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Rapid and efficient treatment of wastewater with high-concentration heavy metals using a new type of hydrogel-based adsorption process

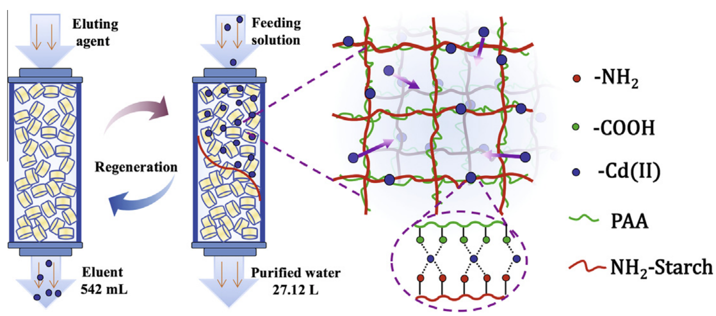
Guiyin Zhou [a], Chengbin Liu [a,*], Lin Chu [a], Yanhong Tang [b], Shenglian Luo [a]

[a] State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, PR China
[b] College of Materials Science and Engineering, Hunan University, Changsha 410082, PR China

HIGHLIGHTS

- NH_2-Starch/PAA as a new integrated adsorbent was successfully prepared.
- The adsorbent exhibited fast sorption rate and high sorption capacity.
- The adsorbent showed high treatment capacity for high concentrated wastewater on fixed-bed column.
- Excellent mechanical strength of adsorbent benefited its separation and reusability.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a new type of double-network hydrogel sorbent was developed to remove heavy metals in wastewater. The amino-functionalized Starch/PAA hydrogel (NH_2-Starch/PAA) could be conducted in a wide pH and the adsorption process could rapidly achieve the equilibrium. The adsorption capacity got to 256.4 mg/g for Cd(II). Resultantly, even though Cd(II) concentration was as high as 180 mg/L, the Cd(II) could be entirely removed using 1 g/L sorbent. Furthermore, the desirable mechanical durability of the adsorbent allowed easy separation and reusability. In the fixed-bed column experiments, the treatment volume of the effluent with a high Cd(II) concentration of 200 mg/L reached 2400 BV (27.1 L) after eight times cycle. The NH_2-Starch/PAA overcame the deficiency of conventional sorbents that could not effectively treat the wastewater with relatively high metal concentrations. This work provides a new insight into omnidirectional enhancement of sorbents for removing high-concentration heavy metals in wastewater.

1. Introduction

Toxic heavy metals, like Cd, can accumulate in the human body and the environment for lengthy periods (Jin et al., 2014). Present, most of major crises are associated with industrial effluent discharge (Bian et al., 2012). Consequently, the concentrations of heavy metals in effluent discharge must be strictly limited. Various techniques have been employed to remove heavy metal ions from industrial effluent, but it is still challenging to control their concentrations to safe level (Gollavelli et al., 2013). Adsorption process has been regarded as one of the most effective techniques to remove heavy metal ions in wastewater (Ali, 2012). However, it is very difficult for conventional sorbents to remove high-concentration heavy metals in wastewater to safe level.

To this end, a great deal of effort has been taken to explore new sorbent materials, such as carbon composites, biomass adsorbents

* Corresponding author.
E-mail address: chem_cbliu@hnu.edu.cn (C. Liu).

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and nano-adsorbents (Tan et al., 2016a; Phetphaisit et al., 2016; Qu et al., 2013). Despite a certain degree of improvement in metal ions adsorption capacity, it is still difficult to decrease heavy metal concentrations to safe level unless using large doses of sorbent for long hours. Furthermore, for the practical application, there are three limitations: (1) slow kinetic, (2) loss of performance and (3) difficult separation. The slow near surface and internal diffusion rates of granular adsorbents seriously limit their overall kinetics where the equilibrium times commonly require some hours (Maneerung et al., 2016). Additionally, these adsorbents are easily subject to blocking and burial of surface adsorption sites, resulting in serious loss of performance (Dou et al., 2013). Although nano-adsorbents possess good dynamics and high adsorption capacities, it is difficult to separate (Stefaniuk et al., 2016; Zhao et al., 2014). The inefficient separation would result in high operation cost and secondary pollution (Ali, 2012). It is still imperative to develop qualified sorbents with high adsorption performance, cost-effectiveness, and ease of operation.

Hydrogel, a three-dimensional cross-linked network of polymers, exhibits a distinctive feature of high swelling in water, providing foreign molecules with fast access into its inner (Hu et al., 2015). However, the low mechanical strength and poor recoverability of hydrogel limit its extensive application. In recent year, some new hydrogels with improved mechanical strength have been developed, such as polyampholyte hydrogels (Sun et al., 2013), nanocomposite hydrogels (Rose et al., 2013) and double-network (DN) hydrogels (Sun et al., 2012). Among them, the DN hydrogel, comprising two interpenetrating and cross-linked polymer networks, is the most effective to improve the mechanical strength of hydrogels (Chen et al., 2015a). Additionally, such a double network concept is proposed to avoid permanent damage of covalent bonds by introducing dynamic interactions including electrostatic interaction, ionic cross-linkers or hydrogen bonding (Du et al., 2014). Thus, this uniqueness of DN hydrogels might open up new opportunities to explore the potential application of these materials as sorbents towards metal ions.

