Metal-Chelating Properties of Poly(2-hydroxyethyl methacrylate–methacryloylamidohistidine) Membranes

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ABSTRACT: Metal-chelating membranes have advantages as adsorbents in comparison with conventional beads because they are not compressible and they eliminate internal diffusion limitations. The aim of this study was to explore in detail the performance of poly(2-hydroxyethyl methacrylate–methacryloylamidohistidine) [poly(HEMA–MAH)] membranes for the removal of three toxic heavy-metal ions—Cd(II), Pb(II), and Hg(II)—from aquatic systems. The poly(HEMA–MAH) membranes were characterized with scanning electron microscopy and ¹H-NMR spectroscopy. The adsorption capacity of the poly(HEMA–MAH) membranes for the selected heavy-metal ions from aqueous media containing different amounts of these ions (30–500 mg/L) and at different pH values (3.0–7.0) was investigated. The adsorption capacity of the membranes increased with time during the first 60 min and then leveled off toward the equilibrium adsorption. The maximum amounts of the heavy-metal ions adsorbed were 8.2, 31.5, and 23.2 mg/g for Cd(II), Pb(II), and Hg(II), respectively. The competitive adsorption of the metal ions was also studied. When the metal ions competed, the adsorbed amounts were 2.9 mg of Cd(II)/g, 14.8 mg of Pb(II)/g, and 9.4 mg of Hg(II)/g. The poly(HEMA–MAH) membranes could be regenerated via washing with a solution of nitric acid (0.01M). The desorption ratio was as high as 97%. These membranes were suitable for repeated use for more than three adsorption/desorption cycles with negligible loss in the adsorption capacity. The stability constants for the metal-ion/2-methacryloylamidohistidine complexes were calculated to be 3.47 × 10⁶, 7.75 × 10⁷, and 2.01 × 10⁷ L/mol for Cd(II), Pb(II), and Hg(II) ions, respectively, with the Ruzic method. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1213–1219, 2005

Key words: membranes; adsorption; hydrophilic polymers

INTRODUCTION

Although metals play important roles in biological processes and some of them are classified as essential, toxic symptoms manifest when a metal-ion level exceeds a certain threshold level. The treatment of wastewater containing soluble heavy metals requires the concentration of the metals into a smaller volume followed by recovery or secure disposal. Heavy-metal removal by polymer microspheres carrying functional groups has attracted the most attention because they may easily be produced in a wide variety of compositions and modified into specific adsorbents by the addition of a variety of metal-complexing ligands. For highly viscous media such as wastewater effluents, however, contact with adsorbents in the form of spherical beads is not desirable because of viscosity limitations.[1] Adsorptive membrane mass transfers in a diffusive-transport mode are more efficient, in which the liquid is made to flow tangentially past the membrane surface, whereas the adsorbate diffuses into the porous membrane to meet the selective metal-complexing ligand immobilized there. For adsorptive membrane development, it is necessary to use a highly permeable polymer carrier. In addition, conventional chromatography with a packed column of gel beads as a support material is not easy to scale up because the pressure drop in packed columns is high, and this leads to compaction of the bed under pressure and low flow rates.[2]

Many publications have reported the performance of adsorptive membranes and their theoretical description and optimal design.[3–5] The porosity, thickness, metal-complexing ligand density, and pore size can dramatically affect the overall performance of adsorptive membranes. Ideal adsorptive membranes should have (1) microporous or macroporous structures, (2) available reactive groups for metal-ion binding, and (3) chemical and physical stability under harsh conditions.

In this article, the performance of a novel metal-chelating poly(2-hydroxyethyl methacrylate–methacryloylamidohistidine) [poly(HEMA–MAH)] membrane, recently produced in our laboratories, for the removal of heavy-metal ions under a wide range of conditions is discussed. An expensive and critical step in the preparation process of a metal-chelating adsorbent is the coupling of a chelating ligand to the ad-

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sorption matrix. Here, comonomer 2-methacryloylamidohistidine (MAH) acted as the metal-chelating ligand, and there was no need to activate the matrix for the chelating-ligand immobilization. Another major issue is the slow release of covalently bonded chelators off the matrix. Metal-chelating ligand release is a general problem encountered in any adsorption technique and causes a decrease in the adsorption capacity. The metal-chelating ligand immobilization step was also eliminated in this approach. MAH was polymerized with 2-hydroxyethyl methacrylate (HEMA), and ligand leakage was also eliminated.

