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Use of hydrous manganese dioxide as a potential sorbent for selective removal of lead, cadmium, and zinc ions from water

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ABSTRACT

Selective removal of three toxic metal ions, Pb(II), Cd(II), and Zn(II), from aqueous solution by amorphous hydrous manganese dioxide (HMO) was evaluated. Two polymeric exchangers, a polystyrene–sulfonic cation exchanger, D-001, and an iminodiacetic acid chelating exchanger, Amberlite IRC 748, were involved for comparison. Hydrogen ion release is accompanied by metal uptake onto HMO, implying that metal sorption could be generally represented by an ion-exchange process. As compared to both exchangers, HMO exhibits preferable sorption toward the toxic metals in the presence of Ca(II) ions at greater levels. FT-IR of the HMO samples laden with different metals indicate that Ca(II) uptake onto HMO is mainly driven by outer-sphere complexation, while that of three toxic metals might be related to inner-sphere complex formation. In addition, uptake of heavy metals onto HMO approaches equilibrium quickly and the exhausted HMO particles can be regenerated readily for repeated use by HCl solution. The results reported strongly display the potential of HMO as an economic and selective sorbent for removal of toxic metals from contaminated waters.

1. Introduction

Heavy metals in water remain a serious threat to environmental and public health [1]. Until now, various techniques, including chemical precipitation, coagulation/flocculation, membrane separation, and ion-exchange, have been developed for efficient removal of heavy metals from contaminated waters. Among these available techniques, ion-exchange technique on polymeric ion-exchangers is widely used for treatment of metal-contaminated wastewater [2–4]. In theory, ion-exchange driven by electrostatic or Columbic interaction is nonspecific for uptake of heavy metal ions. As a result, alkali or alkaline earth ions such as Na^+, Ca^{2+}, and Mg^{2+}, which are ubiquitously present with heavy metals in water, strongly compete against active sites for heavy metals and thus result in a dramatic decrease in the working capacity of ion-exchangers [2,5]. Polymeric chelating exchangers have, to a great extent, shown preferable sorption toward many toxic metals through formation of metal complexes [6–8], but they are often too expensive to justify their application for heavy metal removal from water and wastewater, and some of the chelating resins (e.g., thiol or amine types) are not satisfactory in chemical stability for long-term use.

In the past decades, several hydrous metal oxides have been exploited for heavy metal removal from aqueous media, namely, hydrous Fe(III) [9,10], Al(III) [10,11], Sn(IV) [9,12], Zr(IV) [13], and Mn(IV) oxides [10,12]. for the sorption by hydrous manganese dioxide (HMO) of cationic or anionic pollutants, i.e., heavy metal ions [14], arsenate [15], and phosphate [16], from natural waters has attracted considerable attention, because it would significantly mediate the fate and mobility of the targeted pollutants in water [17,18]. For example, Kanungo et al. [19] and Kanungo et al. [20] studied the sorption of Co(II), Ni(II), Cu(II), and Zn(II) ions on HMO particles in the presence of different electrolytes. They found that these toxic metals can be effectively trapped by HMO through electrostatic forces and formation of inner-sphere complexes. The specific properties of HMO render it a potential sorbent for heavy metal removal from contaminated waters. Nevertheless, most of the available studies in the open Refs. [17,18] were conducted in terms of environmental and geochemical aspects, i.e., the effect of HMO sorption on toxic metal mobility in the aquatic environment, and inadequate efforts were made from a technical viewpoint to evaluate the properties of HMO as a potential sorbent for heavy metal ion removal from contaminated waters. For example, the sorption selectivity of HMO toward targeted metals in the presence of many commonly encountered ions, such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, is of particular significance when it is used in associated wastewater treatment. However, it is still not well understood [21]. Thus, further study is still needed to systematically elucidate HMO sorption toward toxic metals.

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In this current study, we synthesized and characterized amorphous hydrous manganese dioxide, followed by measuring its sorption of three toxic metal cations (Pb(II), Cd(II), and Zn(II)) as a function of solution pH, contact time, and the competing Ca(II) cation. For comparison, two commercially available resins widely used for removal of heavy metals [2,22,23], D-001, a macroporous polystyrene cation exchanger, and Amberlite IRC 748, an iminodiacetic acid chelating exchanger, were employed as reference sorbents. Fourier-transform infrared (FT-IR) spectroscopy was also performed to preliminarily reveal its underlying sorption mechanism.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade and were purchased from Nanjing Zhongdong Reagent Co. (Nanjing, China). D-001 was kindly provided by Zhenguang Resin Co., China. Amberlite IRC 748 was obtained from Rohm Haas Co. (USA). The main physicochemical properties of both resins are presented in Table 1. Prior to use, the resins were washed with 1 M HCl, 1 M NaOH, and alcohol to remove possible impurities, followed by rinsing with deionized water. Then they were converted to Na^+ form by flushing them in a fixed bed with 2 M NaCl for 12 h [22]. Finally, these resins were washed with deionized water and vacuum-desiccated at 333 K for 24 h until they reached a constant weight.

