

Competitive Removal of Pb^{2+} , Cd^{2+} , and Zn^{2+} by Poly(acrylamide-*co*-maleic acid) Hydrogels/Differential Pulse Polarographic Determination

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Received 31 March 2004; accepted 13 July 2004

DOI 10.1002/app.21179

Published online 22 October 2004 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(acrylamide-*co*-maleic acid) [P(AAm/MA)] hydrogels, with various compositions, were prepared from ternary mixtures of acrylamide (AAm)/maleic acid (MA)/water by using ^{60}Co γ -rays. The effect of composition of these hydrogels, on the competitive removal of Pb^{2+} , Cd^{2+} , and Zn^{2+} ions from aqueous solution, was investigated. The hydrogel compositions and their adsorption behaviors were determined by use of differential pulse polarography, a very sensitive electroanalytical technique. It

was observed that the external stimuli of pH, temperature, and ionic strength have an important role on the adsorption. The increments of MA content in P(AAm/MA) hydrogels caused a significant increase in the adsorption these ions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2401–2406, 2004

Key words: hydrogels; adsorption; radiation; differential pulse polarography (DPP); synthesis

INTRODUCTION

Polymeric and copolymeric hydrogels have been extensively studied and many reviews in the field have been reported in the literature.^{1–4} These hydrogels have usually been used for the preconcentration and separation of trace elements from seawater. For separation, the use of hydrogels, containing a chelating functional group that has some features of adsorption, such as durability, reusability, and practical applicability, is very important. For increased and improved metal ion uptake capacity in hydrogels, either comonomers carrying some specific ligands are incorporated into their structures or the chemical structures of repeating units are chemically modified. Some typical examples include poly(*N*-vinyl-2-pyrrolidone-*g*-tartaric acid) and poly(*N*-vinyl-2-pyrrolidone-*g*-citric acid) systems.^{4,5}

Heavy metal ion removal, reported in the literature, can be categorized into two groups: competitive adsorption and noncompetitive or single adsorption. In the first procedure, when an adsorbent is added to a solution that contains ions to be removed and other metal ions, the ions are adsorbed simultaneously with varying degrees of success, depending on their affinities to the functional group of the adsorbent. Noncompetitive adsorption is used to describe the behavior of metal ion removal from aqueous solution containing only one metal. The amount

of adsorbed ions, by noncompetitive adsorption, is approximately twice that which can be achieved by competitive adsorption.⁶

In this article, we report our investigation of external stimuli such as pH, ionic strength, and temperature on the Pb^{2+} , Cd^{2+} , and Zn^{2+} ion-adsorption capacity of poly(acrylamide-*co*-maleic acid) [P(AAm/MA)] hydrogels, under competitive conditions, by using a differential pulse polarography (DPP) technique.

EXPERIMENTAL

Apparatus

A polarographic analyzer system (PAR 174 A), equipped with a mercury drop timer, was used to determine the competitive adsorption of Pb^{2+} , Cd^{2+} , and Zn^{2+} ions from aqueous solutions onto P(AAm/MA) hydrogels. The drop time of the mercury electrode was about 2–3 s (2.75 mg/s). A Kalusek electrolytic cell, with reference-saturated electrode (SCE) separated by a liquid junction, was used in the three-electrode mode; the counterelectrode was a platinum wire. The polarograms were recorded with an LY 1600 X-Y recorder (Linseis GmbH, Selb, Germany). Pulse polarograms were recorded under the conditions of a drop life of 1 s, a scan rate of 5 mV/s, pulse duration of 50 ms, and pulse amplitude of 50 mV.

Chemicals

The two monomers used in this study, acrylamide (AAm) and maleic acid (MA), were supplied by Merck

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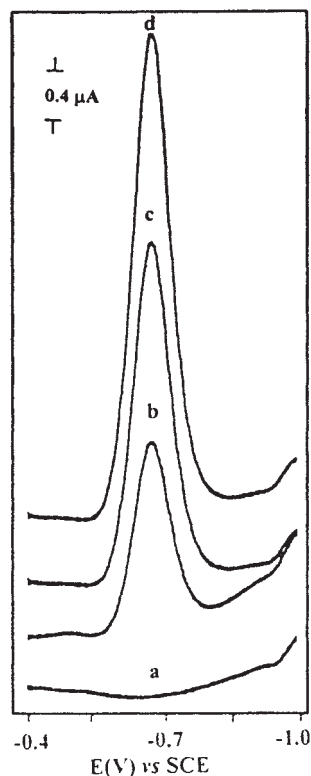


Figure 1 Determination of gel composition of P(AAm/MA) by differential pulse polarography: (a) 10.0 mL, pH = 2.5 B-R buffer solution; (b) a + 0.50 mL P(AAm/MA)-2 extract solution (taken from 500 mL extract solution, $m_{\text{gel}} = 2.9950$ g); (c) 20 μM standard addition of MA; (d) 40 μM standard addition of MA.