EXPERIMENTAL

Materials

L-Histidine methyl ester dihydrochloride and methacryloyl chloride were supplied by Sigma (St. Louis, MO) and used as received. The monomer HEMA was obtained from Fluka AG (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor, and stored at 4°C until use. Azobisisobutyronitrile was provided by Fluka AG. All the other chemicals were reagent-grade and were obtained from Merck AG (Darmstadt, Germany). All water used in the experiments was purified with 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.

Synthesis of the MAH monomer

For the synthesis of the MAH comonomer, the following experimental procedure was applied. L-Histidine methyl ester dihydrochloride (5.0 g) and 0.2 g of hydroquinone were dissolved in 100 mL of dichloromethane. This solution was cooled to 0°C. Triethylamine (12.7 g) was added to the solution. Methacryloyl chloride (5.0 mL) was poured slowly into the solution under a nitrogen atmosphere, and then this solution was stirred magnetically at room temperature for 2 h. At the end of the chemical reaction period, unreacted methacryloyl chloride was removed from the medium by extraction with a 10% NaOH solution. The organic phase was dried with $MgSO_4$ and evaporated in a rotary evaporator. The residue, MAH, was crystallized in an ether–cyclohexane mixture.

Preparation of the poly(HEMA–MAH) membranes

The poly(HEMA–MAH) membranes were prepared with the following procedure. HEMA (2 mL) containing 5 mg of azobisisobutyronitrile as a polymerization initiator and 100 mg of synthesized MAH was mixed with 3 mL of a $0.10M$ $SnCl_4$ solution (porogen). The mixture was then poured into a round glass mold (9 cm in diameter) and exposed to ultraviolet radiation for 10 min under a nitrogen atmosphere. The obtained membranes were washed several times with distilled water and cut into circular pieces (1.0 cm in diameter) with a perforator.

Characterization of the poly(HEMA–MAH) membranes

Swelling test

The swelling ratios of the poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(HEMA–MAH) membranes were determined in distilled water. The swelling experiments were conducted as follows. An initially dry membrane sample with a fixed surface area and thickness (diameter (Φ) = 1.0 cm, thickness = 350 μm) was carefully weighed before being placed in a 50-mL vial containing distilled water. The vial was put into an isothermal water bath with a constant temperature (25 $\pm$ 0.5°C) for 2 h. The membrane sample was taken from the water, wiped with filter paper, and weighed. The weight ratio of the dry and wet samples was recorded.

Microscopic observations

The surface morphology of the membranes was examined with scanning electron microscopy (SEM). The membranes were initially dried in air at 25°C for 7 days before being analyzed. A fragment of the dried membrane was mounted on an SEM sample mount and was sputter-coated with gold for 2 min. The sample was then mounted in a scanning electron microscope (JEM 1200 EX, JEOL, Tokyo, Japan). The surface of the sample was scanned at the desired magnification to study the morphology of the poly(HEMA–MAH) membranes.

NMR studies

The ^{1}H-NMR spectrum was obtained to determine the synthesis of the MAH structure. A JEOL GX-400 300-MHz NMR spectrometer was used.

Adsorption/desorption studies

The adsorption of heavy-metal ions [i.e., Cd(II), Pb(II), and Hg(II)] on poly(HEMA–MAH) membranes from aqueous solutions was studied in batch adsorption-equilibrium experiments. The effects of the adsorption-equilibrium time and the pH of the medium on the adsorption capacity were investigated. Nitrates of the respective metal ions were used throughout the adsorption experiments. Aqueous solutions (25 mL)

