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HEAVY METAL SEPARATION CAPACITY OF A POROUS METHACRYLAMIDO-PHENYLALANINE CONTAINING MEMBRANE BASED ON A POLYHYDROXY-ETHYL METHACRYLATE MATRIX

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ABSTRACT

The abilities of various sorbent materials for heavy metal removal have been reported in the literature. We have developed a novel approach to obtain high metal-sorption capacity utilizing a membrane containing 2-methacrylamidophenylalanine. Metal-complexing ligand 2-methacrylamidophenylalanine (MAPA) was synthesized through the use methacrylo chloride and phenylala-

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nine. Then, poly(2-hydroxyethylmethacrylate-co-2-methacrylamidophenylalanine) (p(HEMA-co-MAPA)) membranes were prepared by UV-initiated photopolymerization of HEMA and MAPA in the presence of the initiator azobisisobutyronitrile. MAPA monomer was characterized by nuclear magnetic resonance spectroscopy. p(HEMA-co-MAPA) membranes were characterized by swelling studies, scanning electron microscopy, Fourier transform infrared spectroscopy, and elemental analysis. These membranes have large pores; the micropore dimensions are approximately 5–10 μm. p(HEMA-co-MAPA) affinity membranes with a swelling ratio of 133.2% and containing 18.9 mmol MAPA/m^2 were used in the removal of the heavy-metal ions of copper, nickel, and mercury from aqueous media containing different amounts of these ions (5–600 mg/L) and at different pH values (2.0–7.0). The maximum adsorption capacities of heavy metal ions onto the MAPA-containing membranes under noncompetitive conditions were 23.8 mmol/m^2 for Cu(II), 29.1 mmol/m^2 for Ni(II), and 50.3 mmol/m^2 for Hg(II). The affinity order was Hg(II) $>$ Ni(II) $>$ Cu(II). The adsorption of heavy metal ions increased with increasing pH and reached a plateau value at approximately pH 5.0. Adsorption of heavy metal ions from artificial wastewater was also studied. The adsorption capacities were 11.9 mmol/m^2 for Cu(II), 7.33 mmol/m^2 for Ni(II), and 9.79 mmol/m^2 for Hg(II). Desorption of heavy metal ions was performed using 0.1 M HNO_3. The p(HEMA-co-MAPA) membranes are suitable for more than five cycles without noticeable loss of capacity.

Key Words: p(HEMA-co-MAPA); Heavy metal removal; Copper (II); Nickel (II); and Mercury (II)

INTRODUCTION

The role of heavy metals in environmental issues has become increasingly more prominent in recent years as ecological awareness has achieved global proportions (1). Recently, chelating polymers have found widespread applications in the enrichment and removal of heavy metals from a variety of matrices (2–6). Several criteria are important in the design of chelating polymers with substantial stability for the selective removal of heavy metal ions: specific and fast complex-building of the metal ions as well as reusability of the chelating polymeric ligands (7). A large number of chelating polymers incorporating a variety of ligands (e.g., polyethyleneimine, iminodiacetate, amidoxime, phosphoric acid, dithiocarbamate, sulfonic/ carboxylic groups, and reactive textile dyes) have been prepared and their analytical properties investigated (8–12). Incorporation of amino acids into polymer matrices has been reported in a series of recent publications (13–17). These researchers based the idea of using different amino acids in matrices because they exhibit reactivity with different chemical substances including metal ions. The relatively high flexibility and durability of amino-acid ligands as well as their significantly low material and manufacturing costs were also important considerations. In addition, amino acids may be easily modified by existing chemical methods to facilitate desorption under mild conditions (17).

For these reasons, we focused our attention on the development of affinity membranes for the assembly of a new class of novel heavy-metal sorbents. In this paper, we report on the preparation of a porous membrane system containing 2-methacrylamidophenylalanine for heavy metal separation. p(HEMA-co-MAPA) membranes were prepared by UV-initiated photopolymerization of HEMA and MAPA monomers in the presence of the initiator azobisisobutyronitrile (AIBN). Adsorption/desorption of Cu(II), Ni(II), and Hg(II) from aqueous media and artificial wastewater was studied.

EXPERIMENTAL

Materials

Phenylalanine was supplied from BDH (U.K.) and used as received. Methacrylo chloride was purchased from Sigma (St Louis, MO, USA). The monomer, HEMA, was obtained from Fluka A.G. (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4°C until use. AIBN was provided from Fluka. All of the other chemicals used were reagent grade from Merck AG (Darmstadt, Germany). The metal salts used were $Cu(NO_3)_2$, $Ni(NO_3)_2$, and $Hg(NO_3)_2$. The pH of each solution was adjusted with nitric acid and sodium hydroxide. All water used in the experiments was purified using a Barnstead (Dubuque, IA, USA) ROpure LP® reverse osmosis unit with a high-flow, cellulose acetate membrane (Barnstead D2731) was subsequently treated by a Barnstead D3804 NANOpure® organic/colloid removal and ion-exchange, packed-bed system. The resulting purified, deionized water had a specific conductivity of 18 megaohm/cm. All glassware was soaked overnight in 4 M nitric acid.

