

Removal of metal ions from aqueous effluents involving new thermosensitive polymeric sorbent

A. Graillet, S. Djenadi, C. Faur, D. Bouyer, S. Monge and J. J. Robin

ABSTRACT

In this work, new thermosensitive copolymers bearing phosphonated groups were synthesized and used to remove metal pollution. Sorption properties are brought by hydrolyzed (dimethoxyphosphoryl)methyl 2-methylacrylate (r_1 MAPC1) monomer. *N-n*-propylacrylamide (NnPAAm) led to the thermoresponsive properties of the copolymers. Low lower critical solution temperature (LCST) values were observed, ranging between 20 and 25 °C depending on the molar ratio of each monomer in the copolymer. Sorption properties of these copolymers towards nickel ions were evaluated for increasing temperatures (10–40 °C), Ni ion concentrations of 20 mg L⁻¹ and pH values between 3 and 7. Best results were observed for temperatures just lower than the LCST (20 °C), when the copolymer was fully soluble in water solution. For temperature higher than the LCST, phosphonic diacid groups accessibility was considerably reduced by the precipitation of the thermosensitive part of the copolymer leading to lower sorption properties. In these conditions, the highest Ni removal by the copolymer was observed for pH = 7, when there was almost no competition between the sorption of H⁺ and Ni²⁺ ions on the phosphonic acid groups. These optimal conditions enabled removal of about 70% of the nickel in the synthetic effluent.

Key words | metallic pollution, phosphonic acid, sorption, thermosensitive polymers

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INTRODUCTION

Several techniques are known to reduce heavy metal content in wastewater. Among them, lime precipitation, ion-exchange and electrolytic methods are currently used (Dean *et al.* 1972; Fu & Wang 2011). However, such techniques can bring environmental problems and do not always allow a full elimination of the metallic pollution. Sorption techniques appear to be an economical alternative method for removing traces of metals from water and avoiding the generation of high sludge volumes. Among all sorption processes described in the literature, polymer enhanced ultrafiltration (PEUF) consists of coupling the sorption of metal ions on high molecular weight polymers with a metal-polymer separation step by ultrafiltration (Palencia *et al.* 2009; Rivas *et al.* 2009; Zamariotto *et al.* 2010). Nevertheless, this ultrafiltration step is energy-consuming and several authors are interested in developing enhanced metal ion separation techniques that require less energy. An interesting possibility is the use of thermosensitive polymers as sorbents (Nonaka *et al.* 2004, 2006; Tokuyama *et al.* 2006, 2010) which allow the use of lower-

cost separation techniques like centrifugation (Nonaka *et al.* 2004), microfiltration or sedimentation (Tokuyama *et al.* 2010). For such application, *N-iso*-propylacrylamide (NiPAM) appears to be the most used monomer to reach thermosensitive properties (Nonaka *et al.* 2004, 2006; Tokuyama *et al.* 2006, 2010; Takeshita *et al.* 2006, 2007) and lead to a lower critical solution temperature (LCST) around 32 °C. To reach sorption properties, a wide range of active groups such as imine (Zamariotto *et al.* 2010), amide (Rivas & Maureira 2008), carboxylic acid (Canizares *et al.* 2005), sulphonic acid (Rivas *et al.* 2000, 2001), phosphinic acid (Nonaka *et al.* 2004, 2006) and phosphonic acid groups (Tokuyama *et al.* 2006) can be used. Among all of them, monomers bearing phosphinic acid and phosphonic acid groups were copolymerized with NiPAM and were reported to bring sorption capacity towards metal ions as well as thermosensitive properties (Nonaka *et al.* 2004, 2006; Tokuyama *et al.* 2006). Nevertheless, the LCST values of all the NiPAM based polymeric sorbents are higher than 32 °C.

