg/mL) in 0.01 M NaCl at pH 4 by shaking for 3 h and then washed with ultrapure water was called surfactant modified laterite (SML).

Standard solution of copper (1000 ppm in 0.5 M HNO_3) was supplied by Merck (Germany). All chemicals were of analytical reagent grade and were used without further purification. Copper nitrate salt, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, was purchased from Merck (Germany). Anionic surfactant, sodium dodecyl sulfate (SDS, with purity > 95%), from Scharlau (Spain, EU), was used to modify the surface of laterite. The effect of ionic strength was studied by the addition of NaCl (Merck). In order to adjust solution pH, HCl, and NaOH (Merck) were used. Ultrapure water system (Labconco, USA) with resistivity 18.2 M Ω was used to produce ultrapure water in preparing all aqueous solutions.

2.2. Adsorption Studies. All adsorption experiments were conducted by batch technique. Initially, the copper stock solution of 2000 ppm was prepared by dissolving precisely calculated amount of copper nitrate salt. Then, the stock solution was appropriately diluted based on experimental requirement.

A known amount of adsorbents solution was thoroughly mixed with 50 mL aqueous copper solution (Cu^{2+}) of 10 ppm in 250 mL Erlenmeyer flasks at $25 \pm 2^\circ\text{C}$ controlled by an air conditioner. The effect of operating condition (pH, adsorbent dosages, contact time, ionic strength, and initial absorbate concentration) on removal of Cu^{2+} was studied. The concentration of Cu^{2+} was determined by flame atomic absorption spectrometry (F-AAS). The removal (R , %) of Cu^{2+} was calculated by

$$\text{Removal } (R, \%) = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

where C_i and C_f are initial concentration and final concentration of Cu^{2+} , respectively.

To study adsorption isotherms, the concentration of Cu^{2+} was varied from 10 ppm to 2000 ppm and pH was adjusted to the desired value. The adsorption capacity of Cu^{2+} ($\Gamma \text{ Cu}^{2+}$) onto SDS modified laterite was determined by the different concentrations of Cu^{2+} solutions before adsorption and after equilibrium process by F-AAS.

2.3. Instrumental Analytical Methods. The concentration of Cu^{2+} was determined by using an atomic absorption spectrometer (AA-6800, Shimadzu, Japan). Hollow cathode lamp (HCL) was used to emit a narrow wavelength of 324.8 nm. The slit width was kept as constant of 0.5 nm for all AAS measurements. The linear relationship between the absorbance and concentrations of Cu^{2+} had a correlation coefficient of at least 0.999.

Concentration of anionic surfactant, SDS used for surface modification of laterite, was determined by spectrophotometry with Ultraviolet Visible spectrophotometer (UV-1650 PC, Shimadzu, Japan) followed our previous paper [36].

FIGURE 1: The XRD pattern of raw laterite.

Potentiometric method was used to determine pH of all solutions. The method was carried out using a HI 2215 Hanna Instruments pH meter by a glass combination electrode. We use three standard buffers (Hanna) to calibrate the electrode before measuring pH of solutions. All measurements were carried out at $25 \pm 2^\circ\text{C}$.

2.4. Characterization Methods. The chemical compositions of laterite were examined by inductively coupled plasma mass spectrometer (ICP-MS Elan 9000, Perkin Elmer, USA) and total carbon analyzer using a TOC V_{CPH} (Shimadzu, Japan).

X-ray diffraction (XRD) was collected on a Bruker D8 Advance X-ray diffractometer, $\text{CuK}\alpha$ radiation ($\lambda = 0.1549\text{ nm}$). Intensity for the diffraction peaks was recorded in the 10° – 70° (2θ) range with a step size of 0.03° .

To evaluate functional groups of laterite and to confirm surface modification of laterite after Cu^{2+} adsorption, Fourier transform infrared spectroscopy was performed with an Affinity-1S (Shimadzu, Japan). The FT-IR spectra were obtained under the same conditions: 25°C , atmospheric pressure, and resolution of 4 cm^{-1} .

3. Modeling by General Isotherm Equation

The obtained isotherms were fitted by a general isotherm equation. The equation was derived by assuming that two adsorption steps can occur at the solid-liquid interface [32].