containing different amounts of heavy-metal ions (30–500 mg/L) were incubated with approximately 200 mg of poly(HEMA–MAH) membranes at different pHs (in the range of 3.0–7.0, which was adjusted with HNO_3 or NaOH at the beginning of the experiment and not controlled afterwards) at 20°C (in a temperature-control chamber), in flasks agitated magnetically at an agitation speed of 600 rpm. After the desired adsorption periods (up to 120 min), the aqueous phases were separated from the membranes, and the residual concentrations of the metal ions in these phases were measured with an atomic absorption spectrophotometer. A Shimadzu (Kyoto, Japan) model AA-6800 flame atomic absorption spectrophotometer was used. For mercury determinations, an MVU-1A mercury vapor unit (Shimadzu, Kyoto, Japan) was employed. Deuterium background correction was applied throughout the experiments, and the spectral slit width was 0.5 nm. The working current/wavelength values and the optimized experimental conditions for the mercury measurements were as follows:

Working current/wavelength: 6 mA/253.6 nm.
Concentration of $SnCl_2$: 1% (w/v).
Concentration of $KMnO_4$: 0.5% (w/v).
Concentration of H_2SO_4: 5% (v/v).

The working current/wavelength values for the cadmium and lead determinations were 8 mA/228.8 nm and 10 mA/283.3 nm, respectively. For each sample, a mean of 10 measurements was recorded. The amount of metal ions adsorbed per unit of mass of the membrane (mg of metal ions/g) was obtained with the following expression:

$$Q = (C_0 - C)V/M \tag{1}$$

where Q is the amount of metal ions adsorbed onto the unit of mass of the adsorbent (mg/g); C_0 and C are the concentrations of the metal ions before and after adsorption (mg/L), respectively; V is the volume of the aqueous phase (L); and M is the amount of the adsorbent (g).

Competitive heavy-metal adsorption from aqueous solutions containing Cd(II), Pb(II), and Hg(II) ions was investigated with a similar procedure. These experiments were performed at a constant pH of 6.0 and at 20°C with solutions containing 3.0×10^{-3} M from each metal ion.

The desorption of heavy-metal ions was achieved with 0.01M HNO_3 as the desorbing agent. The poly-(HEMA–MAH) membranes were loaded with the heavy-metal ions under the following conditions: initial concentration of the metal ions = 200 mg/L, amount of the poly(HEMA–MAH) membranes = 200 mg, volume of the adsorption medium = 25 mL, pH = 6.0, temperature = 20°C, and adsorption time = 60

min. Then, the poly(HEMA–MAH) membranes were placed in the desorption medium and stirred at a stirring rate of 600 rpm up to 120 min. The concentrations of the metal ions in the aqueous phase were determined with the atomic absorption spectrophotometer, as mentioned previously. The desorption percentages were calculated with the following expression:

Desorption ratio (%)

= (Amount of desorbed metal ions/

Amount of metal ions adsorbed) $\times 100$ (2)

RESULTS AND DISCUSSION

### Properties of the poly(HEMA–MAH) membranes

The poly(HEMA–MAH) membranes prepared in this study were rather hydrophilic structures. Therefore, they swelled in aqueous solutions but did not dissolve. Water swelling occurred rapidly, and the equilibrium water uptake was reached in about 60 min. In comparison with PHEMA (58%), the water swelling ratio of the poly(HEMA–MAH) membranes increased significantly (147.9%). Several possible factors may have contributed to this result. First, incorporating MAH actually introduced more hydrophilic functional groups into the polymer chain, which could attract more water molecules into polymer matrices. Second, reacting MAH with HEMA could effectively decrease the molecular weight. Therefore, the water molecules penetrated the polymer chains more easily, and this resulted in an improvement in the polymer water swelling in aqueous solutions.

The SEM micrographs given in Figure 1 show the surface structure and cross section of the poly(HEMA–MAH) membranes. As shown by the surface and cross-sectional surface photographs, the membranes had large pores (transport canals); the pore dimensions were around 1–5 μm. The membrane surface was rough and heterogeneous. These large pores reduced diffusional resistance and facilitated mass transfer.

