

Determination of the Competitive Adsorption of Heavy Metal Ions on Poly(*N*-vinyl-2-pyrrolidone/acrylic acid) Hydrogels by Differential Pulse Polarography

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ABSTRACT: Poly(*N*-vinyl-2-pyrrolidone) and poly(*N*-vinyl-2-pyrrolidone/acrylic acid) hydrogels were prepared by gamma irradiation for the removal of heavy metal ions (i.e., lead, copper, zinc, and cadmium) from aqueous solutions containing different amounts of these ions (2.5–10 mg/L) and at different pH values (1–13). The observed affinity order in adsorption of these metal ions on the hydrogels was Zn(II) > Pb(II) > Cu(II) > Cd(II) under competitive condi-

tions. The optimal pH range for the heavy metal ions was from 7 to 9. The adsorption of the heavy metal ions decreased with increasing temperature in both water and synthetic seawater conditions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2013–2018, 2003

Key words: adsorption; hydrogels; radiation

INTRODUCTION

The oceans contain various kinds of substances in solution. The timescale of oceanic circulation is assumed to be about 1000 years, and the oceans are well stirred. Therefore, seawater is a homogeneous electrolytic solution, which is kept at equilibrium. The concentration of electrolytes is about 0.6M, with heavy metal ions at about 10^{-6} M. Elements above 65 mg/L in seawater have been utilized in industry.¹

It has been reported that amidoxime compounds can be synthesized from nitriles and hydroxylamine and that heavy metal ions are coordinated with the amidoxime group.^{2,3} A metal-chelating resin with an amidoxime group was, therefore, synthesized and applied to the separation and collection of heavy metal ions from dilute solutions.^{4,5} In this regard, polymeric and copolymeric hydrogels have been extensively studied, and many reviews are available in the field.^{6–8} To increase and improve the metal ion adsorption capacity of hydrogels, either comonomers carrying some specific ligands are incorporated into their structures or the chemical structure of repeating units is chemically modified. Typical examples of the former are acrylamide–itaconic acid and acrylamide–maleic acid systems.^{9–12} These hydrogels have been used for the preconcentration and separation of trace elements from seawaters, and their analytical use in

conjunction with atomic absorption spectroscopy has been well established.

Poly(*N*-vinyl-2-pyrrolidone) (PVP) and poly(*N*-vinyl-2-pyrrolidone/acrylic acid) [P(VP/AA)] hydrogels were prepared by radiation-induced polymerization. Recently, we characterized the hydrogels thus prepared with respect to their swelling properties and network structures.¹³ In this study, we examined external stimuli such as pH, ionic strength, and temperature on the Zn(II), Pb(II), Cu(II), and Cd(II) ion adsorption capacity of these hydrogels under competitive conditions. The measurement of the adsorption of trace amounts of these ions was possible by using differential pulse polarography (DPP) technique, which was used to determine the amounts of trace elements usually encountered in biological or environmental samples.

EXPERIMENTAL

Apparatus

A polarographic analyzer system (PAR 174 A), equipped with a mercury drop timer, was used. The drop time of the mercury electrode was approximately 2–3 s (2.75 mg/s). A Kalousek electrolytic cell with a saturated calomel electrode (SCE), separated by a liquid junction was used in a three-electrode configuration. The counterelectrode was platinum wire. The polarograms were recorded with a Linseis LY 1600 X–Y recorder. Pulse polarograms were recorded under the conditions of a drop life of 1 s, a scan rate of 5 mV/s, a pulse duration of 50 ms, and a pulse amplitude of 50 mV.

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Chemicals

N-vinyl-2-pyrrolidone (VP) and acrylic acid (AA) were obtained from Aldrich (Milwaukee, WI) and BDH Chemicals, Ltd. (Poole, UK), respectively. Glacial acetic acid, phosphoric acid, and boric acid, used to prepare Britton–Robinson buffers, and $\text{Zn}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Cd}(\text{NO}_3)_2$ were obtained from Merck (Darmstadt, Germany).

Preparation of the hydrogels

Three components were used in the preparation of P(VP/AA) hydrogels: VP, AA, and distilled water. Aqueous solutions of the monomers (2 mL of VP and 0.5, 1.0, and 2.0 mL of AA) were prepared in 1 mL of pure water in different compositions (respective VP/AA molar ratios = 72.6/27.4, 55.5/44.5, and 39.0/61.0). The monomer solutions thus prepared were placed in poly(vinyl chloride) straws 4 mm in diameter and irradiated by 1.85 kGy in air at ambient temperature in a PX- γ -30 Isslodovateji-type γ irradiator at a fixed dose rate of 3.87 kGy h^{-1} . The hydrogels, obtained in long cylindrical shapes, were cut into pieces 3–4 mm in size and stored for later evaluation.

