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Adsorption of Cu^{2+} on Montmorillonite and Chitosan-Montmorillonite Composite Toward Acetate Ligand and the pH Dependence

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Abstract Chitosan-montmorillonite composite was extensively used for the removal of heavy metals from wastewater. In wastewater, copper (Cu^{2+}) usually coexist with the organic ligands, which had unknown effect on Cu^{2+} adsorption by the composite materials. In order to understand further on that, the adsorption of copper by the composite materials must be studied. In the present study, montmorillonite was coated with chitosan, and X-ray diffraction (XRD) patterns of the composite proved the intercalation of chitosan in the montmorillonite. Fourier transform infrared (FTIR) spectra of the composite identified the presence of amino group on the composite, and that of the composite saturated with metals identified the interaction between the amino groups and metals. Langmuir adsorption isotherm indicated that the composite had more capacity to adsorb Cu^{2+} from wastewater than montmorillonite. The adsorption capacity of Cu^{2+} by montmorillonite and chitosan-montmorillonite composite was studied, respectively, as a function of pH and in the presence of acetate. Compared to the montmorillonite at low ligand concentration (0.08 mmol/L) or low pH (<4.0), the coexisting acetate increased more Cu^{2+} adsorption by the composite. The acetate ligand presented less depression on the adsorption by the composite than that by montmorillonite at high ligand concentration (4 mmol/L) or high pH (>4.5). Therefore, the composite is more suitable for removing Cu^{2+} than montmorillonite in acid aqueous medium.

Keywords Organic ligand · Montmorillonite · Chitosan · Adsorption · Cu^{2+}

1 Introduction

In recent years, considerable attention had been devoted to the development of low-cost innovative materials for reducing heavy metals in aqueous systems to safer levels. Clay-polymer nanocomposites have attracted much interest because of both hydrophilic and hydrophobic surfaces as well as a large surface area. These materials are potentially useful as adsorbents of organic pollution and heavy metals in waste water (He et al 2014; Calagui et al 2014). Smectite group minerals have large adsorption capacities for polymer macromoleculars due to the unique interspace. Montmorillonite (Mt) is used widely as phyllosilicate in nanocomposite (Günister et al 2007) and has been found to be suitable for the removal of metals. It was considered as low-cost adsorbent, having the greatest cation exchange capacity among clay minerals for the removal of heavy metals (Huang et al 2010; Marcussen et al 2009; Zhu et al

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2011). However, Mt would disperse in water and be separated difficultly from aqueous medium because of its hydrated characteristic (Gecol et al 2006).

Chitosan (Cts), the cationic (1-4)-2-amino-2-deoxy-β-D-glucan, are industrially produced in various quality grades from chitin and the second most abundant polysaccharide in nature (Muzzarelli 2011). It has more than 1 mmol/g binding capacity for toxic heavy metals as well as more efficiency in removing metals from wastewater than other natural adsorbents (Varma et al 2004). Nevertheless, the chitosan beads had several disadvantages such as low-specific gravity and weak mechanical properties (Chang and Juang 2004). It formed a hydrogel in aqueous media and dissolved in acidic solution, which led the inaccessibility of the binding sites (Futalan et al 2011).

Thus, chitosan-montmorillonite composite (Com) attracted interest for heavy metal removal from aqueous solution due to improved structure and functions on the removal of heavy metals from aqueous medium versus sole chitosan or Mt (Calagui et al 2014; Depan et al 2014; Gecol et al 2006; Günister et al 2007; He et al 2014; Wang et al 2014; Wang and Chen 2014; Yan and Bai 2005). Moreover, the metal removal efficiency depended on many factors, such as pH variations, the nature of heavy metals, and the organic ligands, which contained with heavy metals in waste water (Yan and Bai 2005). The organic ligands are the production of organic matter decomposition, commonly present in aqueous medium. The carboxyl (–COOH) and phenolic (–OH) groups along with the ligands could form complexes with heavy metals, then changed the reactivity of heavy metal and affected the adsorption obviously (Angove et al 1999; Gao et al 2003; Huang et al 2010; Lackovic et al 2004).

The copper could be released into the environment and possess a serious threat to human, plants, and aquatic lives due to its persistent in nature, non-biodegradability, and bioaccumulation in food chain transfer. It has the form of Cu^{2+} ions chelated with organic or inorganic ligand as the primary forms in natural water or waste water (Sarathy and Allen 2005). The organic ligands could affect the adsorption of heavy metals on minerals (Jiang et al 2012; Su et al 2015). The formed ternary surface complexes or soluble complexes could enhance or suppress the adsorption of heavy metals by the minerals at specific conditions, respectively (Abollino et al 2003; Huang et al 2010; Marcussen et al 2009; Wang and Chen 2014; Zhu et al 2011).