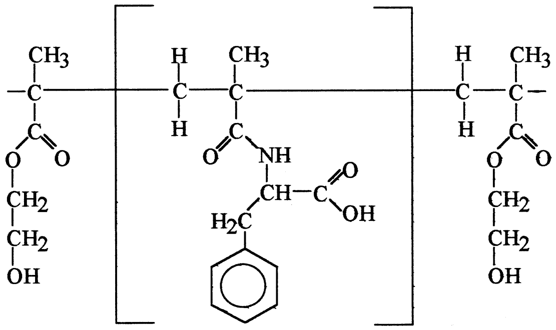
Synthesis of the 2-Methacrylamidophenylalanine Monomer

For synthesis of the 2-methacrylamidophenylalanine (MAPA) monomer, the following experimental procedure was applied: 5.0 g of phenylalanine and 0.2

g of $NaNO_2$ were dissolved in 30 ml of K_2CO_3 solution (5%, v/v). This solution was cooled down to 0°C. Under nitrogen, 6 ml of methacrylochloride was poured slowly into this solution, and the resulting solution was stirred magnetically at room temperature for 2 h. At the end of this chemical reaction period, the solution pH was adjusted to 3.0. Then the solution was extracted with chloroform ($CHCl_3$). The organic phase was dried with $MgSO_4$ and evaporated in a rotary evaporator. The residue (MAPA) was crystalized in an ether and cyclohexane mixture.

Preparation of poly(2-Hydroxyethylmethacrylate-co-Methacrylamidophenylalanine) membranes

The p(HEMA-co-MAPA) membrane was prepared as described. Two milliliters of HEMA, 5 mg AIBN as polymerization initiator, and 100 mg of synthesized MAPA were mixed with 3 ml of 0.1 M $SnCl_4$. The mixture was then poured into a round glass mould (9 cm in diameter) and exposed to UV radiation for 10 min under nitrogen atmosphere. The membrane obtained was washed several times with distilled water and cut with a perforator into circular pieces (1.0 cm in diameter). The polymer structure produced with HEMA and MAPA monomers is given as follows:



HEMA 2-methacrylamidophenylalanine

Characterization of poly(2-Hydroxyethylmethacrylate-co-Methacrylamidophenylalanine) Membranes

Swelling Test

The swelling ratio of the p(HEMA-co-MAPA) membrane was determined in distilled water. The initial, dry membrane sample with a fixed surface area of 1 cm and a thickness of 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 at 25 ± 0.5°C for 2 h. The membrane sample was taken out from the water periodically, wiped using filter paper, and weighed. The weight ratio of dry and wet samples was recorded.

Microscopic Observations

Microscopic observations and photographs of the gold-coated p(HEMA-co-MAPA) membranes were performed by using a scanning electron microscope (SEM) (Raster Electronen Microscopy, Leitz-AMR-1000, Germany).

Elemental Analysis

To evaluate the degree of MAPA incorporation, the synthesized p(HEMA-co-MAPA) adsorbents were subjected to elemental analysis through the use of a Leco Elemental Analyzer (Model CHNS-932).

FTIR Studies

Fourier transform infrared spectroscopy (FTIR) spectra of the p(HEMA) and p(HEMA-co-MAPA) membranes were obtained through the use of a FTIR spectrophotometer (FTIR 8000 Series, Shimadzu, Japan). The dry membrane (approximately 0.1 g) was thoroughly mixed with 0.1 g KBr (IR Grade, Merck, Germany), and pressed to form a tablet. The FTIR spectrum was then recorded.

NMR Studies

The nuclear magnetic resonance spectrum of MAPA monomer protons was taken in $CDCl_3$ on a JEOL GX-400 300 MHz instrument. The residual non-deuterated solvent ($CHCl_3$) served as an internal reference. Chemical shifts were reported in ppm (δ) downfield relative to $CHCl_3$.

Heavy Metal Adsorption/Desorption

Metal adsorption experiments were conducted at pH 2.0–7.0 at concentrations of 5–600 ppm. Twenty milliliters of aqueous metal ion solutions with different concentrations were incubated with the p(HEMA-co-MAPA) membranes (0.01 m^2/L) in flasks stirred magnetically at 600 rpm. All experiments were performed at room temperature. As determined in the preliminary experiments, the equilibrium adsorption time was 60 min; no significant change in the amount of adsorption occurred after 60 min. At the end of the adsorption experiment, membranes were removed from the adsorption medium by filtration, and the concentrations of Cu(II), Ni(II), Hg(II) in the aqueous phase were measured with a graphite-furnace atomic absorption spectrophotometer (AAS) (AAS 5EA, Carl Zeiss Technology, Zeiss Analytical Systems, Germany). Hg(II) concentration was determined by an AAS connected with a hydride generator. The instrument response was periodically checked with known metal solution standards. Three replicates of experiments were performed, and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples to determine the margin of error. The amount of adsorption per unit surface area of the membranes was evaluated by using the following expression.

$$q = \frac{[(C_0 - C_A)V]}{A} \tag{1}$$

Where, q is the amount of metal ions adsorbed onto unit surface area of the membrane (mmol/m^2); C_0 and C_A are the concentrations of the metal ions in the initial solution and in the aqueous phase after adsorption, respectively (mmol/L); V is the volume of the aqueous phase (ml); and A is the surface area of the membrane (m^2).

Adsorption of heavy metal ions from artificial wastewater was carried out in batches. A 20-ml solution containing 0.5 mmol/L of Cu(II), Ni(II), and Hg(II) was incubated with the p(HEMA-co-MAPA) membranes at pH 7.0 at room temperature and stirred magnetically at 600 rpm. Artificial wastewater also contains Zn(II), Fe(III), Co(II), Cd(II), Cr(III), and Al(III). The concentrations of each metal ion in artificial wastewater were 0.5 mmol/L. To adjust salinity, 700 ppm NaCl was added to the artificial wastewater. After adsorption, the concentration of the metal ions in the remaining solution was determined as described above.