Adsorption of Zn(II), Cu(II), Pb(II), and Cd(II) ions on the PVP and P(VP/AA) hydrogels

The PVP and P(VP/AA) hydrogels ($\sim 0.0300 \text{ g}$) were immersed into 15.0 mL of solution in a concentration range of 2.5–10 mg/L ($\text{pH} \cong 7$) and were allowed to stand for 4 days. We detected the time-dependent equilibrium adsorption behavior of Zn(II), Pb(II), Cu(II), and Cd(II) ions onto the hydrogels by recording the peak currents of those ions day by day until they reached a constant (equilibrium adsorption) value. At the end of this time, the adsorbent was taken away by decantation from the solution. The equilibrium concentrations of Zn(II), Cu(II), Pb(II), and Cd(II) in the solution was determined by DPP. We deaerated 10 mL of the solution in the polarographic cell by passing pure nitrogen gas (99.99%) for about 5 min. We recorded the polarograms by scanning the potential from 0.00 to about -1200 mV . The Cu(II), Pb(II), Cd(II), and Zn(II) ions showed peaks at -150 , -350 , -600 , and -950 mV , respectively, in the acidic solution ($\text{pH} = 1$; Fig. 1). After standard additions of $50 \mu\text{L}$ of 500 ppm mixtures of Cu(II), Pb(II), Cd(II), and Zn(II) into the solutions allowed to stand for 4 days with PVP or P(VP/AA) hydrogels ($\sim 0.0300 \text{ g}$) in a concentration range of 2.5 to 10 mg/L, the peak currents increased proportionally, and nonadsorbed ions were detected. Because the initial amounts of the ions were known, the difference was obviously the amount of adsorbed ions.

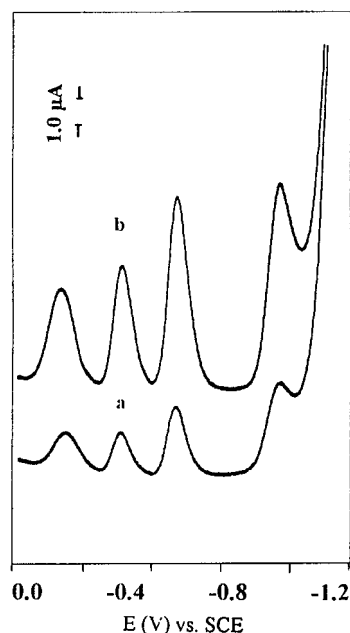


Figure 1 Differential pulse polarograms for the determination of adsorbed Cu(II), Pb(II), Cd(II), and Zn(II) on the P(VP/AA)-1 hydrogel for 2.5 mg/L of solution: (a) 10 mL of extract solution and (b) a standard addition of $50 \mu\text{L}$ of 500 mg/L Cu(II), Pb(II), Cd(II), and Zn(II).

RESULTS AND DISCUSSION

Effect of pH

The PVP and P(VP/AA) hydrogels were synthesized with ^{60}Co γ -rays to investigate the adsorption capacity of PVP and P(VP/AA) for the four metal ions. The details of the procedure and the pH-dependent swelling behavior for these hydrogels were reported in our previous article.¹³ The adsorption characteristics of the adsorbents toward Zn(II), Cu(II), Pb(II), and Cd(II) ions were determined in buffer solutions containing 7.5 mg/L of ions over the pH range 1.0–13.0 at a fixed temperature (20°C). For this work, we tried to use 7.5 mg/L Zn(II), Pb(II), Cu(II), and Cd(II) initial solutions to roughly obtain optimum pH. Instead of using all of the hydrogel composition, we selected the PVP hydrogel for the determination of the adsorption of all the ions, and this showed the general tendency. The maximum adsorption detected for the mentioned ions corresponded to the same (optimum) pH interval. It is well known that pH has two kinds of influences on metal adsorption: an effect on the solubility and specification of the metal ions in aqueous solutions and an effect on the overall charge of the adsorbents. Accordingly, the affinities of the PVP hydrogels for Zn(II), Cu(II), Pb(II), and Cd(II) ions were investigated by batch study at different pH values under competitive conditions, and the results are given in Figure 2. As shown in Figure 2, the adsorption behavior of these