As mentioned before, MAH was selected as the metal-complexing comonomer. In the first stage of the study, MAH was synthesized from histidine and methacryloyl chloride. Then, MAH was incorporated into the bulk structure of the PHEMA membranes. The ^{1}H-NMR spectrum was recorded to determine the synthesis of the MAH structure. The ^{1}H-NMR spectrum indicated the characteristic peaks from the groups in the MAH monomer. These characteristic peaks were as follows ($CDCl_3$, δ): 1.5 (—CH_2), 1.9 (—CH_3), 3.6 (—O—CH_3), 4.7 (vinyl CH), 5.2 (vinyl CH), 5.8 (vinyl CH), and 6.6–8.0 (cyclic NH and CH).
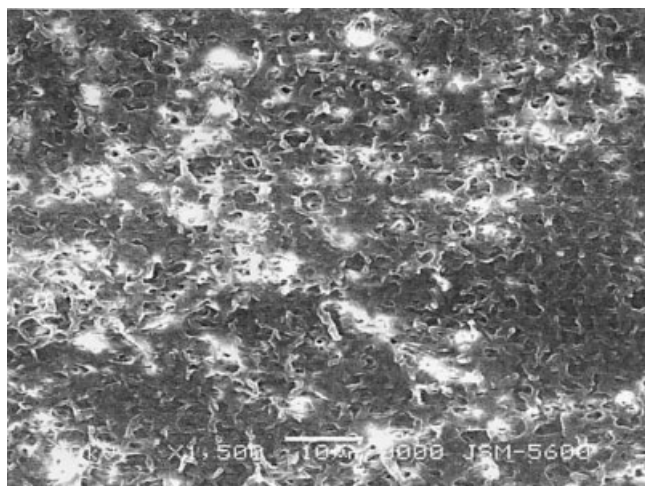
(a)
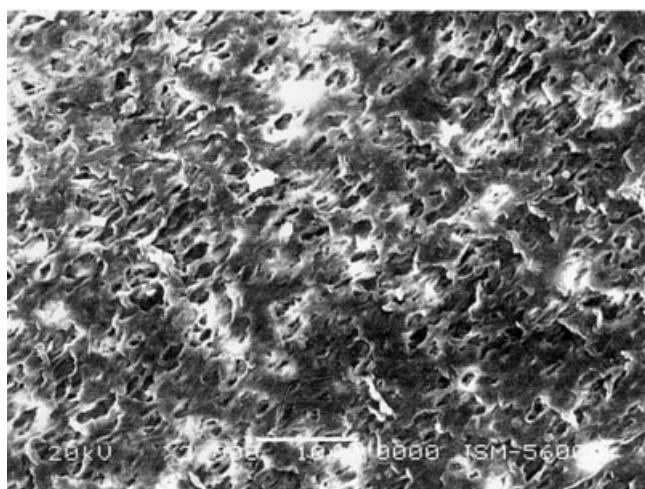
(b)

Figure 1 Representative SEM micrographs of a poly(HE-MA–MAH) membrane: (a) surface structure and (b) cross-sectional surface.

Adsorption of the heavy-metal ions

Adsorption rate

Figure 2 shows the adsorption rates of Cd(II), Pb(II), and Hg(II) ions onto the poly(HEMA–MAH) membranes as a function of time. These batch experiments were performed with single (not together) solutions of the metal ions. Figure 3 reflects the changes in the amounts of the metal ions adsorbed with time, which were calculated with eq. (1). The adsorption conditions are given in the figure legend. The slopes of the curves reflect the adsorption rates. For the Pb(II) and Hg(II) ions, high adsorption rates were observed at the beginning of the adsorption process, whereas for Cd(II) ions, the adsorption rate was lower; plateau values, that is, adsorption-equilibrium times, were gradually reached within 60 min.
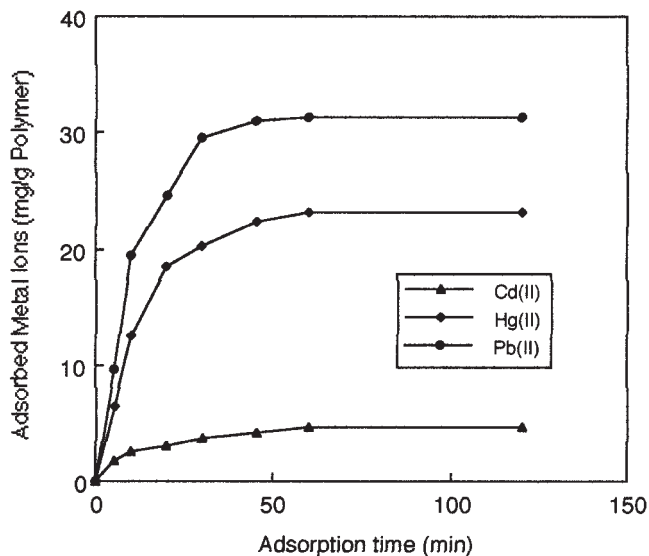

