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Research paper

Characterization of bentonite modified with humic acid for the removal of Cu (II) and 2,4-dichlorophenol from aqueous solution

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ABSTRACT

This study examines the modification of bentonite with humic acid (HAB) as a novel sorbent for simultaneous removal of Cu(II) and 2,4-dichlorophenol (2,4-DCP) from aqueous solution. Batch experiments were conducted employing either single sorption or simultaneous sorption of Cu(II) and 2,4-DCP. Results indicated that the sorption of either Cu(II) or 2,4-DCP onto HAB was little influenced by the presence of the other contaminant. The amount of sorption was 22.40 mg g^{-1} and 14.23 mg g^{-1} for Cu(II) and 2,4-DCP, respectively at 30 °C. Scanning electron microscopy (SEM) indicated that HA was immobilized on the surface of bentonite. Energy dispersive spectroscopic (EDS) analysis indicated that Cu(II) was sorbed onto HAB. X-ray diffraction (XRD) analysis demonstrated that the crystalline structure of bentonite did not change after being modified with HA. Fourier-transform infrared (FTIR) spectra confirmed that new bonds and band intensity emerged after the sorption of Cu(II) and 2,4-DCP onto the HAB. These suggest that simultaneous sorption of 2,4-DCP and Cu(II) onto HAB could occur through: firstly, a mechanism that partitions between 2,4-DCP and HA; and secondly, the ion-exchange mechanism between Cu(II) and bentonite.

1. Introduction

Heavy metals and chlorinated-phenols are dangerous pollutants in wastewater because they are harmful to humans and the environment. Therefore, these pollutants must be removed from wastewater prior to being discharged into the aquatic environment (Babel and Kurniawan, 2003; Bhattacharyya and Gupta, 2008). Natural clays and modified clays working as low-cost adsorbents have received much attention in the recent years because of their applicability in removing heavy metals and phenolic compounds from contaminated water (Ahmaruzzaman, 2008; Lin and Juang, 2009). However, most studies have concentrated on using clay or organoclay to remove heavy metals or organic compounds from aqueous solution independently. In fact, the treatment of mixed wastewater is a significant challenge because metals and organic contaminants have different fates and transport mechanisms.

Several studies have been published regarding the simultaneous sorption of metals and organic compounds using organoclays. Recently, bentonite modified with carboxydecyl triethylammonium and hexadecyl trimethylammonium has been used to remove Pb(II) and chlorobenzene (Lee et al., 2002; Sheng et al., 1999), while bentonite modified with benzyldimethyl octadecylammonium chloride or dioctadecyl dimethylammonium chloride has been utilized for multiple adsorption of 2-chlorophenol and Pb(II) and Cd(II) (Andini et al., 2006; Huang et al., 2015). Bentonite modified with benzyl triethylammonium has also been used for simultaneous sorption of benzene and heavy metals (Oyanedel-Craver et al., 2007). However, carboxydecyl triethylammonium, hexadecyl trimethylammonium and benzyldimethyl octadecylammonium chloride are cationic surfactants; they can also be environmentally hazardous (Sarkar et al., 2010, 2013). Conversely, humic acid is a naturally occurring organic matter which results from microbial and chemical transformations of organic debris, and can be used for clay modification (Zamparas et al., 2013). Studies of bentonite modified with humic acid (HA) for simultaneous sorption of Cu(II) and 2,4-DCP are limited. HA, metal ions and toxic organic pollutants may exist in water simultaneously at different concentrations, and metal ions and HA can form complexes in water (Wang et al., 2008). Hence, sorption behaviours of heavy metals and toxic organic pollutants and their relevant mechanisms may help to uphold environmental standards for complex pollutants (Zhou et al., 2008), where the simultaneous sorption mechanism is still unclear.