The interactions between the Com and the organic ligands were not clear yet. Organic ligands might do effect on the metal adsorption by composite the same as or different from that by minerals. The amino group on Com might cause the different performance of organic ligand in the adsorption of Cu^{2+} by Com from that by Mt (Ngah and Musa 1998; Zhang and Bai 2003).

The aim of the present study was to investigate the influences of organic ligand on the sorption of Cu^{2+} by Com, compare to that with pure Mt, and provide the basis for better application of Com for the removal of Cu^{2+} in the wastewater.

2 Materials and Methods

2.1 Materials

Natural Mt was collected from Southern Clay Products, Inc. (Gonzales, TX) and saturated with sodium chloride. The sediment was washed by deionized (DI) water until no Cl^- remained, and then freeze-dried (VirTis 25 Liter FreezeMobile, the VirTis Company, Gardiner, NY). The cation exchange capacity (CEC) of the clay was 81 cmol$_c$/kg as measured by the Ca-Mg exchange method. The specific surface area was 790 m^2/g as determined by the ethylene glycol monoethyl ether (EGME) method.

Chitosan of medium molecular weight (MW), has viscosity of 200–800 cP, containing a number of glucosamine units with a MW of 161 g/mol was supplied by Sigma-Aldrich (deacetylation degree is 80 %). All the reagents used were of analytical grade and supplied by Sinopharm Chemical Co. (Shanghai, China).

2.2 Synthesis of Chitosan-Montmorillonite Composite

One gram per liter of chitosan solution was prepared first by the addition of corresponding amount of polymer to 10 mmol/L HCl. The polysaccharide solution was magnetic stirred for 4 h, and its pH was adjusted by adding 1 mol/L NaOH. Five hundred milliliters of chitosan solution was slowly added into 500 mL Mt dispersion (1 %, m/v) before 12 h continual stirring, and then the mixtures were centrifuged at 9000 r/min for 30 min. The supernatant was discarded and the residual was mixed with another 500 mL chitosan solution, then stirred for 12 h. The residue was obtained by 30 min centrifuge at 9000 r/min and washed with DI water twice. The obtained material after freeze-dried was

grinded to pass through 60 mesh and stored in a desiccator (An and Dultz 2007; Darder et al 2003; Deng et al 2006). Before use, 2 g Mt and 2 g Com were dispersed separately in a 1-L DI water and stirred constantly for 2 h. All experiments in the present work were conducted at room temperature.

2.3 Characterization of the Composite of Chitosan-Montmorillonite

2.3.1 X-ray Diffraction Analysis of Mt and the Com

The Mt or Com powder was grinded to pass through 140 mesh and filled in the X-ray diffraction (XRD) powder holder for the observation. XRD (Bruker D8 advance diffractometer) measurements were performed on using Cu-Kα radiation. The diffractometer was operated at a tube voltage of 40 kV and a current of 40 mA with 1.2 s counting per 0.02°. The XRD patterns were recorded with the powder in 3–30° (2θ) range, and the d_{001} was calculated with Bragg's law.

2.3.2 Fourier Transform Infrared Spectroscopy Analysis of the Com

Five milliliters of Mt or Com (1000 mg/L) was deposited accumulatively on polished 25×2 mm ZnS windows (ClearTran, International Crystal Labs, Garfield, NJ), air-dried, and dehydrated under a heat lamp (250 W). One milliliter of chitosan solution (2 mg/mL, solved in 10 mmol/L HCl) was deposited on the windows and air-dried. The Fourier transform infrared (FTIR) spectra of the above samples were recorded in transmission model with a resolution of 2 cm^{-1} on a Spectrum 100 infrared spectrometers (Perkin-Elmer). A total of 64 scans were collected and averaged for each spectrum (from 4000 to 700 cm^{-1}). The optical bench of the instrument and the sample chamber were purged with dry N$_2$ for 15 min before each record (Deng et al 2006, 2010).