Figure 2 Adsorption rates of Cd(II), Pb(II), and Hg(II) ions onto poly(HEMA–MAH) membranes (adsorption conditions: initial concentration of metal ions = 100 mg/L, pH = 6.0, temperature = 20°C).

In the literature, different equilibrium adsorption times have been reported for different polymeric adsorbents. Roozemond et al.[6] investigated copper and cadmium uptake by 3,5-dimethyl-1-hydroxymethyl pyrazole attached *p*-aminomethyl-substituted poly-(styrene–divinylbenzene) chelating polymer. They reported that adsorption was rather slow and only after 2 days was the equilibrium reached. Ebraheem and Hamdi[7] studied some divalent ions, including Cd(II),
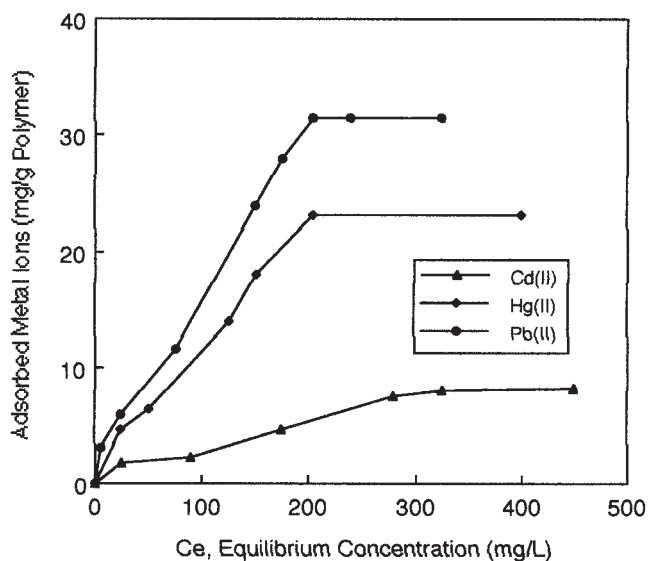

Figure 3 Adsorption capacities of poly(HEMA–MAH) membranes for Cd(II), Pb(II), and Hg(II) ions (adsorption conditions: amount of membrane = 0.19 g, volume of the adsorption medium = 20 mL, pH = 6.0, temperature = 20°C, adsorption time = 60 min).

Ni(II), Cu(II), and Zn(II), on phenol formaldehyde polymer carrying poly(salicylaldoxime-3,5-dimethylene), and they reported 10 h for the equilibrium adsorption time. Latha et al.[8] studied the extraction of Fe(III), Fe(II), Cu(II), and Ni(II) by ethylenediamine-functionalized polyacrylamide, and they indicated that the complexation reaction proceeded very slowly, and after 5 h, the equilibrium was attained. Konishi et al.[9] performed the sorption of Zn(II), Cd(II), and La(III) by biopolymer gel beads of alginic acid, and they reached equilibrium in about 2 h. Reed and Matsumoto[10] studied Cd(II) adsorption kinetics by activated carbon, and they considered 6 h a short adsorption-equilibrium time.

