Competitive Adsorption of Uranyl Ions in the Presence of Pb(II) and Cd(II) Ions by Poly(glycidyl methacrylate) Microbeads Carrying Amidoxime Groups and Polarographic Determination

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ABSTRACT: The adsorption capacity of UO_2^{2+} in the presence of Pb(II) and Cd(II) ions was investigated with amidoximated poly(glycidyl methacrylate) (PGMA) microbeads with an average size of 135 μm packed in a glass column (0.5-cm i.d. and 20-cm length, flow rate = 3 mL/min) under competitive conditions. A differential pulse polarography technique was used for the determination of trace quantities of uptaken elements by the measurement of the reduction peak currents at $-200/-950$, -400, and -600 mV (vs a saturated calomel electrode) for UO_2^{2+}, Pb(II), and Cd(II) ions, respectively. When only UO_2^{2+} was found in the eluate, its adsorption was 85.3% from a 50 μM initial solution. However, when there was UO_2^{2+} with binary systems of Pb(II) or Cd(II), it was 78.2 and 76.3%, respectively. On the other hand, in a ternary mixture of UO_2^{2+} with Pb(II) and Cd(II), the adsorption was found to be 75.2% with the same initial concentration. According to the results, the competitive adsorption studies showed that these amidoximated PGMA microbeads had good adsorption selectivity for UO_2^{2+} with the coexistence of Pb(II) and Cd(II) ions. The ionic strength of the solution also influenced the UO_2^{2+} adsorption capacity of the amidoximated PGMA microbeads. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 4168–4172, 2007

Key words: adsorption; functionalization of polymers; selectivity

INTRODUCTION

Uranium is one of the most seriously threatening heavy metals because of its toxicity and some radioactivity. Excessive amounts of uranium have found their way into the environment through activities associated with the nuclear industry. Uranium contamination poses a threat in some surface and ground waters.[1] In view of the anticipated exhaustion of terrestrial uranium reserves in the near future, research has been directed toward the recovery of uranium from nonconventional sources, such as coal and natural waters (0.1–10 mg of U/m^3) and especially seawater (2.8–3.3 mg of U/m^3). The recovery of uranium from the contaminated water of flooded mines (0.1–15 mg of U/m^3) also presents a very important environmental problem to be solved.[2] The possibility of coexisting UO_2^{2+}, Pb(II), and Cd(II) ions in various industrial wastes and sea water has great probability, and therefore their selective removal is necessary for the recovery of these elements.

Among the various methods described, adsorption is generally preferred for the purification or recovery of uranyl ions from seawater because of its high efficiency and easy handling, the availability of different adsorbents, and its cost effectiveness.[3]

For the separation of uranyl ions for either purification or enrichment, numerous resins with chelating groups have been developed.[4–7] Several criteria are important in the design of chelating polymers with substantial stability for the selective removal or recovery of uranyl ions: specific and fast complexation of the uranyl ions as well as the reusability of the chelating polymeric ligands. A large number of chelating polymers incorporating a variety of ligands (e.g., iminodiacetate, amidoxime, phosphoric acid, amine, dithiocarbamate, oxime, and reactive textile dyes) have been prepared, and their analytical properties have been investigated.[8–10]

Among them, amidoxime-group-containing polymeric adsorbents are noted because of their high selectivity toward uranyl ions and rapid adsorption rate.[11–14] Sekiguchi et al.[15] and Kubota and Shigehisa[16] prepared amidoxime-group-containing resins and showed the recovery of uranyl ions from seawater with a high adsorption yield. Egawa and Harada[17] synthesized a macroreticular chelating resin containing amidoxime by reacting acrylonitrile–divinylbenzene copolymeric beads with hydroxylamine. To the

best of our knowledge, although a great deal of research has been conducted on amidoxime-group-carrying adsorbents, poly(glycidyl methacrylate) (PGMA) beads with surface-grafted chains carrying two amidoxime groups per repeating unit have not been reported in the literature. The unique advantage of the modified PGMA beads is that they contain double amidoxime groups per repeating unit and an additional dimethylene spacer unit between neighboring amidoxime groups in each monomeric unit on the surface. In addition, these novel PGMA beads carrying double amidoxime groups per repeating unit may be more accessible for the adsorption of uranyl ions in aqueous solutions at very low concentration levels (parts per billion) than conventional adsorbents having only one amidoxime group per repeating unit.