(Darmstadt, Germany). Glacial CH_3COOH , H_3PO_4 (85%), H_3BO_3 , and standardized NaOH were used to prepare Britton–Robinson (B-R) buffers. B-R buffer solution was prepared by using 2.3 mL glacial acetic acid, 2.7 mL phosphoric acid, and 2.4720 g boric acid, dissolved by dilution with triple-distilled water to 1.0 L; 50-mL portions of this solution were taken and the pH was adjusted from 2.0 to 8.0 by addition of the appropriate amount of 2.0M NaOH.

Preparation of P(AAm/MA) hydrogels

The P(AAm/MA) hydrogels were prepared simultaneously by using radiation-induced polymerization and crosslinking of AAm and MA in aqueous solutions without use of a crosslinker by the following procedure. Aqueous solutions of monomers were prepared in 1.0 mL of pure water at different compositions (AAm/MA mole ratios: 98.80/1.20; 97.41/2.39; 96.46/3.54; 94.78/5.22). These solutions were placed in poly(vinylchloride) straws of 4 mm diameter and irradiated to 25 kGy in air at ambient temperature in a ^{60}Co γ -irradiator. The hydrogels, obtained in long cylindrical shapes, were cut into pieces (3–4 mm) and

dried in a vacuum oven at 315 K, to reach a constant weight, and subjected to Soxhlet extraction with water. The uncrosslinked polymer and unreacted MA were removed with this extraction from the hydrogel structure. Extracted hydrogels were dried again in a vacuum oven at 315 K to constant weight and stored for later evaluations. The amount of unreacted MA in the extract was determined by a DPP technique. The polarograms of unreacted MA were determined through scanning the potential from -400 to about -1000 mV. MA showed a peak at about -600 mV during the potential scan. Figure 1 shows the peaks of the release of MA from P(AAm/MA)-2 hydrogel and the standard additions of 2.0×10^{-5} M MA solutions. From the differences of the peak currents of MA and the standard addition of MA, the amount of unreacted MA was determined. The mole percentages of MA in the initial mixtures and in the copolymeric hydrogel and percentage gelation are summarized in Table I.

Adsorption of Pb^{2+} , Cd^{2+} , and Zn^{2+} ions from aqueous solution onto P(AAm/MA) hydrogels

P(AAm/MA) hydrogels (~ 0.0300 g) were immersed in 15.0-mL solutions containing 20 μM Pb^{2+} and variable amounts of Cd^{2+} and Zn^{2+} ions, or 20 μM Cd^{2+} and variable amounts of Pb^{2+} and Zn^{2+} ions, and finally 20 μM Zn^{2+} and variable amounts of Pb^{2+} and Cd^{2+} ions. The hydrogels were allowed to stand for 4 days in the above solutions. By the end of this time, the adsorbent was removed by decantation from the solution. The equilibrium concentrations of Pb^{2+} , Cd^{2+} , and Zn^{2+} ions in the solutions were determined by DDP. A 10-mL sample of the solution in the polarographic cell was deaerated by the passage of pure nitrogen gas (99.99%) for about 5 min. The polarograms were recorded by scanning the potentials from -300 to -1300 mV for Pb^{2+} , and the peaks were observed for Pb^{2+} , Cd^{2+} , and Zn^{2+} ions at about -400 , -600 , and -1000 mV, respectively, depending on the pH of the buffer solution (Fig. 2). After standard additions of 100 μL of 20 μM of Pb^{2+} , Cd^{2+} , or Zn^{2+} ions, the peak currents increased quantitatively, and non-adsorbed ions were detected. Because the initial

TABLE I
Molar Percentage of MA in the Feed and the Hydrogels and Gelation Percentage

Gel	MA (mol %)		Gelation (%)
	In feed	In gel	
P(AAm/MA)-1	1.20	0.964 ± 0.013	79.6
P(AAm/MA)-2	2.29	1.776 ± 0.015	74.3
P(AAm/MA)-3	3.54	2.310 ± 0.046	65.3
P(AAm/MA)-4	5.22	3.150 ± 0.015	60.5