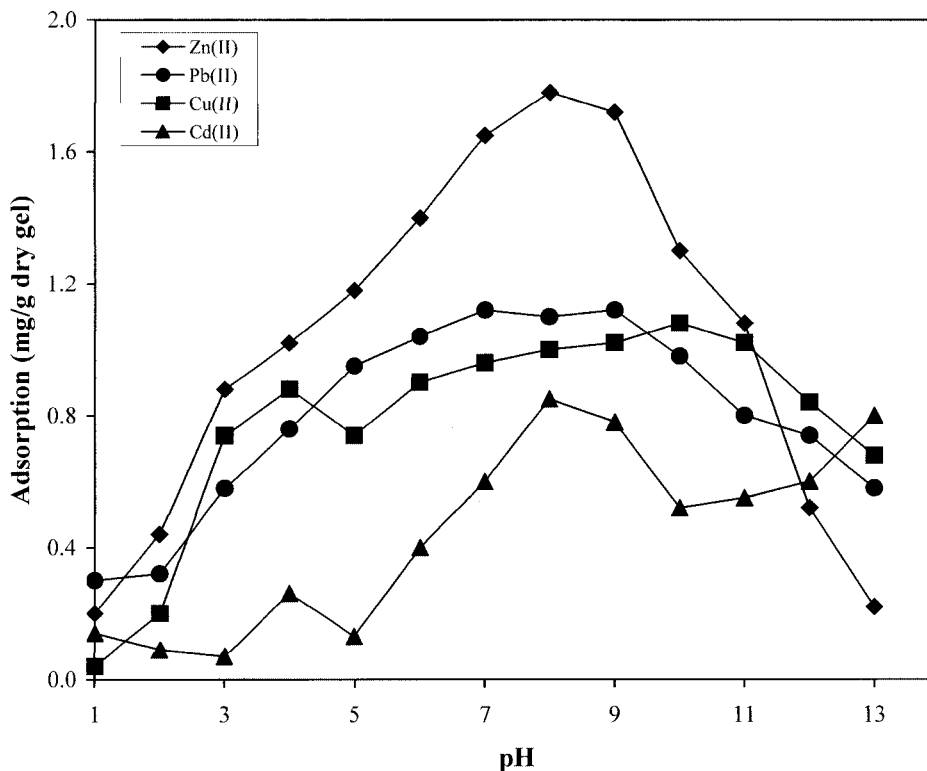


Figure 2 Effect of pH on the adsorption of Cu(II), Pb(II), Cd(II), and Zn(II) for the PVP hydrogels (initial solution = 7.5 mg of metal ions/L).

ions was especially less sensitive to pH changes in lower and higher pH regions. In highly acidic media (pH \approx 1–3) and in highly basic media (pH \approx 11–13), lower adsorption occurred compared to that around the neutral pH range. Several authors have observed the inhibition of metal chelation due to a decrease in pH in different adsorbents.^{14,15} Thus, it has been proposed that protons and metal ions compete for the same binding sites. As shown in Figure 2, the adsorption capacities increased with increasing pH, reaching maximum values at about pH 8, and then decreased. Similar results were also obtained with the P(VP/AA) hydrogels. The maximum adsorption of the metal ions onto the hydrogels may have been due to electrostatic interaction via the carbonyl groups of pure PVP and the acidic groups of the P(VP/AA) hydrogels. The maximum amounts of adsorbed ions on pure PVP at about pH 8 were 1.78 mg of Zn(II)/g of dry gel, 1.10 mg of Pb(II)/g of dry gel, 1.0 mg of Cu(II)/g of dry gel, and 0.85 mg of Cd(II)/g of dry gel. The maximum adsorption values of the P(VP/AA) hydrogels at the same pH were 1.60–0.94 mg of Zn(II)/g of dry gel, 1.08–0.59 mg of Pb(II)/g of dry gel, 1.24–0.35 mg of Cu(II)/g of dry gel, and 0.76–0.48 mg of Cd(II)/g of dry gel depending, on the AA content in the hydrogels. Whatever the pH, Zn(II) ions were always more adsorbed than were Pb(II), Cu(II), and Cd(II) ions for all of hydrogels, regardless of their composition. The

difference in adsorption values could be explained by the different affinity of the heavy metal ions for donor groups (i.e., carboxyl group) in the metal-chelating ligand.

