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Research paper

Preparation and characterization of organo-vermiculite based on phosphatidylcholine and adsorption of two typical antibiotics

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ABSTRACT

In this study, a novel organoclay (PC-VER) was synthesized by modifying vermiculite (VER) with phosphatidylcholine (PC), and the adsorption characteristics of oxytetracycline (OTC) and ciprofloxacin (CIP) on PC-VER were further examined. The structural characteristics of PC-VER were analyzed by XRD, FTIR, TG and SEM/EDS, confirming that PC molecules were successfully introduced into VER. It was found that PC molecules cannot only intercalate into the interlayer space but also can adsorb on the external surface of VER if the solution contains water. This causes the decrease in specific surface area and increase in thermal stability. Zeta potential results show that PC-VER has a positively charged surface when the solution pH below 3. The kinetic study showed that the adsorption process of OTC and CIP both abided by pseudo-second-order model. The film-diffusion was the dominated controlling-step for the adsorption on VER, and both film and intra-particle diffusion controlled the adsorption on PC-VER. The adsorption isotherm could be well described by the Langmuir model, exhibiting an enhanced adsorption of OTC and CIP for PC-VER. Electrostatic attraction is the main mechanism for the adsorption on VER according to the effect of pH values and coexisting cations. For PC-VER, the enhanced adsorption of OTC was mainly controlled by hydrophobic interaction; while electrostatic attraction was a priority for the CIP adsorption. Results obtained from this study displayed that PC-VER could serve as a low-cost, suitable and eco-friendly material for adsorption of antibiotics.

1. Introduction

The surfactant modified clay or clay minerals have aroused great interest due to their wide application in environmental remediation and material synthesis. In general, clay minerals consist of two tetrahedral silica sheets and a central octahedral alumina or magnesia sheet with the exchangeable cations occurring in the interlayer spaces (Chen et al., 2010). These cations can be exchanged easily with organic cations, such as cationic surfactant and biomolecules. The most commonly applied and well-studied organic modifiers are long-chain quaternary alkylammonium cations (Ruiz-Hitzky and Meerbeek, 2006). The modification process converts the clay mineral surface from hydrophilic to hydrophobic. So, these organoclays can be used to adsorb organic pollutants (Borisover et al., 2008), also as subassembly for clay polymer nanocomposites with ameliorative chemical and mechanical stability and thermal properties (Bitinis et al., 2011). However, the long-chain alkyl organic cations usually can block the pore channels of clay mineral and cause a significant diminution in the specific surface area, leading to reduced adsorption sites for pollutants. What's more, modification of clay mineral by cationic surfactant will introduce secondary pollution to the environment due to their toxicity and lack of biocompatibility, which limit their application (Ruiz-Hitzky et al., 2011).

Amphoteric surfactants are usually nontoxic, biodegradable, biological safety, and have excellent water solubility. The surfactants can be used to modify clay minerals in order to improve its adsorption capacity, and their non-toxic nature makes them suitable for environmental remediation. The modification theory is that the surfactants can probably enter the interlayer space by exchanging due to their cationic group, or adsorb on the surface through electrostatic interaction (Qi et al., 2008). Betaine and sulfobetaine, two typical amphoteric surfactants, modified montmorillonite has been synthesized and used to adsorb some organic and inorganic contaminants (Fan et al., 2014; Liu et al., 2015). Thus, we introduce an eco-friendly organic clay using lecithins as a long-chain biosurfactant of natural biological source. Lecithins have been extensively applied in food and pharmaceutical industries (Nieuwenhuyzen and Thomas, 2008; Simovic et al., 2011), and its mixture with clay has

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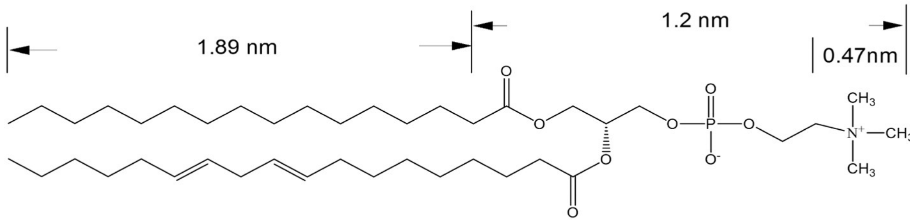

Fig. 1. The chemical structural formula and size label of phosphatidylcholine (PC).

been used as an adsorbent for removal of herbicide from wastewater (Sánchez-Verdejo et al., 2008). The principal constituent of lecithin is the phosphatidylcholine (PC) which is formed by the way that two fatty acid chains are connected to an amphoteric head group via a glycerol backbone (Nagy et al., 2013). PC molecules show the positive charge when the pH value of solution is lower than the isoelectric point, which allow to be exchanged with the cation in clay interlayer space.

Vermiculite, a typical 2:1 expandable clay mineral, is very abundant in China (Vieira and Allan, 2007; Yu et al., 2010), and has mostly been used as the material for construction, refractory, soil amendment and so on. It can be used as an easily provided and inexpensive material (approximately 500 RMB/t in China markets) for preparation of adsorbents. The cation exchange capacity (CEC) of vermiculite is relatively higher than the common clay minerals. Also, they swell less than montmorillonite because of their higher charge in the tetrahedral sheets (Malandrino et al., 2006). The applications of montmorillonite or other silicate materials in adsorption have been extensively studied (Wicklein et al., 2010; Liu et al., 2012; Luo et al., 2016), while the evidence showing the potential of vermiculite in adsorption is rather scarce.