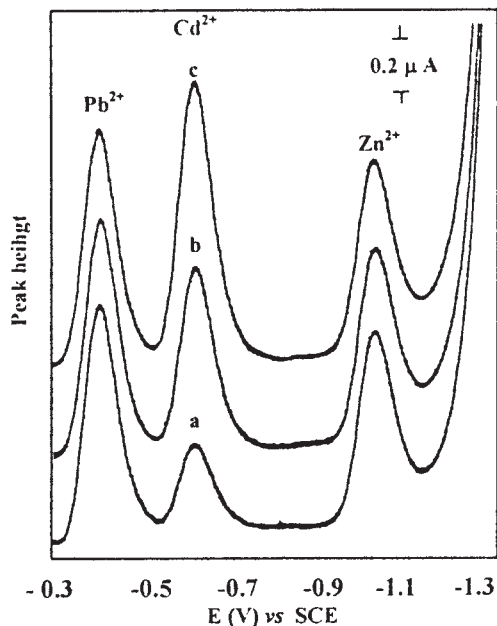


Figure 2 Differential pulse polarograms for competitive adsorption of Cd^{2+} onto P(AAm/MA)-2 in the presence of Pb^{2+} and Zn^{2+} (polarograms were recorded in acidic solution): (a) $20 \mu\text{M}$ Cd^{2+} next to $50 \mu\text{M}$ Pb^{2+} and Zn^{2+} in 15 mL pH = 6 B-R buffer solution [0.0298 g P(AAm/MA)-2 hydrogel was immersed into this solution for 4 days]; (b) $20 \mu\text{M}$ standard addition of Cd^{2+} ; (c) $40 \mu\text{M}$ standard addition of Cd^{2+} .

amounts of the ions were known, the difference was obviously the amount of adsorbed ions.

RESULTS AND DISCUSSION

Synthesis of P(AAm/MA) hydrogels

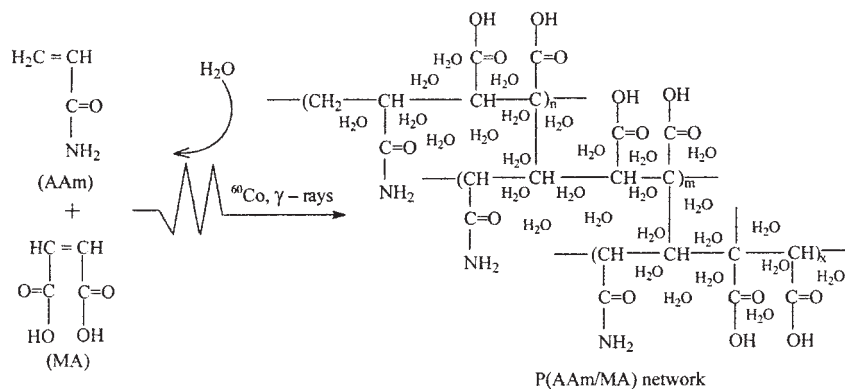
In this study ionizing radiation processing was used for the preparation of P(AAm/MA) hydrogels. Maleic acid does not homopolymerize, as can be expected from its 1,2-disubstituted structure, when it is irradiated in aqueous solution. A parallel trial, irradiating

pure solid maleic acid or its aqueous solutions, provided additional confirmation of expected results. In the presence of monomer with a high polymerization tendency, such as acrylamide, however, it is randomly incorporated into the main chain. Because of its low solubility in water, it was not possible to prepare copolymers with maleic acid contents higher than that stated earlier in the experimental section. When AAm/MA/water is irradiated with γ -rays, free radicals are generated in the aqueous solution. Random reactions of these radicals with the monomers cause formation of AAm/MA networks. When the irradiation dose is increased beyond a certain value, the polymer chains could form crosslinks. A schematic presentation of possible copolymerization between AAm and MA monomers is shown in Scheme 1.

The mole percentages of the AAm and MA monomers in the initial mixtures, the corresponding composition of AAm and MA in the copolymers, and the percentage gelation are summarized in Table I. As shown in this table an increasing mole percentage of MA, in the initial mixture, increases the amount MA in the hydrogel but causes a decrease in the conversion from monomer to hydrogel. These results indicate that MA shows typical properties of a chain-transfer agent during the copolymerization process. The results, pertaining to the composition and conversions, are detailed in Table I.

