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Sorption properties of U(VI) and Th(IV) on two-dimensional Molybdenum Disulfide (MoS_2) nanosheets: Effects of pH, ionic strength, contact time, humic acids and temperature

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HIGHLIGHTS

- U(VI)/Th(IV) sorption is obviously affected by pH but not by ionic strength.
- Inner-sphere surface complexation dominated the two sorption processes.
- The removal efficiency of Th(IV) by MoS 2 is higher than that of U(VI).
- The presence of cations/anions weakly influences the adsorption.
- The U(VI)/Th(IV) sorption process is spontaneous and endothermic.

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ABSTRACT

Herein, the two-dimensional MoS_2 nanosheet was characterized and its performance as an adsorbent for U(VI) and Th(IV) removal from water was evaluated in batch experiments. The results showed that MoS_2nanosheets have a thin thickness and few negligible impurities. Both U(VI) and Th(IV) sorption on MoS_2were obviously enhanced by high pH and the oxygen-containing group on the surface of MoS_2 increased with an increase of pH. However, the sorption was not affected by ionic strength, suggesting that inner-sphere surface complexation dominated the two sorption processes. The removal efficiency of Th(IV) by MoS_2 was higher than that of U(VI) in solutions containing different cations and anions. The adsorption equilibrium for U(VI)/Th(IV) was achieved within 2 h and pseudo-second-order equation showed favorable fit. HA significantly increased the uptake of U(VI)/Th(IV) at pH <7.5/6, while decreased the sorption at pH >7.5/6. Freundlich model provided more fit to the equilibrium data than Langmuir model at pH 5.5. The maximum sorption amount of MoS_2 for U(VI)/Th(IV) run up to 492.72/454.72 $mg \cdot g^{-1}$, obviously higher than the amounts of some other materials. The U(VI)/Th(IV) sorption was a spontaneous and endothermic process. All these results suggested the potential applicable value of MoS_2 nanosheets in removing U(VI) or Th(IV) from aqueous solutions.

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1. Introduction

Water contamination induced by heavy metals is increasingly focused on owing to their toxicity and harm to environment and organisms. Up to now, many technologies have been developed to remove these toxic metal ions from aqueous solutions (Hu et al., 2016). Hereinto, adsorption is considered as an effective and promising water-treatment technique with low cost, ease of operation, flexibility, simple design (Shao et al., 2009; Sun et al., 2015, 2016, 2017; Yao et al., 2018; Yu et al., 2018). Among various adsorbents, functional nanomaterials are extensively used for the sorption of metal ions, such as carbon material (carbon nanotube, carbon nanofibers, graphene oxide), titanate material (titanate nanotube), and magnetic material (Fe_3O_4) (Zhao et al., 2014; Sun et al., 2015, 2016; Hu et al., 2017a; Yao et al., 2017; Chen et al., 2018). However, there is still room for exploring higher efficient adsorbents.

More recently, molybdenum disulfide (MoS_2) nanosheets, as a two-dimensional (2D) material, have received widespread attention as an alternative to graphitic carbon owing to its high-energy capacity ($\sim$1200 mAh g^{-1}) (Chang and Chen, 2011a,b; Chang et al., 2011; Xiao et al., 2011), which is much higher than that of commercial graphite (372 mAh g^{-1}) (Cahen et al., 2008) and graphene nanosheets (600–900 mAh g^{-1}) (Geim and Novoselov, 2007; Yoo et al., 2008; Wang et al., 2010). Furthermore, considering the abundance of exposed sulfur, MoS_2 could be an efficient adsorbent for the removal of metal ions though its strong Lewis acid and base soft–soft interactions (Wang and Mi, 2017). Several cases have proved the adsorption potentials of MoS_2. For example, MoS_2 was proved to be a kind of superb adsorbent for removing Hg^{2+} from water (Jia et al., 2017a). Some modified composite based on MoS_2 also showed high sorption ability for several metals, including Ag^+, Co^{2+}, Pb^{2+}, Li^+, even and Hg^0 vapor and so on (Gash et al., 1998; Chen et al., 2013; Zhang et al., 2016a; Zhao et al., 2016; Aghagoli et al., 2017). Nevertheless, interactions between MoS_2 and other more toxic metal ions in aqueous solutions need to be studied to illustrate the sorption ability and related mechanism of these MoS_2 nanosheets.

