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Polymer monoliths with chelating functionalities for solid phase extraction of metal ions from water

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ABSTRACT

Simple devices for the adsorption and preconcentration of metal ions comprising various monolithic polymers have been prepared by *in situ* polymerization within the 5.5 cm long and 5.6 mm i.d. polypropylene syringes. Poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) monolith was modified with ethylenediamine to obtain the chelating material. The poly(butyl methacrylate-*co*-ethylene dimethacrylate) and poly(lauryl methacrylate-*co*-ethylene dimethacrylate) monoliths were first photografted with glycidyl methacrylate prior to functionalization with ethylenediamine. Alternatively, other chelating functionalities including poly(ethylene imines) varying in molecular weight and shape (linear and branched) as well as lysozyme were also attached to the monolithic supports. We found that the poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) monolith functionalized with ethylenediamine exhibited the best chelating properties characterized with rapid adsorption and a capacity of 111.2 mg/g (537 μmol/g) for Pb^{2+}, 38.1 mg/g (649 μmol/g) for Ni^{2+}, 69.9 mg/g (1100 μmol/g) for Cu^{2+}, and 188.9 mg/g (3633 μmol/g) for Cr^{3+}. The very fast desorption was then achieved using 1.0 mol/L HNO_3 as the eluent. An enrichment factor of 300 was observed for metal ions adsorbed from solutions containing 2 ppb of the metal.

1. Introduction

Heavy metal ions, due to their high toxicity, non-degradability, and persistent hazard, pose a significant risk to human health. Human exposure to these ions, even in minute amounts, which can appear in our food chain and environment, can cause serious disease. The harmful effects caused by metal ions such as Hg^{2+}, Ni^{2+}, Pb^{2+}, and Cr^{3+} include inhibition of cellular activities and disorder of physiological functions, which can lead to serious diseases such as cancers [2]. To address this threat, simple and efficient methods are needed for the enrichment and rapid detection of metal ions, enabling a real-time monitoring. Extensive research in this field has focused on precipitation [3], solvent extraction [4,5], ultra-filtration [6], ion exchange [7–9], and adsorption. The last technique is generally preferred among these approaches because of its simplicity. A vast variety of adsorbents with selected functionalities including nanomaterials [1,10–15], biomass [16–22], mesoporous silica [23–26], organic polymers based beads [27,28], and bentonites [29,30] have already been demonstrated.

Organic polymer-based monolithic columns with large through-pores were developed in the early 1990s to address the problems of traditional columns packed with particles. Those problems were slow diffusional mass transport, and large back pressure at high flow rates [31–33]. Their intrinsic advantages of these monoliths included high permeability, rapid mass transfer, and simple preparation in a variety of shapes and chemistries [34]. Although most of the applications of monoliths concern chromatographic separations of organic compounds and biopolymers, their use in solid phase extraction has recently attracted significant attention [35–39]. Among these monoliths, those chelating metal ions represent a small subgroup. For example, Wang et al. prepared a porous polymer monolith in a cartridge via *in-situ* polycondensation of epoxy monomer bisphenol A diglycidyl ether and ethylenediamine, and used it for the preconcentration and determination of environmental Pb(II) [40]. Uzun et al. prepared a poly(2-hydroxyethyl methacrylate-*co*-*N*-methacryloyl-(L)-cysteine methyl ester) monolith containing chelating cysteine functionality and utilized it for the removal of Cu^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, and Pb^{2+} from aqueous media [41]. Zhang et al. prepared a porous conjugate monolith consisting of graphene oxide in

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carboxymethyl cellulose using an unidirectional freeze-drying [42]. This monolith exhibited a strong ability to adsorb Ni^{2+} ions that were then reduced by $NaBH_4$ to form a catalyst for conversion of 4-nitrophenol to 4-aminophenol. Moyna reported grafting of poly(lauryl methacrylate-*co*-ethylene dimethacrylate) monoliths with vinylazlactone, followed by functionalization with iminodiacetic acid, for application in chelating ion chromatography [43]. A similar process has also been reported by Gillespie et al. [44].

Extreme suitability of crosslinked glycidyl methacrylate-based porous beads for the preparation of chelating resins was discovered several decades ago [45–51]. The epoxy groups of these copolymers can be easily functionalized with a variety of ligands containing amine functionalities to achieve both high selectivity and capacity. For example, Bolton et al. functionalized a poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) monolith with 5-hydroxy-1,10-phenanthroline that chelated palladium ions. The conjugate was then used for catalysis of a Suzuki–Miyaura reaction [52]. Several reports have described attachment of iminodiacetic acid to glycidyl methacrylate-based monolithic structures enabling chelating of metal ions [53–56]. Rahmi et al. prepared a glycidyl methacrylate-based “tip-in chelating monolith” with iminodiacetic acid functionalities, and demonstrated solid phase microextraction of trace elements in natural water prior to their determination by ICP-MS [57]. Saito’s group grafted glycidyl methacrylate on porous polyethylene discs and the product reacted with iminodiacetic acid and tested the disc for chelating of copper ions [53]. Poly(lauryl methacrylate-*co*-ethylene dimethacrylate) monoliths were prepared within fused silica capillaries by Paul’s group and subsequently photografted with glycidyl methacrylate [55]. The grafted monoliths were then further modified with iminodiacetic acid, resulting in columns capable of metal ions separation.