In this study, the adsorption capacity of PGMA microbeads carrying double amidoxime groups per repeating unit was investigated for UO_2^{2+} ions in the presence of Pb(II) and Cd(II) ions from aqueous solutions under competitive and noncompetitive conditions with a differential pulse polarography (DPP) technique. First and foremost, DPP has been used for trace element analyses because of its high sensitivity, resolution, accuracy, and inexpensive instrumentation. Other accessible techniques capable of heavy-metal-ion determination, such as atomic adsorption spectroscopy, UV spectrometry, and γ spectrometry, often do not offer sufficient sensitivity and selectivity for accurate determinations at the trace concentration. These are all time-consuming procedures, and losses of these metals are also possible.

EXPERIMENTAL

Apparatus

A polarographic analyzer system (PAR 174 A) (Princeton Applied Research Company, USA), equipped with a mercury drop timer, was used to determine the competitive and noncompetitive adsorption of UO_2^{2+}, Pb(II), and Cd(II) ions from aqueous solutions onto amidoximated PGMA microbeads. The drop time of the mercury electrode was about 2–3 s (2.75 mg/s). A Kalusek electrolytic cell, with a reference saturated calomel electrode (SCE) separated by a liquid junction, was used in the three-electrode mode; the counter electrode 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 scanning rate of 5 mV/s, a pulse duration of 50 ms, and a pulse amplitude of 50 mV.

Materials

The PGMA microbeads carrying amidoxime groups were prepared as previously described.[18] $UO_2(NO_3)_2\cdot$ 6H$_2$O, Pb(NO$_3$)$_2$, Cd(NO$_3$)$_2$, NaNO$_3$, and NaCl were obtained from Merck (Darmstadt, Germany).

Polarographic determination of the UO_2^{2+} uptake in the presence of Pb(II) and Cd(II) ions

The amidoximated PGMA microbeads with an average size of 135 μm were packed in a glass column (0.5-cm i.d. and 20-cm length). An aliquot of the sample solution (15.0 mL, 50 μM) containing UO_2^{2+}, Pb(II), and Cd(II) or UO_2^{2+} with various amounts of Pb(II) and Cd(II) was passed through the column at a flow rate adjusted to the desired value (3 mL/min).

A 0.1M HCl (pH 1.0) solution (10.0 mL) was put into the polarographic cell and deoxygenated with high-purity nitrogen (99.999%) for about 5 min. The background polarograms were obtained by the scanning of the potential from 0.0 to about −1300 mV (versus SCE). From the eluate solution, 1.0-mL aliquots were collected and transferred to the polarographic cell containing the supporting electrolyte. After the scanning of the potential from 0.00 to about −1300 mV, the UO_2^{2+}, Pb(II), and Cd(II) ions exhibited reduction peaks at −200/950, −400, and −600 mV, respectively (Fig. 1). The analytical determination of the UO_2^{2+}, Pb(II), and Cd(II) ions was performed by the standard addition of 50 μM UO_2^{2+}, Pb(II), or Cd(II) and the evaluation of the peak currents. The amounts of adsorbed ions on the amidoximated PGMA microbeads were estimated by the measurement of the peak heights of the extracted aliquot and their comparison with the peak height obtained after standard additions. The optimum conditions for the analytical determination of the investigated ions by DPP were found to be pH 1.0, peak potentials at −200/950, −400, and −600 mV for the UO_2^{2+}, Pb(II), and Cd(II), respectively, a scanning rate of 5.0 mV/s, a pulse amplitude of 50 mV, a pulse duration of 50 ms, and an ambient temperature of 25 ± 3°C. The average value of three measurements is reported. The standard deviations of the measured adsorption values were less than 10% of the mean.