To show the regeneration of the p(HEMA-co-MAPA) membranes, repeated adsorption-desorption cycles were completed five times by using the same affinity membranes. Desorption of heavy metal ions was performed using 0.1 M HNO_3. The p(HEMA-co-MAPA) membranes carrying 23.8 mmol Cu(II)/m^2 , 29.1 mmol Ni(II)/m^2, and 50.3 mmol Hg(II)/m^2 were placed in this desorption medium and stirred at 600 rpm for 30 min at room temperature. The final metal ion concentration in the aqueous phase was determined by AAS. The desorption ratio was calculated from the amount of metal ions initially loaded on the membranes and the final metal ion concentrations in the desorption medium.

RESULTS AND DISCUSSION

Properties of poly(2-Hydroxyethylmethacrylate-co-methacrylamidophenylalanine) Membranes

p(HEMA-co-MAPA) membranes prepared in this study are hydrophilic structures. Therefore, they swell in aqueous solutions but do not dissolve. Figure 1 shows the swelling behavior of p(HEMA) and p(HEMA-co-MAPA) membranes in water. Swelling occurs rapidly, and the water uptake reaches equilibrium in approximately 60 min. Compared with p(HEMA) (58%), the swelling ratio of the poly(HEMA-co-MAPA) membrane increases significantly (133.2.9%). Several possible factors may contribute to this result. First, the incorporation of 2-methacrylamidophenylalanine introduces hydrophilic functional groups into the polymer chain, which can attract more water molecules into polymer matrices. Second, reacting 2-methacrylamidophenylalanine with HEMA could effectively decrease the molecular weight and reduce the crystallinity. Therefore, the water molecules penetrate into the polymer chains more easily and result in an improvement of polymer-water swelling in aqueous solutions.

The SEM micrographs given in Fig. 2 shows the surface structure and the cross-section of the p(HEMA-co-MAPA) membranes. As seen from the surface

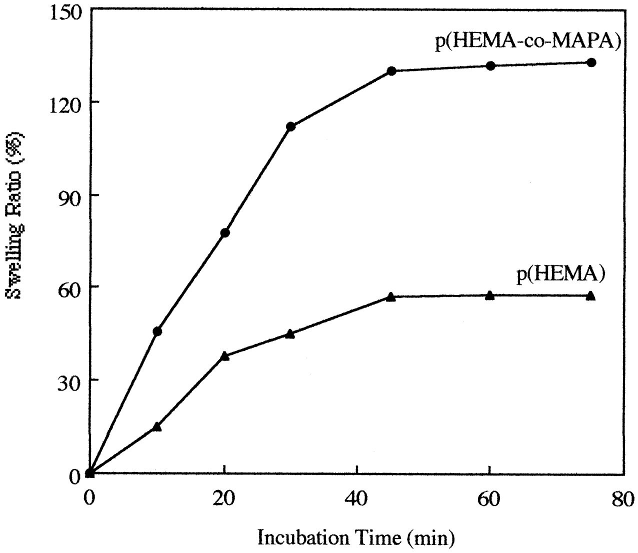


Figure 1. Swelling properties of pHEMA and p(HEMA-co-MAPA) membranes in water as a function of incubation time.

