Applied Clay Science 88–89 (2014) 33–38

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Montmorillonite as a multifunctional adsorbent can simultaneously remove crystal violet, cetyltrimethylammonium, and 2-naphthol from water

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ARTICLE INFO

Article history:
Received 18 May 2012
Received in revised form 11 December 2013
Accepted 13 December 2013
Available online 7 January 2014

Keywords:
Montmorillonite
Adsorption
Wastewater treatment
Organic contaminants

ABSTRACT

The adsorptive behaviors of crystal violet (CV), cetyltrimethylammonium (CTMA), and 2-naphthol to montmorillonite (Mt) using a simultaneous-adsorption process were studied in this work. The adsorption results showed that under the experimental concentrations both CV and CTMA were almost completely removed by Mt. XRD and FTIR characterization results showed that the adsorbed CV and CTMA formed CTMA–CV aggregates within the interlayer spaces of Mt, and these aggregates served as accommodation spaces for the adsorption of 2-naphthol. The adsorption isotherms of 2-naphthol fitted linear equation well in the simultaneous-adsorption process, suggesting that partition should be the dominant mechanism for uptaking 2-naphthol. Combining the fact that CV alone formed aggregates showed nonlinear adsorption isotherms and much weaker adsorption capacity towards 2-naphtol than CTMA alone formed aggregates, one would expect that CTMA played a dominant role in the adsorption of 2-naphthol to CTMA–CV aggregates. In addition, the CTMA–CV aggregates have better adsorption capacity towards 2-naphthol than the combination of CTMA aggregates and CV aggregates do. FTIR results showed that CV could adjust the arrangement of CTMA in the CTMA–CV aggregates, which might be the reason for the enhanced adsorption capacity. Results of this work suggest that montmorillonite can be used as a low-cost and high-efficient adsorbent for the simultaneous removal of different types of organic contaminants from water.

1. Introduction

Montmorillonite (Mt) is a 2:1 type clay mineral composed of one octahedral sheet sandwiched by two tetrahedral sheets. Due to isomorphous substitution effect, Mt layers contain negative charges, which are counterbalanced by inorganic cations (e.g., Na^+, Ca^{2+}) (Brigatti et al., 2006). These inorganic cations are exchangeable, making Mt efficient adsorbent for various cationic contaminants, such as heavy metals (Bailey et al., 1999; Bhattacharyya and Gupta, 2008; Krishna and Susmita, 2006), cationic dyes (Eren and Afsin, 2008; Gupta and Suhas, 2009; Rytwo and Ruiz-Hitzky, 2003), and cationic surfactants (Li and Rosen, 2000; Li et al., 2006; Ma and Zhu, 2007). After the adsorption of organic cations, interlayer space of Mt can change from hydrophilic to hydrophobic, and the resulting materials, also known as organoclays, have been used as efficient adsorbents for hydrophobic organic contaminants (HOC) (Chen et al., 2005; Ramesh et al., 2007; Rytwo and Gonen, 2006; Shen, 2002, 2004; Zhu et al., 2007). Therefore, Mt can simultaneously remove both organic cations and HOC from wastewater, and it has been considered as a low-cost and high-efficient adsorbent for wastewater containing different organic contaminants (Ma and Zhu, 2007; Özcan et al., 2005; Rytwo and Gonen, 2006; Wei et al., 2009; Zhu and Ma, 2008).

Since Mt generally shows high affinity towards organic cations, the removal efficiency of HOC by Mt has drawn much more attention in the simultaneous-adsorption process (i.e., one-step-adsorption process). Several previous studies showed that the adsorptive behavior of HOC on Mt in this adsorption process strongly depends on the structure of intercalated organic cation (Ma and Zhu, 2007; Shen, 2002; Wei et al., 2009), similar to the adsorptive behavior of traditional organoclay, previously synthesized before the adsorption of HOC. For example, Wei et al. (2009) reported that in the simultaneous-adsorption process 2-naphthol was adsorbed on crystal violet (CV) intercalated Mt by a surface adsorption mechanism; while Ma and Zhu (2007) proposed that phenol was partitioned into the pseudo-organophase formed by cetyltrimethylammonium (CTMA) aggregates.

