

Poly(*N*-vinylpyrrolidone-co-2-acrylamido-2-methylpropanesulfonate sodium): Synthesis, Characterization, and its Potential Application for the Removal of Metal Ions from Aqueous Solution

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ABSTRACT: In the current study, poly(*N*-vinylpyrrolidone-co-2-acrylamido-2-methylpropanesulfonate sodium), poly(VP-co-AMPS), was prepared and used for the removal of Cu^{2+} , Cd^{2+} , and Ni^{2+} ions via a polymer-enhanced ultrafiltration (PEUF) technique. The copolymer was synthesized by radical polymerization in an aqueous medium with a comonomer feed composition of 50:50 mol %. The molecular structure of the copolymer was elucidated by ATR-FTIR and ^1H NMR spectroscopy, and the average molecular weight was obtained by GPC. The copolymer composition was determined to be 0.42 for VP and 0.58 for AMPS by ^1H NMR spectroscopy. The copolymer and homopolymers exhibited different retention properties for the metal ions. PAMPS exhibited a high retention capacity for all of the metal ions at both pH values studied. PVP exhibited selectivity for nickel ions. Poly(VP-co-AMPS) exhibited a lower retention capacity compared to PAMPS. However, for poly(VP-co-AMPS), selectivity for nickel ions was observed, and the retention of copper and cadmium ions increased compared to PVP. The homopolymer mixture containing PAMPS and PVP was inefficient for the retention of the studied metal ions. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41272.

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INTRODUCTION

Over the years, industrial development has caused increased levels of heavy metals in the environment, which affect the food chain and, ultimately, human health.¹ Heavy metal ions are detected in the industrial wastewater generated from mining activities, petroleum refining, battery manufacture, paint production, and photographic industries.² Most of the industrial effluents contain more than one toxic metal. For example, effluents produced at a copper mine contain a high level of Cu^{2+} and traces of Cd^{2+} , Ni^{2+} , and Mn^{2+} .³ The removal of heavy metal ions from aqueous solutions is one of the main topics of current interest for wastewater treatment. The materials and technology currently available to clean effluent are not completely efficient. Therefore, it is necessary to continue the search for improved methods and materials.

Polymer enhanced ultrafiltration (PEUF) is a relatively low-pressure membrane filtration process used for the retention of trace metals as well as their enrichment and removal from dilute aqueous solutions.^{4–9} Many researchers have shown great interest in this relatively new technique due to the strict regulations for improving water quality, low cost, simplicity of installation, and

higher efficiency compared to conventional treatment processes, such as chemical precipitation, coagulation and flocculation, electrochemical treatment, ion-exchange, and adsorption.^{10–15} PEUF involves two steps including binding of a water-soluble polymer to a metal ion followed by the retention of the metal–polymer complex on the membrane. The pore size of ultrafiltration (UF) membranes must be less than the size of the polymer molecules and the metal–polymer complexes regardless of the type of conformational changes that these materials might undergo under different conditions, such as pH, ionic strength, and temperature.^{16–18}

The interactions between functional groups on the polymer and the metal ions in solution can result in the formation of a coordinate bond or ionic bond. However, weaker interactions can also occur (e.g., trapping of metal ions in the polymeric bulk).^{19,20} The factors that influence the polymer–metal ion interaction can be divided into two groups (i.e., those that depend on the polymer and those do not depend on it). The first group includes the nature of the functional groups attached to the backbone, molecular weight, polydispersity, structure, and copolymer composition, distance separation between functional groups and backbone, and degree of branching. The

second group includes the pH and ionic strength of the medium, nature and charge of the metal ion, nature of the counter ion of the metal ion, and temperature.^{19,21} Metal ion chelation polymers, which are known as polychelators, contain one or more electron donor atoms, such as N, S, O, and P, that can form coordinate bonds with most of the toxic heavy metals.²²

The use of poly(2-acrylamido-2-methylpropanesulfonate sodium) (PAMPS) in the PEUF technique for removal of heavy metal ions from water has been reported, and the results indicated significantly high retention percentages for various metal ions.^{23–26} Despite these good results, the regeneration of the polymer retention capacity after several cycles of metal ion “charge–discharge” and the selectivity to a cationic specie in mixtures of different metal ions (competitive conditions) can be improved. One method for improving these results involves the copolymerization of AMPS with a nonionic monomer that exhibits a higher tendency to form coordination bonds with one of several metal ions in a mixture, which would also reduce the number of ionic bonds between the metal ions and the copolymer compared to PAMPS. With a lower number of ionic polymer-metal bonds, polymer regeneration via a washing method in the PEUF technique would require an eluent with a lower acid concentration to remove the metal, which would potentially increase the lifetime of the polymer and the UF membrane.²⁷