The Com was further treated individually with the following cations: Na$^+$, K$^+$, Cu^{2+}, Al^{3+}, and Mn^{2+}. Each treatment included of 1 mL Com dispersion (5 mg/mL) and the addition of 25 mL 0.1 mol/L NaCl, KCl, CuCl$_2$, AlCl$_3$, or MnCl$_2$, respectively. The material was saturated with cations twice in each treatment. In Cu^{2+} exchange treatment, to avoid from the formation of Cu(OH)$_2$ precipitation, reaction solution was acidified with HCl to achieve pH 4.5–5.0. High dose of the cation was greater than several hundred times the CEC of Com

with each individual washing, for nearly complete exchange of cations on the Com. The excess of electrolytes in the cation treatments was removed by repeatedly washed with DI water (Deng et al 2006, 2010). The residue after centrifuge was suspended with 1 mL DI water. The dispersion of the Com was deposited on the windows and air-dried. The following operation was the same as mentioned above.

2.4 Isotherm Adsorption of Cu^{2+} by Mt or Com

An amount of adsorbent (2 mg, 1 mL dispersion of Mt or Com) was placed in a centrifuge tube, into which 5 mL Cu(NO$_3$)$_2$ solution (2–100 mg/L, pH 5.0) was added. Preliminary experiments had shown that the adsorption is complete within 24 h. The experiments were performed in a shaker bash for 24 h at 200 r/min. After centrifuge at 9000 r/min for 30 min, the Cu concentration in the initial solution and the equilibrium solution were determined using a flame atomic absorption spectroscopy (SpectrAA 220FS, Varian, USA). The amount of Cu^{2+} adsorbed on the composite was calculated by the difference between the content of metal in initial solution and that one in equilibrium solution, corrected with the blank, and it was expressed in milligrams per gram.

2.5 Cu^{2+} Adsorption as Influenced by Concentrations of Organic Ligands

Batch experiments were performed by shaking tubes with 1 mL dispersion of Mt or Com and 10 mL Cu(NO$_3$)$_2$ solutions (10 mg/L) in the presence of 1 mL acetate solutions (1–50 mmol/L) at 200 r/min for 24 h. The Cu(NO$_3$)$_2$ solutions were added with acetate (organic ligand + Cu^{2+}) or 12 h later (organic ligand before Cu^{2+}) than acetate, respectively. The following processes were the same as mentioned in Section 2.4.

2.6 The pH Variation Influence on Cu^{2+} Adsorption Toward Organic Ligands

The sodium acetate/acetic acid buffer was prepared at 0.08 or 4 mmol/L and was mixed with 2 mL dispersion of Mt or Com in the presence of 10 mL Cu(NO$_3$)$_2$ solutions (20 mg/L). Subsequently, the suspension was adjusted with HCl or NaOH to pH 3.0, 3.5, 4.0, 4.5, 5.0, and 5.5, respectively. The suspension was shaken for 24 h and the following processes were the same as in Section 2.4.

2.7 Calculation of the Chemical Form of Cu with MEDUSA

The chemical form of Cu at the experiment condition was calculated with the MEDUSA (32 bit, version updated at Dec. 16, 2010) and the Visual Minteq (version 3.0).

3 Results and Discussion

3.1 Characterization of Com

It was clear that d-spacing in X-ray data moves to smaller angles for the wider interlayer distance in the Com (Fig. 1). The d-spacing for the pure Mt was found at 6.98° (2θ), which corresponded to an interlayer distance of 1.26 nm. When the chitosan intercalated the Mt, the increased d-spacing of chitosan-montmorillonite composite was found at 5.78° (2θ), corresponding to an interlayer distance of 1.52 nm. The intercalation of the chitosan in the Mt interlayer was confirmed by the increase of d_{001} from 1.26 to 1.52 nm (An and Dultz 2007; Darder et al 2003).

As shown in Fig. 2a, the bands at 1535 cm^{-1} (–NH$_3^+$ bending) and 1381 cm^{-1} (C–H bending) on the spectrum of the Com were assigned to chitosan characteristic band. On the other hand, 3625 cm^{-1} (interlayer O–H stretching) and 1044 cm^{-1} (Si–O stretching) were inherited from that of Mt. The broad peak on the

spectrum of Com dominated at 3421 cm^{-1} included the N–H stretching of chitosan (3371 cm^{-1}) and the O–H stretching of Mt and/or chitosan (3400 and 3459 cm^{-1}). These results showed that the interaction had taken place between chitosan molecules and clay particles on the surface (Günister et al 2007). These discussions were in agreement with the observation of the XRD studies that the Mt formed complexes with chitosan.

Compared to that of pure Com, the spectrum (Fig. 2b) of the Com saturated with metals showed a little shift from 1517 to 1530 cm^{-1} (–NH$_3^+$ bending), indicating the proton exchange happened (Crini 2005). Neither obvious shift nor intensity change on the stretching of O–H and bending of N–H (3625 and 1632 cm^{-1}, respectively) was observed. That observation certified that the ion exchange reaction with –NH$_3^+$ happened more easily rather than the chelation with –NH$_2$ or –OH (Crini 2005; Gerente et al 2007).

