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Cube sugar-like sponge/polymer brush composites for portable and user-friendly heavy metal ion adsorbents

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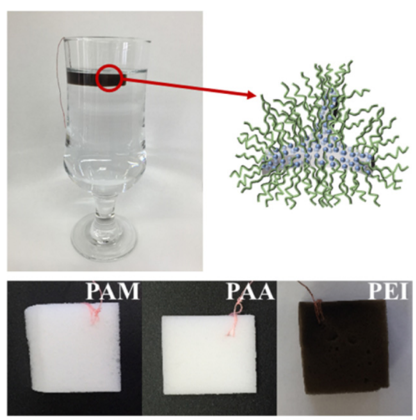
HIGHLIGHTS

- A simple method to instantly remove heavy metals is valuable to individual users.
- Portable and user-friendly heavy metal ion adsorbents are developed.
- Polymer-grafted sponges exhibit the best adsorption capacity and biocompatibility.

GRAPHICAL ABSTRACT



Polymer brush-grafted sponge

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ABSTRACT

Portable, non-toxic, and user-friendly sponge composites decorated with polyelectrolyte (PE) brushes were developed for the fast and efficient removal of heavy metal ions from waste water or drinking water. The polyacrylamide (PAM) and polyacrylic acid (PAA) brushes were grafted onto the sponge via "grafting-from" polymerization. For the polyethyleneimine (PEI) brush, "grafting-to" polymerization was used. A polydopamine (Pdop) layer was first coated on the sponge. Then, PEI was grafted onto the Pdop-coated sponge via a Michael addition reaction. The PEI-grafted sponge exhibited the best adsorption capacity and the fastest reaction rate of all the brushes due to the numerous adsorption sites of the PEI. The adsorption performance of two different PEI-grafted sponges depended on the molecular weight (MW) of the PEI. Simply by being dipped into a glass of water, non-toxic PEI-grafted sponge instantly removed the low concentration heavy metal ions, demonstrating a practical application for individual users.

1. Introduction

Heavy metal ions in industrial waste water have become a serious threat to wildlife and human health due to their high toxicity

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and non-biodegradability. Because they can be accumulated in the human body along the food chain, cases of serious side effects have been reported [1–3]. Conventional technologies for removing heavy metal ions involve ion exchange, chemical precipitation, filtration, electro-dialysis, and adsorption [4–20]. Conventional wastewater treatment consists of preliminary, primary, secondary and tertiary treatments that are based on biological, physical and chemical processes. Some of the disadvantages of these treatments are the constant high electrical energy requirements and the design, supervision, maintenance, and the general cost of construction that would require highly skilled workers [4–6]. There is also the issue of ecological disposal of the sludge waste. Because of the effectiveness of the adsorption process, numerous adsorbents have been proposed to efficiently remove heavy metal ions from waste water. Bulk material-based adsorbents can be effectively used for removal of heavy metals because of advantages of the relatively economic and easy processes. T.S. Anirudhan group examined the potential use of polymer-grafted sawdust as an adsorbent for the removal of Cr(VI) from water [21]. H.G. Park group demonstrated the potential industrial applications of biomaterials for the removal of heavy metals using alginate-based cotton [22]. Many research groups also proved that biochar is a promising adsorbent for heavy metals [23–26]. Nanoadsorbents are of particular interest in waste water treatment because of their high surface-to-volume ratio, which leads to a higher uptake capacity [7–20]. However, it has been recently reported that the unintended leakage of nanomaterials into the environment can cause a significant threat to the environment and public health [27,28]. Most of the reported nanoadsorbents are flow type and disperse in the water during adsorption, which are very vulnerable to leakage in the process of separation. Ironically, nanoadsorbents intended for environmental remediation could themselves be hazardous to the environment. Furthermore, previously reported nanoadsorbents and adsorption processes are not suitable for small scale applications or individual users. A simple method to instantly remove heavy metal ions would be valuable to individual users who either do not have access to purified water or who find themselves in an emergency situation without the appropriate tools.