In this article, the interactions among copolymer poly(VP-co-AMPS) and Cu^{2+} , Cd^{2+} , and Ni^{2+} were studied for the first time using a washing method in the PEUF technique. The interaction of these ions with PAMPS, PVP and a blend of both homopolymers with the same functional group molar ratio as in poly(VP-co-AMPS) were also analyzed.

EXPERIMENTAL

Materials

AMPS was prepared by neutralizing 2-acrylamido-2-methylpropane sulfonic acid (>99%, Sigma) with 1M NaOH (Merck) in an aqueous solution, and VP (99%, Sigma) was distilled under reduced pressure. The following reagents were used as received from suppliers without any further treatment: potassium persulfate (KPS, >99%, Sigma), MBA (>99%, Sigma), poly(vinylpyrrolidone) solution (PVP K60, 51% in H_2O , 160 kDa, Fluka), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99%, Merck), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (>99%, Merck) and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (>99%, JT Baker). D_2O (Aldrich, 98%) was used to prepare the solutions for ^1H NMR analyses. Aqueous solutions of HNO_3 and NaOH (0.1M, Merck) were prepared. A stirred cell ultrafiltration system (Amicon) and regenerated cellulose membranes (Millipore) of different MWCO (molecular weight cut-off) were used for diafiltration experiments.

Synthesis of Polymers

The linear copolymer poly(VP-co-AMPS) was synthesized by free radical polymerization in aqueous media with an equimolar composition of monomers in the feed, and their total concentration was 0.175 M (2.5 wt %). The monomer mixture, which was in a 250 mL borosilicate bottle (with PTFE screw cap), was deoxygenated by bubbling with nitrogen gas for 10 min, and

then, 1 mol % of KPS was added as a radical initiator. The reagent mixture was maintained at 60°C for 24 h without stirring. Next, the product was diluted in water, purified and fractionated by diafiltration using a stirred cell ultrafiltration system with regenerated cellulose membranes of MWCO of 30 and 10 kDa. Then, the >30 and >10 kDa fractions were lyophilized and dried under vacuum to a constant mass. The yield of the copolymer with respect to both fractions was determined gravimetrically. The PAMPS homopolymer was obtained with the same procedure used to obtain the copolymer.

Characterization of Polymers

Spectroscopic Characterization. The copolymer was dissolved in D_2O at a concentration of 10 mg mL^{-1} , and the ^1H NMR spectra was acquired using a Mercury 400-BB spectrometer operating at a frequency of 400 MHz. The composition of each monomer in the copolymer was calculated based on the analysis of its spectrum. The spectrum was normalized and integrated using the MestReNova program (version 6.0.2). The infrared spectra of the copolymer and homopolymer (PAMPS) were obtained on a Spectrum One (Perkin-Elmer) spectrometer using the attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) method. The spectra were recorded with 32 scans at a resolution of 4 cm^{-1} .

Gel Permeation Chromatography (GPC). The number (M_n) and weight (M_w) average molecular weight and the polydispersity index (M_w/M_n) of the synthesized polymers poly(VP-co-AMPS) and PAMPS (fractions of >30 kDa separated by diafiltration), as well as of the commercial polymer PVP K60 (without previous fractionation) were obtained via GPC using a liquid chromatograph (HPLC) Perkin Elmer Series 200 equipped with a Flexar® refractive index detector, Flexar® isocratic pump and a PL aquagel-OH MIXED-H column (Polymer Laboratories). A mobile phase consisting of 0.2M NaNO_3 and 0.01M NaH_2PO_4 buffer at pH 9 was used. The flow rate was maintained at 0.5 mL min^{-1} . The samples were dissolved in the same mobile phase mentioned above prior to injection. The molecular weight was determined based on the calibration curve obtained from monodisperse polyethyleneglycol (PEG) standard samples, which possessed a molecular weight between 232 and 263 000 g mol^{-1} (molar mass at the peak maximum).