Effect of pH

The adsorption of heavy metal ions, on a polymer backbone containing acidic pendant groups, is usually a strong function of the pH⁷ because the acidic pendant groups on these polymer backbones release protons in response to changes in pH. The adsorption characteristics of the adsorbents toward Pb^{2+} , Cd^{2+} , and Zn^{2+} ions were investigated in 15 mL buffer solutions containing $20 \mu\text{M}$ ions over the pH range of 2.0–8.0 at a fixed temperature (20°C). Figure 3(a)–(c)



Scheme 1

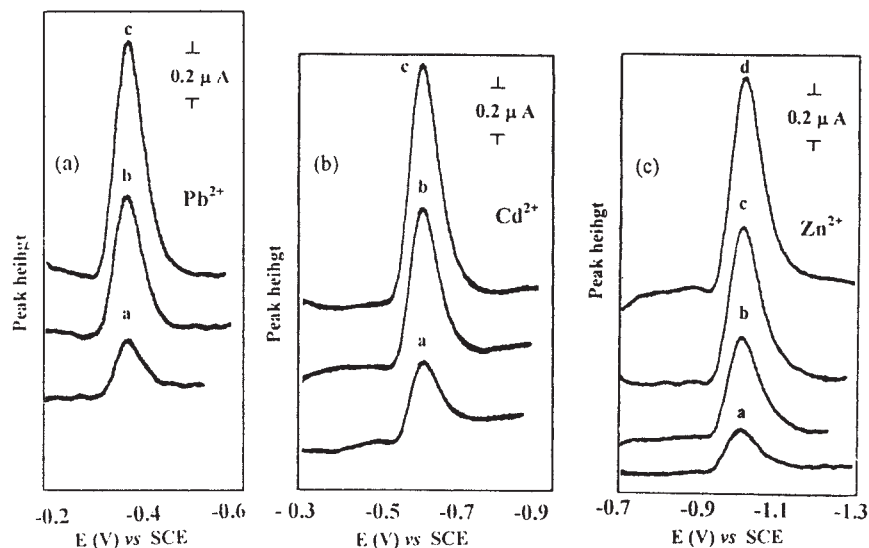


Figure 3 Differential pulse polarograms for the adsorption of Pb^{2+} onto P(AAm/MA)-1 hydrogels (polarograms were recorded in acidic solution): (a) $20 \mu\text{M M}^{2+}$ in 15.0 mL pH = B-R buffer solution [$\cong 0.0306$ g P(AAm/MA)-1 hydrogel was immersed into this solution for 4 days]; (b) $20 \mu\text{M M}^{2+}$ standard addition; (c) $40 \mu\text{M M}^{2+}$ standard addition.

show polarograms for the adsorption of single Pb^{2+} , Cd^{2+} , and Zn^{2+} ions onto P(AAm/MA)-1 hydrogels. Figure 4(a)–(c) show the change in the amount of adsorbed Pb^{2+} , Cd^{2+} , and Zn^{2+} ions of P(AAm/MA) hydrogels with various MA contents. An increase in the MA content in the hydrogel caused an increase in the amount of Pb^{2+} , Cd^{2+} , and Zn^{2+} ions. This behavior may be attributed to the increments of the carboxyl groups on the backbone chain of the hydrogels. The higher amounts of carboxylate groups mean higher electrostatic interaction between the cationic ions and the anionic groups. Although the maximum adsorption of Pb^{2+} and Cd^{2+} ions corresponds to pH = 6, a slight change for Zn^{2+} ion was observed between pH 2 and 8. This behavior was attributed to the second dissociation constant of MA ($\text{p}K_{a2} = 6.07$), where the hydrogen ions of the acidic pendant groups are completely dissociated at about this pH.