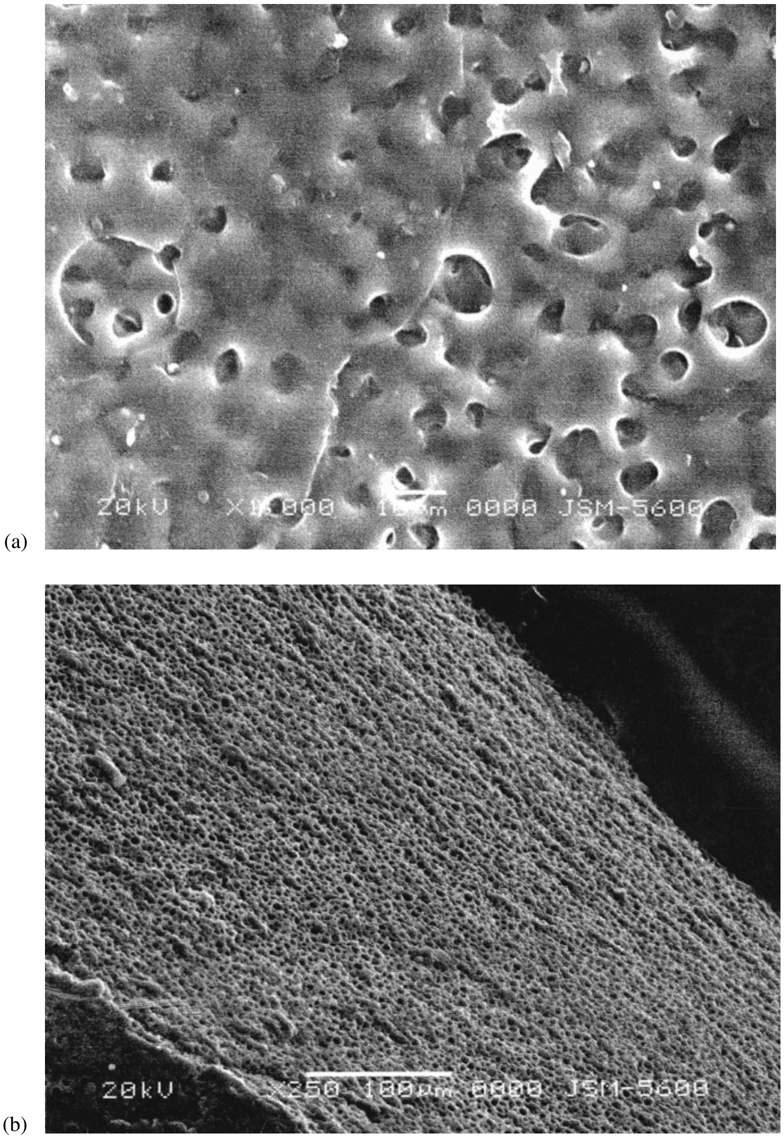


Figure 2. The representative SEM micrographs of p(HEMA-co-MAPA). (a) Surface. (b) Cross-sectional area.

and cross-sectional surface photographs, the membranes have large pores (transport canals); the micropore dimensions range from 5 to 10 μm. The membrane surface seems rough and heterogeneous. These large pores reduce diffusional resistance and facilitate mass transfer of heavy metal ions because of high inner surface area. This type of membrane surface also provides higher heavy metal chelation and enhances adsorption capacity.

MAPA was selected for its affinity to create heavy metal ion complexes . In the first stage of this study, MAPA was synthesized from phenylalanine and methacrylo chloride. Then, MAPA was incorporated into the bulk structure of the p(HEMA) membranes. The FTIR spectra of p(HEMA) and p(HEMA-co-MAPA) have the characteristic stretching vibration band of hydrogen bonded alcohol, O—H, around 3,440 cm^{-1} (Fig. 3). The FTIR spectrum of p(HEMA-co-MAPA) have characteristic amide I and amide II absorption bands at 1,625 cm^{-1} and 1,574 cm^{-1}, respectively. However, the hydrogen-bonded alcohol stretching-band intensity of plain p(HEMA) is higher than that of the p(HEMA-co-MAPA) membrane due to the incorporation of the MAPA co-monomer in the polymer structure.

To evaluate the degree of MAPA incorporation, elemental analysis of the synthesized p(HEMA-co-MAPA) adsorbent was performed. The incorporation of the MAPA was calculated as 18.9 $mmol/m^2$ and was based on the theoretical amount of nitrogen contributed by the monomer mixture.

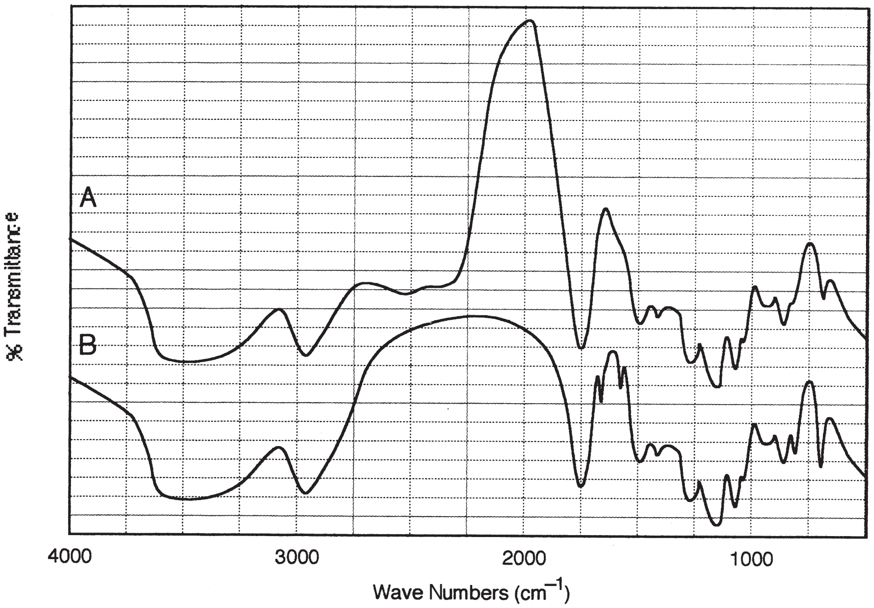


Figure 3. FTIR Spectra of (A) p(HEMA) and (B) p(HEMA-co-MAPA).