The general isotherm equation is

$$\Gamma = \frac{\Gamma_{\infty} k_1 C (1/n + k_2 C^{n-1})}{1 + k_1 C (1/n + k_2 C^{n-1})}, \quad (2)$$

where Γ is amount of Cu^{2+} adsorbed; Γ_{∞} is the maximum adsorption amount; k_1 and k_2 are equilibrium constants for the first layer adsorption and clusters of n molecules or multilayer adsorption. C denotes the equilibrium concentration of Cu^{2+} in solution.

The selected fitting parameters were described in our previously published papers [35–37].

TABLE 1: The chemical composition of raw laterite.

Content (%)	Value
Al_2O_3	15.0
Fe_2O_3	40.1
SiO_2	33.2
MnO_2	0.7
P_2O_5	0.5
Na_2O	
K_2O	~ 0.8
CaO	
C	0.7

4. Results and Discussion

4.1. Characterization of Laterite

4.1.1. Characterization of Raw Laterite. Table 1 shows the chemical compositions of raw laterite material. The inorganic components were determined by ICP-MS while carbon content was measured by TC. The results in Table 1 indicate that the main chemical compositions of laterite are metal oxides in which Fe_2O_3 , SiO_2 , and Al_2O_3 are dominated. The composition of laterite used in the present study is similar to the published papers [45, 46].

The XRD pattern of laterite is represented in Figure 1. The predominated morphologies were found as quartz (SiO_2), hematite (Fe_2O_3), and goethite ($\text{FeO}(\text{OH})$). The peaks at $2\theta = 45, 66$ indicated Al_2O_3 with very low intensity. The mineralogical phases of laterite used in this study is close to laterite used in other researches [5, 45].

Figure 2 indicates the FT-IR spectra of laterite without any modification. As can be seen in Figure 2, the band at 3622.32 and 3406.29 was assigned to $-\text{OH}$ group of Si and Al. Another band at 1645.28 was assigned to inner layer water molecules [5, 45]. The bands at 1031.92 , 1036.84 , 912.33 , and 796.60 appeared in the spectra because of the presence of Si–O–Fe, Al–OH, Fe–OH vibrations. The Fe–O bonds stretching at 534.28 and 464.84 were also obtained due to the presence of hematite in structure of laterite. The results of FT-IR are in good agreement with ICP-MS and XRD given above.

FIGURE 2: The FT-IR spectra of raw laterite.

4.1.2. Characterization of Laterite after SDS Preadsorption and Copper Adsorption. Anionic surfactant sodium dodecyl sulfate (SDS) with a concentration of 0.01 M (higher than critical micelle concentration, CMC) was used to modify the surface of laterite in 0.01 M NaCl (pH 5). In order to evaluate the change in mineral phase and surface modification and of laterite after preadsorption of SDS (SML) and sequential adsorption of Cu^{2+} with initial concentration of 100 ppm in 10 mM NaCl (pH 5), the XRD and FT-IR techniques are also used.

Figures 3(a) and 3(b) show that the morphologies still contain quartz (SiO_2), hematite (Fe_2O_3), and goethite ($\text{FeO}(\text{OH})$). These are similar to raw laterite, demonstrating that the structure of laterite does not change after adsorption SDS and adsorption of Cu^{2+} . However, the intensity of special peaks assigned for each mineral phase was changed. The intensity of specific peak for SiO_2 is enhanced while the others of Fe_2O_3 and $\text{FeO}(\text{OH})$ are reduced after preadsorption of SDS (Figure 3(a)) compared with original laterite. SDS is an anionic surfactant that can easily attract positive mineral (Fe_2O_3 and $\text{FeO}(\text{OH})$) than negative one of SiO_2 . For the case of laterite after consequential adsorption of cation Cu^{2+} , the peak indicated for SiO_2 decreased dramatically while the others for Fe_2O_3 and $\text{FeO}(\text{OH})$ slightly increased [5, 27].