This work focuses on a new thermosensitive sorbent showing LCST values close to room temperature. Such thermal properties can be reached using poly(*N-n*-propylacrylamide) (p(*Nn*PAAm)) as acrylamide moiety. Copolymer LCST values close to 25 °C are thus reachable, reducing the process temperature by 10 °C. Sorption properties are brought by the phosphonic acid groups of hydrolyzed-(dimethoxyphosphoryl)methyl 2-methylacrylate (*n*-MAPC1) monomer. Synthesis of new thermosensitive copolymers bearing different molar ratio of phosphonic acid groups is described in this paper. Thermal sensitivity of these copolymers was characterized to ensure the relevance of such copolymers to reduce the energy-consumption of the process. Moreover, sorption experiments carried on 20 mg L⁻¹ nickel ions concentration effluents proved the efficiency of these copolymers to treat wastewater containing metallic pollution. Sorption was evaluated for temperatures between 10 and 40 °C and for initial effluent pH values between 3 and 7.

METHODS

Materials

Chemicals

Phosphonated monomer, (dimethoxyphosphoryl)methyl 2-methylacrylate (MAPC1) (Lot Number: SP-41-003) has been kindly supplied by Specific Polymers (Montpellier, France) and used as received. *N-n*-propylacrylamide (Lot Number: 22-71-8) has been purchased from Monomer-Polymer and Dajac Labs (Trevose, USA). Azobisisobutyronitrile (AIBN) has been purchased from Sigma-Aldrich and used after recrystallization in methanol. Other chemicals have been purchased from Sigma Aldrich and used as received.

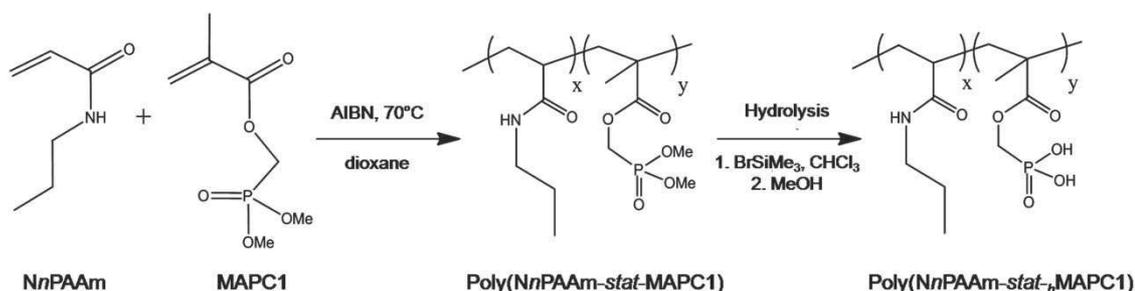


Figure 1 | Synthesis of poly(*Nn*PAAm-*stat-n*-MAPC1).

Synthesis of poly(*Nn*PAAm-*stat-n*-MAPC1)

All polymerization were conducted in dioxane in schlenk tubes by free radical polymerization (Figure 1). Typical procedure for the synthesis of poly(*Nn*PAAm-*stat-n*-MAPC1) 90/10 is described here. Both monomers *Nn*PAAm (3.0 g, 2.65 × 10⁻² mol) and MAPC1 (0.62 g, 2.94 × 10⁻³ mol), solvent (20 mL) and AIBN (24.2 mg, 1.47.10⁻⁴ mol), were first introduced and the obtained solution was degassed by three freeze pump thaw cycles and then heated at 70 °C. Obtained copolymers were purified by precipitation in a large volume of cold hexane and dried under reduced pressure. Hydrolysis of dimethylphosphoryl (O = P-(OMe)₂) functions were achieved with bromotrimethylsilane (BrSiMe₃) and methanol. Copolymers were finally washed by dialysis against pure distilled water at 18 °C in order to remove unreacted molecules. All molecular weights were determined by size exclusion chromatography (SEC) in DMAc, 0.1 wt% LiCl at 50 °C with polystyrene (PS) standards. All ¹H or ³¹P nuclear magnetic resonance (NMR) spectrometry analyses have been run on a Bruker 400 MHz spectrometer with D₂O as deuterated solvent.