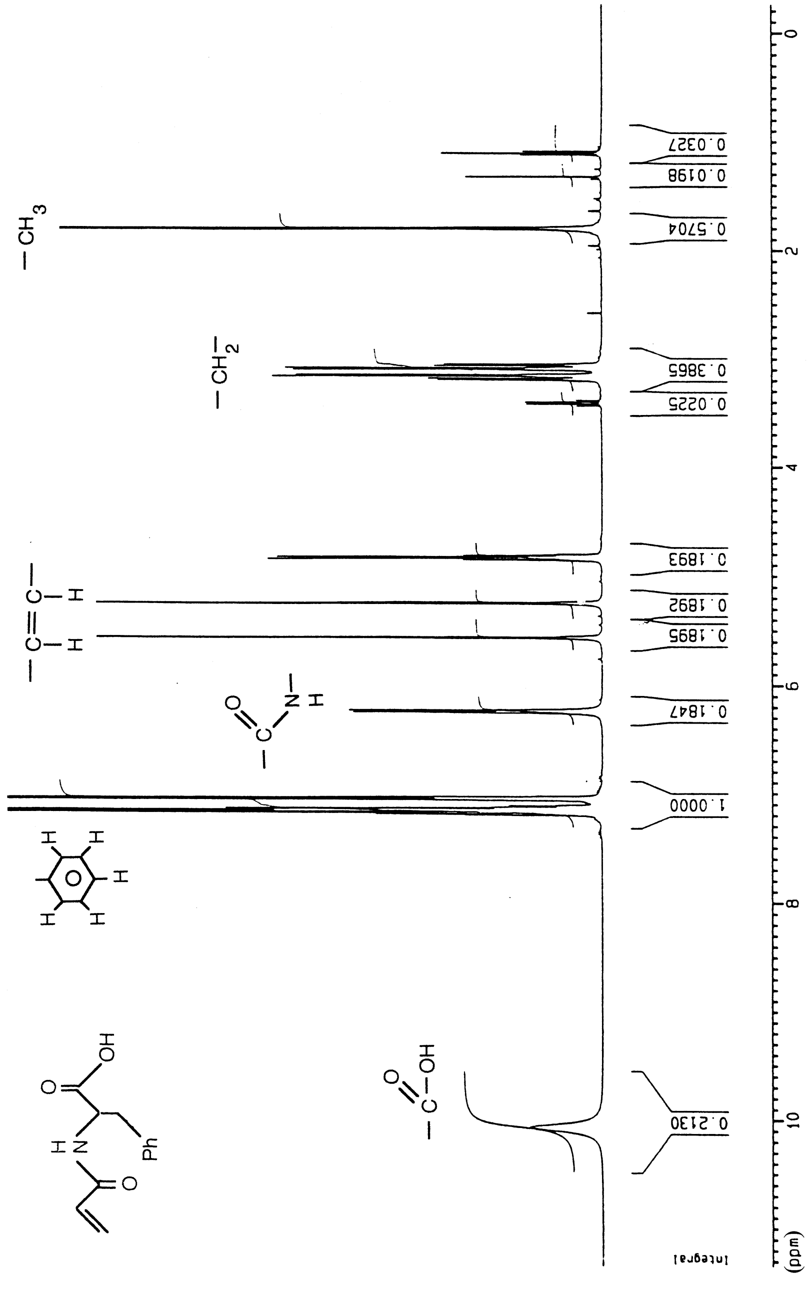


Figure 4. NMR spectrum of MAPA monomer.

^{1}H-NMR was used to determine the synthesis of MAPA structure (Fig. 4). The ^{1}H-NMR spectrum ($CHCl_3$ standard) indicates the characteristic peaks from the groups in the MAPA monomer: δ 2.84 (t; 3H, J = 7.06 Hz, CH_3), δ 3.05–3.19 (m; 2H, CH_2), δ 4.80–4.85 (m; 1H, methin), δ 5.24 (s; 1H, vinyl H), δ 5.56 (s; 1H, vinyl); δ 6.24 (d; 1H, J = 7.4 Hz, NH), δ 7.04–7.20 (m; 5H, aromatic), δ 10.07 (s; 1H, OH).

Adsorption of Heavy Metal Ions

Adsorption Rate

Figure 5 shows adsorption rates of heavy metal ions by p(HEMA-co-MAPA) membranes as a function of time. High adsorption rates are observed at the beginning of adsorption, and then saturation values (i.e., adsorption equilibrium) are gradually achieved within 20 min. Adsorption of heavy metal ions was rather fast, especially when the metal ion concentration was high. This may be due to high driving force, which is the heavy metal ion concentration difference be-

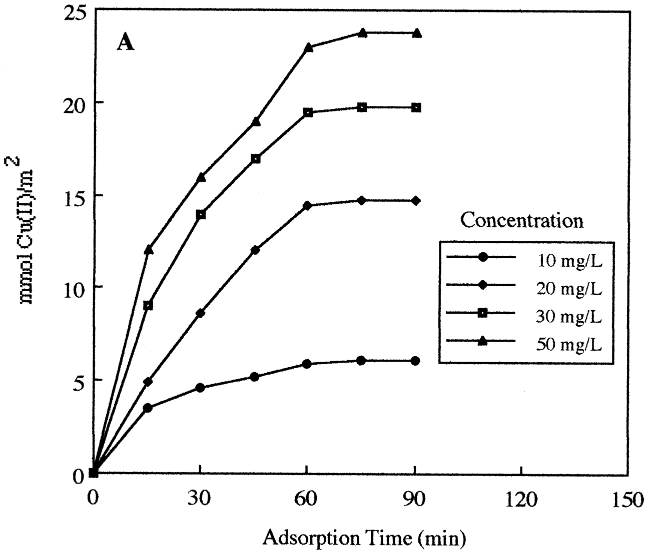


Figure 5. Adsorption rates of heavy metal ions on the p(HEMA-co-MAPA) membranes at pH 6.0: (A) for Cu(II), (B) for Ni(II), (C) for Hg(II).