The shift of –NH$_3^+$ bending indicated that the –NH$_3^+$ might act as a binding site in this adsorption process. The dominated interaction mechanism of Cu^{2+} adsorption with composite might be the ion exchange interaction. Considering that adsorption of metals on Mt due to the cation exchange on the protonated hydroxyl groups (Abollino et al 2008; Huang et al 2010; Malandrino et al 2006; Wang and Chen 2014; Zhu et al 2011) also, the organic ligand might have influence on the Cu^{2+} adsorption by Com and Mt similarly (Varma et al 2004).

**Fig. 1** The XRD patterns of montmorillonite and chitosan-montmorillonite
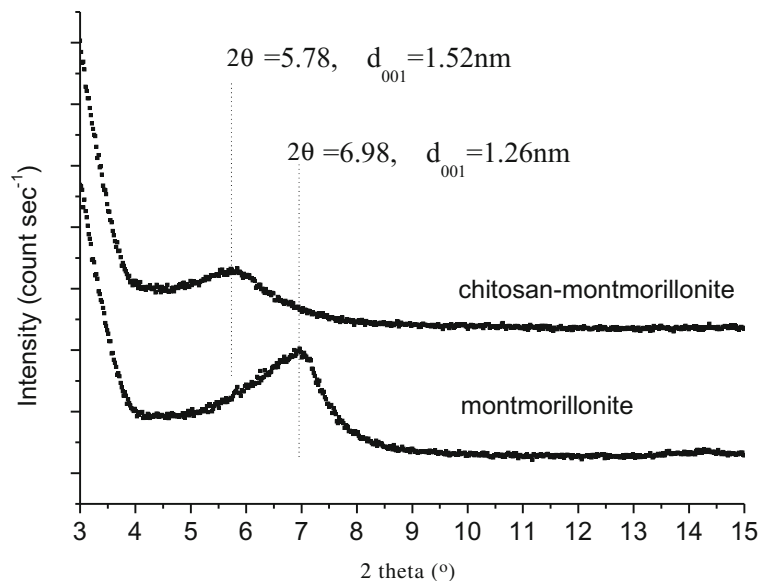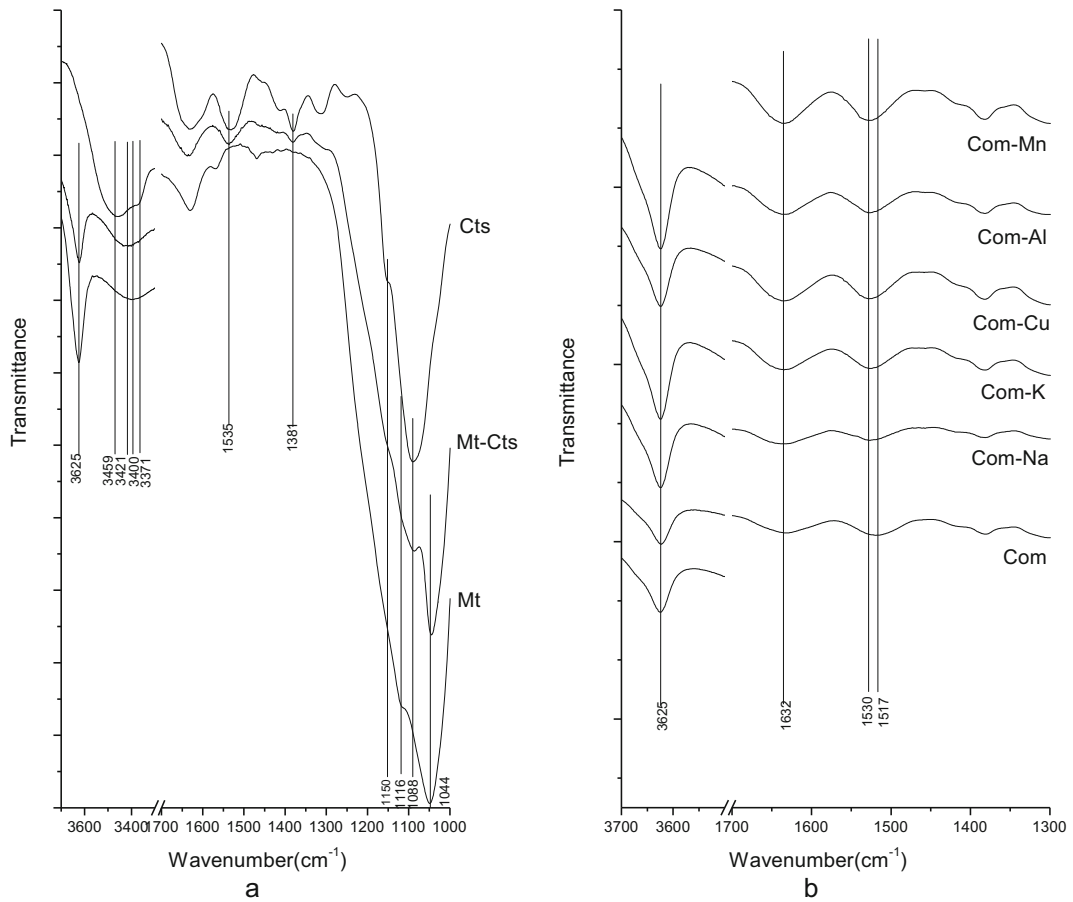
Fig. 2 **a** FTIR spectra of montmorillonite (Mt), chitosan (Cts), and Mt-Cts composite (Com). **b** FTIR spectra of Com and Com saturated with Na, K, Cu, Al, and Mn cations, respectively (the optical bench of the instrument and the sample chamber were purged 15 min with dry N_2 before record)