Here, a new type of amino-group functionalized DN hydrogel sorbent was designed and prepared. To the best our knowledge, it is the first time that DN hydrogel was used as sorbent to remove heavy metals in wastewater. The Cd removal performance was strengthened in this study because it is a highly focused pollutant in water in Hunan Province, China. The actual industrial effluent from local smelting plant was treated with the new adsorbent. Metal ions adsorption onto the DN hydrogel was examined in batch experiments to evaluate its adsorption performance, and the binding mechanism was primarily highlighted based on the FTIR and XPS analysis. Extended column experiments were conducted to evaluate the potential for practical application. This work would be expected to potentially develop a step change in sorbent materials in the arena of industrial effluent treatment.

2. Experimental

2.1. Chemicals and materials

Soluble starch and acrylic acid (AA) were obtained from industry. Ammonium persulfate (APS), N,N-methylenebisacrylamide (MBA), epichlorohydrin (ECH), and triethylene tetramine (TETA) were purchased from Sinopharm Chemical Reagent Co. Ltd. China. Other chemicals were used as received. Analytical grade cadmium nitrate was employed to prepare the Cd(II) stock solutions. The actual industrial effluent was taken from Shuikoushan Smelting Plant, Hengyang, Hunan province, China.

2.2. DN hydrogel synthesis

Firstly, starch aqueous solution was heated at 90 °C to form a transparent, low-viscosity solution. Then, a 0.6 mL aqueous solution in a cylinder mold, containing 14 wt% dissolved starch, 14 wt% AA, 0.25 mol% APS initiator and 1.5 mol% MBA cross-linking agent (the mole ratios were referred to AA), was heated at 60 °C for 2 h to complete gelation process to get a pristine starch/PAA hydrogel (Starch/PAA). Next, after an immersion into 2 mL of dimethyl sulfoxide solution of sodium hydroxide (0.1 g) and ECH (0.15 mL) for 1 h at 60 °C, the Starch/PAA was further immersed into 2 mL of deionized water containing sodium hydroxide (20 wt%) and TETA (0.2 mL) for 6 h at 60 °C to obtain NH_2-Starch/PAA. The NH_2-Starch/PAA was washed with deionized water to remove unreacted reagents. According to the synthetic ratio, the cost of the dry NH_2-Starch/PAA is approximately US$ 7.0×10^3/t, much lower than those of commonly used sorbents (see Supporting Information).

2.3. Characterizations

The surface morphology of NH_2-Starch/PAA was examined by scanning electron microscopy (SEM, FEI QUANTA 200). The functional groups of the samples were characterized by Fourier transform infrared spectra (FTIR, Nicolet 5700). The surface chemistry of NH_2-Starch/PAA before and after adsorbing Cd(II) was determined by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher Scientific, England). The thermogravimetric analysis (TGA, TG/DTA7300) was measured under a nitrogen atmosphere from room temperature to 700 °C at a heating rate of 10 °C/min. Compression test was performed on a universal testing machine (HZ-1007C) with compression/decompression rate of 2 mm/min. The pH value at the point of zero charge (pH_{PZC}) was measured by ΔpH method in a series of 0.01 M NaCl at different pH. The swelling experiment was performed by immersing the dried NH_2-Starch/PAA in an excess of water at room temperature to reach swelling equilibrium. The swelling ratio (SR) was calculated as $SR = (W_s - W_d)/W_d$, where W_s and W_d represented the weights of swollen gel and corresponding dried gel, respectively.

2.4. Batch adsorption experimental

According to reactor size, the hydrogel sorbent (1 g/L weight of dry gel) was cut into small pieces and added into Cd(II) solutions with preselected concentrations. For all adsorption tests, the initial pH values of the Cd(II) solutions were adjusted with HCl solution or NaOH solution. After the adsorption processes, the sorbents were conveniently separated by decantation and the residual metal ions in solution were analyzed by atomic absorption spectrometer (AAS, Hitachi Z-2000, Japan). For the regeneration, the Cd(II)-adsorbed sorbents were eluted with 0.1 M HCl solution, regenerated with 0.1 M NaOH solution, and then washed with deionized water to remove adsorbed alkali.

2.5. Fixed-bed column adsorption experimental

A simulated effluent, containing 200 mg/L Cd(II) and 0.01 M NaI, CH_3COOK, $MgSO_4$ and $CaCl_2$, was treated using two columns in series. The pH of the simulated effluent was adjusted to 5.0. The column parameters are summarized in Table S1. When NH_2-Starch/PAA sorbent in the first column was close to adsorption capacity, this column was transferred and regenerated with 0.1 M HCl and NaOH solution, and the other two columns were shifted forward in sequence. In this way, in a continuous processing loop, the first column always had the highest adsorption loading and the second