(continued)

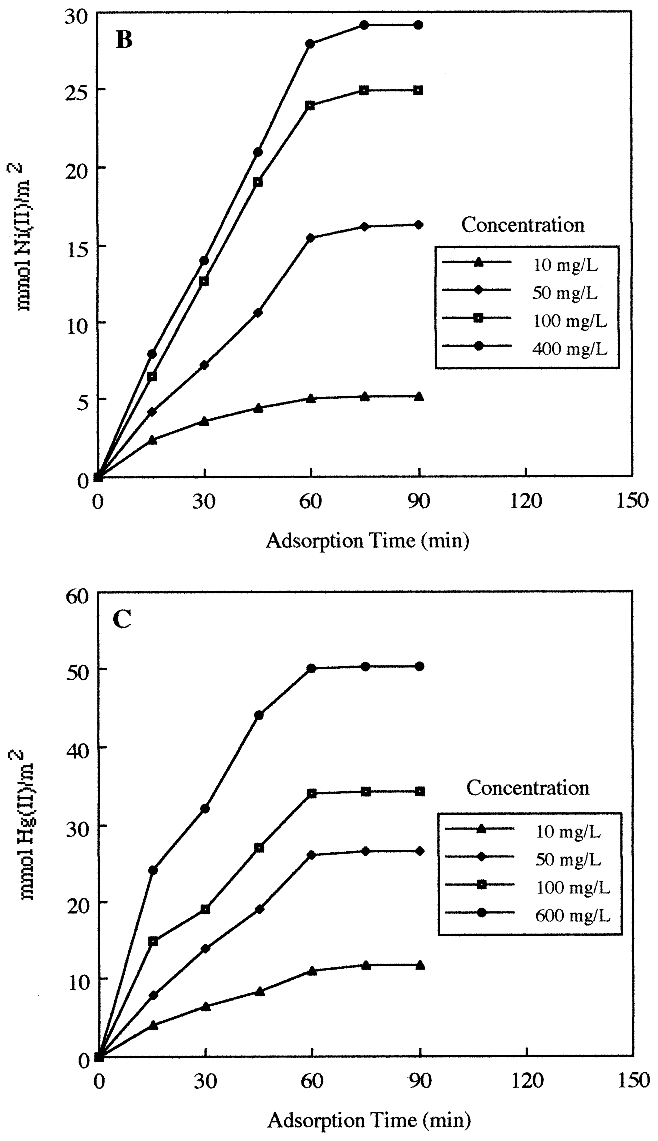


Figure 5. Continued.

tween the adsorption medium and the membrane phases. It should be also noted that Hg(II) was adsorbed much faster than Cu(II) and Ni(II) due to much higher affinity of the MAPA groups to Hg(II) ions. The order of adsorption rate is Hg(II) > Cu(II) > Ni(II).

A wide range of equilibrium adsorption times were reported in the literature with various sorbent systems in membrane and microsphere forms. For example, Reed and Matsumoto (18) considered 6 h as a short equilibrium time in their kinetic studies of cadmium adsorption with activated carbon sorbent). Marchese et al. (19) investigated separation of cobalt, nickel, and copper ions with alanine liquid membranes and reported that equilibrium was achieved in about 4–5 h. Shreedhara-Murthy and Ryan (20) investigated mercury, copper, cadmium, lead, and uranium adsorption on cellulose-dithiocarbamate resins and reported that the adsorption rates were very slow. Egawa et al. (21) studied uranium adsorption on polyacrylonitrile fibers containing amidoxime groups and reported a 7-h equilibrium adsorption time. Teramoto et al. (22) reported that a spiral-type supported liquid-membrane model reached steady state in about 4 h. Roozemond et al. (23) studied copper and cadmium uptake of 3,5-dimethyl-1-hydroxymethyl pyrazole attached to a p-aminomethyl-substituted poly(styrene-co-divinylbenzene) chelating polymer. They showed that adsorption is rather slow; the resin did not reach equilibrium for 2 days. Ebrahem and Hamdi (24) studied various divalent ions, including Ni(II), Cu(II), Zn(II), and Cd(II) on a phenol formaldehyde polymer containing poly(salicylaldoxime-3,5-diylmethylene), and reported a 10-h equilibrium adsorption time. Latha et al. (25) studied ethylenediamine- functionalized polyacrylamide resin for extraction of several metal ions, such as Fe(III), Fe(II), Cu(II), and Ni(II), and they reported that the reaction proceeds very slowly (equilibrium time 5 h) . Note that in such an adsorption process, several parameters determine the adsorption rate, such as adsorbent structural properties (e.g., size, porosity, surface area), amount of sorbent, metal ion properties (e.g., hydrated ionic radius), initial concentration of metal ions, chelate-formation rate, and existence of other ions that may compete with the ions of interest for the active adsorption sites. All the studies mentioned here have been performed in different conditions. Therefore, it is almost impossible to compare the adsorption rates reported. However, the adsorption rates obtained with the affinity membranes that we produced seem to be very satisfactory.

Effects of Initial Concentration of Metal Ions

An important variable in the adsorption of heavy metal ions is whether the capacity of the metal-complexing groups is affected by heavy metal concentration. Figure 6 shows the adsorption capacities of the p(HEMA-co-MAPA) membranes for the ions from the single-metal aqueous solutions under study. The amount of adsorption was increased when the initial heavy metal concentration was increased until saturation was reached. The maximum adsorption capacities of the p(HEMA-co-MAPA) membranes in the studied range were 23.8 mmol/m^2, 29.1 mmol/m^2, and 50.3 mmol/m^2 for Cu(II), Ni(II), and Hg(II), respectively. The affinity order of the membrane was Hg(II) $>$ Ni(II) $>$ Cu(II).