Competitive adsorption

The Zn(II), Pb(II), Cu(II), and Cd(II) ion adsorption from aqueous solutions in a concentration range of 2.5–10 mg/L at about pH 8.0 via the pure PVP and P(VP/AA) hydrogels were determined under competitive conditions (simultaneous adsorption from solutions containing all of the metal ions), as described in the Experimental section and as illustrated in Figure 3 and Table I. The adsorption was affected by the initial metal concentration, as shown in Figure 3. When this concentration increased, the adsorption of metal ions via these hydrogels from solution increased strongly and then leveled off. This plateau corresponded to the saturation of the carbonyl and acidic groups. The metal ion adsorption values for the pure PVP were found in the range 0.74–2.00 mg of Zn(II)/g of dry gel, 0.54–1.90 mg of Pb(II)/g of dry gel, 0.34–1.34 mg of Cu(II)/g of dry gel, and 0.40–1.15 mg of Cd(II)/g of dry gel. The metal ions could 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

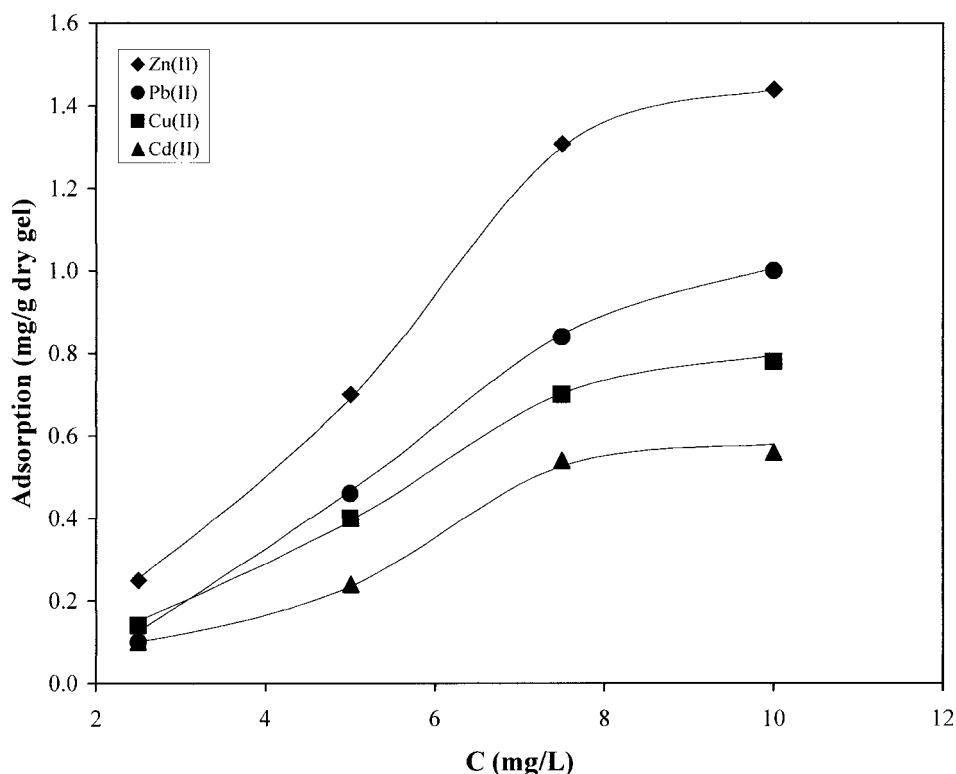


Figure 3 Effect of concentration of Cu(II), Pb(II), Cd(II), and Zn(II) on the adsorption capacities of P(VP/AA)-2 hydrogels.

exchange of electrons and the formation of a chemical bond between the metal ions and the PVP surfaces (especially with the carbonyl groups of the PVP chain). However, AA incorporation significantly decreased adsorption of these ions. The amounts of adsorbed ions on P(VP/AA) were found to be in the range 0.70–1.70 mg of Zn(II)/g of dry gel, 0.44–1.38 mg of Pb(II)/g of dry gel, 0.28–1.28 mg of Cu(II)/g of dry gel, and 0.29–0.96 mg of Cd(II)/g of dry gel for P(VP/AA)-1; 0.25–1.44 mg of Zn(II)/g of dry gel, 0.10–1.00 mg of Pb(II)/g of dry gel, 0.14–0.78 mg of Cu(II)/g of dry gel, and 0.10–0.72 mg of Cd(II)/g of dry gel for P(VP/AA)-2; and 0.16–1.17 mg of Zn(II)/g of dry gel, 0.09–0.98 mg of Pb(II)/g of dry gel, 0.12–0.42 mg of Cu(II)/g of dry gel, and 0.08–0.68 mg of Cd(II)/g of dry gel for P(VP/AA)-3 (Table I). The

observed affinity order was Zn(II) > Pb(II) > Cu(II) > Cd(II).

