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Cysteine functionalized poly(hydroxyethyl methacrylate) monolith for heavy metal removal

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ABSTRACT

The aim of this study was to investigate the performance of monoliths composed of hydroxyethyl methacrylate (HEMA) to which *N*-methacryloyl-(L)-cysteine methyl ester (MAC) was polymerized for removal of heavy metal ions. Poly(HEMA-MAC) monolith was produced by bulk polymerization. Poly(HEMA-MAC) monolith was characterized by FTIR and scanning electron microscopy (SEM). The poly(HEMA-MAC) monolith with a swelling ratio of 89%, and containing 69.4 μmol MAC/g were used in the adsorption studies. Adsorption capacity of the monolith for the metal ions, i.e., Cu^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, and Pb^{2+} were investigated in aqueous media containing different amounts of the ions (10–750 mg/L) and at different pH values (3.0–7.0). The maximum adsorption capacities of the poly(HEMA-MAC) monolith were 68.2 mg/g for Zn^{2+}, 129.2 mg/g for Cu^{2+}, 245.8 mg/g for Pb^{2+}, 270.2 mg/g for Hg^{2+}, and 284.0 mg/g for Cd^{2+}. pH significantly affected the adsorption capacity of MAC incorporated monolith. The competitive adsorption capacities were 587 μmol/g for Zn^{2+}, 1646 μmol/g for Cu^{2+}, 687 μmol/g for Pb^{2+}, 929 μmol/g for Hg^{2+}, and 1993 μmol/g for Cd^{2+}. The chelating monolith exhibited the following metal ion affinity sequence on molar basis: $Cd^{2+} > Cu^{2+} > Hg^{2+} > Pb^{2+} > Zn^{2+}$. The formation constants of MAC–metal ion complexes have been investigated applying the method of Ruzic. The calculated values of stability constants were 5.28×10^4 L/mol for Cd^{2+}, 4.16×10^4 L/mol for Cu^{2+}, 2.27×10^4 L/mol for Hg^{2+}, 1.98×10^4 L/mol for Pb^{2+}, and 1.25×10^4 L/mol for Zn^{2+}. Stability constants were increased with increasing binding affinity. The chelating monoliths can be easily regenerated by 0.1 M HNO_3 with higher effectiveness. These features make poly(HEMA-MAC) monolith a potential adsorbent for heavy metal removal.

1. Introduction

Industrial wastewater is one of the major sources of aquatic pollution. Among the aquatic pollutants, heavy metals have gained relatively more significance in view of their persistence and toxicity [1]. These metal ions are metabolic poisons and enzyme inhibitors [2]. They can cause mental retardation and semipermanent brain damage. Metals are classified as persistent environmental toxins because they cannot be rendered harmless by chemical or biological remediation processes [3]. Toxic metals are released into the environment in a number of different ways. Coal combustion, sewage wastewaters, automobile emissions, battery industry, mining activities, tanneries, alloy industries, and the utilization of fossile fuels are just a few examples [4]. Many methods of treatment for industrial wastewaters have been reported in the literature, among these methods are precipitation, membrane filtration, neutralization, ion exchange, coprecipitation/adsorption [5]. Among these techniques, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents, and cost effectiveness [6]. The necessity to reduce the amount of heavy metal ions to acceptable levels in wastewater streams, and subsequent possible re-use of these metal ions, has led to an increasing interest in selective polymer adsorbents [7–15]. Several criteria are important in the design of chelating polymers with substantial stability for the selective removal of heavy metal ions: specific and fast complexation of the metal ions as well as the reusability of the chelating polymeric ligands [16]. A large number of polymers incorporating a variety of chelating-ligands (e.g., poly(ethyleneimine), iminodiacetate, amidoxime, phosphoric acid, dithiocarbamate, thiazolidine) have been prepared and their adsorption and analytical properties investigated [17–20]. Recently, reactive amino acids bearing polymers and their different applications have been reported in a series of recent publications [21–26]. The idea of using different amino acid based chelating ligands by the scientists stems from the fact that these chelating ligands are very reactive with metal ions [19–23]. The higher structural flexibility and durability of these ligands as well as significantly lower material and manufacturing costs are also very important [27]. In

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addition, amino acid based metal-complexing ligands may be easily modified by existing chemical methods to facilitate desorption under mild conditions.

The macroporous structure of monoliths allows the overcoming of some of the disadvantages of bead-based columns [28]. Monoliths have lower mass transfer resistance and pressure drop than conventional packed-bed columns [29]. In this case, all liquid phase flows through the pores and mass exchange occurs significantly faster compared to conventional packings [30]. Because of easy and cheaper preparation, high capacity and performance and high porosity, the monolithic stationary phases have been applied in diverse applications [31–33].

According to the above, there is an emerging need for the development of novel adsorbents. Therefore we have focused our attention on the preparation of poly(hydroxyethyl methacrylate) monolithic column containing *N*-methacryloyl-(L)-cysteine methyl ester (MAC). The results of adsorption/desorption studies with Cu^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+} and Zn^{2+} ions were reported here.