Synthesizing polymer brushes, i.e., surface-anchored polymer chains, is a very convenient way to increase the density of surface functional groups [29–36]. Polymer brush is a layer of polymer chains attached to a surface by the end of the polymer chain [29]. Two different approaches, "grafting-from" and "grafting-to" polymerizations, are used to graft the polymer brushes onto the substrate. The "grafting-from" approach involves immobilizing an initiator system on the surface of a solid substrate, and the polymer layer is polymerized in situ at the initiator sites on the substrate [29]. The "grafting-to" method attaches end-functionalized polymers to the appropriate functional groups on a solid surface [29]. Functional groups on inorganic surfaces are generally limited to monolayers with just one or a few ion-exchanging (or chelating) functionalities per anchoring molecule incorporated onto the inorganic surface. In contrast, polymer brushes possess numerous repeating units and therefore numerous functional groups (i.e., one functional group per repeating unit). Furthermore, polymer brushes can be strongly anchored onto the surface of a wide range of materials via chemically robust covalent bonds [29–36]. B. Yameen group designed cationic or anionic polymer brush-grafted magnetic nanoparticles for highly efficient water remediation [37]. L. Tang group also reported amine-based polymer brush-grafted magnetic nanoparticles for highly effective adsorption of heavy metal ions [38]. Y. Guan group demonstrated Cu^{2+}-modified polymer brush-grafted magnetite nanoparticles for proteins adsorption [39]. Thus, polymer-brush-grafted magnetic nanoadsorbents are used to increase the uptake capacity and the separation ability of adsorbents [37–42]. However, in the absence of magnetic field, these nanoadsorbents are susceptible to leakage during the separation process.

This disadvantage of nanoadsorbents led us to develop a large, portable and user-friendly adsorbent in a single, practical unit, without the potential risk of leakage exhibited by nanoadsorbents. Building hierarchically large structures onto a single, practical unit (e.g., from centimeter (or meter) to micrometer and nanometer scales) is crucial for the synthesis of portable and user-friendly adsorbents. Sponges are portable, easy to use, and ubiquitous materials, which are possibly a desirable template for fabricating portable adsorbents because they possess centimeter-scale (or potentially meter-scale) dimensions, millimeter-scale pores and micrometer-scale interconnected skeletons. Herein, we report portable, non-toxic, and user-friendly heavy metal ion adsorbents composed of sponge/polymer brush composites.

2. Experimental

2.1. Materials

The melamine formaldehyde sulfate (MF) sponge was purchased from a local supermarket. The MF sponge can be also synthesized according to the literature [43]. Tetraethyl orthosilicate (TEOS, 99.999%), ammonium hydroxide solution (NH_4OH, 28–30%), 2-propanol (99.999%), ethanol (EtOH, 96.5%), 3-(Trimethoxysilyl)propyl methacrylate (MPS, 98%), acrylic acid (AA, 99%), acrylamide (AM, ≥99.8%), dopamine hydrochloride (100%), tris(hydroxymethyl)aminomethane (≥99.8%), polyethyleneimine solution (PEI, M_w = 750,000, 50 wt% in H_2O), polyethyleneimine (PEI, M_w = 25,000, ≤1% water), lead(II) nitrate ($Pb(NO_3)_2$, ≥99.0%), copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$, 99–100%), 4-nitrophenol sodium salt dihydrate (4-NPh, 99.9%), NaOH (93%), hydrochloric acid (HCl, 35–37%), acetonitrile (≥99.8%), and sodium borohydride ($NaBH_4$, 98%) were purchased from Sigma-Aldrich. The α,α'-azobis(isobutyronitrile) (AIBN, 98%) was purchased from JUNSEI. All chemicals were used as received. Deionized (DI) water with a resistance 18.2 MΩ cm was obtained using a Millipore Simplicity 185 system.

2.2. Synthesis of MF sponge/SiO_2/PAM or PAA

A solution containing 2-propanol (30 mL), DI water (5.4 mL) and NH_4OH (0.9 mL) was prepared and stirred for 1 min. Then, 0.9 mL of TEOS and the MF sponge (2 × 2 × 1 cm) were added into the solution, followed by stirring for 4 h. After synthesizing silica nanoparticles onto the MF sponge (MF sponge/SiO_2), the resulting silica-coated sponge (MF sponge/SiO_2) was washed 3 times with DI water and dried in an oven at 50 °C. The MF sponge/SiO_2 was immersed into an MPS solution (MPS (0.25 mL)/EtOH (30 mL) under reflux (80 °C) for 10 h. After the MPS coating, the resulting sponge (MF sponge/SiO_2/MPS) was washed 3 times with DI water. To graft each polymer onto the MF sponge/SiO_2/MPS, 0.1 g of monomer (AA or AM) and 2.5 mg of initiator (AIBN) were completely dissolved in 30 mL of acetonitrile. The MF sponge/SiO_2/MPS was immersed into the monomer solution and further reacted under reflux at 80 °C for 10 h. Finally, the resulting sponge was washed 3 times with DI water and dried in an oven at 50 °C.

2.3. Synthesis of MF sponge/Pdop/LMW or HMW-PEI

A solution containing EtOH (8 mL), DI water (18 mL) and NH_4OH (80 μL) was prepared and stirred for 30 min. Then, 2 mL of dopamine hydrochloride solution (0.05 g/1 mL) and the MF sponge (2 × 2 × 1 cm) were added into the solution, followed by stirring for 6 h. After synthesizing the polydopamine (Pdop) onto the MF sponge (MF sponge/Pdop), the resulting sponge was washed 3