RESULTS AND DISCUSSION

Detailed information on the synthesis and structural characterization of the amidoximated PGMA microbeads was given in our earlier publication.[18] UO_2^{2+}, Pb(II), or Cd(II) solutions (15 mL) in the concentration range of 0–500 μM were passed through the column at a flow rate of 3 mL/min. From the each aliquot, 10.0-mL portions were collected and transferred to the polarographic cell. The pH of this solution was adjusted to 1.0 with concentrated HCl to supply the necessary electrolyte medium for the polarographic procedure. Polarograms were taken by the scanning of
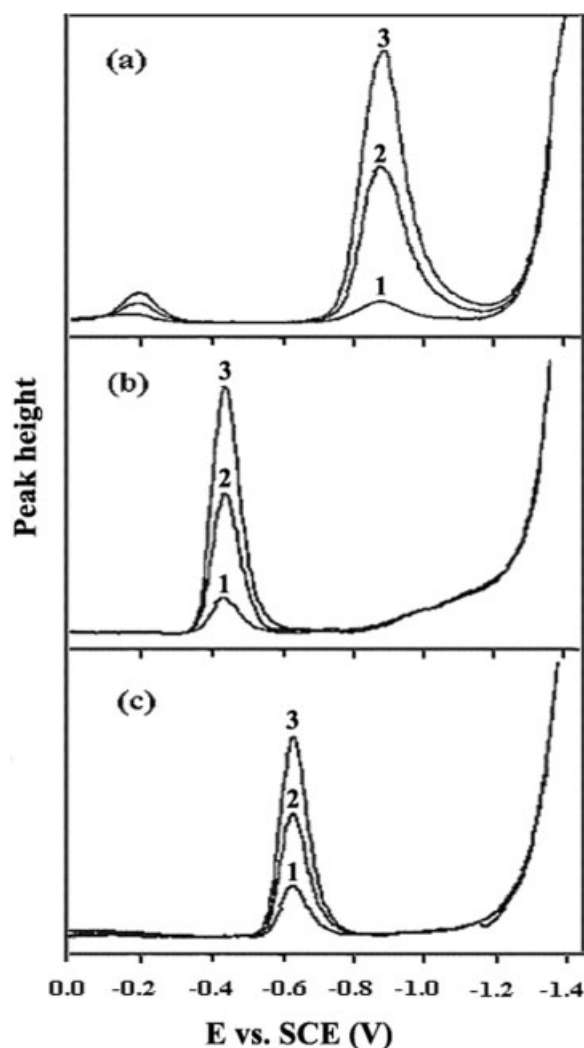
Figure 1 DPP polarograms for the determination of adsorbed metal ions on amidoximated PGMA microbeads from 50 μM solutions: (a) UO_2^{2+} [(1) 10 mL of an eluate solution plus 100 μL of HCl (pH ~ 1.0), (2) a standard addition of 50 μM UO_2^{2+}, and (3) a standard addition of 50 μM UO_2^{2+}], (b) Pb(II) [(1) 10 mL of an eluate solution plus 100 μL of HCl (pH ~ 1.0), (2) a standard addition of 50 μM Pb(II), and (3) a standard addition of 50 μM Pb(II)], and (c) Cd(II) [(1) 10 mL of an eluate solution plus 100 μL of HCl (pH ~ 1.0), (2) a standard addition of 50 μM Cd(II), and (3) a standard addition of 50 μM Cd(II)].