Figure 4 shows that FT-IR spectra of modified laterite by preadsorption of SDS are similar to the raw one (Figure 4(a)). In addition, the relative intensity of asymmetrical and symmetrical stretching of $-\text{CH}_2-$ presented at 2926.01 and 2854.65 cm^{-1} decreases dramatically in the spectra of SML while these peaks appear with very high intensity in spectra of SDS powder (data not shown). This confirms that the hydrophobic interaction can work on the surface of laterite. In addition, the characteristic peaks of SO_4^{2-} at about 1247 cm^{-1} and 1218 cm^{-1} appear very strong in spectra of SDS while all bands disappear in the spectra of SML. It is demonstrated that SDS has sulfate head groups in contact with the surface of laterite via the electrostatic attraction at the current salt concentration (10 mM NaCl). In other words, the modification of laterite was successful due to the presence of bilayer and/or admicelles on the surface of laterite [36].

As can be seen in Figure 4(b), the band at 3442.94 assigned to $-\text{OH}$ is very big due to the hydroxo complex of $\text{Cu}(\text{II})$. The bands at 1031.92, 1036.84, and 912.33 that appeared in the spectra of raw laterite are shifted to lower wavenumber at 1029.99, 1004.91, and 910.40 because the surface of laterite is changed. In addition, the peaks of $-\text{CH}_2-$ present at 2926.01 and 2854.65 cm^{-1} of SML could not be seen in the spectra of SML after Cu^{2+} adsorption. These results suggest the adsorption of copper molecules onto SML via electrostatic attraction and nonelectrostatic interactions between Cu^{2+} and organic compounds in laterite.

4.2. Surface Modification of Laterite by SDS. Anionic surfactant SDS with a concentration of 0.01 M was used to modify the surface of laterite in 0.01 M NaCl (pH 5). The obtained adsorption capacity of SDS on laterite (with solid-liquid ratio 200 mg/mL) is 0.01 mmol/g. Although the adsorption SDS on laterite is small, the loading implies the presence of bilayer and/or admicelles of SDS [36]. As a result, the surface charge of laterite is negative which can enhance adsorption of cationic heavy metal Cu^{2+} . Figure 5 indicates that the removal efficiency of Cu^{2+} in 1 mM NaCl (pH 5) with initial concentration of 10 ppm increases from 61.6% to 89.5% after the surface modification of laterite by SDS.

Typical concentration of $\text{Cu}(\text{II})$ in wastewater and surface water is quite low. The limited concentration according to national technical regulation on water quality of Vietnam is equal to 1 mg/L for class B (low quality water). It should be noted that when the concentration of $\text{Cu}(\text{II})$ in aqueous solution is less than 2.5 mg/L the removal efficiency of copper through adsorption using SML is approximately 99%. Furthermore, the maximum contaminant level (MCL) standard according to USEPA for Cu is 0.25 mg/L. It implies that the SML is a promising material to remove $\text{Cu}(\text{II})$ from aqueous solutions.

Effective parameters on adsorptive removal of copper ion by using SML are systematically studied, as given below.

4.3. Adsorptive Removal of Copper Ion by Using Surfactant Modified Laterite

4.3.1. Effect of pH. Solution pH plays an important role in the adsorption of copper ion onto surfactant modified laterite (SML) because it can affect the surface charge of SML and charging behavior of chemical speciation of copper. At $\text{pH} > 7$, the high precipitation of Cu^{2+} can take place which influences the concentration of Cu^{2+} in solution. The effect of initial pH on the adsorption of Cu^{2+} by SML was investigated in the pH range of 3–7 in 1 mM NaCl (Figure 6). This implies that the negatively charged SML surface can easily attract Cu^{2+} by electrostatic attraction.

As can be seen in Figure 6, the removal of Cu^{2+} using SML increases with increasing solution pH from pH 4 to pH 6 because of the competition between H^+ (at low pH) and cation Cu^{2+} on the surface of SML. However, the desorption of SDS is increased at $\text{pH} > 7$ so that the removal efficiency of Cu^{2+} decreases. Thus, optimum pH for removal of Cu^{2+} by SML is pH 6 which agrees well with optimum pH in the

FIGURE 3: The XRD patterns of laterite after preadsorption of SDS (a) and after sequential adsorption of Cu^{2+} (b).

