

Intercalation and adsorption of ciprofloxacin by layered chalcogenides and kinetics study



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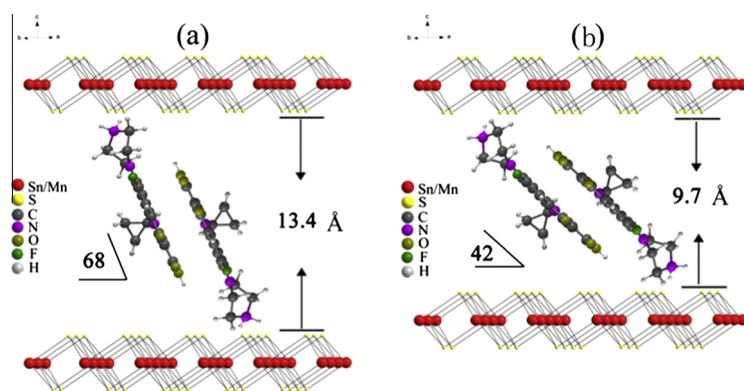
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GRAPHICAL ABSTRACT



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ABSTRACT

The hydrothermally synthesized layered chalcogenide, $K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5–0.95$) (KMS-1), was applied to remove ciprofloxacin from aqueous solution. Kinetic data showed the removal reaction followed a pseudo-second-order kinetic model and the rate controlling step was both through external film and intraparticle diffusion. The adsorption of CIP by KMS-1 is endothermic and the maximum adsorption capacity of KMS-1 was 199.6, 230.9 and 269.5 mg/g at temperature of 10, 25 and 40 °C, respectively. The heavy metal ions had great effect on the removal efficiency of CIP and the degree of inhibition followed the order: $Pb^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$. The shift of Bragg peaks from XRD at various pH accompanying CIP removal and FE-SEM images confirmed that cation exchange is the major mechanism for the adsorption of CIP by KMS-1. In the pH range of 4.0–7.0, the intercalation of cationic CIP adopted a tilted orientation of di-molecular CIP in KMS-1 with the titling angle of 68° and 42°, respectively. A vertical arrangement of the zwitterionic CIP adsorbed on the surface of KMS-1 was also confirmed. These results suggested that KMS-1 is an effective adsorbent to remove CIP from water.

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1. Introduction

Ciprofloxacin (CIP) is an important antibiotic widely used as medicine for human and animals [1–3]. For the past decades,

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excessive drug contamination including CIP has been discharged from hospital and drug manufacturers into the environment. The agricultural soil leaching and incomplete metabolism of CIP in host also contributed to the pollutant source of wastewater. Although wastewater was disposed through sewage treatment plants, CIP might be poorly removed due to the bacteria-inhibiting effect and then accumulated into the surface water gradually [3–5]. Actually, CIP can be detected in wastewater and surface water with concentrations of several hundred ng/L [6,7]. The excessive presence of CIP in the environment can develop antibiotic resistance in bacteria as well as lead to deleterious effects on the aquatic organics [8,9]. Therefore, searching effective methods to remove CIP from waster source has become a vital concern. Various methods have been attempted to remove CIP from water, such as biodegradation [10], oxidation [11,12], photocatalytic degradation [13] and adsorption [3]. Undoubtedly, adsorption is one of the most promising technologies due to its easy operation, economic factor and high efficiency [9,14–18].

Until now, most of adsorbents used to remove CIP from wastewater are oxide-related materials, such as carbon-based material [8,19,20], natural mineral material [7,21–25] and synthetic metal oxides [26]. The carbon-based materials, including carbon nanotubes, activated carbon, and carbon xerogel, were usually functionalized with groups containing oxygen atoms for CIP removal. The presence of oxygen atoms on their surface can interact with CIP for higher removal efficiency. It was already shown that the CIP can be removed by typical mineral material such as sodium montmorillonite, rectorite, birnessite, kaolinite and nano-sized magnetite, but the removal mechanisms of these adsorbents may be different [7,21–25]. The cationic CIP could intercalate into the sodium montmorillonite and make the interlayer spacing changed. While, the zwitterion forms of CIP was removed by surface adsorption of sodium montmorillonite [7]. The uptake of CIP by rectorite and birnessite was resulted from cation exchange between cationic CIP and the exchangeable cation on the surface or between the interlayers [21,24]. Although the cation exchange was the dominant mechanism of CIP adsorption on kaolinite with desorption of exchangeable cation, there were no intercalation into the kaolinite [23]. The adsorption of CIP at the magnetite surface mediated by carboxylic groups [25]. The results of CIP removal by synthetic metal oxides, such as aluminum hydrous oxides and iron hydrous oxides, showed that only one oxygen atom of the carboxylate group of CIP could bind with the hydrous oxide surface of adsorbents and the other oxygen atom from keto group could further bind with Fe atom of iron hydrous oxides [26].