the potential from 0.00 to about −1300 mV versus SCE. The UO_2^{2+} ion showed two reduction peaks at −200 and −950 mV in 0.1M HCl during the potential scanning [Fig. 1(a)]. These peaks at −200 and −950 mV correspond to the reduction of U(VI) to U(V) and U(VI) to U(III) on a mercury electrode, respectively. However, the peak at −950 mV, which was well resolved and appeared suitable to be investigated for analytical use, had a maximum peak current at pH 1.0 and showed quantitative increments with the additions of a standard UO_2^{2+} solution. The same procedure was also applied to Pb(II) and Cd(II) ions. The reduction peaks were observed at −400 mV for Pb(II)

and at −600 mV for Cd(II) [Fig. 1(b,c)]. These peaks also showed quantitative increments with the additions of their standard solutions. The amounts of adsorbed UO_2^{2+}, Pb(II), and Cd(II) ions were determined from the differences between the peak currents of the eluate solutions and their amounts after standard additions. The UO_2^{2+}-, Pb(II)-, and Cd(II)-ion adsorption capacities of amidoximated PGMA microbeads as a function of the initial concentration are illustrated in Figure 2. The adsorption capacities first increased with the initial metal-ion concentrations of UO_2^{2+}, Pb(II), and Cd(II) and then reached a plateau value at an initial concentration of 250 μM for each metal ion. This is a typical curve of chemical adsorption.[19] At the plateau, the amount of the adsorbed UO_2^{2+} ion was determined to be 3.95 μmol/g of dry polymer. The adsorption behavior of Pb(II) and Cd(II) ions, which have lower adsorption capacities than UO_2^{2+}, shows adsorption isotherms similar to that of UO_2^{2+} ions. The adsorption capacity of amidoximated PGMA microbeads for UO_2^{2+}, Pb(II), and Cd(II) ions at an initial concentration of 250 μM was 3.95, 3.00, and 2.05 μmol of metal ion/g of dry polymer, respectively. The order adsorption affinity, based on the amount of metal-ion uptake (μmol of metal ion/g of dry polymer), was as follows: UO_2^{2+} > Pb(II) > Cd(II). Rivas et al.[20] used a commercial poly(amidoxime) chelating polymer and investigated the adsorption affinity of Cu(II), Hg(II), Pb(II), and UO_2^{2+} ions by a batch technique. It was found that this resin exhibited an affinity for UO_2^{2+} and Pb(II) ions but no affinity for the other metal ions. The differential adsorptions of the different ions could be attributed to the facilities of the diffusion of the metal ions and adsorption (or entrapment) within the mesh sizes of these polymers. The specificity of the metal-chelating ligand (i.e., amidoxime groups) might have also contributed to this high
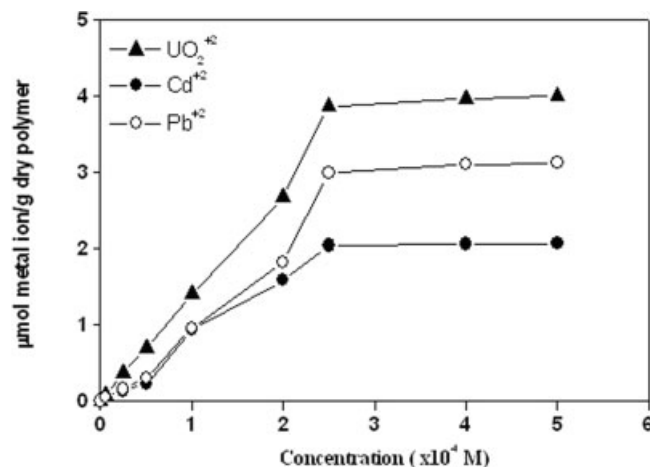