The metal ions can be adsorbed nonspecifically by physical adsorption, associated with the weak forces of physical attraction such as van der Waals forces, or by chemical adsorption associated with the change of electrons and the formation of a chemical bond between the metal ions and the P(AAm/MA) chains (especially with the carboxylic acid groups of the MA units). The adsorption of Pb^{2+} , Cd^{2+} , and Zn^{2+} ions onto P(AAm/MA) hydrogels may be ionic in nature because the acidic groups of these hydrogels in metal ion solutions were completely dissociated at pH corresponding to $\text{p}K_{a2}$. The slight decrease at further increase in pH may be attributable to possible hydroxide precipitation of the heavy metal ions. Maximum adsorption values of Pb^{2+} , Cd^{2+} , and Zn^{2+} ions on P(AAm/MA)-3 were $1.7 \mu\text{mol Pb}^{2+}/\text{g}$ dry gel, 1.3

$\mu\text{mol Cd}^{2+}/\text{g}$ dry gel, and $1.8 \mu\text{mol Zn}^{2+}/\text{g}$ dry gel. On the other hand, the adsorption capacity of P(AAm/MA) hydrogels was increased by 20% for Pb^{2+} , 37% for Cd^{2+} , and 34% for Zn^{2+} with the increase of MA content in the hydrogel. The difference in the adsorption values can be explained by the different affinities of the heavy metal ions for donor groups (i.e., carboxyl group) in the metal-chelating ligand MA.

Competitive adsorption

The competitive adsorption, of Pb^{2+} , Cd^{2+} , or Zn^{2+} ions, was studied by taking a definite amount of one of the mentioned ions in the presence of a changing amount of the other ions. For this purpose, $20 \mu\text{M Pb}^{2+}$ solutions were prepared in 15 mL B-R buffer solutions (pH = 6) containing Cd^{2+} and Zn^{2+} ions within a concentration range of 10 to $50 \mu\text{M}$. P(AAm/MA) hydrogels (~ 0.0300 g) were immersed in the above solutions and allowed to stand for 4 days. The effect of increasing amounts of Cd^{2+} and Zn^{2+} ions on the adsorption of Pb^{2+} was investigated for P(AAm/MA) hydrogels with various MA contents. The same procedures were repeated for $20 \mu\text{M Cd}^{2+}$ or Zn^{2+} ions but, in this case, Zn^{2+} and Pb^{2+} ions or Cd^{2+} and Pb^{2+} ions were used within a concentration range of 10 to $50 \mu\text{M}$. As shown in Figure 5(a)–(c), the adsorption of Pb^{2+} , Cd^{2+} , or Zn^{2+} ions onto P(AAm/MA) hydrogels, under competitive conditions, was decreased by 47, 33, and 30% for P(AAm/MA)-1; 50, 31, and 31% for P(AAm/MA)-2; and 41, 30, and 25% for P(AAm/MA)-3. When the concentrations of the other two ions were increased, the adsorption of the metal

