Applied Clay Science 146 (2017) 35–42

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Chitosan and surfactant co-modified montmorillonite: A multifunctional adsorbent for contaminant removal

Lifang Zhu[a], Linhan Wang[b], Yin Xu[b,*]

[a] Zhejiang University of Water Resources and Electric Power, Zhejiang 310018, China
[b] Environmental Science and Technology Department, Xiangtan University, Xiangtan 411105, China

ARTICLE INFO

Keywords:
Montmorillonite
Organoclay
Contaminants
Adsorption
Water treatment

ABSTRACT

The demands for multifunctional adsorbents are increasing in these days because wastewater may simultaneously contain various types of contaminants. In this work, montmorillonite (Mt) was modified with both hexadecyltrimethylammonium (HDTMA) and chitosan (CTS), with the purpose of synthesizing multifunctional adsorbents that can efficiently adsorb hydrophobic organic contaminants, heavy metal cations, and dyes from water. The structural characteristics of the resulting modified samples (H/C-Mt) were first investigated using XRD, FTIR, TG, and Zeta potential measurements. According to the obtained results, both chitosan and HDTMA were intercalated into Mt interlayers, forming hydrophobic organo-phases. With increasing CTS loading amount, the basal spacing of C/T-Mt gradually increased, and the Zeta potential evolved from negative to positive. C/T-Mt could effectively uptake phenol, Cd^{2+}, Conger red (CR), and crystal violet (CV) from water. The organo-phases created by HDTMA were responsible for the uptake of phenol on C/T-Mt, while the functional groups on CTS (e.g., $-OH$, $-NH_2$) contributed to the adsorption of Cd^{2+}. The positively charged surfaces of C/T-Mt, together with the hydrophobic interactions between C/T-Mt and contaminants, contributed to the effective uptake of CR on C/T-Mt. As for CV, the hydrophobic interactions should be the main reason for its adsorption on C/T-Mt. The obtained results suggested that C/T-Mt could be a multi-functional adsorbent for the effective uptake of different types of contaminants from water.

1. Introduction

Clay minerals and their modified products, as a large family of sorbents, have drawn much attention nowadays, in that they are relatively low-cost and environmentally friendly, and can be used to effectively adsorb a wide variety of contaminants (Chen et al., 2014, 2016; Gates et al., 2009; Lee and Tiwari, 2012; Ma and Zhu, 2006, 2007; Wang et al., 2010; Wu et al., 2001, 2009; Zhu et al., 2007, 2009a,b, 2011, 2014a,b, 2015a,b). Hereinto, montmorillonite (Mt) and its modified products have received particular interests. As a typical 2:1 type clay mineral with abundant exchangeable interlayer cations, Mt itself can effectively adsorb various cationic contaminants (e.g., heavy metal cations, cationic dyes) through a cation exchange process (Gupta and Bhattacharyya, 2014; He et al., 2001; Jovic-Jovicic et al., 2008, 2010, 2013; Leodopoulos et al., 2015; Wei et al., 2009; Zhu et al., 2014a, 2016). In addition, the structure and properties of Mt can be easily modified using a diversity of modifiers (cationic surfactant, polymers, hydroxylmetal polycations, etc.), and the resulting synthesized materials can be used as efficient adsorbents for various contaminants (Lee and Tiwari, 2012; Ma and Zhu, 2006, 2007; Ruan et al., 2008; Ruiz-Hitzky et al., 2010; Zhu et al., 2015b, 2016). Combining with the factors that Mt is low-cost, environmentally friendly, and abundant in reserve, Mt-based adsorbents have promising applications in various pollution control areas (Beall, 2003; de Paiva et al., 2008; Nafees and Waseem, 2014; O'Day and Vlassopoulos, 2010; Zhu et al., 2015b, 2016).