Figure 2 Effect of the concentration of UO_2^{2+}, Pb(II), and Cd(II) on the adsorption capacity of amidoximated PGMA microbeads.
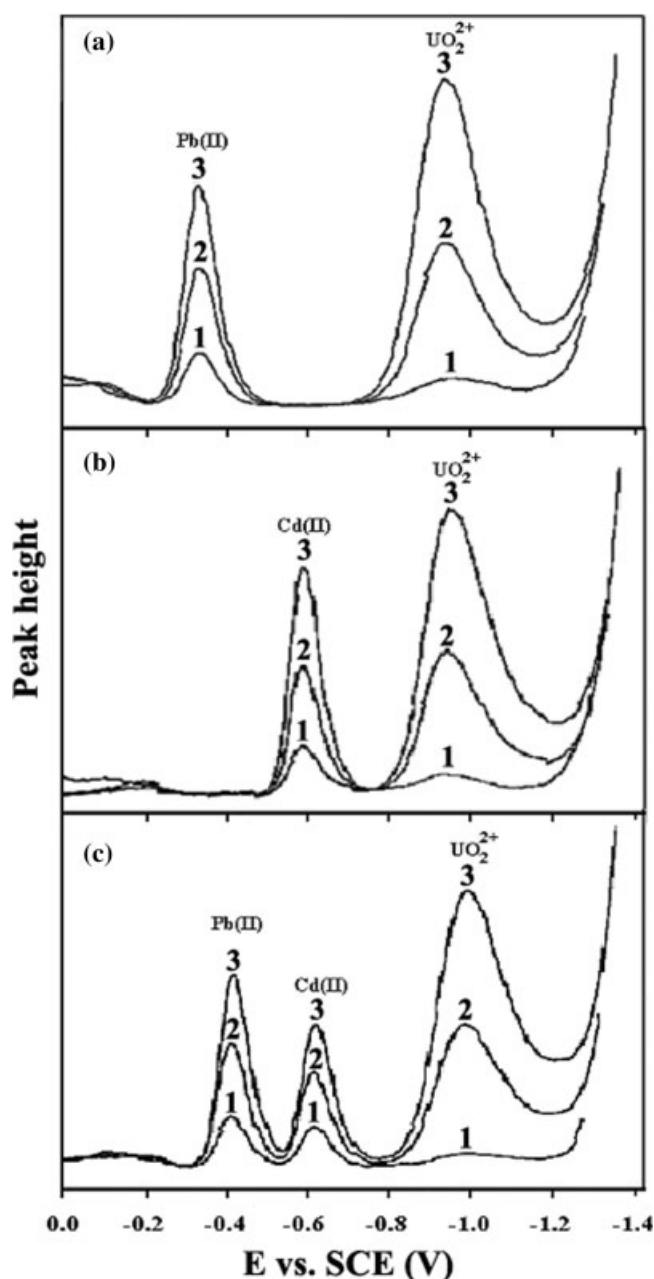
Figure 3 DPP polarograms for the determination of adsorbed UO_2^{2+} ions on amidoximated PGMA microbeads from 50 μM solutions in the presence of (a) Pb(II) [(1) 10 mL of an eluate solution plus 100 μL of HCl (pH $\sim$ 1.0), (2) a standard addition of 50 μM UO_2^{2+} and Pb(II), and (3) a standard addition of 50 μM UO_2^{2+} and Pb(II)], (b) Cd(II) [(1) 10 mL of an eluate solution plus 100 μL of HCl (pH $\sim$ 1.0), (2) a standard addition of 50 μM UO_2^{2+} and Cd(II), and (3) a standard addition of 50 μM UO_2^{2+} and Cd(II)], and (c) Pb(II) and Cd(II) [(1) 10 mL of an eluate solution plus 100 μL of HCl (pH $\sim$ 1.0), (2) a standard addition of 50 μM UO_2^{2+}, Pb(II), and Cd(II), and (3) a standard addition of 50 μM UO_2^{2+}, Pb(II), and Cd(II)].

adsorption capacity for UO_2^{2+}. In this respect, this high adsorption capacity for UO_2^{2+} ions is due to the hydrophilic nature of the two amidoxime groups in the amidoximated PGMA microbeads, which had an

adequate affinity to UO_2^{2+} ions. The long side chain of the amidoximated PGMA leads to a higher free volume that can help the UO_2^{2+} ions to diffuse toward the chelating groups easily. In addition, one amidoximated glycidyl methacrylate unit possesses two amidoxime groups that can share four pairs of electrons with a single UO_2^{2+} ion and cage the metal ion tightly.