FIGURE 4: The FT-IR spectra of laterite after preadsorption of SDS (a) and after sequential adsorption of Cu^{2+} (b).

FIGURE 5: The removal of Cu^{2+} at the initial concentration of 10 ppm in 1 mM NaCl (pH 5) using laterite and surfactant modified laterite (SML).

case of adsorption heavy metal ions on surfactant modified alumina (SMA) [2, 3]. However, alumina is much more expensive compared with laterite so SML is more suitable than SMA for removing heavy metal ions in developing countries.

FIGURE 6: The removal of Cu^{2+} by surfactant modified laterite (SML) as a function of pH ($\text{Ci}(\text{Cu}^{2+}) = 10 \text{ ppm}$; contact time 90 min; adsorbent dosage 5 mg/mL; 1 mM NaCl).

The point of zero charge of laterite is about 7.4 [45, 46], meaning that at $\text{pH} < 7.4$ laterite has positive charge, since surface modification of laterite with SDS was conducted at pH

FIGURE 7: The removal of Cu^{2+} by SML at different contact time ($\text{Ci}(\text{Cu}^{2+}) = 10 \text{ ppm}$; pH 6; adsorbent dosage 5 mg/mL; 1 mM NaCl).

4.0 to promote preadsorption of SDS on laterite surface. After preadsorption of SDS, the concomitant of proton occurred so pH of solution increased around 0.6 units (from pH 5.0 to 5.6). This trend is similar to the case of SDS adsorption on Al_2O_3 [36]. However, net surface charge of SML is negative which enhances adsorption of Cu^{2+} significantly. After copper adsorption, pH of solutions decreased (from 5.0 to 4.7), demonstrating that adsorption of cation Cu^{2+} induces the desorption of SDS with proton into solution.

4.3.2. Effect of Contact Time. Contact time affects the completeness of adsorption equilibration. The effect of contact time on the adsorptive removal of Cu^{2+} by using SML is presented in Figure 7. Figure 7 shows the removal efficiency of Cu^{2+} from aqueous solution by using SML growing with time from 10 min to 180 min. It is suggested that adsorption reaches equilibrium at 90 min. After 180 min, the removal decreases because high concentration of Na^+ in NaCl background can displace Cu^{2+} . The equilibrium adsorption in this study is longer than the case of adsorptive removal of Cu^{2+} by natural kaolin clay (only 30 min) and the removal of Cu^{2+} by goethite mineral (60 min) [47, 48]. Nevertheless, 90 min is acceptable and is selected as the optimum contact time for removal of Cu^{2+} by using SML in 1 mM NaCl (pH 6).

4.3.3. Effect of Adsorbent Dosage. The adsorbent dosage has a significant effect on the adsorption process because it can influence the total surface area of adsorbent and number of binding site. The amount of SML was varied from 0.05 to 6.0 g of adsorbent that corresponded from 1.0 to 12 mg/mL (Figure 8).

Figure 8 reveals that the removal of Cu^{2+} by SML increases with increasing adsorbent dosage from 1 to 12 mg/mL. It may be explained by the increased large number of available binding sites for adsorption or increased net specific surface area with an increase of dosage [49]. However, an increase in adsorbent causes the increase of the adsorption capacity; then the adsorption capacity decreases due to the aggregation of colloidal particles at high adsorbent dosage

FIGURE 8: Removal (R) and adsorption capacity (Γ) of Cu^{2+} by SML as a function of adsorbent dosage ($\text{Ci}(\text{Cu}^{2+}) = 10 \text{ ppm}$; pH 6; contact time 90 min; 1 mM NaCl).

FIGURE 9: The removal of Cu^{2+} by SML at different NaCl concentrations ($\text{Ci}(\text{Cu}^{2+}) = 10 \text{ ppm}$; pH 6; contact time 90 min; adsorbent dosage 5 mg/mL).

[50]. Optimum adsorbent dosage is found to be 5 mg/mL and is fixed for the remaining studies.