As is well known, the adsorptive characteristics of Mt-based adsorbents strongly depend on the modifiers used to synthesize these adsorbents (Ma et al., 2016a,b; Sarkar et al., 2012; Wang et al., 2004; Xi et al., 2010; Xu et al., 2014; Zhang et al., 2011; Zhou et al., 2010, Zhu et al., 2015b; Zhu et al., 2016). According to numerous previous studies, cationic surfactant modified Mt (organo-Mt, OMt) can create hydrophobic organic-phases, which can effectively uptake hydrophobic organic contaminants (HOC) through a partition-dominated process (Borisover et al., 2012; Khenifi et al., 2009; Sarkar et al., 2012; Slade and Gates, 2004; Zhou et al., 2015; Zhu et al., 2015b; Zhu et al., 2016). Hydroxymetal polycations modified Mt (Inorgano-Mt, IMt) contain large specific surface areas and abundant reactive functional groups

* Corresponding author.
E-mail address: xuyin@xtu.edu.cn (Y. Xu).

http://dx.doi.org/10.1016/j.clay.2017.05.027
Received 28 August 2016; Received in revised form 21 May 2017; Accepted 24 May 2017
Available online 31 May 2017
0169-1317/

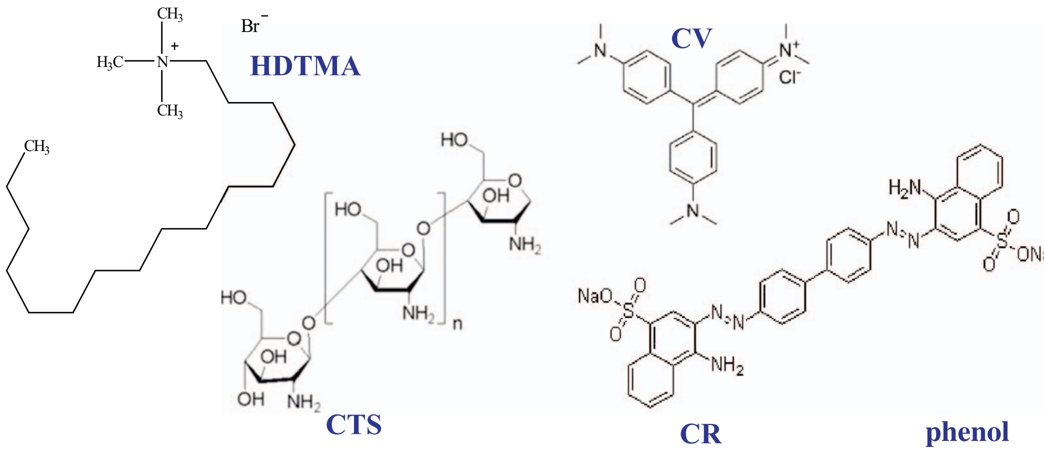

Fig. 1. The molecular structures of the organic chemicals.

(e.g., − OH), and they can be efficient adsorbents for both heavy metal cations and oxyanions (Kasama et al., 2004; Ma et al., 2015; Saha et al., 2001, 2002; Tian et al., 2009; Wu et al., 2001, 2009; Zhou et al., 2010; Zhu et al., 2014b, 2016). Some cationic polymers contain special functional groups (e.g., −OH and $-NH_2$) and large charge density, and Mt modified with these polymers may effectively uptake heavy metal cations and anionic dyes (Churchman, 2002; Kang et al., 2009; Yang et al., 2010; Yue et al., 2007). However, despite of the diversity of the Mt-based adsorbents, most of them generally are only efficient for one or two particular types of contaminants. For example, OMt are efficient for the removal of HOC but generally not so efficient for heavy metal cations; IMt have seldom been used for the adsorption of HOC.

As the simultaneous presence of various types of contaminants in wastewaters is quite common, particularly in the effluents from industrial zones (where different factories are located in the same area) and the leachate from landfills, developing multifunctional adsorbents is drawing increasing interests (Andini et al., 2006; Jovic-Jovicic et al., 2010, 2013; Ma and Zhu, 2006; Ma et al., 2016a; Zhu and Zhu, 2007; Zhu et al., 2009b). Several previous studies modified Mt with more than one type of modifiers, and the resulting materials could simultaneously remove various types of contaminants from water (Ma and Zhu, 2006; Ma et al., 2016a,c; Zhu and Zhu, 2007; Zhu et al., 2009b). Zhu and Zhu (2007) showed that inorgano-organo Mt (IOMt), which were synthesized by modifying Mt with both hydroxyaluminum polycations (Al_{13}) and hexadecyltrimethylammonium (HDTMA), could simultaneously uptake phosphate and HOC from water. Ma et al. (2016c) modified Mt with both Al_{13} and a zwitterionic surfactant, and the resulting IOMt could be multifunctional adsorbents for uptaking phenol, phosphate, and Cd^{2+} from water. According to above studies, choosing proper chemical reagents to modify Mt can be a facile approach to synthesize multifunctional adsorbents.