During the radiation-induced polymerization of VP with AA, the amount of carboxylic acid groups in the AA units may have decreased as a result of intramolecular and intermolecular anhydride formation. This behavior may have caused a decrease in the equilibrium degree of swelling and the degree of ionization of the P(VP/AA) hydrogels, depending on AA content. The degree of swelling of these hydrogels decreased with increasing AA content due to the decrement of average molecular weight between crosslinks.¹³ Therefore, the efficiency of diffusion of the metal ions could be prevented within the mesh size of these hydrogels. As a result, adsorption decreased with increasing AA content. Different poly-

TABLE I
Effect of Concentration on the Adsorption of Zn(II), Pb(II), Cu(II), and Cd(II) Ions for PVP and P(VP/AA) Hydrogels (mg of adsorbed/g of dry gel; pH \cong 8)

Initial concentration (mg/L)	PVP				P(VP/AA)-1				P(VP/AA)-2				P(VP/AA)-3			
	Zn(II)	Pb(II)	Cu(II)	Cd(II)	Zn(II)	Pb(II)	Cu(II)	Cd(II)	Zn(II)	Pb(II)	Cu(II)	Cd(II)	Zn(II)	Pb(II)	Cu(II)	Cd(II)
2.5	0.74	0.54	0.34	0.40	0.70	0.44	0.28	0.29	0.25	0.10	0.14	0.10	0.16	0.09	0.12	0.08
5.0	1.38	1.04	0.93	0.72	0.76	0.58	0.46	0.33	0.70	0.46	0.40	0.24	0.28	0.33	0.20	0.25
7.5	1.78	1.10	1.00	0.85	1.60	1.08	1.24	0.76	1.40	0.65	0.65	0.54	0.94	0.59	0.35	0.48
10.0	2.00	1.90	1.34	1.15	1.70	1.38	1.28	0.96	1.44	1.00	0.78	0.56	1.17	0.98	0.42	0.68

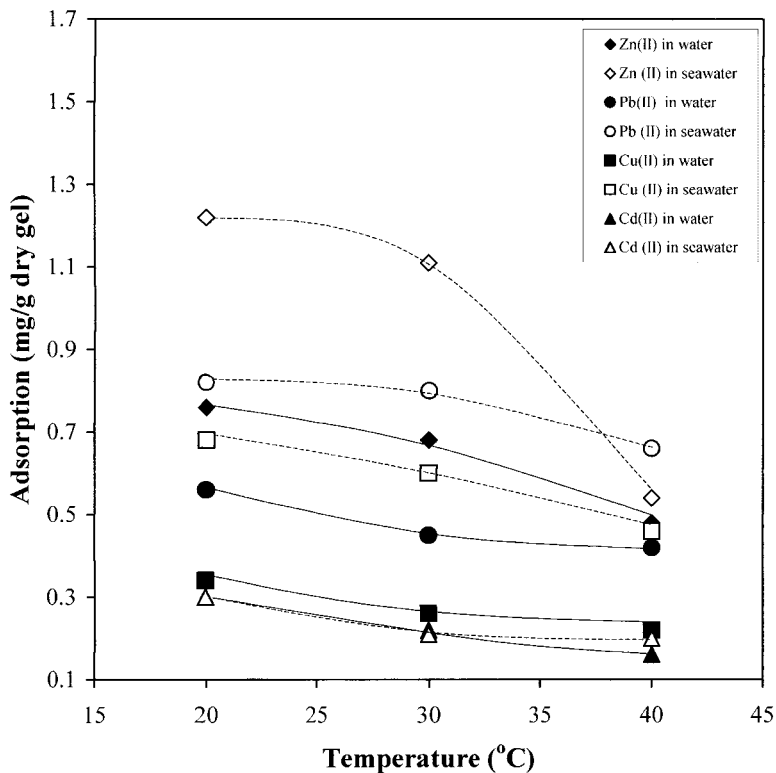


Figure 4 Variation with temperature of adsorbed Cu(II), Pb(II), Cd(II), and Zn(II) ions on PVP hydrogels from water and synthetic seawater (0.55M NaCl and 3 mM NaHCO₃).