All these individual studies published in the literature were performed under different experimental conditions. In such adsorption processes, there are several parameters that determine the adsorption rate, such as the stirring rate in an aqueous phase or the flow rate in a column system, the structural properties of the adsorbent used (e.g., surface topography, porosity, and swelling degree), the loading of metal-complexing agents, the amount of the adsorbent, the metal-ion properties (e.g., hydrated ionic radius and coordination complex number), the initial concentration of metal ions, the chelate-formation rate between the metal chelate ligand and the metal ions, and the existence of other metal ions that may compete with the metal ion of interest for the same active adsorption sites. Consequently, it is not reasonable to make a healthy comparison of the adsorption rates reported. However, by only considering adsorption-equilibrium times, we can conclude that the approach proposed in this study, in which poly(HEMA–MAH) membranes were used, may be considered an important improvement in the adsorption kinetics.

Adsorption capacity

The heavy-metal-ion adsorption capacities of the poly-(HEMA–MAH) membranes are presented as a function of the equilibrium concentration of the metal ions in the adsorption medium in Figure 3. These batch experiments were performed with single solutions of Cd(II), Pb(II), and Hg(II) ions. The adsorption conditions are given in the figure legend. It is well-known that in the absence of complexing agents, the hydrolysis and precipitation of the metal ions are affected by the concentration and form of the soluble metal species.[10–12] We estimated the theoretical precipitation concentrations of hydroxides of the respective metal ions at different pH values with solubility product (K_{sp}) values given by Skoog et al.[13] The amount of metal ions adsorbed per unit of mass of the poly(HEMA–MAH) membranes (i.e., adsorption capacity) increased with the initial concentration of the metal ions. To reach the plateau values, which represent the sat-

uration of the active sites on the membranes [in other words, to obtain the maximum adsorption capacities of the poly(HEMA–MAH) membranes], the initial metal-ion concentrations were increased up to 500 mg/L. The maximum adsorption capacities of the membranes were 8.2, 31.5, and 23.2 mg/g for Cd(II), Pb(II), and Hg(II) ions, respectively. The order of affinity based on the weight uptake by the poly(HEMA–MAH) membranes was as follows: Pb(II) > Hg(II) > Cd(II). The maximum adsorption capacities of the membranes, on a molar basis, were 0.073, 0.152, and 0.118 mmol/g for Cd(II), Pb(II), and Hg(II) ions, respectively. Therefore, the order of affinity, on a molar basis, was again as follows: Pb(II) > Hg(II) > Cd(II).