2. Experimental

2.1. Materials

Cysteine methyl ester and methacryloyl chloride were supplied by Sigma (St Louis, USA) and used as received. 2-Hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Fluka A.G. (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4 °C until use. *N*,*N*,*N*′,*N*′-Tetramethylene diamine (TEMED) was also obtained from Fluka. Poly(vinylalcohol) (PVAL; MW: 100.000, 98% hydrolyzed) was supplied from Aldrich Chem. Co. (USA). All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany). All water used in the adsorption experiments was purified using a Barnstead (Dubuque, IA) ROpure LP® reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure® organic/colloid removal and ion exchange packed-bed system.

2.2. Synthesis of N-methacryloyl-(L)-cysteine methyl ester

Details of the preparation and characterization of the *N*-methacryloyl-(L)-cysteine methyl ester were reported elsewhere [34]. Briefly, the following experimental procedure was applied for the synthesis of MAC monomer: 5.0 g of L-cysteine methylester and 0.2 g of $NaNO_2$ were dissolved in 30 mL of K_2CO_3 aqueous solution (5%, v/v). This solution was cooled to 0 °C. 4.0 mL of methacryloyl chloride was poured slowly into this solution under nitrogen atmosphere and then the solution was stirred magnetically at room temperature for 2 h. At the end of this period, the pH of this solution was adjusted to 7.0 and then was extracted with ethyl acetate. The aqueous phase was evaporated in a rotary evaporator. The residue (i.e., MAC) was crystallized in ethanol and ethyl acetate.

2.3. Preparation of poly(HEMA-MAC) monolith

Poly(HEMA-MAC) monolith was prepared by an in situ polymerization within a glass tube using H_2O_2/TEMED as the initiator system. Acetonitrile was included in the polymerization recipie as the diluent (as a pore former). Initiator H_2O_2/TEMED was dissolved in the mixture of monomer (HEMA: 2 mL, EGDMA: 1 mL, porogenic diluent, acetonitrile: 2 mL). The monomer mixture was transferred into 2 mL ethanol/water mixture (50/50, v/v) and then sonicated to obtain a clear solution and was then purged with nitrogen for 15 min. The glass tube (200 mm × 10 mm inside diameter) was filled with the above mixture and then sealed. The polymerization was allowed to proceed at 60 °C for 4 h. The tube was then attached to a chromatographic system. Ethyl alcohol (50 mL) and water (50 mL) were pumped through the column at a flow-rate of 1.0 ml/min to remove the unreacted monomers and porogenic diluent present in the monolith after the polymerization was completed. The poly(HEMA-MAC) monolith was washed with acidic thiourea solution for 48 h at room temperature. The poly(HEMA-MAC) monolith was cleaned again with 0.1 M HNO_3 and then it was stored in buffer containing 0.02% sodium azide at 4 °C until use. The PHEMA monolith was prepared same polymerization recipe without MAC.

2.4. Characterization studies

Porosity of the monolith was measured by the nitrogen sorption technique, performed on Flowsorb II (Micromeritics Instrument Corporation, Norcross, USA). The specific surface area of monolith in dry state was determined by multipoint Brunauer–Emmett–Teller (BET) apparatus (Quantachrome, Nova 2200E, USA). 0.5 g of monolith was placed in a sample holder and degassed in a N_2-gas stream at 150 °C for 1 h. Adsorption of the gas was performed at −210 °C and desorption was performed at room temperature. Data obtained from desorption step was used for the specific surface area calculation. The pore volume and average pore diameter were determined by BJH (Barrett, Joyner, Halenda) model on adsorption.

Water uptake ratio of the monolith was determined in distilled water. The experiment was conducted as follows: initially dry monolith was carefully weighed before being placed in a 50-mL vial containing distilled water. The vial was put into an isothermal water bath at a fixed temperature (25 °C) for 2 h. The monolith sample was taken out from the water, wiped using a filter paper, and weighed. The weight ratio of dry and wet samples was recorded. The water content of the monolith was calculated using the weights of monolith before and after uptake of water.

The monoliths were examined using scanning electron microscopy (SEM). The samples were initially dried in air at 25 °C for seven days before being analyzed. A fragment of the dried monolith was mounted on a SEM sample mount and was sputter-coated for 2 min. The sample was then mounted in a scanning electron microscope (Model: JSM 5600, Jeol, Japan). The surface of the sample was then scanned at the desired magnification to study the morphology of the monolith.

FTIR spectroscopy was used in the range 4000–400 cm^{-1} to study surface chemistry of MAC monomer and poly(HEMA-MAC) monolith in the solid state (FTIR 8000 Series, Shimadzu, Japan).

2.5. Removal of heavy metal ions from aqueous solutions

The removal tests of heavy metal ions from aqueous solutions were studied for the PHEMA and the poly(HEMA-MAC) monoliths. The monolith column equipped with a water jacket for temperature control was degassed under reduced pressure (by using water suction pump). Equilibration of the column was performed by passing four column volumes of phosphate buffer (pH 7.4) before injection of the heavy metal solution. In a typical adsorption system, 50 mL of the aqueous solution (in the range of 5–750 mg/L) was passed through the monolithic column, by a peristaltic pump for 2 h. Nitrate salts were used for metal ion source. The pH was maintained in a range of ±0.1 units until equilibrium was attained. Investigations were made for pH values in the range of 3.0–7.0. The concentration of the heavy metal ions in the aqueous phase, after the desired treatment periods was measured using a graphite furnace atomic absorption spectrophotometer (GFAAS, Analyst 800/PerkinElmer, USA). The concentration of the Hg^{2+} in