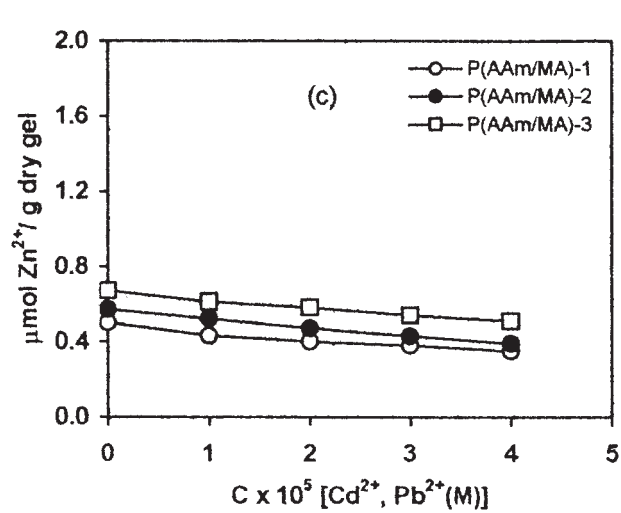
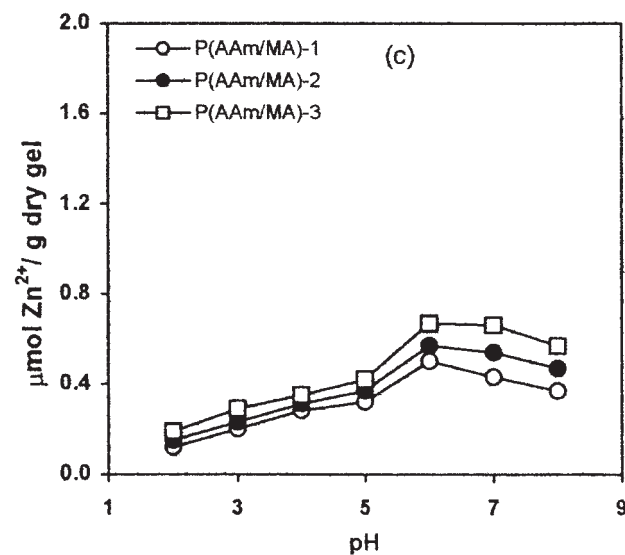
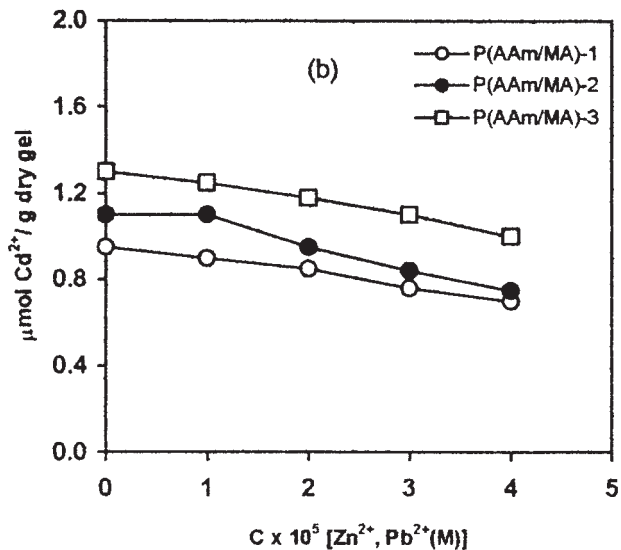
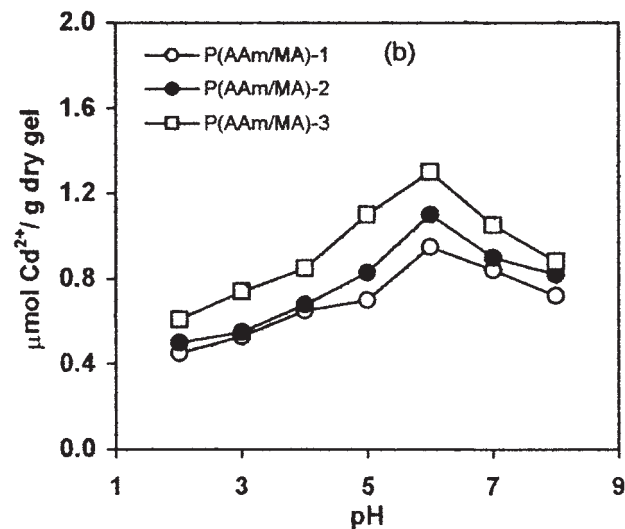
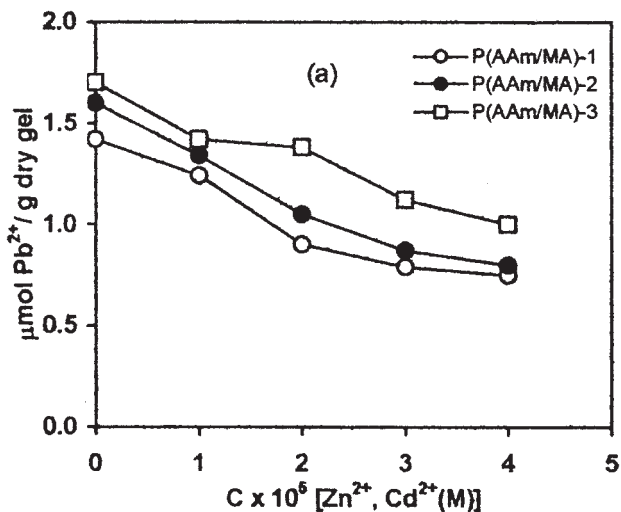
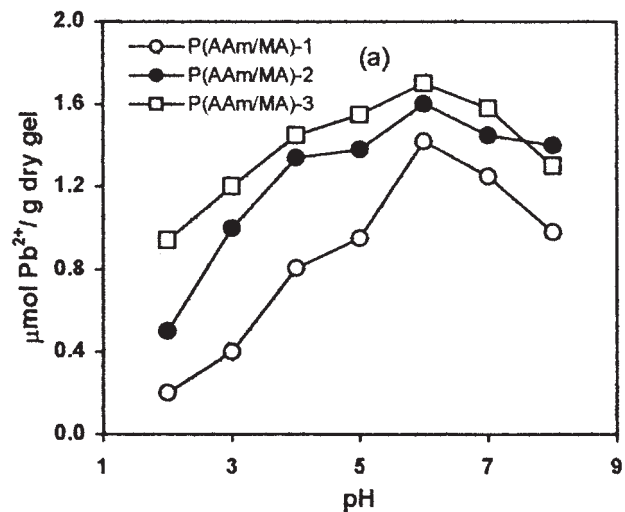


Figure 4 Effect of pH on the adsorption of Pb²⁺, Cd²⁺, and Zn²⁺ for P(AAm/MA) hydrogels.