Different affinity adsorbents with a wide range of adsorption capacities for heavy-metal ions have been reported in the literature. Shreedhara-Murthy and Ryan[14] found 3.9–14.4 mg of Cd(II)/g removal by cellulose–dithiocarbamate resins. Roozemond et al.[6] reported an adsorption capacity of 40 mg of Cd(II)/g with pyrazole-containing poly(styrene–divinylbenzene) sorbents. Liu et al.[15] investigated Cd(II) adsorption onto an N-(hydroxymethyl)thioamide-anchored macroreticular acrylonitrile–divinylbenzene copolymer and found 22.4 mg of Cd(II)/g adsorption capacity. Konishi et al.[9] reported 4.5 mg of Cd(II)/g with alginic acid gels. Denizli et al.[16] used Procion Blue MX-3B attached PHEMA-based microspheres and achieved 4.2 mg of Cd(II)/g adsorption capacity. Shah and Devi[17] used a dithizone-anchored poly(vinyl pyridine) support and reported a specific adsorption capacity up to 144 mg of Hg(II)/g. Liu et al.[15] achieved 72 mg of Hg(II)/g adsorption capacity with an N-hydroxymethyl thioamide resin. Cestari and Airoldi[18] found 186 mg of Hg(II)/g by 3-trimethoxysilyl-1-propanethiol-immobilized silica. Jyo et al.[19] reported 40 mg of Hg(II)/g with phosphoric acid treated poly(glycidylmethacrylate–divinylbenzene) beads. Say et al.[20] used dithiocarbamate-incorporated monosize polystyrene microspheres for the adsorption of organomercury species; the maximum adsorption capacities were reported to be 122 mg/g for CH_3HgCl, 114 mg/g for C_2H_5HgCl, and 20 mg/g for C_6H_5HgCl. Chen and Wilson[21] used a living *Escherichia coli* strain for the bioaccumulation of Hg(II), and the highest bioaccumulation level was 17.6 mg of Hg(II)/g of dry biomass. Özer et al.[22] reported that the adsorption capacities of *Rhizopus arrhizus* and a living *E. coli* strain were 71 and 17.6 mg of Hg(II)/g, respectively. Denizli and Pişkin[23] reached an adsorption capacity of 125 mg of Pb(II)/g with Alkali Blue 6B attached poly-[ethyleneglycoldimethacrylate–hydroxyethylmethacrylate (EGDMA–HEMA)] microspheres. Dev and Rao[24] used a polystyrene–vinylbenzene macroreticular resin functionalized with bis(*N*,*N*′-salicylidene)1,3-propanediamine and reported an adsorption capacity of 80.8 mg of Pb(II)/g. Therefore, in comparison with
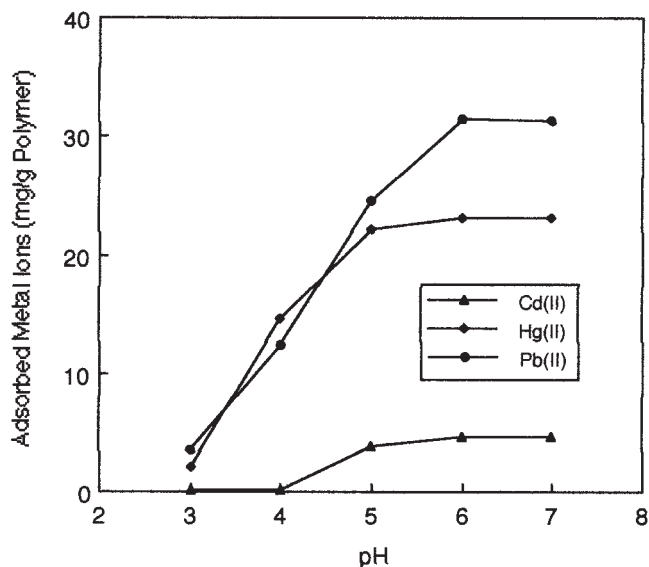
Figure 4 Effect of the pH on the adsorption capacity of poly(HEMA–MAH) membranes for Cd(II), Pb(II), and Hg(II) ions (adsorption conditions: initial concentration of metal ions = 200 mg/L, amount of membranes = 0.19 g, volume of the adsorption medium = 20 mL, temperature = 20°C, adsorption time = 60 min).

the values in the literature, the adsorption capacities of the poly(HEMA–MAH) membranes obtained in this study [i.e., 8.2, 31.5, and 23.2 mg/g for Cd(II), Pb(II), and Hg(II) ions, respectively] are quite satisfactory for the removal of these ions from aqueous solutions.

Effect of pH

It is well-known that metal-ion adsorption on both nonspecific and specific adsorbents is pH-dependent.[11,12,14] Therefore, to establish the effect of pH on the adsorption of metal ions onto poly(HEMA–MAH) membranes, batch equilibrium studies at different pH values in the range of 3.0–7.0 were carried out. In this group of experiments, the initial concentrations of the metal ions were 200 mg/L, and the adsorption-equilibrium time was 60 min. Figure 4 shows the effect of pH on the adsorption of Cd(II), Pb(II), and Hg(II) ions onto poly(HEMA–MAH) membranes. The adsorption of the heavy-metal ions increased with increasing pH and reached a plateau value at pH 6.0.

Competitive adsorption

In this group of experiments, the competitive adsorption of Cd(II), Pb(II), and Hg(II) ions onto the poly-(HEMA–MAH) membranes was also investigated. These experiments were performed at a constant pH of 6.0 and at 20°C with solutions containing 3.0×10^{-3} M from each metal ion. As shown in Table I, the adsorbed amount of Pb(II) ions was higher than those

obtained for Cd(II) and Hg(II) ions. The adsorption capacities were 2.90 mg/g for Cd(II) ions, 14.80 mg/g for Pb(II) ions, and 9.40 mg/g for Hg(II) ions. From these results, the order of affinity under competitive conditions was the same as that obtained for single-ion solutions, that is, Pb(II) > Hg(II) > Cd(II).

