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Sorption of tetracycline on organo-montmorillonites

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ABSTRACT

Tetracycline (TC) is a veterinary antibiotic that is frequently detected as pollutant in the environment. Powerful adsorbents are required for removing TC. The present paper compares the TC adsorption capacity of Na-montmorillonite (Na-mont) with six organo-montmorillonites (organo-monts). Three quaternary ammonium cations (QACs) with different alkyl-chain lengths were used as modifiers. Powder X-ray diffraction indicated that the d_{001} values of organo-monts increased with increasing the QACs loading and alkyl-chain length. The CECs of the organo-monts were substantially lower than that of Na-mont and decreased with QACs chain length and increased loading. The modeling of the adsorption kinetics revealed that the processes of TC adsorption on the tested samples could be well fitted by the pseudo-second-order equation. The maximum adsorption capacities of TC on the organo-monts (1000–2000 mmol/kg) were considerably higher than that on Na-mont (769 mmol/kg). Both the Langmuir and Freundlich model could fit the adsorption isotherms. The TC adsorption to the organo-monts increase significantly with decreasing the pH below 5.5 because of the electrostatic interaction, and a high QACs loading performed better than a low loading at around pH 3.

1. Introduction

Tetracycline (TC) is widely used to treat diseases of animals and is incorporated into animal feeds to promote growth efficiency [1]. However, TC is poorly absorbed in the digestive tract of animals and has been excreted in feces or urine as a mixture of the parent compound and metabolites [2]. Residues of TC are quite persistent in the soil and sediment and can accumulate by repeated manure applications [3]. Frequent misuse of antibiotics promotes the expansion of antibiotic-resistance among bacterial populations and affects plant growth and development [4]. Moreover, the application of manure in fields implies that TC also has the potential to reach the sediment and aquatic environment [1]. The interaction of TC with clay minerals [5], humic acids [2], soil-slurry mixtures [6], sediments [7] and specific adsorbents for removal of TC and comparable organic pollutants [8] has been investigated.

Clays, including montmorillonite, have drawn particular attention as suitable materials for environmental remediation. The adsorption of TC on clays is greatly influenced by the pH [9], the ionic strength [9] and the dissolved organic cations [10]. As the pH increases, the cationic form of TC decreases in abundance, with a concomitant increase in neutral and anionic forms. The adsorption affinity of TC on clays generally decreases with increasing pH and ionic strength, as cation-exchange is considered the dominant sorption mechanism [11]. For example, Figueroa et al. [9] reported that adsorption of TC to montmorillonite and kaolinite decreased as pH increased from 4 to 9 and found an adsorption capacity as high as 111 mmol/kg at pH 5.5 for TC adsorption on Na-mont. The montmorillonite surface properties might be greatly modified with surfactants by ion-exchange reactions. Organo-monts can change the hydrophilic surface to increasingly hydrophobic surface depending on the surfactant concentration [12]. Attention has also been paid to the sorption of organic pollutants on organo-monts [13]. The short-chain organo-monts are more effective than long-chain organo-monts in adsorbing non-ionic organic compounds [14]. Groisman et al. [15] observed that compounds with low or medium hydrophobicity were better adsorbed on the short-chain organo-monts than on the clay mineral, whereas the more hydrophobic compounds were better adsorbed on the

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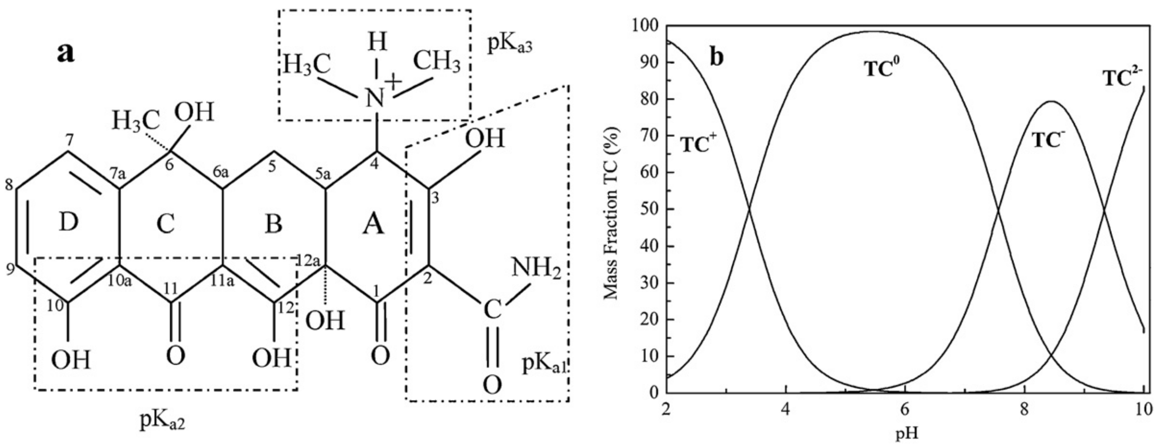