Recently, layered chalcogenides, $K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5–0.95$) (KMS-1) and $[CH_3NH_3]_{2x}Mn_xSn_{3-x}S_6 \cdot 0.5H_2O$ ($x = 0.5–1.1$) (CMS), were shown to effectively and selectively remove heavy metal ions such as Cd^{2+} , Pb^{2+} , Hg^{2+} and Cu^{2+} , by ion exchange with a high adsorption capacity over wide pH range [27–29]. Nowadays, the wastewater is often contaminated by complex pollutants, including heavy metal ions and organic pollutant such as antibiotics. Therefore, it is necessary to develop and evaluate the activities of adsorbents in the presence of complex contaminants. In this context, KMS-1 was applied to remove CIP from aqueous solution in order to evaluate the ability of this important kind of adsorbent for removal of organic pollutant by use of CIP as a pollutant model. To the best of our knowledge, the removal of organic pollutant by layered chalcogenides including KMS-1 from water had never been reported before. The effects of solution pH, contact time, initial concentration and temperature on the removal of CIP were investigated in detail. Furthermore, various kinetics and isotherms of adsorption were also discussed. The adsorption mechanism was proposed through probing the results of X-ray diffraction (XRD), Fourier transformation infrared analyses (FTIR), Field emission scanning electron microscopy (FE-SEM), Transmission electron

microscope (TEM), Energy dispersive X-ray (EDX) and zeta potential. Two possible conformations of the exchanged cationic CIP in the interlayer spacing were also proposed. These pioneering results would shed light on the adsorption mechanism of layered chalcogenides for organic pollutant, which might greatly contribute to the application of chalcogenides adsorbents in the treatment of complex wastewater.

2. Materials and methods

2.1. Materials

K_2CO_3 ($\geq 99.0\%$), Sn (99.99%), Mn (99.99%), S (99.99%) and ciprofloxacin hydrochloride (CIP-HCl, 98%) were purchased from Aladdin Company (Shanghai, China), and other reagents were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further purification.

Due to the different pK_a values ($pK_{a1} = 6.1$ and $pK_{a2} = 8.7$), CIP can be cationic, zwitterionic and anionic species in solution with different pH values [20]. Fig. S1 showed the speciation of CIP at different pH conditions. CIP exists in a cationic form mainly in an acidic solution with pH below 6.1 due to the protonation of amine group. CIP exits as an anion group when its pH is higher than 8.7 due to the loss of a proton from the carboxyl group. When solution pH was between 6.1 and 8.7, zwitterionic CIP is the dominant species resulted from the charge balance of the two groups mentioned above.

The preparation of CIP and Na^+CIP^- solid: The pH of about 800 mg/L of CIP-HCl solution was adjusted to 7 or 10 using NaOH solution by pH meter (UB-7, Denver, USA). The pH of the solution was kept for about 6 h. Due to the limited solubility of CIP at different pH, a certain amount of CIP and Na^+CIP^- solid will be precipitated. After that, the solid was filtered by filter membrane and dried in vacuum at 60 °C. The CIP and Na^+CIP^- solid were finally obtained for pH = 7 and pH = 10, respectively.

2.2. Preparation of KMS-1 material

KMS-1 was prepared according to Manos's methods [28]. In a typical synthesis, K_2CO_3 (5.52 mmol), Sn (11 mmol), Mn (5.52 mmol), S (33.1 mmol) and H_2O (7.34 mL) were mixed in a 25 mL of Teflon-lined autoclave. The autoclave was sealed and placed in furnace at 200 °C for four days. Then the autoclave was allowed to cool down at room temperature. The product was isolated by filtration and followed by washing with ultrapure water, CS_2 and ethanol, respectively. Finally, they were dried in vacuum at 60 °C.

2.3. Batch adsorption experiment

All adsorption experiments were carried out in 250 mL of conical flask by mixing a given dose of KMS-1 with a certain volume of CIP solution (or including competitive ions) in a thermostatic shaker. The initial pH of CIP solution was adjusted to a certain value using NaOH and HCl solution by pH meter. After adsorption, the mixture was immediately centrifuged, and the supernatant was analyzed for the CIP concentration by a high performance liquid chromatography (HPLC) (1200 infinity, Agilent, USA).

2.4. Characterization of KMS-1 before and after adsorption

Powder X-ray diffraction (PXRD) patterns were obtained at room temperature with an X'Pert ProMPD diffractometer (X'Pert Pro, PANalytical B.V., Holland) using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) beam in the 2θ range of 5–80°. The elemental composition and

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