



A highly efficient polyampholyte hydrogel sorbent based fixed-bed process for heavy metal removal in actual industrial effluent

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ABSTRACT

High sorption capacity, high sorption rate, and fast separation and regeneration for qualified sorbents used in removing heavy metals from wastewater are urgently needed. In this study, a polyampholyte hydrogel was well designed and prepared via a simple radical polymerization procedure. Due to the remarkable mechanical strength, the three-dimensional polyampholyte hydrogel could be fast separated, easily regenerated and highly reused. The sorption capacities were as high as 216.1 mg/g for Pb(II) and 153.8 mg/g for Cd(II) owing to the existence of the large number of active groups. The adsorption could be conducted in a wide pH range of 3–6 and the equilibrium fast reached in 30 min due to its excellent water penetration for highly accessible to metal ions. The fixed-bed column sorption results indicated that the polyampholyte hydrogel was particularly effective in removing Pb(II) and Cd(II) from actual industrial effluent to meet the regulatory requirements. The treatment volumes of actual smelting effluent using one fixed bed column were as high as 684 bed volumes (BV) (7736 mL) for Pb(II) and 200 BV (2262 mL) for Cd(II). Furthermore, the treatment volumes of actual smelting effluent using tandem three columns reached 924 BV (31,351 mL) for Pb(II) and 250 BV (8483 mL) for Cd(II), producing only 4 BV (136 mL) eluent. Compared with the traditional high density slurry (HDS) process with large amount of sludge, the proposed process would be expected to produce only a small amount of sludge. When the treatment volume was controlled below 209.3 BV (7103 mL), all metal ions in the actual industrial effluent could be effectively removed (<0.01 mg/L). This work develops a highly practical process based on polyampholyte hydrogel sorbents for the removal of heavy metal ions from practical wastewater.

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1. Introduction

Heavy metal wastewater is the current outstanding problem in the field of water pollution. Due to the high toxicity and non-biodegradability of heavy metals (Liu et al., 2013), it is very urgent to seek effective methods to remove heavy metals from wastewater (Bian et al., 2012). Various treatment technologies have been applied for the removal of toxic metal ions pollutants from wastewater, including ion exchange, filtration, chemical

precipitation, solvent extraction, sorption and so on (Jin et al., 2014a). Although various techniques for the removal of toxic metal ions have been developed, sorption is considered a facile effective technique due to its cost-effective, versatile and simple to operate for removing trace-levels metal ions from aqueous systems (Ali, 2012).

Recently, the research on adsorbents for the removal of toxic metal ions has been focused on nanomaterial-based adsorbents which possess large surface areas, easy modification, and large number of active sites for binding metal ions (Sun et al., 2013b). Still, the separation and reusability of nanomaterials is a tedious job (Ali, 2012), and the residual nanomaterials in water will undoubtedly bring new security concerns as well (Lowry et al., 2012; Zhao et al., 2014). Therefore, the adsorbents with good separation and

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regeneration properties show incomparable advantages over nanomaterial-based adsorbents. Bulk materials used as sorbents are in favor of separation, but the low adsorption capacity and slow adsorption rate of them is a real problem (Cao et al., 2012).

Hydrogel, a three-dimensional cross-linked network of polymers, exhibits a distinctive feature of high swelling in water (Wang et al., 2010b). They have been considered as a type of mechanically weak materials (Calvert, 2009), and thus little attention is focused on them as possible structural materials. Recently several tough hydrogels with good mechanical properties, such as double-network hydrogels (Sun et al., 2012; Chen et al., 2013; Nakajima et al., 2012), polyampholyte hydrogels (Sun et al., 2013a), and hydrogel composites (Huang et al., 2007), have revealed the potential as structural materials (Shibayama, 2012). Among these hydrogels, polyampholyte hydrogels bear randomly dispersed cationic and anionic repeat groups, forming tough and viscoelastic hydrogels with multiple mechanical properties. Also, the supramolecular structure of polyampholyte hydrogels can be tuned to change multiple function properties over wide ranges by diverse functional unit combinations (Sun et al., 2013a). Additionally, excellent water penetration of hydrogel is highly accessible to foreign molecules (Kudaibergenov and Ciferri, 2007). This uniqueness of polyampholyte hydrogel motivates us to exploit this kind of materials as adsorbents for removing heavy metals in water. To our knowledge, there is no report about sorbents based on polyampholyte hydrogel.

This study presents a novel polyampholyte hydrogel strengthened with graphene oxide, which also provided a framework for the formation of 3D structure. This polyampholyte hydrogel possesses some advantages: good mechanical property for easy separation and durable recycling, large amount of carboxyl and amino groups for high sorption capacity, and high swelling for fast sorption. As a result, the polyampholyte hydrogel as adsorbents was successfully used in the treatment of actual industrial wastewater. The experimental parameters of the adsorption characteristics, fixed-bed column sorption and regeneration/recycling tests were investigated. This work is expected to potentially develop a step change in adsorbent materials for removing heavy metal ions in wastewater.