2.2. Preparation and characterization of hydrous manganese dioxide

HMO particles were prepared according to the method proposed by Parida et al. [24]. In detail, 100 ml of solution containing 30 g of $MnSO_4 \cdot H_2O$ was added to 350 ml of NaOCl solution (containing 19.25 g of active chlorine). After constant agitation at 120 rpm for 1 h, the suspension was allowed to settle. The precipitate was washed first with 0.5 M HCl to remove excessive alkali, followed by rinsing with double-deionized water. Finally, the solid HMO particles were filtered and dried for further study.

X-ray diffraction (XRD) spectra of HMO particles were recorded by an XTRA X-ray diffractometer (Switzerland). FT-IR spectra of HMO particles before and after metal sorption were taken from a Nexus 870 FT-IR spectrometer (USA) with a pellet of powered potassium bromide and sorbent in the range 500–4000 cm^{-1}. The specific surface area of HMO was measured using an N_2 adsorption and desorption test at 77 K (Micromeritics ASAP-2010C, USA).

2.3. Batch sorption and regeneration experiments

A sample of 50 mg of a given sorbent particle was introduced into 250-ml polyethylene flasks containing 100 ml of a solution of known heavy metal concentration. Ca^{2+} was introduced as a competing ion by dissolving its nitrate in water. When necessary, 0.50 M HNO_3 was used to adjust the solution pH in the range 2–8 throughout the experiment. Detailed chemical compositions of the sorption systems are described in the figure captions. The flasks were then transferred to a Model G-25 incubator shaker with a thermostat (New Brunswick Scientific Co. Inc.) and shaken at 200 rpm for 24 h. Preliminary kinetic experiments indicated that 12 h was sufficient to reach sorption equilibrium on HMO particles and the polymeric exchangers. The HMO beads exhausted by heavy metals during sorption were transferred to another flask after being filtered, and 50 ml of 0.5 M HCl solution was added for their regeneration. The regenerated HMO particles were repeatedly used for heavy metal sorption. Note that all the batch experiments were performed in duplicate for data analysis.

For kinetic determination, the initial solution volume was set as 1000 ml, and 0.5-ml aliquots were sampled at various time intervals. The amount of each metal loaded onto the sorbent was calculated by conducting a mass balance before and after the test.

Table 1
Physical and chemical properties of two resins used in the study.

Properties	D-001	Amberlite IRC 748
Functional group	Sulfonic	Iminodiacetic acid
Matrix	Styrene–divinylbenzene, macroporous	Styrene–divinylbenzene, macroporous
Particle size	0.6–1.0 mm	0.50–0.65 mm
Total exchange capacity	4.10 meq/g	1.35 meq/ml[a]

[a] Provided by the manufacturer.

2.4. Measurements of heavy metals in solution

Concentrations of all the heavy metals were determined by atom absorption spectroscopy (Thermal Co. US). When the content was less than 1 mg/L, it was determined by atom fluorescence spectrophotometry (AFS) with an online reducing unit (AF-610A, China) with $NaBH_4$ and HCl solution.

3. Results and discussion

3.1. Physicochemical properties

The physicochemical properties of HMO particles have been well characterized elsewhere [24]. Here we just determined the crystallinity and surface area of the HMO particles. As indicated by XRD spectra (Fig. S1 in the supplementary information), the HMO particles are amorphous in nature, and their BET surface area is around 100.5 m^2/g, which is in close agreement with that reported by Parida et al. [24]. Physicochemical properties of two polymeric exchangers employed herein are presented in Table 1.

3.2. Effect of solution pH on metal sorption

The effect of solution pH on heavy metal removal by HMO was examined, and the results are presented in Fig. 1. As shown, the uptake capacity of each metal is increased with increased solution pH. In addition, solution pH is decreased when sorption occurs, particularly in the pH range from 4 to 7, indicating that H^+ release is accompanied by metals sorption. Kanungo and Parida [25] and Tamura et al. [26] suggested that metal ion (M) uptake by HMO could be represented as follows:

$$-\mathrm{Mn-OH} + \mathrm{M}^{2+} \rightleftarrows -\mathrm{Mn-O-M}^{+} + \mathrm{H}^{+} \tag{1}$$

$$-\mathrm{Mn-OH} + \mathrm{M}^{2+} \rightleftarrows (-\mathrm{Mn-O})_2-\mathrm{M} + 2\mathrm{H}^{+} \tag{2}$$

Both reactions can be classified as typical ion-exchange processes. As inferred from Eqs. (1) and (2), it is plausible that lower pH values are less favorable for metals sorption, which is consistent with the results presented in Fig. 1.

3.3. Sorption isotherms

Sorption isotherms of HMO toward three metals were obtained at 298 K. For simplicity, the experimental results illustrated in Fig. 2a–c are correlated by the Freundlich and Langmuir models [27],

$$q_e = K_f C_e^n \tag{3}$$

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m}, \tag{4}$$

where K_f and n are the Freundlich constants to be determined, q_m (mmol/g) is the maximal sorption capacity, and K_L (L/mmol) is a bind-