



Manganese oxide nanoparticles impregnated graphene oxide aggregates for cadmium and copper remediation



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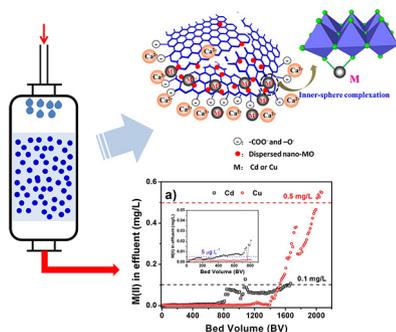
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HIGHLIGHTS

- GO-MO was prepared for simulated wastewater treatment in column settings.
- GO-MO has fast sorption kinetics and high sorption selectivity to the target metals.
- The intraparticle diffusivity was quantified for the sorption kinetics.
- The spent GO-MO can be thoroughly regenerated with an acid-salt binary solution.

GRAPHICAL ABSTRACT



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ABSTRACT

Loading metal oxide nanoparticles (NPs) into porous granular materials with excellent hydraulic characteristics offers a promising option to break the technical barriers of direct application of NPs in scaled-up water decontamination. By taking advantage of graphene oxide (GO) mediating the formation of manganese oxide (MO) nanoparticles at the same time aggregating to form macroporous structure under highly alkaline conditions, we fabricated a novel GO-MO composite ($D = \sim 160 \mu\text{m}$). The intraparticle diffusivity of Cd(II) and Cu(II) onto GO-MO was determined to be 3.17×10^{-9} and $4.67 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, respectively, similar to macroporous resin. The GO-MO showed synergistic sorption capacity for Cd(II) and Cu(II) compared to bulky MO and GO due to the high dispersion of MO NPs ($< 10 \text{ nm}$) in the aggregated GO matrix and Donnan membrane effect. The GO-MO also had strong sorption selectivity in the presence of Ca(II) and humic acid. HADDF-EDS characterization visually showed that Cu(II) and Cd(II) was selectively adsorbed to MO even in the presence of 50 times higher competing Ca(II) ions, which was quantified as $\sim 93\%$ of the total adsorbed metal for both Cu(II) and Cd(II) by XPS analysis. Moreover, GO-MO was successfully employed in the column operation with effective treatment volume of ~ 1650 and $\sim 1995 \text{ BV}$ for simulated Cd(II)- and Cu(II)-contaminated wastewater, respectively. The exhausted GO-MO can be effectively regenerated using acid-salt binary solution with desorption rate $> 97\%$. The results from this study may offer insights to rationally design highly efficient engineered nanocomposites for water purification.

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1. Introduction

Heavy metals such as Pb(II), Cd(II) and Cu(II) in water can pose huge threats to living organisms and ecosystem even at trace levels [1,2]. Therefore, their decontamination from various waters has been a constant and significant concern. In the past years, a variety of methods, including chemical precipitation [3], nanofiltration and ultrafiltration [4,5], coagulation [6], adsorption [7] and biological treatment [8] were developed or improved to reduce or even eliminate heavy metals from water. Among these techniques, adsorption is one of the most frequently used and promising taken into account its prominent performance and simplicity of operation as well as environmental benignity [9]. For adsorption, the key aspect is engineering highly efficient and specific adsorbents. Among various adsorbents, nanosized metallic oxides of specific affinity to target heavy metals, including Mn(IV), Fe(III), Zr(VI), Ti(IV) oxides or hydroxides, are most promising in selective removal of heavy metals [10,11]. Nevertheless, till now, these materials are far from scaled-up application due to the great pressure drop in column application caused by their fine particle sizes.

A common practice to overcome the above technical barrier is loading metal oxide nanoparticles (NPs) onto porous support with good hydraulic properties, such as zeolite [12], crushed brick [13], and activated carbon [14]. However, the serious aggregation of the embedded NPs within these supports unavoidably causes pore blockage particularly in micropores or mesopores, which significantly hurts sorption efficiency [15]. Zhang et al. proposed a strategy to reduce particle aggregation by loading metal oxide NPs onto ion exchange resins covalently bound with non-diffusible charged functional groups [16]. The charged groups promoted the dispersion of the metal oxide particles, and dramatically increased their utilization efficiency for targeted metal sequestration. Unfortunately, the pore blockage issue was not solved, and the slow diffusion/sorption process in such composites still prevents their engineering application. Therefore, composites with larger pores and abundant charged groups are still in demand.

