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Application of graphene-like layered molybdenum disulfide and its excellent adsorption behavior for doxycycline antibiotic

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HIGHLIGHTS

- Graphene-like layered molybdenum disulfide (g-MoS_2) was prepared and characterized.
- g-MoS_2 showed high adsorption capacity of 310 mg/g for doxycycline in aqueous solution.
- The adsorption follows the pseudo second-order kinetic model.
- The adsorption isotherms fit Langmuir model well.
- Doxycycline strongly adsorbs on g-MoS_2 via π–π dispersion, hydrophobic effect and electrostatic interaction.

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ABSTRACT

Graphene-like layered molybdenum disulfide (g-MoS_2) was prepared by hydrothermal synthesis method, which was characterized by atomic force microscopy (AFM), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS). The performance of using g-MoS_2 as an adsorbent for removal of doxycycline (DC) antibiotic from aqueous solution was investigated. The adsorption kinetics, isotherms, thermodynamics and effects of solution pH, ions strength on the adsorption were evaluated in batch adsorption experiments. Compared with the purchased commercial MoS_2, g-MoS_2 showed higher adsorption capacity around 310 mg g^{-1} in the range of pH 4–9. Although both pseudo-first and second order equation described the adsorption kinetics rationally, pseudo-second-order model showed better fit with high R^2. Langmuir model provided the best fit to the equilibrium data and the Langmuir maximum adsorption capacity was found to be 556 mg g^{-1} at pH 6. The adsorption was a spontaneous and endothermic process deduced by the thermodynamic analysis. With Na^+ in the solution could promote the adsorption. The adsorption mechanism was probably π–π interaction, hydrophobic effect and electrostatic interaction. All these results indicated that the prepared g-MoS_2 was a potential adsorbent for the removal of DC antibiotic from aqueous solution.

1. Introduction

Pharmaceutical antibiotics have been extensively used in the therapy of human and animal infections because of their specific antimicrobial properties and minor adverse side effects [1,2]. However, residues of these antibiotics are frequently detected in soil, surface water, groundwater, and even drinking water, which are now regarded as a new class of worldwide pollutants [3–5]. Specifically, the tetracycline antibiotics (TCs), a group of commonly used antibiotics, have been led to great concerns [6–8] .

The traditional removal of TCs by wastewater treatment technologies is generally incomplete [9,10]. Recently, the adsorption and removal of TCs have been received worldwide attention. Several materials, such as activated carbon [11–16], carbon nanotubes [17,18], graphene oxide [19], polymer resin [20,21], mesoporous silica materials [22,23], clay minerals [24–30], biomass ashes [31], sludge [32–36], humic acid [37] have been researched, and the corresponding results showed that the adsorption performance of these materials was dependent on pH conditions, ionic level of the pharmaceutical and the feature of the surface charge of the adsorbents, etc. However, there is still a room for the development of efficient adsorbents and technologies for the removal of such pollutants.

Graphene-like molybdenum disulfide (g-MoS_2), a novel quasi-two-dimensional layered material, is a good candidate as an adsorbent for TCs removal due to its special layered structure, large surface areas and strong covalent forces with van der Waals

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interaction. Recently, the researches of g-MoS_2 in hydrogen evolution, lithium battery performance and electrochemical performance, *etc.* have been attracted a great deal of scientific interest [38]. The former research also indicated that good adsorption performance of MoS_2 was presented in removal aromatic sulfur compounds in fuels [39]. However, its adsorption performance in removal pollutants of antibiotics from water has not been reported till now.

In this study, we explored the application of g-MoS_2 in adsorption and removal of TCs from aqueous solution. Doxycycline (DC), one of the most commonly used TCs was chosen as the model drug and its structure was shown in Fig. 1. The adsorption kinetics, isotherms, thermodynamics and effects of solution pH, ions strength on the adsorption were evaluated in batch adsorption experiments. These results will provide a theoretical foundation for further application of g-MoS_2 in removing antibiotics from wastewaters.

2. Experimental

2.1. Materials

All chemicals were of analytical reagent grade and used without further purification. DC was obtained from Sigma–Aldrich Chemical Co. (99% purity). The commercial MoS_2 was purchased from Sinopharm Chemical Reagent Co.