Polymer-Enhanced Ultrafiltration

The heavy metal ion retention capacity of the polymers was evaluated using the PEUF washing method. Prior to the experiment, an aqueous solution containing cadmium, nickel, and copper nitrates (i.e., 6 mM of each individual metal ion (18 mM of total metal ions)) was prepared. Then, 10 mL of a metal ion solution along with 10 mL of a 40 mM polymer aqueous solution (concentration with respect to repeat unit; polymer fraction of >30 kDa) were placed into the UF cell. The molar ratio between the repeat unit of the polymer and each individual metal ion was 6.7/1, and with respect to total metal ions, the molar ratio was 2.2/1.

The ultrafiltration was performed with a regenerated cellulose membrane of MWCO of 10 kDa under a total pressure of 3.5 bar and powerful stirring while maintaining a constant total cell volume, which was achieved by passing water at a specific pH

from the reservoir through the UF cell containing the polymer-metal ion solution.

Permeate fractions (15 mL) were collected up to a total volume of 165 mL, and their metal ion concentrations were analyzed by atomic absorption spectroscopy (Unicam Solaar M5).

The experiments were performed with polymer-metal ion solutions at pH 3.2 and 5.7. The water contained in the reservoir was adjusted to the same pH value as in the UF cell solution. 0.1M HNO₃ or 0.1M NaOH was used to adjust the pH of the solutions. PAMPS, PVP, poly(VP-co-AMPS) and a blend of both homopolymers with the same functional group molar ratio (sulfonate and pyrrolidone) as in poly(VP-co-AMPS) were evaluated. An experimental blank was evaluated prior to each diafiltration experiment. These blank runs consisted of the filtration of the metal ion solution at the same experimental conditions but in the absence of the polymer. A description of the filtration system has been previously reported.²⁸

To determine the retention capacity of the metal ions in the solution, the (1) retention (*R*) and (2) filtration factor (*F*) need to be defined.

Retention is the fraction of metal ions remaining in the cell according to the expression:

$$R = [M_{\text{cell}}]/[M_{\text{init}}] \quad (1)$$

where $[M_{\text{cell}}]$ corresponds to the absolute quantity of metal ions that are retained in the cell and $[M_{\text{init}}]$ is the absolute quantity of metal ions in the feed.

The filtration factor (*F*) is the ratio between the total volume of permeates (V_p) and the volume of retentate (V_{cell}):

$$F = V_p/V_{\text{cell}} \quad (2)$$

Depending on the experimental data, a graph (retention profile) where *R* is plotted as a function of *F* can be drawn.

RESULTS AND DISCUSSION

Characterization of Polymers

The polymers poly(VP-co-AMPS) and PAMPS were obtained as white solids that appeared as finely divided flakes, which were highly soluble in water, and their reaction yields were 81 and 85%, respectively.

To determine the approximate composition of each monomer in the poly(VP-co-AMPS) copolymer, it was analyzed using solution-phase ¹H NMR spectroscopy. Figure 1 shows the ¹H NMR spectrum of the poly(VP-co-AMPS) copolymer. Two signal regions can be observed, which were identified as Regions 1 and 2. This spectrum confirms the polymerization of the comonomers and the absence of residual free monomers because the vinyl signals were not observed between 5.5 and 6.5 ppm.²⁹

Region 1 is located in the high field of the NMR spectrum between 1.0 and 3.0 ppm. In addition, Region 1 has a diverse origin that includes the protons of the polymer backbone (signals A1, A2, V1) with the exception of those belonging to the CH groups attached to the pyrrolidone ring (signal V2). The methylene groups that are more protected inside the pyrrolidone ring (signals V3, V4) and the geminal methyl groups of

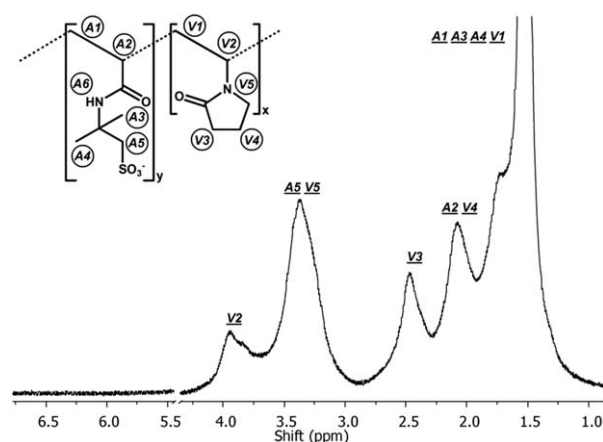


Figure 1. ¹H NMR spectrum of the poly(VP-co-AMPS) copolymer.

the AMPS monomer residue (signals A3, A4) also contribute to the signal of Region 1.