Graphene oxide (GO) is a layered material with very high density of charged oxygen-containing groups such as carboxyl and hydroxyl groups [17–19], and it can reduce the impregnated NPs aggregation and the pore blockage. This makes GO a suitable support for metal oxide NPs. The layered structure of GO could also reduce the pore diffusion resistance during adsorption. One possible problem of such a 2-D composite is its application in column settings due to the layered structure would cause low hydraulic conductivity. However, GO has a distinguished feature that it aggregates at very alkaline pH as a result of inter- and intra-folding of GO nanosheets due to the strong electrostatic repulsion between negatively charged deprotonated oxygen-containing groups [20]. This feature would greatly improve the hydraulic conductivity of GO. Coincidentally, high alkaline conditions are required for synthesis of many metal oxide NPs, in which manganese oxides (MO) with pH_{pzc} of 2–3 is considered to be one of the most efficient adsorbents for heavy metal removal due to its negative surface charge at a broad pH range and specific and strong binding to many metal cations [21]. In this study, by taking advantage of both features, we synthesized a GO-MO composite at alkalinity of 5%. This aggregated composite is expected to have a layered GO substructure, large pores created by the folding of GO nanosheets and therefore would have high hydraulic conductivity but low diffusion restriction. It is also expected that the abundant functional groups and layer structure of GO would facilitate the loading and dispersion of MO NPs and result in high sorption capacity. Therefore, such a composite can achieve excellent balance between adsorption efficiency and hydraulic conductivity. To verify these hypotheses, Cd(II) and Cu(II) were chosen as the representative metals and their diffusion coefficients into this adsorbent as well as the sorption capacity and selectivity were determined in batch experiments. Column experiments were also carried out to examine the performance of this adsorbent for practical application. XPS and scanning TEM (STEM) measurements were further made to probe the underlying sorption mechanism.

2. Materials and methods

2.1. Chemicals

All chemicals used in the experiments are analytical grade (AR) without further treatment. Humic acid (HA) was obtained from Aldrich-Sigma (Shanghai, China), and other chemicals were all provided by Aladdin Industrial Corporation. Cadmium and copper stock solution (1 g L^{-1}) were prepared by dissolving the corresponding chloride salts in ultrapure water (resistivity $> 18.2 \text{ M}\Omega \text{ cm}^{-1}$).

2.2. Synthesis of GO-MO

Few-layer GO nanosheets were fabricated from graphite powder based on a modified Hummers method [22]. The GO-MO composites were synthesized according to the following procedures: Firstly, 0.1 M MnCl_2 solution was mixed with 10 g L^{-1} GO solution, and then the solution pH was adjusted to 7 followed by continuous agitation at 298 K for 24 h. Then, the Mn(II)-preloaded GO was collected and subsequently soaked into a binary NaOCl-NaOH solution of 5% alkalinity and 6% active chlorine. The above mixture was continuously stirred at 298 K for another 24 h to allow the complete oxidation of Mn(II) to Mn(IV). Finally, the solids were separated and alternately rinsed with 1 mM HCl and deionized water till neutral pH. Then, the obtained composites were freeze-dried and stored in a desiccator. The schematic of the fabrication process is provided in Fig. S1, Supporting Information (SI).

2.3. Batch sorption experiments

Batch sorption experiments were conducted in 100 mL Erlenmeyer flasks. Typically, 0.01 g sorbent was added into 50 mL Cd(II) or Cu(II) solution with given concentration. The solution pH was adjusted using 0.1 M HCl and NaOH when desired. The flasks were vibrated at 298 K and 180 rpm for 24 h using an orbit shaker with gas bath. We note that 24 h was sufficient to achieve reaction equilibrium according to preliminary kinetic experiments. For sorption kinetics experiments, 0.1 g GO-MO or GO was dispersed into 500 mL Cd(II) or Cu(II) solution with preset concentration, and aliquots of 0.5 mL were collected at pre-determined time intervals to evaluate sorption kinetics.

2.4. Fixed-bed experiments

The fixed-bed experiments were conducted in a column with length of 130 mm and diameter of 12 mm packed with 3 mL aliquot of wet GO-MO (equivalent to 0.5 g dry particles). A peristaltic pump (Longer Pump, China) was employed to pump the water up-to-down at constant flow rate. The superficial liquid velocity (SLV) and the empty bed contact time (EBCT) of the column tests are provided in the corresponding figure captions. For the column regeneration test, a binary solution of 0.2 M HCl and 4% CaCl_2 was supplied as the regenerant.

2.5. Analysis

The loading of MO on GO was determined by acid digestion followed by analysis of Mn content using a TAS-990 flame atom adsorption spectrophotometer (AA, Persee Inc., China). The Cd(II) and Cu(II) concentrations if higher than 0.5 mg L^{-1} were also measured using the AA, otherwise an atom fluorescence spectrophotometer (AFS-230E) (Haiguang Co., Ltd) was used.

2.6. Nanocomposite characterization

The specific surface area and pore size distribution of the GO support, bulky MO and GO-MO samples were determined using a BET surface area analyzer (ASAP2020, USA) based on N_2 adsorption-desorption tests at 77 K. The surface morphology of GO-MO

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