Fig. 3 The isotherm adsorption of Cu^{2+} by montmorillonite (Mt) or chitosan-montmorillonite (Com) (the *error bars* show the absolute errors in repetition of adsorbed mass; the *dash line* and the *dot line* show the Langmuir fitting on adsorption by Mt and Com, respectively)
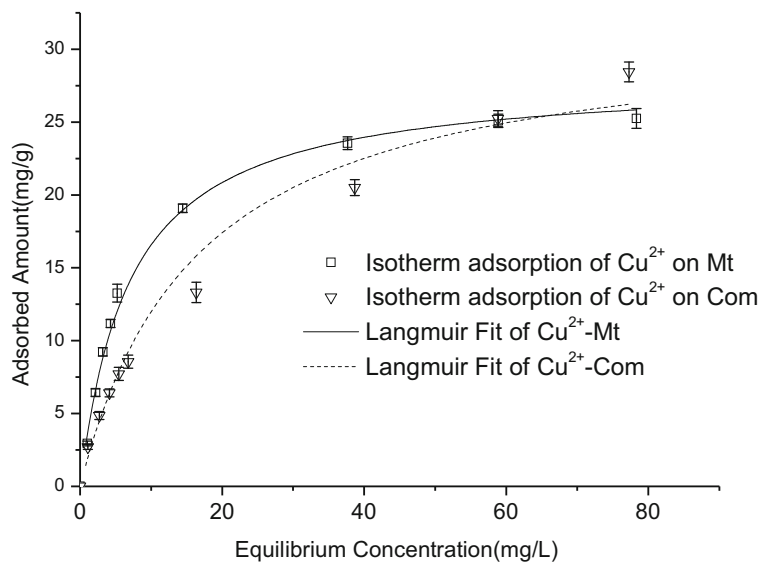
Fig. 4 The influence of acetate ligand (AL) at various concentrations on the adsorbed amount of Cu^{2+} by the montmorillonite (Mt) or chitosan-montmorillonite (Com); the introduction sequence, adding acetate ligand 12 h before Cu^{2+} and adding acetate ligand and Cu^{2+} simultaneously were abbreviated as "AL before Cu^{2+}" and "AL + Cu^{2+}," respectively
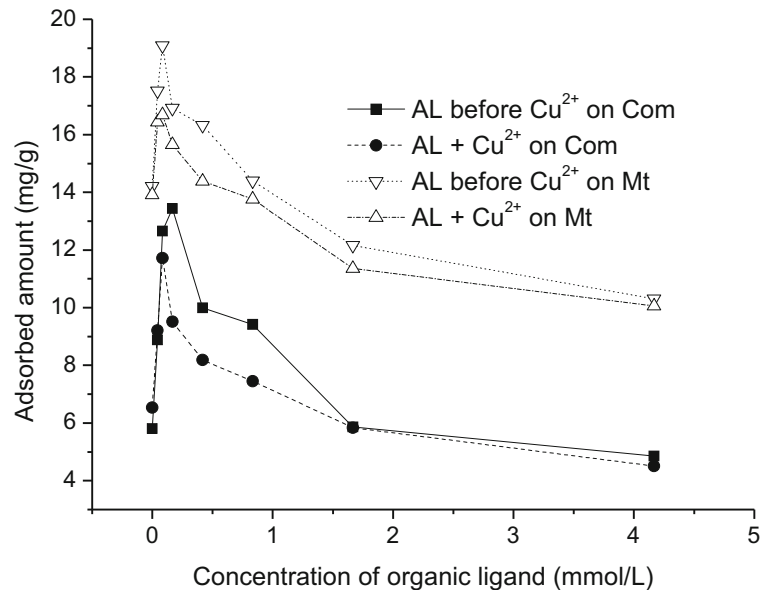
3.2 Isotherm Adsorption of Cu^{2+} on Com or Mt