Figure 5 Effect of concentration of Pb²⁺, Cd²⁺, and Zn²⁺ on the adsorption capacities of P(AAm/MA) hydrogels.

ion was decreased and nearly leveled off. This could be attributed to the saturation of the carboxylate groups on the polymer chain. Therefore, the efficiency of diffusion of the metal ions could be prevented within the mesh size of these hydrogels. According to these results, the effective order in the adsorption under competitive conditions could be arranged as $Zn^{2+} > Cd^{2+} > Pb^{2+}$. On the other hand, the competition of adsorption for all the ions on P(AAm/MA)-3 was more effective compared to that on the other hydrogels. In addition, all three copolymers, containing different amounts of carboxylic acid groups, removed Pb^{2+} ions most preferentially, followed by Cd^{2+} and Zn^{2+} ions under noncompetitive conditions ($Pb^{2+} > Cd^{2+} > Zn^{2+}$). With respect to Pb^{2+} removal, the ion of the metal with higher atomic number is removed preferentially compared to those with the same valences but lower atomic number.

Effect of ionic strength and temperature

The influence of the temperature and ionic strength on the adsorption behavior of the hydrogels at 20, 30, and 40°C (with thermostatic control) in water and synthetic seawater solutions (3 mM $NaHCO_3$ + 0.55M NaCl, pH \cong 7.0) was investigated. As shown in Figure 6, the ionic strength, attributed to $NaHCO_3$ and NaCl solutions, had a more pronounced effect on the uptake properties of the hydrogels. An increase in the ionic strength generally reduced the swelling arising from the difference in the concentration of mobile ions between the gel and solution. Because of decreasing swelling and collapsing of the chains in the hydrogel system, the possible interaction between Pb^{2+} , Cd^{2+} , or Zn^{2+} ions and the polymer chain increased and caused a slight increase in the adsorption (6.0% for Pb^{2+} , 9.0% for Cd^{2+} , and 4.6% for Zn^{2+} at 20°C).

As expected, an increase in the temperature from 20 to 40°C caused a drastic decrease in the amount of adsorbed ions. The amounts of the adsorbed Pb^{2+} , Cd^{2+} , or Zn^{2+} ions were decreased 58, 18, and 56% in water and 52, 20, and 55% in synthetic seawater solu-

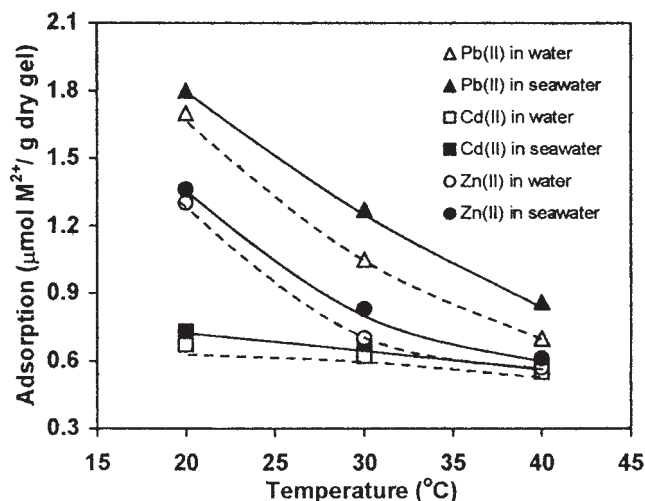


Figure 6 Variation with temperature of adsorbed Pb^{2+} , Cd^{2+} , and Zn^{2+} ions on P(AAm/MA)-3 hydrogels from water and synthetic seawater (0.55M NaCl and 3 mM $NaHCO_3$).

tions, respectively. It is well known that the adsorption decreases with temperature and the temperature-dependency studies also revealed that the observed phenomenon had an adsorption nature.⁷ These hydrogels are potential adsorbents to be used for the removal of Pb^{2+} , Cd^{2+} , or Zn^{2+} ions from wastewater and aqueous effluents.

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