4.3.4. Effect of Ionic Strength. Ionic strength affects electrostatic attraction between ionic adsorbates and charged surface adsorbent. For adsorption of Cu^{2+} onto SML, ionic strength also induces a change of existence of SDS molecules on laterite surface. As can be seen in Figure 9, the removal efficiency is lowest in the absence of salt, demonstrating that the electrostatic interaction causes adsorption. Furthermore, adsorption at 50 mM NaCl concentration is lower than that at 10 mM. This result can be explained by desorption of SDS at high salt concentration. Desorption of SDS is enhanced with increasing NaCl concentration from 10 to 50 mM. When increasing salt, the concentration of Cl^- is high so the removal is decreased. However, the removal increases with an increase of NaCl concentration from 1 to 10 mM, suggesting that not

FIGURE 10: Adsorption isotherms of Cu^{2+} onto SDS modified laterite (SML) as a function of equilibrium concentration of Cu^{2+} at different NaCl concentrations. Points are experimental data; solid lines are results of the 2-step adsorption model.

TABLE 2: The fit parameters for Cu^{2+} adsorption onto SML which are maximum adsorbed amount $\Gamma_{\infty, \text{Cu}^{2+}}$, the equilibrium constants $k_{1, \text{Cu}^{2+}}$ and $k_{2, \text{Cu}^{2+}}$ for first layer adsorption and multilayer adsorption, respectively, and the number of cluster of Cu^{2+} ion $n_{\text{Cu}^{2+}}$.

C salt (mM NaCl)	$\Gamma_{\infty, \text{Cu}^{2+}}$ (mg/g)	$k_{1, \text{Cu}^{2+}}$ (g/mg)	$k_{2, \text{Cu}^{2+}}$ (g/mg) ⁿ⁻¹	$n_{\text{Cu}^{2+}}$
1	150	3.0×10^2	8.0×10^2	2.4
10	185	5.0×10^2	8.0×10^2	2.5
50	110	1.5×10^2	7.5×10^2	2.5

only electrostatic but also nonelectrostatic between Cu(II) and/or Cu(II) speciation and organic substances in laterite induces adsorption. The effect of salt concentration will be discussed in the adsorption isotherms section.

4.4. Characteristics and Mechanisms of Copper Ion Adsorption Isotherms on SDS Modified Laterite

4.4.1. Adsorption Isotherms of Copper Ion on SDS Modified Laterite by a Two-Step Adsorption Model. The effect of ionic strength on adsorption of copper ion on SDS modified laterite (SML) is clearly demonstrated in the isotherms (Figure 10). At pH 6, the Cu^{2+} adsorption capacity increases with increasing NaCl from 1 to 10 mM. At higher salt concentration (from 10 to 50 mM), the adsorption capacity reduces with an increase of salt. The increase in salt concentration increases the number of cations Na^+ (counterions) on the negatively charged layer of SML, reducing the electrostatic effect of SML Cu^{2+} ion. It is quite different from the case of adsorption of copper ion on strawberry leaf powder [51] in which the effect of Na^+ , K^+ , Mg^{2+} , and Ca^{2+} on the copper adsorption is not significant. In our case, the electrostatic attraction between the positive charge of Cu^{2+} ion and negative charge of SML is effectively screened by increasing NaCl concentrations

from 10 to 50 mM. Nonelectrostatic interactions are more important in adsorption at low ionic strength (1 to 10 mM NaCl). These results agree well with the effect of ionic strength on the removal of copper ion using SML shown in previous section.

Figure 10 indicates that, at different salt concentrations, the experimental results can be represented well by the general isotherm equation (2) with the fitting parameters in Table 2.

As shown in Table 2, increasing ionic strength from 1 to 10 mM causes an increase in $k_{1, \text{Cu}^{2+}}$ but a decrease in $k_{1, \text{Cu}^{2+}}$ when increasing salt from 10 to 50 mM. It is noted that the changes in $k_{2, \text{Cu}^{2+}}$ and the number of Cu^{2+} clusters are not significant ($k_{2, \text{NH}_4^+} \approx 8.0 \times 10^2$ and $n_{\text{Cu}^{2+}} \approx 2.5$). The value of $k_{1, \text{Cu}^{2+}}$ is also related to the slope of isotherm. As a result, at high salt concentration, the slope is lower than that at low salt. It suggests that desorption of SDS from the bilayer of admicelles is enhanced by increasing salt concentration from 10 to 50 mM while at low salt concentration the link between sulfate groups of SDS and Cu^{2+} is not strong as other interactions.