The saturation adsorption capacity of Com was greater than that of pure Mt when the equilibrium concentration was up to 60 mg/L (Fig. 3). Within the concentration range studies, the equilibrium data of Com and pure Mt were consistent with the Langmuir model with high correlation coefficients (0.996 for Cu-Mt system and 0.983 for Cu-Com system). The maximum amount (qe) of Cu^{2+} adsorbed on composite (34.91 mg/g) was greater than that adsorbed on Mt (27.61 mg/g).

Therefore, we can assume that the adsorption of Cu^{2+} occurs mainly through a monolayer on homogenous adsorption sites of both Mt and composite. The site homogeneity on composite might result from the protonated amino, and NH_3^+ groups might be the main ion exchange sites.

3.3 Influences of Organic Ligands at Different Concentrations on Cu^{2+} Adsorption

As shown in Fig. 4, acetate at low concentration (0.08 mmol/L) promoted prominently Cu^{2+} adsorption, while at high concentration (>1 mmol/L), it inhibited adsorption on either Mt or Com. Adding acetate before Cu^{2+} resulted more adsorption than adding the acetate and Cu^{2+} solution together, for either Com or Mt. Moreover, the inhibition was more apparent on Mt than on Com.

The diagram (Fig. 5) from MEDUSA program indicated the acetate dependence of Cu formation. With the increasing of acetate concentration, part of the free Cu^{2+} converts to $Cu(Acetate)^+$ and the remained free Cu^{2+} was about 70 % of the total Cu when the acetate was 4 mmol/L.

Fig. 5 The form analysis of Cu^{2+} at different concentrations of acetate ligands with MEDUSA
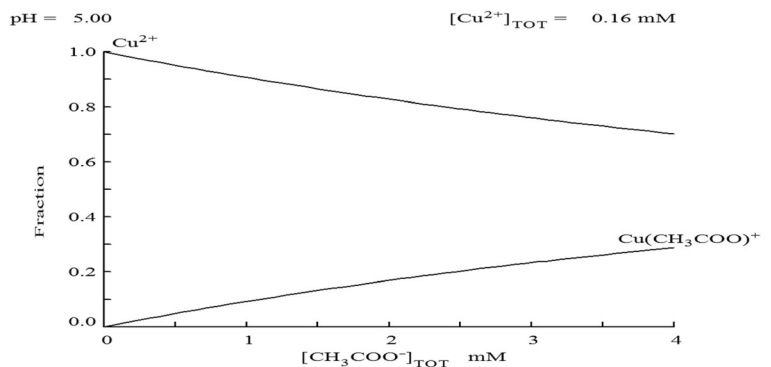
Fig. 6 The pH dependence of adsorbed amount of Cu^{2+} by Mt or Com (two concentrations of ligands at 0.08 or 4 mmol/L, pH 3.0 to 5.5; the ligands and the adsorbent are **a** acetate-Mt and **b** acetate-Com, respectively)
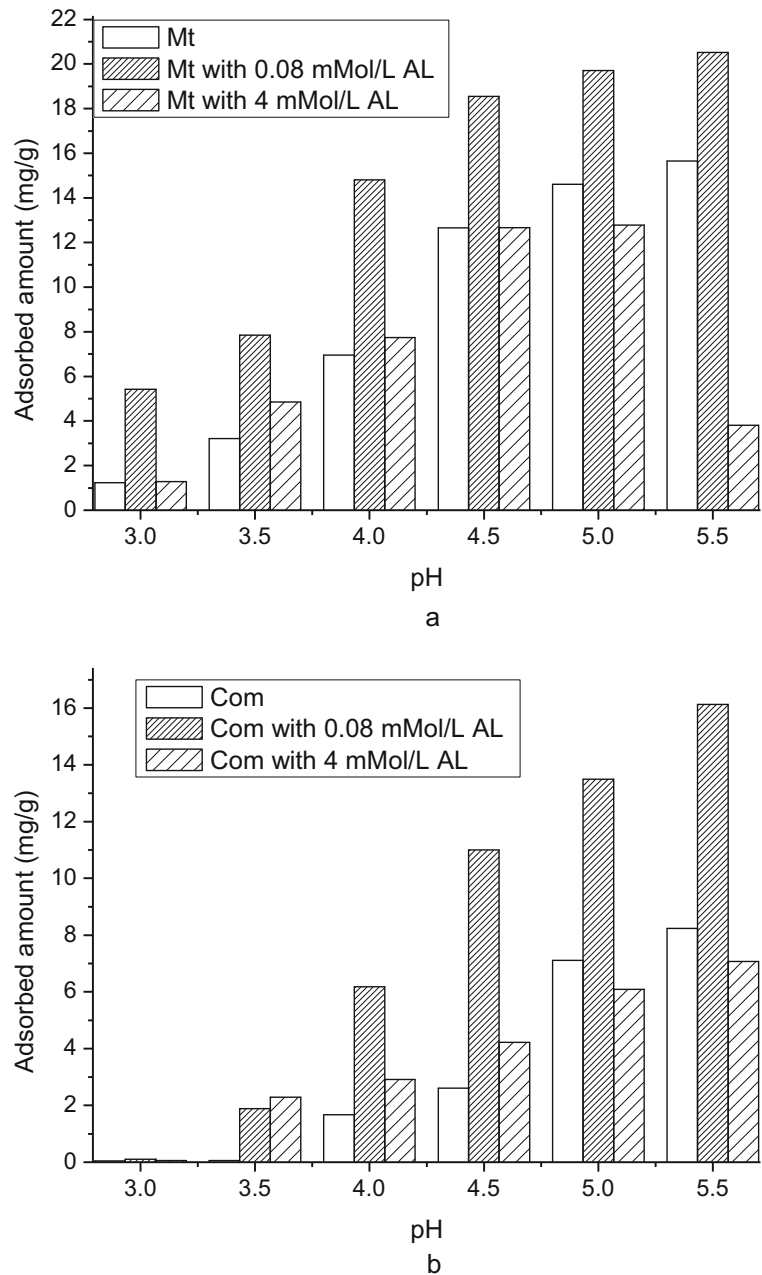