Region 2, which is located between 3.0 and 4.2 ppm, is generated by the CH₂ and CH groups that are attached to the nitrogen of the pyrrolidone ring (V5, V2) and by the methylene group next to the sulfonate of the polymerized AMPS (A5). The broad and intense signal due to the solvent (D₂O/H₂O) was observed between 4.4 and 5.4 ppm, and it has been deleted for clarity. The amidic protons were not detected in the ¹H NMR spectrum of the copolymer due to the complete exchange of protons of the amidic groups with deuterated water.

Based on the previous assignments of the proton groups in Regions 1 and 2 to the molecular structure of the copolymer, equations were formulated to calculate the monomer composition as a function of the area of the signals in these regions. The areas of Regions 1 and 2 were normalized and integrated using the MestReNova program (Version 6.0.2). The values of the integrals were replaced in the respective composition equations, and the calculations produced the monomer molar fractions (cumulative) in the copolymer. The formulated composition equations are:

$$[\text{VP}] = \frac{V}{A+V} \quad (3)$$

$$[\text{AMPS}] = \frac{A}{A+V} \quad (4)$$

$$V = \frac{(I_{R1}) - 9A}{6} \quad (5)$$

$$A = \frac{(I_{R2}) - 3V}{2} \quad (6)$$

where [VP] and [AMPS] are the molar fractions of VP and AMPS in the copolymer, respectively. “V” is the value of the integral of a proton originating from all of the VP residues in the copolymer, and “A” is the value of the integral of a proton originating from all of the AMPS residues in the copolymer. “*I_{R1}*” is the value of the integral of Region 1, and “*I_{R2}*” is the value of the integral of Region 2.

The results of the composition calculations for poly(VP-co-AMPS) resulted in monomer mole fractions of 0.42 for VP and

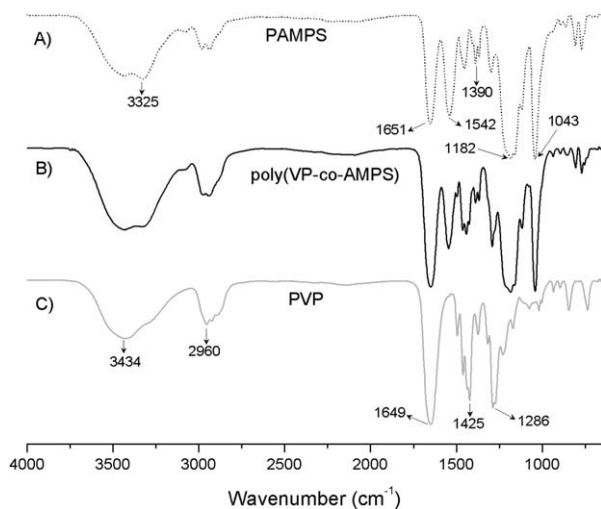


Figure 2. ATR-FTIR spectra of (A) PAMPS, (B) poly(VP-co-AMPS) and (C) PVP.

0.58 for AMPS. In addition, according to a recent study, the monomers of the poly(VP-co-AMPS) system have reactivity ratios less than unity ($r_{VP} = 0.15$ and $r_{AMPS} = 0.22$), under identical synthesis conditions to those used in the present study.³⁰ Therefore, the microstructure of this copolymer is characterized by an moderately alternating sequence of monomer units of VP and AMPS.