The current study therefore aims to investigate the sorption of Cu(II) and 2,4-DCP on a humic acid modified bentonite (HAB) sorbent under mono- or bi-solute conditions. The mechanisms of simultaneous Cu(II) and 2,4-DCP sorption were studied both by assessing the contaminants removal from aqueous solution and thorough characterization (SEM,

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FTIR, XRD and EDS) of the adsorbent surface and structure. This helped to provide evidence for the potential of this new material for treating heavy metal-organic co-contaminated wastewater.

2. Materials and methods

2.1. Preparation of HAB

The bentonite used in this study was mainly a Na-montmorillonite (Na-Mt) supplied by Fenghong Co. Ltd. (Jian, Zhejiang, China) and having a cation exchange capacity (CEC) of 75.4 meq 100 g^{-1} (Su et al., 2011). Humic acid, $Cu(NO_3)_2$ and 2,4-dichlorophenol (2,4-DCP) were of analytical reagent grade and used without further purification. Firstly, humic acid was dissolved in 0.1 M NaOH, and undissolved impurity was discarded. Then, pH of the solution was adjusted to 1.0–1.5 using 6 M HCl and placed in a water bath at 60–70 °C. Following precipitation HA was centrifuged separately. These steps were then repeated. Finally, the precipitated HA was dried in an oven at 40–50 °C overnight. A solution containing 2,4-DCP and Cu(II) was prepared by dissolving a known amount of 2,4-DCP and $Cu(NO_3)_2$ in deionized water to desired concentrations and stored in a refrigerator prior to use. The pH of the solution was adjusted using 0.1 M NaOH or HCl.

HA (0.5 g) was dissolved in 75 mL of 0.1 M NaOH. Then, bentonite (4.0 g) was added to the solution containing HA. The pH was adjusted to 6.0 and then the mixture was put into a shaker incubator at 30 °C and 150 rpm for 18 h. Finally, the precipitation was collected and subsequently washed with distilled water. The moist solid material was dried in an oven at 60–70 °C and ground with a mortar, and HAB was screened through a 110-mesh sieve to obtain particles used as the absorbent.

2.2. Characterization

Solid morphology of the bentonite and the HAB was determined using a scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDS) (JSM 7500F, JEOL, Japan). Utilizing a voltage of 5.0 kV, samples for SEM measurement were magnified 10,000 times.

The infrared spectra of bentonite and HAB were obtained using a Fourier transform infrared (FTIR) spectrometer (FTIR Nicolet 5700, Thermo Corp., U.S.A.). Samples for FTIR measurement were prepared by mixing 1% (*w*/w) specimen with 100 mg of KBr powder and pressing the mixture into a sheer slice. The average of 9 scans was collected for each measurement using a resolution of 2 cm^{-1}.

The crystal characteristics of the modified bentonite before and after use were determined using an X-ray diffraction (XRD) instrument (PANalytical X'Pert Pro MPD, Netherlands) with filtered Cu Kα radiation operated at 40 kV and 40 mA. The XRD pattern was recorded from 10° to 80° of 2θ with a scanning speed of 0.02° at 2θ per second.

2.3. Batch experiment method

Sorption of Cu(II) and 2,4-DCP using HAB and unmodified bentonite (UB) was conducted employing batch experiments for single- and bi-solute reactions. Experiments were performed using 50 mL capped plastic centrifuge tubes containing 25 mL of 100 mg L^{-1} Cu(II) or 2,4-DCP solutions added to 0.1 g of HAB in a shaker incubator operated at a desired temperature and 250 rpm. After being shaken for a certain period of time, the suspensions were centrifuged at 3000 rpm for 5 min. The supernatants were then collected and analyzed for Cu(II) concentration utilizing a flame atomic adsorption spectrophotometer (Varian, Spectra AA 240), while the 2,4-DCP was examined using a UV–Vis spectrophotometer at 286 nm wavelength (752 N, Shanghai, China). In simultaneous sorption experiments, Cu(II) and 2,4-DCP were added to a solution containing 0.1 g of HAB. The sorption conditions were the same as that for single-solute sorption. The sorption capacity was calculated using the following equation (Fu et al., 2009):

$$Q_t(\mathrm{mg/g}) = \frac{(C_0 - C_t)\cdot V/1000}{W} \quad (1)$$

where, Q_t is the amount sorbed at time t (mg g^{-1}); C_0 is the initial concentration of Cu(II) or 2,4-DCP (mg L^{-1}); C_t is the concentration of the Cu(II) or 2,4-DCP in the solution at time t (mg L^{-1}); V is the volume of solution (mL); and W is the weight of the sorbent used (g).