The competitive adsorption of UO_2^{2+} in the presence of various amounts of Pb(II) and Cd(II) ions on amidoximated PGMA microbeads was also investigated as described in the Experimental section. The polarograms obtained under competitive conditions for the UO_2^{2+}–Pb(II) and UO_2^{2+}–Cd(II) binary systems and for the UO_2^{2+}–Pb(II)–Cd(II) ternary system are presented in Figure 3(a–c). The results obtained for the competitive adsorption of UO_2^{2+} with Pb(II), UO_2^{2+} with Cd(II), and UO_2^{2+} with Pb(II) and Cd(II) with increasing concentrations of the coexisting metal ions are illustrated in Figure 4. As shown in this figure, the adsorption capacity of amidoximated PGMA microbeads for UO_2^{2+} ions was slightly affected by the initial concentration of Pb(II) and Cd(II) ions. For this procedure, the coexisting ions were taken at the same concentration and at 2, 4, 8, and 10 times the concentration of the UO_2^{2+} ion.

According to the results, when only UO_2^{2+} was found in the eluate, its adsorption was 85.3% from a 50 μM initial solution. However, when there was UO_2^{2+} with the binary systems of Pb(II) or Cd(II) in equal amounts (50 μM), it was 78.2 and 76.3%, respectively. On the other hand, in a ternary mixture of UO_2^{2+} with Pb(II) and Cd(II), the adsorption was found to be 75.2% under the same conditions. When the coexisting amounts were further increased up to 10 times that of UO_2^{2+}, the adsorption of UO_2^{2+} decreased to 72.9, 71.3, and 70.2% for UO_2^{2+}–Pb(II), UO_2^{2+}–Cd(II, and UO_2^{2+}–Pb(II)–Cd(II) under competi-
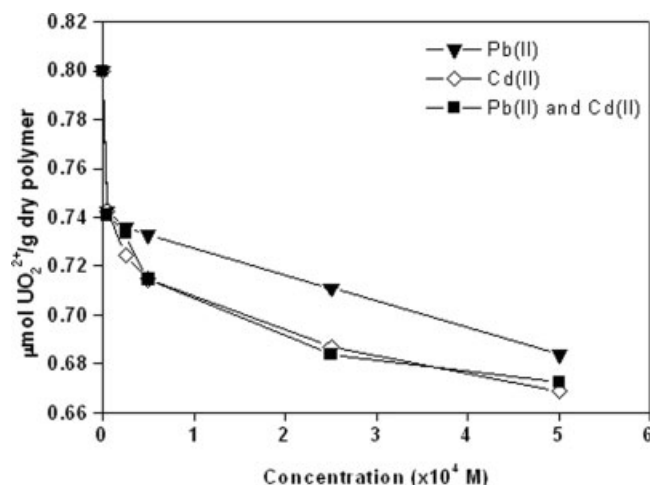

Figure 4 Effect of the Pb(II) and Cd(II concentrations on the UO_2^{2+}-ion adsorption capacity for amidoximated PGMA microbeads.

tive conditions, respectively. It was concluded that there was no serious effect on the adsorption of UO_2^{2+} even when the concentration of the coexisting ions was 10-fold. In these competitive adsorption tests, in a ternary mixture of UO_2^{2+} with Pb(II) and Cd(II), the selectivity coefficient of UO_2^{2+} ions with these two metal ions, at 250 μM initial concentrations, was $\alpha_{UO_2^{2+}}$/Pb(II) = 3.17 and $\alpha_{UO_2^{2+}}$/Cd(II) = 2.67. In light of these finding, in the presence of Pb(II) and Cd(II) ions, amidoximated PGMA microbeads have a great advantage for the selective adsorption of UO_2^{2+} ions. This can be applied to the separation of UO_2^{2+} in aqueous systems containing Pb(II) and Cd(II) ions.