Generally, the mechanism of the interaction between MoS_2 and adsorbed heavy metal ions was proved to have three types. Ion exchange is the first possible mechanism because MoS_2 nanosheets usually exhibit negative surface charge with H^+ or Li^+ as a counterion and finally form metal-sulfur bonding (Zhi et al., 2016; Jia et al., 2017b). Inner layer metal-S complexation is the second potential mechanism. One case showed that Hg^{2+} could replace H^+ ions to complex with one or two sulfur atoms at a high or low Hg-to-MoS_2 ratio (Ai et al., 2016). Pb^{2+} was also found the similar complexation phenomenon with sulfur atoms (Chen et al., 2013). The third potential mechanism is outer layer electrostatic attraction. Co^{2+} was found that the outer layer electrostatic attraction was dominant in the sorption process (Aghagoli et al., 2017). It is note that there may be one or more mechanisms to occur in the sorption. As it is known that the sorption capability of an adsorbent can be strongly affected by the chemical and physical conditions of aqueous solutions. Various environmental factors, such as pH, ionic strength, contact time, solid contents, and all kinds of coexistent ions, can influence the sorption ability, the kinetics and the isotherms of the adsorbent. Therefore, it is necessary to investigate these effects in the future to probe into the interaction mechanisms between toxic metal ions and MoS_2 nanosheets.

In this paper, we explored the macroscopic and microscopic characteristics of MoS_2 nanosheets and its application in uptake and removal of two poisonous radionuclides from aqueous solutions, i.e., Uranium (U) and Thorium (Th). In practice, both uranium and thorium are often discharged into water environment, and then may enter the biosphere with the water cycle. Once it enters the living bodies provoke the inner irradiation, and result in appearance of cancer (Sheng et al., 2008, 2014). Therefore, it is meaningful to investigate both the two metals interactions with the 2D MoS_2 nanosheets. Here, SEM, TEM, AFM, Zeta potentials, XRD, FT-IR, and EDS were used to characterize the adsorbent, i.e., MoS_2 nanosheets. And in batch experiments, the adsorption kinetics, isotherms, thermodynamics and effects of solution pH, ionic strength, solid content, coexisting ions on the sorption of both U and Th were evaluated. This study firstly checks the sorption capacity of MoS_2 nanosheets for U/Th, and explores interaction theory between them. The results will provide the theoretical foundation for the further application of MoS_2 in removing radionuclides from waste water.

2. Materials and methods

2.1. Preparation of materials

All chemical reagents used in this research were analytical-grade from Nanjing XFNANO Materials Tech. Co. Ltd. and without further purification. The specific method of synthesis of MoS_2 was as the following procedure. The sodium molybdate (90 mg $Na_2MoO_4{\cdot}2H_2O$) and thioacetamide (180 mg C_2H_5NS) were dissolved in deionized water (60 mL) and formed a transparent mixed solution. Then the solution was transferred into Teflon-lined stainless-steel autoclave (100 mL) and heated at 240 °C for 24 h. After being cooling and centrifugation, the products were repeatedly washed with deionized water and 100% ethanol for several times to remove impurities. Finally, the MoS_2 nanosheets were got after drying in a vacuum oven at 60 °C for 12 h. And the samples were preserved until being used.

The $UO_2(NO_3)_2{\cdot}6H_2O$ was dissolved into distilled water under nitrogen gas conditions to obtain the stock solution of U(VI). A stock solution of $Th(NO_3)_4$ was prepared by dissolving ThO_2 in HNO_3. Both stock solutions were diluted to the required concentrations.

Humic acid (HA) was extracted from the soil in Hua-Jia county, Gansu province, China. Its physicochemical property has been fully studied previously and it was proved to have strong interaction with adsorbate and adsorbent (Reiller et al., 2005; Sheng et al., 2010).