It has already been reported (*vide supra*) that functionalization of poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) monoliths with chelating groups has been achieved using two different approaches: (i) grafting onto preformed monoliths consisting of monomers, and (ii) direct copolymerization of glycidyl methacrylate monomers. It is unclear which of these preparation methods represents a better approach. In this report, we compare these two pathways leading to polymer monoliths with functionalities designed for the rapid preconcentration and enrichment of heavy metal ion pollutants from their aqueous solutions.

2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA), butyl methacrylate (BMA, 99%), lauryl methacrylate (LMA, 99%), and ethylene dimethacrylate (EDMA) were obtained from Acros (Morris Plains, NJ, USA), and purified by passing them through an aluminum oxide column for removal of inhibitor. Benzophenone (BP), 2,2-dimethoxy-2-phenylacetophenone (DMPAP), 3-(trimethoxysilyl)propyl methacrylate were also purchased from Acros. Cyclohexanol, 1-dodecanol, 1,4-butanediol, 1-propanol, ethylenediamine (EDA), ethylenediaminetetraacetic acid disodium salt (EDTA), and all other reagents were obtained from Beijing Chemical Reagent Company (Beijing, China). Branched poly(ethylene imine) (PEI) with a molecular weight of 25 kDa was purchased from Sigma Aldrich (St Louis, MO, USA), and lysozyme was purchased from RED Company (Beijing, China) and used as received. Linear PEI with molecular weights of 3, 30, and 70 kDa were purchased from Wuhan Qianglong New Chemical Materials Corporation (Wuhan, China). The polypropylene (PP) syringes with 5.5 cm long and 5.6 mm i.d. were products of Agela Technologies Company (Beijing, China).

2.2. Instrumentation

Photopolymerization and photografting of monoliths were carried out using an ultraviolet light source MUA-165 (Mejiro Genossen, Japan) with an intensity of 20 mW/cm^2 at 365 nm.

Scanning electron micrographs and energy dispersive X-ray spectra of monoliths were obtained using a Hitachi Hybrid scanning electron microscopy SU-1510 (Hitachi High-Technologies, Tokyo, Japan) integrated with an energy dispersive X-ray spectrometer Quantax 200 XF 5010 (Bruker, Germany).

The pore size distribution and pore volume of monoliths were measured using a mercury porosimeter Auto Pore 9500 (Micromeritics, Norcross, GA, USA) with a maximum applied pressure of 420 MPa.

A SpectrAA 55B atomic absorption spectrophotometer (Varian, Palo Alto, USA) was used for the quantitation of metal ions.

2.3. Surface modification of polypropylene syringes

Prior to preparation of the monolith, the inner wall of the polypropylene syringe was vinylized with grafted poly(ethylene dimethacrylate) following a procedure described elsewhere, but with minor modifications [58]. In brief, the syringe was first washed with 1.0 mL ethanol and 1.0 mL acetone for five times to remove any residual impurities on the surface and dried in a stream of nitrogen. The syringe was filled with a 0.5 mL of deoxygenated 5 wt% BP solution in methanol and irradiated with the UV-lamp for 3 min followed by a rinse with methanol. The syringe was then filled with 0.5 mL deoxygenated 15 wt% EDMA solution in methanol and irradiated for another 3 min. Finally, the syringe was washed thoroughly with methanol and dried in nitrogen.

2.4. Preparation of generic monoliths

A polymerization mixture comprised of 24% functional monomers (GMA, BMA, or LMA), 16% EDMA, 60% porogens (all wt%). In addition, 1 wt% DMPAP initiator with respect to monomers was also added. A mixture of cyclohexanol (20%) and 1-dodecanol (40%) were used as porogens for the preparation of poly(GMA-EDMA) monoliths. Poly(BMA-EDMA) monoliths were prepared in presence of 1,4-butanediol (34%) and 1-propanol (26%) as porogens and a mixture consisting of 1,4-butanediol (45%) and 1-propanol (15%) was used for the preparation of poly(LMA-EDMA) monoliths. The polymerization mixtures were homogenized by sonication for 10 min and degassed by purging with nitrogen for 5 min. The mixtures was then drawn into the vinylized PP syringe and irradiated with UV light for 6 min. The resulting monoliths were washed with methanol to remove the unreacted components. Both poly(BMA-EDMA) and poly(LMA-EDMA) monoliths were photografted with GMA in two steps. Pores of these monoliths were filled with a deoxygenated solution of benzophenone (5 wt%) in methanol and irradiated with UV (20 mW/cm^2) at 365 nm for 15 min. The monolith was then washed with methanol and dried. The second step included filling pores of the monolith with 15 wt% glycidyl methacrylate solution in methanol, exposing to UV (20 mW/cm^2) at 365 nm for 15 min, followed by washing with methanol and water.

2.5. Pore surface functionalization of the monoliths

Functionalization of the monoliths with chelating groups was carried out with 50 wt% aqueous EDA or alternatively with 10 wt% aqueous solutions of poly(ethylene imines) in a thermostated oven at 80 °C for 24 h. The monoliths were then flushed thoroughly with