According to the simulation results in Fig. 5, the 0.08 mmol/L acetate had little effect on the formation of Cu, yet, the experiment showed that 0.08 mmol/L acetate promoted the adsorption of Cu^{2+} both by Mt and Com, indicating that the reason for the promotion might be the change of adsorption sites on adsorbent rather than change of the adsorbate.

Mt can adsorb heavy metals via cation exchange in the interlayers resulting from the interaction between ions and negative permanent charge at pH 5.0. Organic ligands improved the adsorption at its low concentration while inhibited the adsorption at its high concentration. The adsorption could be affected by the forming of ternary surface complexes and the metal complex, respectively (Abollino et al 2008; Malandrino et al 2006; Marcussen et al 2009; Zhu et al 2011). The ternary surface complexes could be supposed as ligand-metal-sorbent on the Mt.

Fig. 7 The form analysis of Cu^{2+} at different pH with MEDUSA (83.3 μM acetate ligands)

$[Cu^{2+}]_{TOT} = 0.16\ mM$ $[CH_3COO^-]_{TOT} = 83.30\ \mu M$
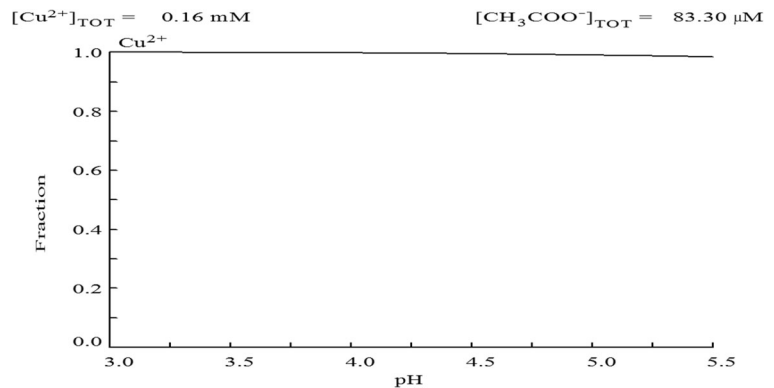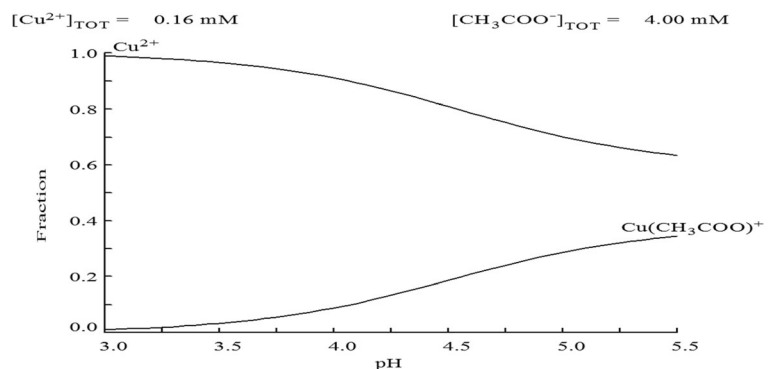