Desorption/reuse

The desorption of the adsorbed metal ions from the poly(HEMA–MAH) membranes was also studied in a batch experimental setup, and a 0.01M HNO₃ solution was used as the desorbing agent. The desorption ratios for the Cd(II), Pb(II), and Hg(II) ions from the membranes loaded with the respective metal ions (loaded from single metal-ion solutions) at a concentration of 200 mg/L were obtained (Table II). As shown in Table II, higher than 97% desorption ratios were obtained after three adsorption/desorption cycles. When HNO₃ was used as the desorption agent, the coordination spheres of the chelated metal ions were disrupted, and subsequently, metal ions were released from the solid surface into the desorption medium.

Stability constants of the metal-ion/MAH complexes

It is of great importance to know the formation constants for MAH/metal-ion complexes to understand the affinities of heavy-metal ions to poly(HEMA–MAH) membranes. The formation constants for the MAH/metal-ion complexes were investigated with the Ruzic method.[25] According to this data treatment, the plotting of $[M]_{ionic}/(M_T - [M]_{ionic})$ versus $[M]_{ionic}$ should yield a straight line if one type of complex is predominant (M_T is the total metal concentration and $[M]_{ionic}$ is the concentration of the labile metal species). From the slope, the metal binding capacity of the ligand (C_L) is determined. From the intercept according to eq. (3), the apparent stability constant ($K_{stability}$) can be defined as follows:

$$\{[M]_{ionic}/(M_T - [M]_{ionic})\} = 1/K_{stability}C_L \qquad (3)$$

TABLE I
Competitive Adsorption of Cd(II), Pb(II), and Hg(II) Ions from a Mixture onto Poly(HEMA–MAH) Membranes

Metal ion	Metal ions adsorbed (mg/g of polymer)	Metal ions adsorbed (mmol/g of polymer)
Cd(II)	2.90	0.026
Pb(II)	14.80	0.072
Hg(II)	9.40	0.047

TABLE II
Adsorption–Desorption Cycles for Cd(II), Pb(II), and Hg(II) Ions

Cycle no.	Adsorption (mg/g)			Desorption (%)		
	Cd(II)	Pb(II)	Hg(II)	Cd(II)	Pb(II)	Hg(II)
1	2.60	24.80	12.40	98.8	99.2	98.6
2	2.56	24.60	12.23	98.3	98.8	98.2
3	2.51	24.30	12.01	97.4	97.8	97.2

With this method, a straight line was obtained from the plot of $[M]_{ionic}/(M_T - [M]_{ionic})$ versus $[M]_{ionic}$. The straight-line relationship indicates that the interaction of the metal ions with MAH occurred via one type of functional group. The $K_{stability}$ values for the MAH/metal-ion complexes were 3.47×10^6, 7.75×10^7, and 2.01×10^7 L/mol for Cd(II), Pb(II), and Hg(II) ions, respectively. The maximum amounts of the metal ions adsorbed were consistent with the $K_{stability}$ values obtained.

CONCLUSIONS

At least 20 metals are classified as toxic, and half of them, including cadmium, arsenic, mercury, chromium, copper, lead, nickel, selenium, silver, and zinc, are emitted into the environment in quantities that pose risks to human health.[26,27] Among them, perhaps the most toxic are cadmium, lead, and mercury. The necessity of reducing the amount of heavy metals in wastewater streams and the subsequent possible reuse of these metal ions have led to increasing interest in selective adsorbents. A novel metal-chelating poly-(HEMA–MAH) membrane was applied for the removal of Cd(II), Pb(II), and Hg(II) ions from aquatic systems. When the pH of the medium and the adsorption-equilibrium time were optimized, the maximum amounts of the metal ions adsorbed were 8.2 mg/g for Cd(II) ions, 31.5 mg/g for Pb(II) ions, and 23.2 mg/g for Hg(II) ions. The order of affinity, Pb(II) > Hg(II) > Cd(II), did not change when the metal ions competed. The $K_{stability}$ values were in good agreement with the amounts of metal ions adsorbed. The repeated adsorption/desorption cycles showed the feasibility of the poly(HEMA–MAH) membranes for heavy-metal removal.

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