The IR spectra of all of the samples exhibited characteristic bands of the expected functional groups [see Figure 2(A–C)] and the absence of vinyl signals ($\nu_{C=C}$ to $1635\text{--}1620\text{ cm}^{-1}$).³¹ This result is evidence of the polymerization of the monomers and the purity of the obtained product. The PVP homopolymer [see Figure 2(C)] exhibited signals corresponding to C–N stretching between the pyrrolidone ring and the polymer backbone (1286 cm^{-1}), the stretching of the C=N partial double bond in the pyrrolidone ring (1425 cm^{-1}), C=O stretching of the carbonyl group (1649 cm^{-1}), C–H asymmetric stretching of CH_2 (2960 cm^{-1}) and the stretching vibration of the hydroxyl groups (3434 cm^{-1}), which is generated by the absorbed atmospheric water due to its highly hygroscopic properties.^{32–34} For the PAMPS homopolymer [see Figure 2(A)], the characteristic signals that were observed corresponded to N–H stretching of amine groups (3325 cm^{-1}), C=O stretching of the primary amide (1651 cm^{-1}), C–N and CNH bending of amine groups (1542 cm^{-1}), bending of the gem-dimethyl groups (1390 cm^{-1}), O=S=O asymmetric stretching (1182 cm^{-1}) and O=S=O symmetric stretching (1043 cm^{-1}) of sulfonate groups. Finally, as shown in Figure 2(B), the IR spectrum of poly(VP-co-AMPS) contains signals that are very similar to those from both homopolymers.

According to the GPC experiments (see Table I) performed on the fractions of poly(VP-co-AMPS) and PAMPS retained by the 30 kDa (MWCO) membrane, the M_w value of the copolymer was higher than that of PAMPS. Additionally, the yields of the copolymer and PAMPS with respect to their fractions of >30 kDa were 34 and 4%, respectively. These results are in good agreement with of Kurenkov et al.³⁵ who reported the

dependence of M_w of the copolymers poly(VP-co-AMPS) as a function of the molar composition of AMPS in the initial monomer mixture, during copolymerization of AMPS with VP. This dependence pass through maximum at the equimolar ratio of the monomers in the starting mixture ([AMPS] : [VP] = 50 : 50). The maximum in the dependence is caused by the donor-acceptor character of the reaction of AMPS with VP; AMPS shows a medium electron-acceptor power, and VP, a medium electron-donor power.

Metal-ion Retention Capacity

In this study, we studied the retention capacity for divalent metal ions (Cu^{2+} , Ni^{2+} , and Cd^{2+}) using PAMPS, PVP, poly(VP-co-AMPS) and a blend of PVP and PAMPS at a pH of 3.2 and 5.7. These polymers have different interactions with the metal ions.

PAMPS is a strong polyelectrolyte, which is dissociated in water. This homopolymer exhibited the highest retention capacity (around of 60%) of the three metal cations at both pH values studied (see Figure 3). This behavior is mainly attributed to the electrostatic interaction of metal ions with sulfonate groups,²⁵ which are easily accessible to all ions because of their external position (separated between 9 and 10 \AA) on the helical structure of PAMPS. This structure is caused by the presence of an asymmetric center at the central carbon of acrylamides units leading to the formation of hydrogen bonds between units with the same conformation.³⁶ Moreover, the electrostatic repulsion between the sulfonate groups (in aqueous medium) avoids the folding of the linear polymers with AMPS groups in its structure, further contributing to the accessibility of the metal ions.³⁷

The metal ion retention capacity of PAMPS was almost the same at both pHs (3.2 and 5.7), which means that the hydrogen ions do not compete with the metal ions in this pH range. This acid-base behavior of PAMPS in the pH range studied is consistent with the $pK_a \approx 1.5$ reported in the literature for sulfonic acid group.³⁸ In both pHs, the retention curve decreases slowly as a function of F , which indicates that it is possible to weaken the electrostatic interaction between the polymer and metal ion.

On the other hand, PVP exhibited a different behavior towards the metal ions compared to PAMPS. Figure 4 shows the retention profiles using the polychelator PVP. This polymer has an electron donor amide group that acts as a ligand for complexing metal ion.¹⁹

The absence of ionizable functional groups in the PVP allows higher folding of these macromolecules (in aqueous medium) and therefore, the accessibility of the PVP amide groups to metal ions (during the “polymer–metal ion” complex formation) is less

Table I. GPC Results for PAMPS, PVP, and Poly(VP-co-AMPS) (42 : 58)

	GPC		
	M_w	M_n	M_w/M_n
Poly(VP-co-AMPS) (42:58)	106,040	83,453	1.271
PAMPS	99,398	54,688	1.818
PVP	146,231	54,421	2.687