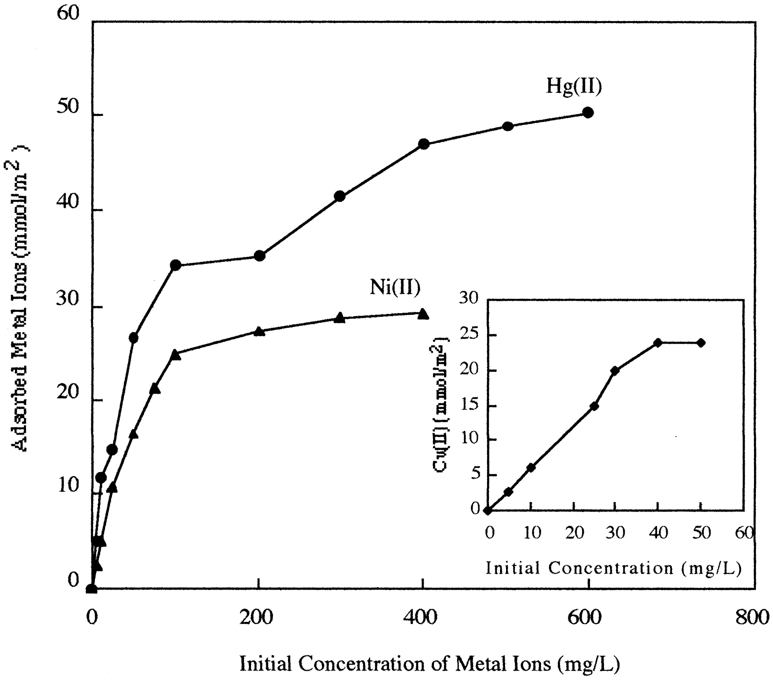


Figure 6. Heavy-metal ion-adsorption capacity of the p(HEMA-co-MAPA) membrane. pH was 5.0 and total membrane surface area in each batch was 0.01 m^2/L.

The p(HEMA-co-MAPA) membrane carries 18.9 mmol MAPA/m^2. One MAPA molecule interacts with one to three metal ions; the ratio is dependent on the type of metal. Note that the nitrogen and oxygen atoms of MAPA molecule are available for interaction with heavy metal ions. The heavy-metal ion adsorption on the p(HEMA) membranes (carrying no MAPA) are relatively low, about 0.54 mmol/m^2 for Cu(II), 0.96 mmol/m^2 for Ni(II), and 2.26 mmol/m^2 for Hg(II). Note that these membranes are highly susceptible to swelling when in water and are also microporous; therefore, they may absorb heavy metal ions within the pores of the swollen membrane. In addition, the hydroxyl and carbonyl groups of p(HEMA-co-MAPA) may interact with heavy metal ions (similar to solvation with water), which may also cause nonspecific-adsorption.

Sorbents used in heavy metal removal are generally in particulate form. Reed and Matsumoto reported that 90–120 mmol Cd(II)/m^2 were removed with activated carbon of different porosities (18). Egawa et al. found 62.1 mmol uranium/m^2 removal by acrylonitrile-divinylbenzene copolymer beads that contained amidoxime as an adsorbent (21). By using methylmethacrylate-divinylbenzene beads with poly(styrene-divinylbenzene) sorbents composed of a aminomethylphosphonic acid, macroreticular, chelating polymeric resin, Maeda and Egawa showed very low adsorption capacities with 1.5 mmol Pb(II)/m^2 and 1.6 mmol Cu(II)/m^2 (26). Denizli et al. used dye-affinity poly(hydroxyethylmethacrylate) membranes for heavy metal adsorption (27–29). The maximum adsorption capacities were 5.6–19.9 mmol Cu(II)/m^2 and 16.3–130.3 mmol Hg(II)/m^2. It seems that the adsorption capacities achieved with the p(HEMA-co-MAPA) membranes that contain amino acids are satisfactory.

Effects of pH

Metal ion adsorption onto nonspecific and specific sorbents is pH dependent [18–21]. In the absence of complexing agents, the hydrolysis and precipitation of the metal ions are affected by the concentration and form of soluble metal species. The solubility of metal ions is governed by hydroxide or carbonate concentration. Reed and Matsumoto reported that hydrolysis of metal ions, such as Cu(II), As(III), Cd(II), and Hg(II), becomes significant at approximately pH 7.5–8.5 (18). Therefore, in the present study we varied the pH between 2.0–7.0. The effect of pH on heavy metal adsorption is shown in Fig. 7. The adsorption capacities in-

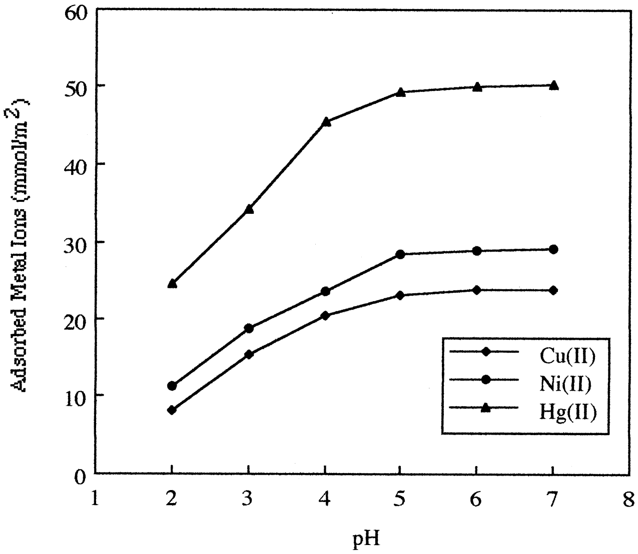


Figure 7. Effect of pH on adsorption of heavy metal ions on the p(HEMA-co-MAPA) membranes. Initial concentration of metal ions: 50 mg/L for Cu(II), 400 mg/L for Ni(II), 600 mg/L for Hg(II), and total membrane surface area in each batch was 0.01 m^2/L.