Fig. 1. Molecular structure of TC (a) and the speciation diagram of TC as a function of pH (b) [9].

long-chain organo-monts. However, the sorption behavior of TC on the organo-monts has not yet been fully explored. In the present work, the ability of modified montmorillonites as potential adsorbents for TC was therefore further investigated and compared with Na-mont.

Conventional surfactants used as modifying the clay are quaternary ammonium cations (QACs). The QACs have a general form as $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$. In general, the organo-monts displays different adsorptive properties for organic pollutants, depending on the molecular size and the nature of R and R′ and the degree of ion-exchange. The present work therefore focused on the effect of the chain length and the amount of QACs in the organo-monts on the adsorption behavior of TC. Both kinetic and adsorption isotherms were carried out at pH 5.5, where TC is uncharged. The influence of the pH on the adsorption of TC was also tested. Throughout the text the notation adsorption will be used, although the binding of TC with the modified clays may occur between the clay layers, which also could be considered as absorption.

2. Materials and methods

2.1. Materials

Methanol and acetonitrile (chromatographic pure) were obtained from Fisher Scientific (Pittsburgh, PA, USA) and used for high-performance liquid chromatography (HPLC) analysis. Other reagents were of analytical grade. All solutions were prepared with double distilled water (DDW).

Tetracycline hydrochloride (T3383, 96% purity) was obtained from Sigma-Aldrich Chemical Company (St. Louis, USA) without further purification. The chemical structure is depicted in Fig. 1a and the speciation diagram of TC as a function of pH in Fig. 1b. The pK_a values are 3.3, 7.7 and 9.7 [9]. Fresh TC stock solutions (1.5 mmol/L) were prepared for each experiment.

The QACs used for the clay modification were tetramethylammonium bromide (TMAB), dodecyltrimethylammonium bromide (DDTMAB) and hexadecyltrimethylammonium bromide (HDTMAB). Some basic properties of the QACs are listed in Table 1.

2.2. Na-mont and organo-monts

Montmorillonite was purchased from Sanding Company (Zhejiang, China) and was purified and saturated by Na^+ ions. The sample was named as Na-mont and its cation-exchange capacity (CEC) was 138.8 meq/100 g, as measured by the NH_4OAc method [16] (Table 2).

For the preparation of the organo-monts the procedure described was followed [17]. 1.0 g of Na-mont was dispersed in 100 mL DDW, and then a desired amount of QACs was slowly added. The mixture was incubated in a water bath of 80 °C for 10 h under stirring slightly. Finally, the suspension was washed with DDW until it was free of Br^- (checked by titration with $AgNO_3$). The organo-monts were prepared with an amount of QACs equivalent to f times the CEC (f = 0.2, 1.0). The fraction f of organic cation is defined as:

$$f = \frac{m_{\text{cation}}/M_{\text{cation}}}{CEC \times m_{\text{clay}}} \quad (1)$$

Table 1
Basic physicochemical properties of the tested surfactants.

Compound (abbreviation)	Formula	Molar mass (g/mol)	Aqueous solubility (g/L)	Structure
Tetramethylammonium bromide (TMAB)	$C_4H_{12}BrN$	154.04	100	$CH_3{-}N^{+}(CH_3)_2{-}CH_3$
Dodecyltrimethylammonium bromide (DDTMAB)	$C_{15}H_{34}BrN$	308.35	30.83	$CH_3{-}N^{+}(CH_3)_2{-}(CH_2)_{11}CH_3$
Hexadecyltrimethylammonium bromide (HDTMAB)	$C_{19}H_{42}BrN$	364.45	50	$CH_3{-}N^{+}(CH_3)_2{-}(CH_2)_{15}CH_3$