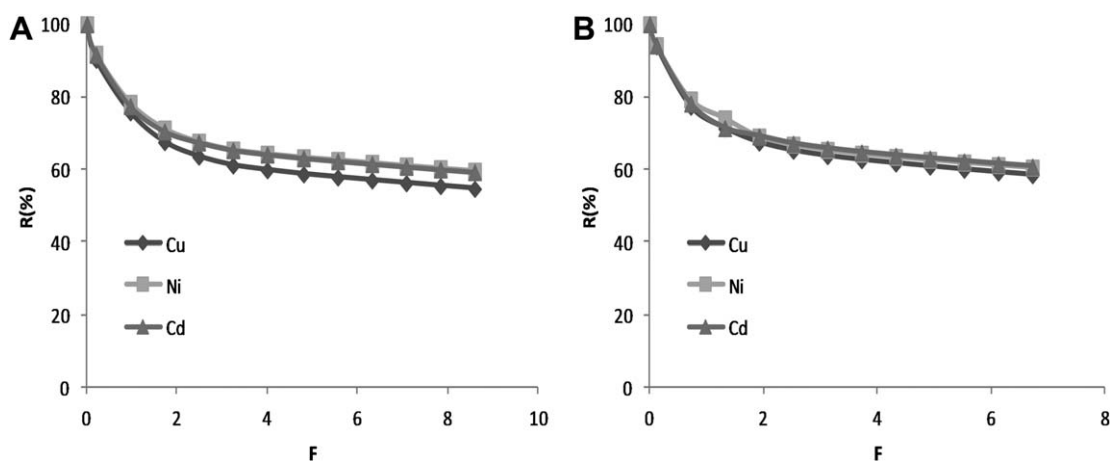


Figure 3. Metal retention profile using PAMPS at (A) pH 3.2 and (B) pH 5.7.

than the accessibility of the PAMPS sulfonate groups to these same ions. It is also likely that a single metal ion is coordinated with more than one amide group within each macromolecule of PVP, whereas each sulfonate group of a PAMPS macromolecule coordinates a single metal ion. Previous hypotheses explain the lower retention percentages of the (three) metal ions generated by PVP compared with PAMPS.

The retention profiles of PVP exhibited a different shape compared to PAMPS. For PVP, the retention curve decreases to a value of F at ~ 4 , and then, it remains constant. This result is due to the chelating interaction between PVP and nickel ions being stronger than the electrostatic interaction with PAMPS. Therefore, the nickel ions are strongly retained by the ultrafiltration cell.

The results of PVP indicated that selective retention for Ni^{2+} was achieved compared to null retention of Cu^{2+} and Cd^{2+} at both pH values. The nickel ion selective coordination with PVP suggests a more adaptable macromolecular conformation of PVP to nickel ions in the coordination sites, probably because of its smaller ionic radius compared to Cd^{2+} and Cu^{2+} .³⁹

In addition, the retention of nickel ions was higher at a pH of 5.7 compared to a pH of 3.2, which is most likely due to the amide being protonated at a more acidic pH causing metal repulsion and lower retention. Other research has shown that protonation of PVP in acidic aqueous medium occurs mainly

in oxygen (not on nitrogen) of amide group, providing a positive charge to the polymer. The estimated $\text{p}K_a \approx 2\text{--}3$ indicates that $\sim 17\%$ of pyrrolidone groups are protonated at pH 3.2, while almost none is protonated at pH 5.7.^{40–43} Furthermore, the oxygen in the pyrrolidone group also participates in the formation of coordination bonds with divalent transition metals (M^{2+}), and at $\text{pH} < 4$ the hydrogen ions compete with the metal ions, avoiding the interaction between the last ions and the PVP carbonyl oxygens.⁴⁰ This explains the lower percentage retention of nickel ions at pH 3.2 than at pH 5.7.