Recently, several studies also modified Mt with both polymers and cationic surfactants to synthesize novel OMt (Wang et al., 2010; Zhu et al., 2010). Zhu et al. (2010) suggested that with high charge density, cationic polyacrylamide could adjust the arrangement of HDTMA on the obtained OMt, resulting in better adsorption capacity toward HOC as compared with HDTMA modified Mt This type of OMt could also efficiently uptake anionic dyes, as their surfaces are positively charged (Guo et al., 2012; Wang and Wang, 2007a). According to the structural characteristics of this type of OMt, we expect that by choosing proper cationic polymer (e.g., those with −OH and $-NH_2$ groups) for the modification, the resulting OMt might be ideal multifunctional adsorbents for various types of contaminants.

In this work, Mt was modified with both HDTMA and chitosan (CTS), with the purpose of synthesizing multifunctional OMt for various types of contaminants. The structural characteristics of the resulting materials (H/C-Mt) were investigated using XRD, FTIR, TG, and zeta potential measurements. Then, phenol, Cd^{2+}, Congo red (CR), and crystal violet (CV) were selected as representatives of HOC, heavy metal cations, anionic dyes, and cationic dyes, respectively, and the adsorption capacities of H/C-Mt toward these contaminants were examined. The obtained results showed that H/C-Mt can be a multifunctional adsorbent for the effective uptake of the tested contaminants from water.

2. Materials and methods

2.1. Materials

The natural Mt (from Inner-Mongolia, China) has a cation exchange capacity (CEC) of 108 meq/100 g, with the structural formula of $Ca_{0.392}Na_{0.016}K_{0.020}$ $(Si_{7.92}Al_{0.08})$ $(Al_{2.518}Fe_{0.450}Mg_{1.104}Ti_{0.036}Mn_{0.004})$ $O_{10}(OH)_2{\cdot}nH_2O$ and the purity > 95% (Zhu et al., 2009b, 2011). The impurities are mainly composed of silica (~4%), and Mt was directly used as received. CTS, HDTMA-Br, phenol, CR, CV, and $CdCl_2$ were supplied by Guangzhou Chemical Reagent Factory (China). The molecular structure of the used organic chemicals is given in Fig. 1. All the chemicals were of analytical grades and used as received.

2.2. Synthesize of the adsorbents

To synthesize the HDTMA-CTS-Mt adsorbents, the Mt dispersion, CTS solution, and HDTMA-Br solution were separately prepared (all in mass/volume ratio). CTS was dissolved with HCl (Wang and Wang, 2007b), and the $-NH_2$ groups on CTS were protonated, i.e., positively charged. Then, the CTS solution and HDTMA-Br solution were mixed under vigorous stirring to obtain the modifier solution, which was then followed by the addition of Mt dispersion. The mixture was stirred at 60 °C for 4 h. The obtained products then were aged at 60 °C for another 10 h, which was followed by extensive washing with distilled water by centrifugation. The final products then were dried at 60 °C. The added amount of HDTMA was set at 60% of Mt's CEC, and the amounts of CTS were equal to 2%, 4%, or 6% of Mt's weight. Accordingly, the resulting OMt were denoted as 60H/2%C-Mt, 60H/4%C-Mt, and 60H/6%C-Mt, respectively.

For comparison purpose, this work also synthesized traditional HDTMA alone modified Mt (H-Mt). The same amount of HDTMA (i.e., 60% of Mt's CEC) and similar synthesizing conditions were used for the synthesis of H-Mt.

2.3. Characterization methods

Basal spacing values of the obtained samples were detected on a Bruker D8 ADVANCE X-ray diffractometer operating at 40 kV and