3. Results and discussion

3.1. Sorption of Cu(II) and 2,4-DCP onto bentonite and HAB

In order to determine whether the humic acid modified bentonite (HAB) can be used for simultaneous sorption of Cu(II) and 2,4-DCP, they were sorbed individually onto the HAB and the unmodified bentonite (UB). This involved undertaking batch experiments where a solution containing 100 mg L^{-1} Cu(II) or 100 mg L^{-1} 2,4-DCP at pH 6.5 and 30 °C was used. It was observed that initial sorption of Cu(II) was rapid on both UB and HAB in the first 10 min, while it took more than 60 min for the sorption of Cu(II) on the UB or HAB to reach equilibrium (Fig. 1a). This indicated that HAB did not improve the sorption rate of Cu(II) compared to that of UB. It might have resulted from the sorption of Cu(II) onto the adsorbents through an ion-exchange mechanism in which the interlamellar cations of clay such as Na^+ was replaced. This could be explained by the high CEC of bentonite (75.4 meq 100 g^{-1}) (Barbier et al., 2000; Donat et al., 2005).

However, HAB slightly enhanced the sorption of Cu(II), for example, UB sorbed about 22 mg g^{-1} Cu(II) while HAB sorbed nearly 23 mg g^{-1}. This suggests that there is little complexation between HA and metal ions on the surface of bentonite because these complexation processes are usually very fast as indicated by complexation studies of HA with metal ions (El-Eswed and Khalili, 2006). This has also been confirmed by previous works that reported the sorption of HA on bentonite reached equilibrium in approximately 24 h (Banat et al., 2000; Wang et al., 2008). Hence, it is proposed here that the sorption of Cu(II) onto the HAB is due to the ion-exchange mechanism rather than complexation mechanism.

Similarly to Cu(II), the initial sorption of 2,4-DCP was rapid for both UB and HAB, and the sorption reached equilibrium in less than 60 min (Fig. 1b). However, a high sorption capacity of 2,4-DCP onto HAB (16.4 mg g^{-1}) was observed in comparison to UB (3.4 mg g^{-1}). A higher sorption capacity of 2, 4-DCP onto HAB could be attributed to the interaction between 2,4-DCP and HA on the surface of HAB. This was because HA was one of the major components of humic substances which contained both hydrophilic and hydrophobic molecules (Anirudhan and Suchithra, 2010). So, the hydrophobic interaction between HA and 2,4-DCP might have improved the sorption of 2,4-DCP on HAB (Xi et al., 2007). In contrast, 2,4-DCP was adsorbed onto the unmodified bentonite (UB) only by reaching into the interlamellar sorption sites of the clay. Therefore, the low sorption capacity of 2,4-DCP on UB was observed. This was also supported by a study demonstrating a low adsorption of phenol onto bentonite (Banat et al., 2000).

3.2. Simultaneous sorption of Cu(II) and 2,4-DCP onto HAB

It was reported that complexation of heavy metals and humic acid could play an important role in simultaneous sorption since the presence of humic acid in water would provide additional binding sites for heavy metals, thus promoting metal sorption on fly ash (Wang et al., 2008). In this study, to determine whether competition occurred between Cu(II) and 2,4-DCP during their sorption onto HAB, a comparison was made of simultaneous sorption and single sorption of Cu(II) and 2,4-DCP onto the adsorbent. Cu(II) sorption onto HAB was similar regardless of the presence of 2,4-DCP (Fig. 2a). This indicated that there

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