Numerous studies have shown that the arrangement of the intercalated cations can evidently influence the capacity of organoclays for adsorbing HOC (Chen et al., 2005; Churchman et al., 2006; Zhu et al., 2007, 2010). For the organoclays synthesized with small, compact organic cations (e.g., tetramethylammonium, TMA), increasing the

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http://dx.doi.org/10.1016/j.clay.2013.12.010

intermolecular distance of the intercalated cations will lead to larger exposed siloxane surface areas (main adsorption sites for HOC), which then can increase the adsorption capacity of this type of organoclays (Ruan et al., 2008; Shen, 2004). With respect to the organoclays synthesized with large, flexible organic cations (containing at least one long alkyl chains, e.g., CTMA), adjusting the arrangement of alkyl chain aggregates within the interlayer space of organoclays may also enhance their adsorption capacity (Zhu et al., 2007, 2010). According to these findings, several methods have been developed to improve the adsorption capacity of the organoclays. For example, reduced-charge Mt has been used to synthesize TMA-Mt, and the resulting organoclays will have larger surface areas and better adsorption capacity (Ruan et al., 2008). Cationic polymers (e.g., polyacrylamide) have been employed to simultaneously intercalate Mt with CTMA. Due to the high charge/volume ratio of the cationic polymers, the arrangement of CTMA can be adjusted, and the resulting organoclays show better adsorption capacity towards HOC (Zhu et al., 2010). As such, in the simultaneous-adsorption process the adsorptive behaviors of HOC may also be influenced by the arrangement of the intercalated organic cations, especially when wastewater contains different types of organic cations, since the co-existing organic cations may influence each other's arrangement within the interlay space of Mt. However, the related researches have not been well concerned yet until now.

The objectives of this work are (1) to investigate how the arrangement of cationic dyes and cationic surfactants can be influenced by each other within the interlayer spaces of Mt, and (2) to examine the adsorptive behaviors of the resulting organoclays towards HOC in the simultaneous-adsorption process. CV, CTMA, and 2-naphthol were selected as representatives of cationic dye, cationic surfactant and HOC, respectively. Results of this work may provide new information for understanding the adsorptive behaviors of organoclays and for the application of Mt in the treatment of wastewater containing multiple organic contaminants.

2. Materials and methods

2.1. Materials

The raw Mt sample (purity > 95%) with the structural formula of $Na_{0.016}\ K_{0.020}Ca_{0.392}[Al_{2.518}Fe_{0.450}\ Mg_{1.104}Ti_{0.360}Mn_{0.004}][Si_{7.910}Al_{0.090}]O_{20}(OH)_4 \cdot nH_2O$, was obtained from Inner-Mongolia, China (Zhu et al., 2007, 2010). The net charge of the clay mineral was $-0.82\ e$ per unit cell, and its cation exchange capacity (CEC) was 108 cmol/kg. Cetyltrimethylammonium bromide, CV, and 2-naphthol of analytical grade were supplied by Shanghai Chemical Co. (China). All of the reagents were used as received.

2.2. Adsorption experiment

For comparison, the following batch adsorption experiments were carried out: (1) simultaneous adsorption of CV and 2-naphthol to Mt; (2) simultaneous adsorption of CTMA and 2-naphthol to Mt; and (3) simultaneous adsorption of CV, CTMA, and 2-naphthol to Mt. The obtained organoclays in above three adsorption systems were denoted as CV–Mt, CA–Mt, and CA–CV–Mt, respectively. The added amount of CV was controlled at 0.2 or 0.4 times CEC of Mt, and the added amount of CTMA was controlled at 0.2, 0.4, or 0.6 times CEC of Mt. The initial concentrations of 2-naphthol ranged from 5 to 200 mg/L. During the adsorption processes, 0.2 g Mt was combined with 20 mL solution (containing desired amount of above chemicals) in 25 mL glass centrifuge tubes. Then the tubes were sealed with Teflon-lined caps and shaken for 8 h at 25 °C. Preliminary experiments showed that the adsorption equilibrium was reached within 8 h. After centrifugation at 2000 g for 30 min, the concentration of 2-naphthol in supernate was detected using a UV–vis spectrophotometer at the wavelength of 224 nm. Control experiments showed that in the tested concentration range, both CV and CTMA could be almost completely adsorbed by Mt (over 99.5%), and the remaining CV and CTMA did not have evident influence on the detection of 2-naphthol.