To demonstrate PC-modified vermiculite as potential materials for immobilizing antibiotics, the oxytetracycline (OTC) and ciprofloxacin (CIP) adsorption study were carried out. OTC and CIP are widely used for human and animals, and are frequently detected in the water environment. These antibiotics might be hardly removed through sewage treatment system because their low degradation and bacteria-inhibiting effect, and then gradually accumulated into the surface water, resulting in drug resistance as well as deleterious effects for aquatic plants (Li et al., 2015; Schmitt et al., 2006). Recent studies show that clay minerals can remove both TC (exactly similar to OTC) and CIP from aqueous solutions through different mechanisms, such as ion exchange, electrostatic attraction and surface complexation (Wang et al., 2011; Wang et al., 2010; Zhao et al., 2015). To our best knowledge, the adsorption of antibiotics by vermiculite and organo-vermiculite has not been previously investigated. In this study, PC-modified vermiculite were prepared under different solution conditions and its structural properties were characterized by XRD, FTIR, TG, SEM/EDS, BET and zeta potential. The adsorption behavior of OTC and CIP to VER and PC-VER, including the adsorption kinetics, isotherms, mechanisms and the factors affecting the adsorption (dosage, solution pH, coexisting cations and heavy metal ions) were investigated.

2. Materials and methods

2.1. Materials

The high-purity vermiculite was obtained from Sigma-Aldrich with a small amount of mica impurities (impurity rate < 3%). The chemical composition (wt%) of VER was as follows: SiO_2 39.8%, Al_2O_3 13.7%, MgO 22.6%, Fe_2O_3 14.4%, CaO 3.2%, K_2O 7.1%, Na_2O 0.52%, TiO_2 0.78%. The cation exchange capacity (CEC) of VER was 0.855 meq g^{-1}, measured by the ammonium-exchange method (Tran et al., 2015a), with Mg^{2+} as the major exchangeable interlayer cation. The lecithin from soybean with 90% phosphatidylcholine (PC, $C_{42}H_{80}NO_8P$, FW: 758.06) content was purchased from Aladdin Chemistry Co. Ltd. The molecular structure formula and size label of PC is illustrated in Fig. 1. PC molecules were insoluble in water but soluble in ethanol, and can be emulsified in aqueous solution. Oxytetracycline hydrochloride (OTC) and ciprofloxacin hydrochloride (CIP) was produced by Aladdin Chemistry Co. Ltd. and their molecular structure and pK_a values are shown in Fig. 2. Both OTC and CIP dissolve easily in water (>1 g L^{-1}) and can be cationic, zwitterionic and anionic species in solution with different pH values (OTC: $pK_{a1} = 3.3$, $pK_{a2} = 7.7$ and $pK_{a3} = 9.7$; CIP: $pK_{a1} = 6.1$ and $pK_{a2} = 8.7$) (Carrasquillo et al., 2008; Wang et al., 2011). All other chemicals such as absolute CH_3CH_2OH, NaOH, HNO_3, NaCl, $CaCl_2$, Cu $(NO_3)_2 \cdot 3H_2O$, Zn $(NO_3)_2 \cdot 6H_2O$, which were of analytical grade and used as received.

2.2. Preparation of organo-vermiculite

The PC modification of vermiculite was synthesized as below: a certain amount of PC was completely dissolved in 20 mL absolute ethanol until the molar ratio of PC over the total amount of exchangeable sites in VER was 2.565 mmol g^{-1} (3.0 CEC). Then 1.0 g of vermiculite and 180 mL distilled water (or ethanol) was added into the above solution; the pH of the dispersion was adjusted by 0.1 M HNO_3 to obtain pH = 2.0. The obtained mixture was ultrasonically dispersed within 10 min

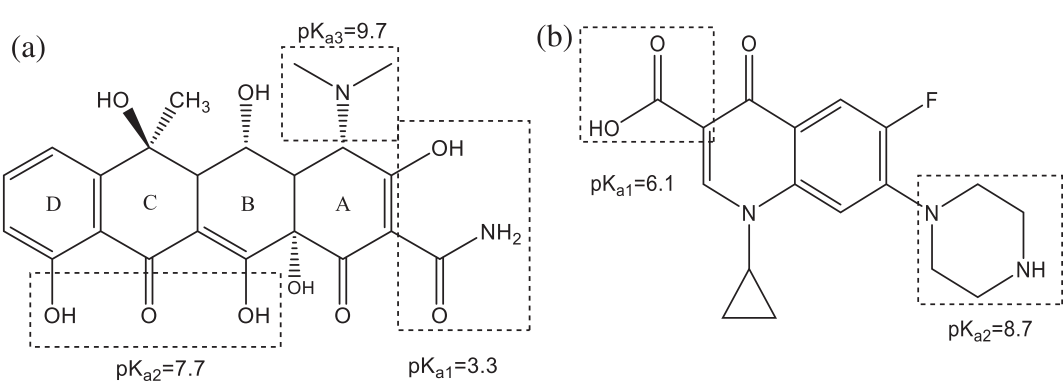

Fig. 2. Chemical structure of OTC (a) and CIP (b) with indications of the functional groups of different pK_a values.