Figure 5 shows the retention profile of poly(VP-co-AMPS). The copolymer exhibited a different binding capacity compared to the PAMPS and PVP homopolymers. In comparison to PAMPS, the copolymer exhibited a decreased retention capacity for all of the ions at both pH values. The lower molar fraction of sulfonate groups in the copolymer compared to PAMPS (58% vs. 100%) could be the cause of the decreasing retention, but evidently this reduction was not directly proportional to the mole fraction of sulfonate groups, because the values obtained were similar to those of PAMPS with only 17, 15, and 4% less retention of Cu^{2+} , Cd^{2+} , and Ni^{2+} , respectively (at pH 5.7 and $F = 7$). This means, that in the case of the copolymer may coexist electrostatic and coordination interactions between the monomer units (VP and AMPS) and the three metal ions. The combined effect of the electrostatic and coordination interactions on the retention of the

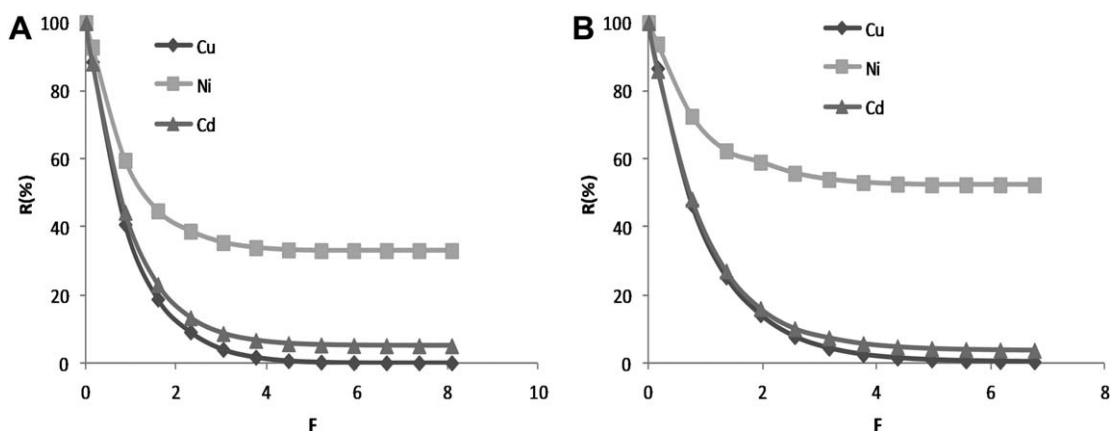


Figure 4. Metal retention profile using PVP at (A) pH 3.2 and (B) pH 5.7.

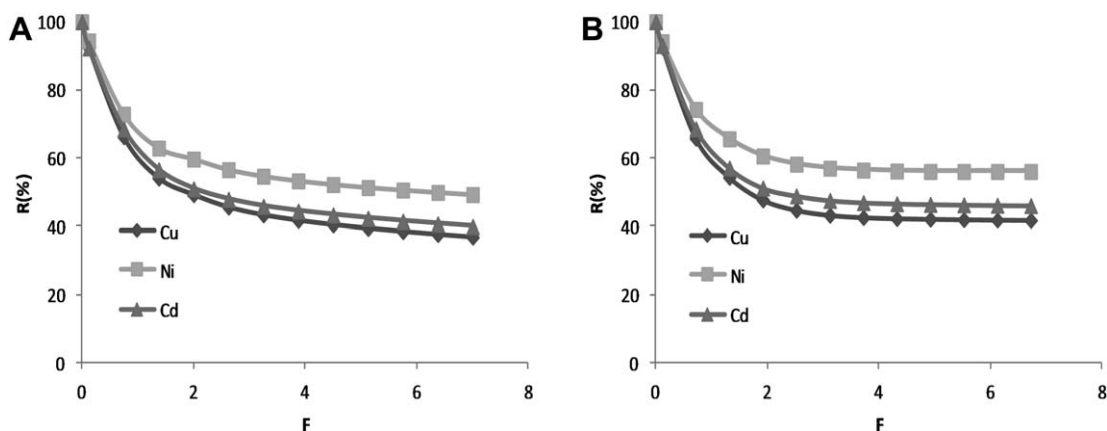


Figure 5. Metal retention profile using poly(VP-co-AMPS) at (A) pH 3.2 and (B) pH 5.7.

metal ions is greater than the sum of the individual effects of these interactions. The synergistic interactions can be caused by the random distribution of comonomers (VP and AMPS) in the copolymer, which tends to alternation (azeotropic system) according to their reactivity ratios previously determined ($r_{VP} = 0.15$ and $r_{AMPS} = 0.22$).³⁰ As a consequence of the absence of AMPS-rich sequences in the copolymer main chain, its macromolecular structure does not assume a helical conformation as the PAMPS (as mentioned above) and instead, it is likely that other types of conformations produce a more flexible backbone and higher availability of $-\text{CONH}-$ groups to form coordinate bonds with ions.