The presence of salts in wastewaters or seawater is one of the important factors that may affect the adsorption behaviors of metal ions. Increasing the ionic strength reduces the electrostatic forces between the polymer chain and metal ions. The charged ions may probably be suppressed because of the ionic atmosphere of the polyelectrolyte, and at the same time, the ionic atmosphere of the counterions restricts the approach of the metal ions to the ligand groups. Therefore, the influence of the ionic strength on the adsorption capacities of the amidoximated PGMA microbeads in $NaNO_3$ and NaCl solutions within the range of 0.1–0.5M was investigated, and the results obtained for a 250 μM initial UO_2^{2+} concentration are illustrated in Figure 5. We observed that the ionic strength of $NaNO_3$ had a more pronounced effect than NaCl. The decrease of the adsorbed UO_2^{2+} ions in the presence of $NaNO_3$ and NaCl was 46.7 and 31.7% at the same ionic strength (0.5M), respectively. This could be attributed to the ionic interaction of the amidoximated sites with electrolytes species, resulting in the prevention of UO_2^{2+} adsorption.

The influence of electrolytes in a synthetic seawater solution (3 mM $NaHCO_3$ and 0.55M NaCl) on the adsorption capacity of a 250 μM initial concentration of UO_2^{2+} on the amidoximated PGMA microbeads was also studied. As shown in Figure 6, the ionic
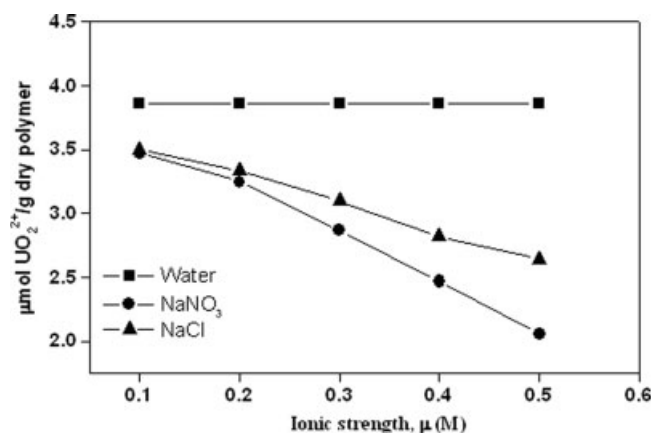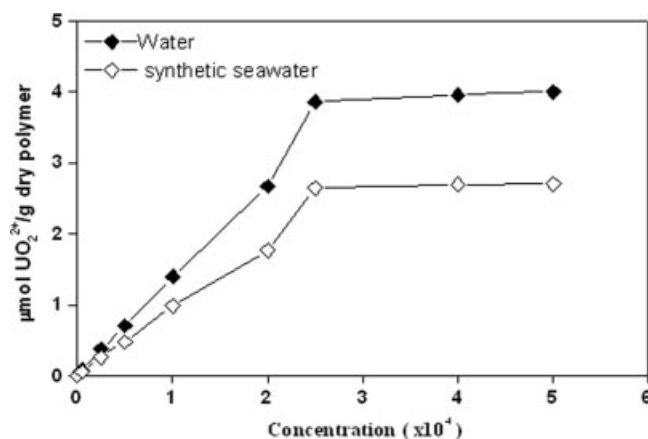

Figure 6 Effect of the UO_2^{2+}-ion concentration on the adsorption capacity for amidoximated PGMA microbeads in water and synthetic seawater.

strength corresponding to $NaHCO_3$ and NaCl had a more pronounced effect than pure water on the uptake property of the amidoximated PGMA microbeads. The concentration of the adsorbed UO_2^{2+} ion in synthetic seawater was decreased by 32.0% in comparison with pure water. In synthetic seawater, bicarbonate ions (HCO_3^-) and amidoxime groups in the amidoximated PGMA can form ionic interactions, which induce an electrostatic repulsion of UO_2^{2+} ions. Therefore, competition exists between bicarbonates and UO_2^{2+} ions for adsorption sites and decreases the adsorption capacity.

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Figure 5 Effect of the ionic strength on the UO_2^{2+}-ion adsorption capacity for amidoximated PGMA microbeads.