creased with an increase in pH, reaching plateau values at around pH 5.0. Plateau values were 23.8 mmol/m^2 for Cu(II), 29.1 mmol/m^2 for Ni(II), and 50.3 mmol/m^2 for Hg(II). The difference in adsorption values can be explained by the different affinity of the heavy metal ions for the donor atoms (i.e., oxygen and nitrogen) in the MAPA amino-acid ligand.

Adsorption from Artificial Wastewater

Adsorption capacities of the p(HEMA-co-MAPA) membranes from artificial wastewater for Cu(II), Ni(II) and Hg(II) are shown in Table 1. The adsorption capacities of the p(HEMA-co-MAPA) membranes from artificial wastewater for all metal ions were much lower than the experiments under competitive conditions and using single solutions. The adsorption capacities were 11.9 mmol/m^2 for Cu(II), 7.33 mmol/m^2 for Ni(II), and 9.79 mmol/m^2 for Hg(II). p(HEMA-co-MAPA) membranes exhibit the following metal ion affinity sequence: Cu(II) > Hg(II) > Ni(II). In the wastewater experiments, p(HEMA-co-MAPA) membranes adsorbed Cd(II), Zn(II), Fe(II), Co(II), Al(III), and Cr(III). The presence of other metal ions in the artificial wastewater decreases the adsorption capacities of p(HEMA-co-MAPA) membranes for Cu(II), Ni(II), and Hg(II).

Regeneration of Membranes

To be useful in metal ion recycling processes, chelated metal ions should be easily desorbed under suitable conditions. Desorption experiments were per-

Table 1. Adsorption of Heavy Metal Ions from Artificial Wastewater on the p(HEMA-co-MAPA) Membranes. Concentration of Each Metal Ion: 0.5 mmol/L; pH: 7.0; Total Membrane Surface Area in Each Batch: 0.01 m^2/L; Adsorption Time: 60 min.

Ions	Adsorbed Ion (mmol/m^2)
Cu(II)	11.92 ± 0.5
Ni(II)	7.33 ± 0.4
Hg(II)	9.79 ± 0.8
Zn(II)	4.15 ± 0.7
Fe(III)	5.85 ± 0.9
Cd(II)	7.17 ± 0.2
Co(II)	5.48 ± 0.5
Cr(III)	6.04 ± 0.4
Al(III)	7.53 ± 0.5

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Table 2. Heavy Metal Ions Adsorption Capacity of p(HEMA-co-MAPA) Membranes After Repeated Adsorption-desorption Cycles. Initial Concentrations of Metal Ions: 1 mmol/L; pH: 7.0; Total Membrane Surface Area in Each Batch: 0.01 m^2/L; Adsorption Time: 60 min.

	Cu(II)		Ni(II)		Hg(II)	
Cycle No.	Adsorption ($mmol/m^2$)	Desorption (%)	Adsorption ($mmol/m^2$)	Desorption (%)	Adsorption ($mmol/m^2$)	Desorption (%)
1	23.8	97.7	29.1	97.6	50.3	96.5
2	23.5	98.2	28.4	98.4	49.8	98.2
3	23.0	97.5	28.0	99.7	49.6	97.3
4	22.6	96.5	27.7	98.6	49.4	98.4
5	22.0	97.9	27.5	97.3	49.1	96.9

formed using 0.1 M HNO_3 as the desorption agent. The p(HEMA-co-MAPA) membranes loaded the maximum amounts of metal ions were placed within the desorption medium, and the amount of metal ions desorbed in 30 min was measured. Table 2 shows the adsorption-desorption values of heavy metal ions by p(HEMA-co-MAPA) membranes after several cycles of consecutive adsorption and desorption. This table clearly shows that the novel p(HEMA-co-MAPA) membranes containing amino acids can be used repeatedly without significant loss of adsorption capacities for all metal ions studied here.

CONCLUSION

We have shown that polymeric membranes that contain 2-methacryloamidophenylalanine have high adsorption capacity for metal ions both under noncompetitive and competitive conditions. Adsorption capacities were as high as 23.8 $mmol/m^2$ for Cu(II), 29.1 $mmol/m^2$ for Ni(II), and 50.3 $mmol/m^2$ for Hg(II). p(HEMA-co-MAPA) membranes show the following metal ion affinity order: Hg(II) $>$ Ni(II) $>$ Cu(II). Further, we have shown that these porous membranes can be used for heavy metal removal from artificial wastewater and demonstrated that the adsorption capacities of the p(HEMA-co-MAPA) membranes from artificial wastewater for all metal ions were much lower than for those ions studied under noncompetitive conditions. The adsorption capacities were 11.92 $mmol/m^2$ for Cu(II), 9.79 $mmol/m^2$ for Hg(II), and 7.33 $mmol/m^2$ for Ni(II). Repeated adsorption and desorption cycles showed that p(HEMA-co-MAPA) membranes, with their novel amino acid ligands, are feasible tools for heavy metal adsorption.

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