On the other hand, the copolymer exhibited slight selectivity for nickel ions due to the presence of VP monomer units. In comparison to PVP, the copolymer exhibited a higher retention of copper and cadmium ions due to the AMPS groups, which are able to exchange cations. It is also possible to observe differences in the retention profiles of the copolymer at different pH values. At a pH of 3.2, the retention curve decays slowly similar to PAMPS. However, at pH 5.7, the retention curve remains constant from F near to 4. This result indicates that the VP groups are activated as a complexing agent at a pH higher resulting in strong interactions.

Figure 6 shows the retention profile of metal ions using a blend of both PAMPS and PVP homopolymers. The results clearly

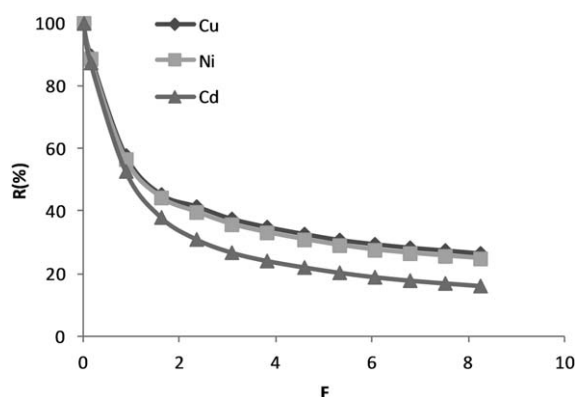


Figure 6. Metal retention profile using a blend of homopolymers PAMPS and PVP at pH 5.7.

indicate a lower retention of all of the metal ions resulting in an inefficient system. In the blend of PAMPS and PVP, the electrostatic repulsion between macromolecules PAMPS probably promotes the formation of hydrogen bonds between the carbonyl groups of PVP and secondary amino groups of PAMPS. This favors the steric shielding of charged groups on the PAMPS, the occlusion of a high proportion of these groups in the PAMPS-PVP interpolymer complex, and the decrease of available carbonyl groups to coordinate metal ions. On the other hand, the copolymer macromolecules probably tend to form less hydrogen bonds between them, compared to hydrogen bonds formed between the PAMPS and PVP chains in the blend of the two homopolymers, due to the electrostatic repulsion caused by the presence of the sulfonate groups distributed almost alternately along the macromolecular copolymer structure.³⁰ As a result of the above, the metal ions retention capacity of the blend PAMPS: PVP was lower than that of the copolymer. Therefore, this result demonstrates the efficient use of the copolymer compared to the mixture of the two homopolymers under the same conditions.

Finally, it is important to highlight the potential use of poly(VP-co-AMPS) (42:58) copolymer in the removal of copper, cadmium, and nickel ions from aqueous media. This copolymer provides similar results to those obtained by PAMPS but with a lower charge density (due to the relative decrease of sulfonate groups), which simultaneously implies the decrease in the number of ionic polymer-metal (II) bonds and the increase in the number of coordination polymer-metal (II) bonds. These properties could allow that “poly(VP-co-AMPS)/metal ions” complex can be washed with eluents of low concentration of acid, instead of the eluents of high concentration of acid usually used during the polymer regeneration process via the washing method in the PEUF technique. This may provide the additional benefit of increasing the lifetime of the copolymer and of the ultrafiltration membrane, compared to the use of the PAMPS.

CONCLUSIONS

In the current study, poly(VP-co-AMPS) was synthesized, characterized, and its metal ion retention capacity was analyzed and compared to their homopolymers (i.e., PAMPS and PVP) and a blend of both homopolymers.

The copolymer was prepared by free radical polymerization in aqueous media with a comonomer feed composition of 50 : 50 mol %. The copolymer was characterized by ^1H NMR spectroscopy, which confirmed the presence of both monomeric units in the copolymer.

The retention of metal ions by the copolymer and homopolymers varied. PAMPS exhibited a high retention capacity of all of the metal ions at both pH values studied. PVP exhibited selectivity for nickel ions. The copolymer exhibited a lower retention capacity compared to PAMPS. However, for the copolymer, selectivity toward nickel ions was observed, and the retention of copper and cadmium ions increased compared to PVP. The mixture of homopolymers (i.e., PAMPS and PVP) was inefficient for the retention of the studied metal ions.

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