On the contrary, protonated amino groups and positive charges appeared in Com at pH < 6.3 (An and Dultz 2007), and the ternary surface complexes might be metal-ligand-sorbent in the Com. The amino groups on the chitosan were in favor of the formation of ternary surface complex, resulted in more promotion on the Cu^{2+} adsorption by Com than by Mt. Moreover, Cu(Acetate)$^+$ was formed with the increasing of acetate ligand. It was more difficult for that to be adsorbed on the Mt, because the ionic radius of complexes was too large to enter the interspace. But this suppression was not apparent on the adsorption by Com, because the protonated amino contended with ligand for the bonding of Cu^{2+}.

Meanwhile, the addition of acetate before Cu^{2+} adsorption was more beneficial to the formation of ternary complexes on the Com or Mt and had no promotion on the forming of soluble complex.

3.4 Effect of pH on Cu^{2+} Adsorption by Com or Mt Toward Organic Ligands

The influence of pH on the adsorption of Cu^{2+} by Mt and Com was studied and the results obtained are represented in Fig. 6a, b. As expected, the adsorption behavior significantly changed with the pH variation and became greater at higher pH both on the Mt and Com in the absence of acetate. Acetate (0.08 mmol/L) enhanced the adsorption by either Mt or Com in the pH interval between 3.0 and 5.5. Four millimoles per liter acetate increased the adsorption by either Mt or Com at pH < 4.5, but suppressed the adsorption by Mt at pH 4.5–5.5. Moreover, 4 mmol/L acetate enhanced the adsorption on Com at low pH, but inhibited that at pH 5.0–5.5.

The diagrams using MEDUSA are present in Figs. 7 and 8. In the presence of 0.08 mmol/L acetate ligand, the change of free Cu^{2+} could not be observed with the increase of pH. On the other hand, the free Cu^{2+} converted to Cu(Acetate)$^+$ obviously with the increase of pH when the acetate was 4 mmol/L. The free Cu^{2+} was 60 % of the total Cu when pH was 5.5 in Fig. 8.

For the adsorption on Mt, the organic acid will convert to the neutral form (–COOH) at low pH, not the anionic forms anymore, and therefore, they can be adsorbed in the interlayer of Mt with Cu together (forming Cu-neutral ligand complexes). This might be the reason why the adsorption of Cu was greater in the presence of the ligand at low pH.

Fig. 8 The form analysis of Cu^{2+} at different pH with MEDUSA (4 mM organic ligands)

$[Cu^{2+}]_{TOT} = 0.16\ mM$ $[CH_3COO^-]_{TOT} = 4.00\ mM$

Low pH was more favorable to form ternary surface complexes, and high pH was helpful to form Cu(Acetate)$^+$ soluble complexes, respectively. So, 0.08 mmol/L acetate promoted more Cu^{2+} adsorption on Mt and Com at low pH as compared to that at high pH. Moreover, the promotion by 4 mmol/L acetate reversed to inhibition when the pH increased from 4.0 to 5.0. For the Com, the positive charge of amino group has increased at low pH, and there formed the metal-ligand-sorbent ternary complexes on the surface. That was why the increased adsorbed amount of Cu^{2+} on Com was greater than that on Mt at same condition.

The effect of organic ligand on Cu^{2+} adsorption by Com depended on the pH, nature, and the concentration of ligands. In conclusion, the ligand tended to promote Cu^{2+} adsorption at low pH and inhibited Cu^{2+} sorption at high pH.

4 Conclusions

Compared to Mt, the Com had more capacity to adsorb the Cu^{2+}, while the Cu^{2+} adsorption curve of Mt was much better fitting with Langmuir model than that on Com. Acetate ligands at low concentrations or low pH improved adsorption capacity on the Com than that on the Mt. The inhibition from the ligands was cut down on the Com than Mt. Acetate showed better effect on the Com for the removal of Cu^{2+} (up to 60 mg/L) from acidic wastewater.

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