2.3. X-ray diffraction and FTIR characterization

The X-ray diffraction (XRD) patterns of the Mt samples were recorded using a Bruker D8 ADVANCE X-ray diffractometer, operating at 40 kV and 40 mA with Cu Kα radiation. After the equilibrium adsorption of CV and/or CTMA, the resulting organoclays were separated from the water by 2 min centrifugation at 2000 *g*. Then the separated organoclay pastes were pressed on sample support and followed immediately by XRD measurement. The patterns were recorded for a 2θ range between 1° and 20° at a scanning speed of 2°/min. After that, the organoclays samples were dried at 60 °C for 12 h and then ground to pass 100 mesh sieves. The dry powders were then pressed on the sample support for further XRD measurement. Basal spacings were determined from the 2θ values of the corresponding basal reflections.

FTIR characterization for the dry samples was carried out on a Brucker Vertex-70 FTIR spectrophotometer. The spectra over the range of 4000–400 cm^{-1} were recorded with a resolution of 1.0 cm^{-1}. Proper amount of sample was mixed with KBr and milled to fine powder using a mortar and pestle. The powder was then made into a fragile pellet using a compression machine, and then the pellet was placed inside a supporting cell for infrared analysis. Sixty four interferograms were collected for each sample.

3. Results and discussion

3.1. Characterization results

XRD has been proved as a powerful tool in characterizing the structure of organoclays. The potential arrangements of intercalated organic cations were proposed according to the obtained basal spacing of organoclays and the size of organic cations (He et al., 2006; Xi et al., 2005). In this work, the XRD patterns of both dry and water saturated organoclays were obtained (Fig. 1), and accordingly the basal spacings were calculated (Table 1S). According to previous studies (He et al., 2006; Xi et al., 2005), CTMA should first adopt lateral-monolayer arrangement and then lateral-bilayer arrangement within the interlayer space of dry CA–Mt, as its loading level increased from 0.2 CEC to 0.6 CEC. Water saturated CA–Mt has larger basal spacing than the corresponding dry CA–Mt and the wet Mt, consistent with previous studies (Zhu et al., 2011), indicating the incorporation of large amount of water molecules to the interlayer space of the wet samples.

The basal spacing of dry CV–0.2Mt is 1.46 nm, which means that the gallery height is only 0.5 nm, suggesting flat arrangement of CV within the interlayer space of 0.2CV–Mt. After water saturation, the basal spacing of CV–0.2Mt increased to 1.99 nm. Double peaks corresponding to the basal spacings of 1.46 nm and 1.87 nm are shown for dry 0.4CV–Mt. For the wet 0.4CV–Mt, however, it has only one diffraction peak at 2.11 nm. These results also suggest that large amount of water molecules have entered into the interlayer space of wet CV–Mt.

The basal spacings of dry CA–CV–Mt are much larger than those of dry CA–Mt and dry CV–Mt, and they are generally proportional to the loaded amount of CTMA and CV, indicating the simultaneous intercalation of CTMA and CV into the interlayer spaces of CA–CV–Mt. After water saturation, the basal spacings of CA–CV–Mt can be further expanded. However, the expansion is quite small (no more than 0.1 nm) for most of the CA–CV–Mt, except for 0.4CA–0.2CV–Mt and 0.6CA–0.2CV–Mt, the two samples with lower CV but higher CTMA loading levels. In addition, although CA–0.4CV–Mt have large basal spacings in dry state than CA–0.2CV–Mt, the former series showed smaller basal spacing after water saturation. Combing with the fact that CA–Mt (with relatively high CTMA loading) swell more significantly than CV–Mt and CA–CV–Mt after water saturation, one can tell that