2.2. Instrumentation

UV–Vis absorption spectra were obtained using UV-2401PC spectrometer (Shimadzu). A 1-cm path-length quartz cuvette was used. Atomic force microscopy (AFM) images were recorded using Multimode-V microscope in contact mode. AFM samples were prepared by drop casting the g-MoS_2 suspension in ethanol onto freshly cleaved mica surfaces and dried under room temperature. The surface area (BET method) was calculated by the nitrogen adsorption–desorption isotherms at 77 K using a TriStar II 3020 surface area and porosity analyzer (Micromeritics Instrument Corp.). X-ray powder diffraction (XRD) patterns were recorded using a D/MAX-2550 diffractometer, equipped with a Cu Kα radiation source (λ = 1.5418A). Transmission electron microscopy (TEM) micrographs were taken with a JEOL-JEM-2010 (JEOL, Japan) operated at 200 kV. The samples used for TEM were prepared by dispersing some products in ethanol, then placing a drop of the solution onto a copper grid and letting the ethanol evaporate slowly in air. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCA Lab MKII X-ray photo-electron spectrometer using the Mg Kα radiation.

2.3. Synthesis of g-MoS_2

The g-MoS_2 was prepared as described by Ramakrishna Matte et al. [40]. 1 mmol MoO_3, 2.5 mmol KSCN and 10 mL of deionized water were mixture and put in 25 mL Teflon-coated autoclave at 453 K for 24 h by hydrothermal treatment. The product was washed with water for six times, and dried at 378 K.

2.4. Adsorption and removal of DC by g-MoS_2

The batch experiments were carried out in 50 mL stoppered conical flasks containing the mixture of 4 mg g-MoS_2 and 15 mL DC aqueous solution. The flasks were wrapped with aluminum foils to avoid photodegradation and then were mounted in a thermostatic shaker bath with a shaking speed of 130 rpm at a preset temperature of 303 K for adsorption. For batch kinetic studies, the initial DC concentration was 100 mg L^{-1} while pH was 3.8 without being adjusted. At different reaction time, 5 mL supernatant was aspirated and centrifuged at 4000 rpm for 15 min, and then analyzed immediately using UV-2401 spectrophotometer at 345 nm. Adsorption isotherm studies were carried out with initial DC concentration of 20–140 mg L^{-1}, and the solution pH maintained about 3.8, 6.0, 9.0 by adjusting with 0.01 mol L^{-1} HCl or NaOH if necessary. Adsorption thermodynamics experiments were performed with the initial DC concentration of 20, 60, and 100 mg L^{-1} with initial solution pH at controlled temperatures of 288, 303 and 318 K. For pH and ionic strength sorption experiments, the initial concentration of DC was 100 mg L^{-1}. The solution pH varied from 2 to 11, while the ionic strength of the solution was adjusted by dissolving 0–7.5 g NaCl solid before adding g-MoS_2. All experiments were run in duplicate, and linear calibration curve (absorbance versus concentration) was used to determine the concentration of the DC. The amount of DC was determined in initial and equilibrium solutions, and the adsorption capacity, q_e(mg g^{-1}), was calculated using the following equation

$$q_e = V(C_0 - C_e)/m \quad (1)$$

where C_0 is the initial adsorbate concentration (mg L^{-1}), C_e is the residual concentration at equilibrium in solution (mg L^{-1}), V is the volume of solution (L), and m is the mass of g-MoS_2 (g).

3. Results and discussion

3.1. Characterization of g-MoS_2

AFM, XRD, TEM, EDS, XPS and BET were employed to characterize g-MoS_2 prepared by hydrothermal synthesis method. AFM image was presented in Fig. 2 and height profiles of g-MoS_2 confirmed that the existence of MoS_2 stacks with an average thickness of 4–5 nm, which showed the presence of a few layers of graphene-like MoS_2. According to the literature [40], the number of counting layers of g-MoS_2 was 8–12, which could be named

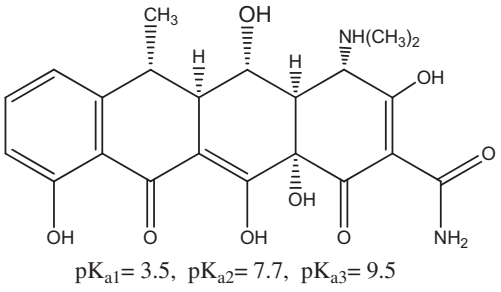

Fig. 1. The structure of doxycycline.

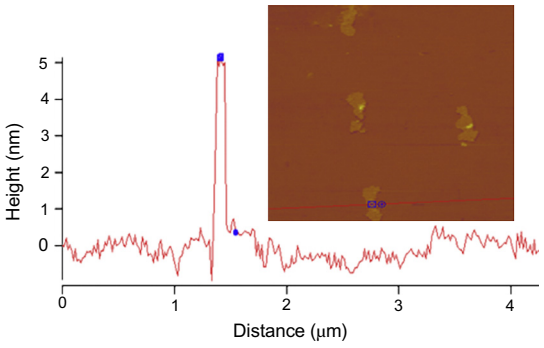

Fig. 2. AFM images and associated height profile of g-MoS_2 layers.