2. Materials and methods

2.1. Materials

Graphene oxide (GO) was prepared by oxidation of natural graphite powder (320 mesh, Qingdao Tianhe Graphite Co. Ltd) according to a modified improved Hummers' method (Marcano et al., 2010). Acrylic acid (AA) and methyl methacrylate (MMA) were distilled under reduced pressure before use. Ammonium persulfate (APS), N,N-methylenebisacrylamide (MBA), N,N,N',N'-tetramethylethylenediamine (TEMED), sodium dodecylsulfonate (SDS) and triethylene tetramine (TETA) were purchased from commercial sources and used as received. The actual industrial effluent was taken from Shuikoushan smelting plant located in Hengyang, Hunan province, China. All aqueous solutions were prepared with deionized water.

2.2. Preparation of polyampholyte hydrogel

Polyampholyte hydrogel was synthesized using radical copolymerization and functionalized by aminolysis reaction. In a typical preparation procedure of polyampholyte hydrogel, the radical copolymerization of AA (0.4 mL) and MMA (0.2 mL) was initiated by APS (0.003 g) in 2 mL of 5 mg/mL GO aqueous suspension, using MBA (0.012 g) as crosslinking agents, TEMED (5 μ L) as the

crosslinking accelerator and SDS (0.2 g) as emulsifying agent. The reaction last for 2 h at 60 °C to get a hydrogel product. Then the hydrogel was immersed into 10 mL of 0.1 g/mL TETA aqueous solution for 2 h at 90 °C to complete the ammonolysis of methyl ester. At last, the polyampholyte hydrogel was washed with deionized water to remove SDS and unreacted reagents. The cost of the polyampholyte hydrogel production is approximately US\$ 6.3×10^3 /t, much lower than those of some reported sorbent materials (see Supporting Information).

2.3. Characterization

The structure of the polyampholyte hydrogel was examined by scanning electron microscopy (SEM, FEI QUANTA 200). The functional groups in the hydrogel were characterized by Fourier transform infrared spectra (FTIR, Nicolet 5700) and Raman spectra (Labram-010). The N and O contents of the samples were determined by an elementary analysis (vario EL III). The thermogravimetric analysis (TGA, TG/DTA7300) was measured under a nitrogen atmosphere from room temperature to 700 °C with heating rate of 10 °C/min. The surface chemistry properties of the hydrogel during the adsorption process were determined by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher Scientific, England). The compression test of the hydrogel was performed on a universal testing machine (HZ-1007C) with compression/decompression rate of 1 mm/min. The pH values at the point of zero charge (pH_{PZC}) of the hydrogel were measured in a series of 0.01 M NaCl with different initial pH. The swelling experiment was performed by immersing the hydrogel in an excess of water at room temperature to reach swelling equilibrium. The swelling ratio (SR) of the hydrogel was calculated as $SR = (W_s - W_d)/W_d$, where W_s and W_d represent the weights of swollen hydrogel and dry hydrogel, respectively.

2.4. Batch adsorption experiments

Batch adsorption experiments were conducted to explore the adsorption properties and mechanism of the polyampholyte hydrogel which was swollen with deionized water before adsorption. The sorbent dosage was calculated by the weight of dry hydrogel. Analytical grade Pb(NO₃)₂ and Cd(NO₃)₂ were employed to prepare the Pb(II) and Cd(II) stock solutions. The pH values of the solution were adjusted by 0.1 M HCl or NaOH solutions, and NaClO₄ or LiClO₄ were added as background electrolyte. The concentrations of residuary metal ions in solution were measured by an atomic absorption spectrometer (AAS, Hitachi Z-2000, Japan). The metal-adsorbed hydrogel was eluted with 0.1 M HCl solution, then regenerated with 0.1 M NaOH solution, and washed with deionized water to neutral. All the experimental data were the average of triplicate determinations with less than 5% relative errors.

2.5. Fixed-bed column sorption experimental

Fixed-bed column sorption experiments were carried out at ambient temperature using the polyampholyte hydrogel (2 mm $\times$ 2 mm $\times$ 2 mm) packed in fixed-bed columns. Two feeding solutions (FS) with different metal concentration were treated: FS1 (simulated effluent) contains 40 mg/L Pb, Cd, Ca, Mg, Na and K or FS2 (actual industrial effluent) contains 2.225 mg/L Pb, 4.175 mg/L Cd, 203.7 mg/L Zn, 14.75 mg/L Mn, 4.675 mg/L Ni, 9.675 mg/L Cu, 0.042 mg/L Cr and 10.02 mg/L Fe. The FS was pumped down-flow through the column by a peristaltic pump. A hydrochloric acid (HCl) solution with an upper concentration limit of 0.1 M was used as the eluting agent for desorption. The column parameters are summarized in Table 1.

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