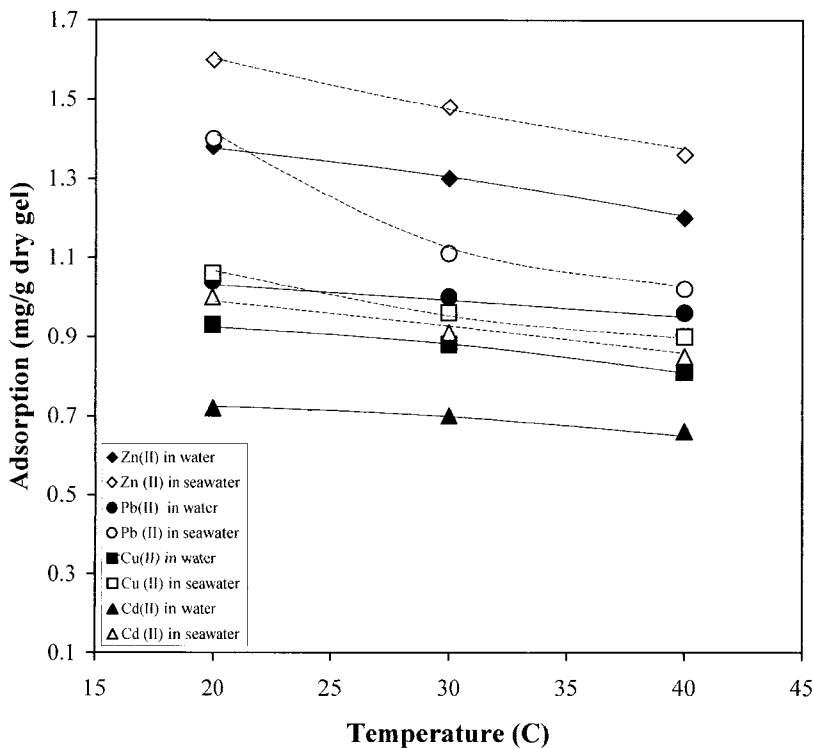


Figure 5 Variation with temperature of adsorbed Cu(II), Pb(II), Cd(II), and Zn(II) ions on P(VP/AA)-1 hydrogels from water and synthetic seawater (0.55M NaCl and 3 mM NaHCO₃).

meric adsorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Roozmond et al.¹⁶ showed 40 mg of Cd(II)/g and 32 mg of Cu(II)/g with pyrazole-containing poly(styrene-divinylbenzene) adsorbents. Denizli et al.¹⁷ used Alkali Blue 6B-attached poly(ethylene glycol dimethacrylate-2-hydroxyethyl methacrylate) [P(EGDMA-HEMA)] adsorbents, in which the maximum adsorption capacities were 2.3 mg of Cu(II)/g, 5.52 mg of Cd(II)/g, and 128 mg of Pb(II)/g. Because analytical tools used in many works usually include spectrophotometric techniques, the concentration of synthetic solution containing the mentioned ions had higher values than in this study. With the polarographing technique, trace quantities of heavy metals could be determined in real samples without preconcentration.

Effect of ionic strength and temperature

The effect of temperature and ionic strength on the adsorption capacities of the hydrogels at 20, 30, and 40°C (with thermostatic control) in water and synthetic seawater (0.55M NaCl and 3 mM NaHCO₃) solution were investigated, and the results obtained for Zn(II), Pb(II), Cu(II), and Cd(II) ions are shown in Figure 4 for PVP and in Figure 5 for P(VP/AA)-1. As shown in these figures, with the comparison of adsorbed Zn(II), Pb(II), Cu(II), and Cd(II) ions, we observed that the ionic strength or Na⁺ ions had a more pronounced effect on the adsorption properties of the hydrogels. An increase in the ionic strength generally decreases the swelling because the difference in concentration of mobile ions between the gel and solution is reduced with a decrease in the osmotic swelling

pressure of the ions inside the gels. Because of a decrease in swelling and the collapsing of the chains in the gel system, the possible interactions between Zn(II), Pb(II), Cu(II), and Cd(II) ions and the polymer chain increased. An increase of temperature from 20 to 40°C caused a decrease in the amount of adsorbed Zn(II), Pb(II), Cu(II), and Cd(II) ions. Because the adsorption decreased with temperature, the temperature-dependence studies also revealed that the observed phenomenon had an adsorption nature.

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