4.4.2. Adsorption Mechanisms and Advantages of Copper Ion onto SDS Modified Laterite.

Adsorptive removal of copper

TABLE 3: Adsorption capacity of Cu^{2+} on natural materials or modified natural materials and SML.

Adsorbent	Adsorption capacity (mg/g)	References
Zeolite, clinoptilolite	1.64	[12]
HCl-treated clay	83.3	[42]
Marine alga, <i>Ecklonia maxima</i>	90	[43]
Red paddy soil	0.21	[44]
SDS modified laterite	185	This study

ion (Cu^{2+}) is enhanced by using anionic surfactant, SDS modified laterite (SML). The effective conditions on adsorption of Cu^{2+} ion by SML were systematically studied in Section 4.3. The two-step model was established to describe the Cu^{2+} adsorption onto SML, suggesting that adsorption of Cu^{2+} could replace admicellar bilayers of SDS molecules on the laterite surface at high salt concentration. Adsorption of Cu^{2+} decreases with an increase of ionic strength at high salt concentration because desorption of SDS is enhanced by increasing salt concentration [35] which is in good agreement with discussion in Section 4.3.1. It is also represented by two-step adsorption model with decreasing $k_{1,\text{Cu}^{2+}}$ when increasing NaCl concentration from 10 to 50 mM. At low salt concentration, the main interactions inducing adsorption may be lateral, hydrogen bonding, surface complexation, and Van der Waals interactions between Cu^{2+} and organic substances in the laterite.

Adsorption mechanisms of Cu^{2+} ion on SML are also supported by the results of FT-IR spectra (see Section 4.1.2). The bands of CH_2^- of SML did not occur after adsorption of Cu^{2+} in 10 mM NaCl, suggesting that the adsorption of Cu^{2+} onto SML is mainly controlled by the electrostatic attraction between the negatively charged sulfate groups of bilayer admicelles and positive charge of Cu^{2+} . It seems to be similar to the case of Cu^{2+} on natural kaolinite clays [48]. Nevertheless, at low ionic strength, the attraction between positive Cu^{2+} and negative SML is not so strong compared with other interactions. In this case, nonelectrostatic interactions between Cu^{2+} and/or speciation of Cu^{2+} with organic substances in laterite mainly contribute to adsorption.

Some published papers focused on sorption of Cu(II) onto different kinds of sorbents. Nevertheless, sorption of Cu(II) onto SML has not been reported. Furthermore, SML used in the present study has very high adsorption capacity (185 mg/g) compared with other natural sorbents or modified natural materials (Table 3). It demonstrates that SML is novel material for removal of Cu(II) from aqueous solution.

5. Conclusions

For the first time, we investigated adsorption characteristics of copper ion (Cu^{2+}) on sodium dodecyl sulfate (SDS) surfactant modified laterite (SML) in aqueous solution. The adsorption experiments were quantified by flame atomic absorption spectrometry (F-AAS). The raw laterite, laterite after preadsorption of SDS, and sequential adsorption of Cu^{2+} were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The

optimum conditions for adsorptive removal of Cu^{2+} using SML were found as pH 6, contact time 90 min, adsorbent dosage 5 mg/mL, and ionic strength 10 mM NaCl. Adsorption isotherms of Cu^{2+} on SML at different NaCl concentrations were fitted well by a two-step adsorption model. The adsorption of Cu^{2+} on SML decreased with an increase of NaCl concentration due to the enhancement of SDS desorption with increasing salt concentration but at low NaCl concentrations (1 to 10 mM), adsorption Cu^{2+} on SML increased with an increase of salt. Adsorption mechanisms of Cu^{2+} onto SML were mainly controlled by electrostatic attraction between the positive charge of Cu^{2+} and the negatively charged layer SML at high ionic strength while at low ionic strength nonelectrostatic interactions between Cu^{2+} and organic compounds in laterite induced adsorption. The SML was demonstrated as a novel adsorbent to remove Cu^{2+} from aqueous solutions.

Competing Interests

The authors declare that they have no competing interests.

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