Determination of thermosensitive behaviour

Thermosensitivity of the poly(*Nn*PAAm-*stat-n*-MAPC1) was estimated by a change in the transmittance through the polymer solution with temperature. The measurement of the transmittance was carried out on 5 g L⁻¹ copolymer aqueous solutions with a Perkin Elmer Lambda 35 UV-Visible spectrometer equipped with a Peltier temperature programmer PTP-1 + 1. A wavelength of 500 nm was selected. Temperature ramp was 0.2 °C per minute between 10 and 40 °C.

Sorption experiments

Sorption experiments were carried out by dialysis to avoid the influence of the separation process in the determination

Table 1 | Characterization of poly(N*n*PAAm-*stat*-*h*MAPC1)

Copolymer abbreviation	Molar ratio of N <i>n</i> PAAm:MAPC1 in the feed	Molar ratio of N <i>n</i> PAAm: <i>h</i> MAPC1 in the copolymer ^a	Phosphonic acid group in the copolymer (mmol.g _{poly} ⁻¹) ^a	<i>M_n</i> (g mol ⁻¹) ^b	$\bar{D} M_w/M_n$ ^b
poly(N <i>n</i> PAAm)	–	–	–	120,000	2.7
poly(N <i>n</i> PAAm- <i>stat</i> - <i>h</i> MAPC1) 95/05	95:05	94:06	0.453	79,400	2.2
poly(N <i>n</i> PAAm- <i>stat</i> - <i>h</i> MAPC1) 90/10	90:10	89:11	0.830	64,350	2.5
poly(N <i>n</i> PAAm- <i>stat</i> - <i>h</i> MAPC1) 80/20	80:20	80:20	1.51	65,400	2.4
poly(N <i>n</i> PAAm- <i>stat</i> - <i>h</i> MAPC1) 70/30	70:30	70:30	2.25	71,000	2.6

^aComposition in the copolymer calculated by ¹H NMR spectroscopy.

^b*M_n*: number average molecular weight, *M_w*: mass average molecular weight, \bar{D} : polydispersity index. Values determined by size exclusion chromatography with PS standards in DMAC solution containing 0.1 wt% LiCl, *T* = 50 °C.

of sorption properties. Ten millilitres of copolymer aqueous solution of different polymer concentrations (between 1.25 and 10 g L⁻¹) were introduced in a tubular ester cellulose dialysis membrane with a molecular weight cut-off of 2,000 D avoiding the diffusion of the copolymer in the inner solution. Copolymer solution was then brought into contact through this tubular membrane to 100 mL of a solution containing 20 mg L⁻¹ of Ni²⁺. The quantity of Ni trapped by the copolymer was determined by measuring the concentration of the outer solution before and after sorption experiment, a blank experiment with pure water as inner solution enabled consideration of the dilution factor induced by the addition of the inner solution. Experiments were carried during 8 hours after having verified that this time was needed to reach equilibrium. Temperature and pH influences on the sorption capacity were studied. Metal ion concentrations were assessed by atomic adsorption spectroscopy with a Perkin Elmer AAnalyst 400, an AutoPrep 50 dilutor and a S10 auto-sampler.

RESULTS AND DISCUSSION

Synthesis of poly(N*n*PAAm-*stat*-*h*MAPC1)

All copolymers were synthesized by free radical polymerization with variation of the molar ratio *h*MAPC1:N*n*PAAm in the feed from 5:95 to 70:30. Such range of copolymers were synthesized in order to select the one that best conciliates sorption properties and low energy consumption. Copolymer structures were confirmed by ¹H and ³¹P NMR spectroscopy and Table 1 shows that poly(N*n*PAAm-*stat*-*h*MAPC1) with

various composition can be obtained by varying the composition of MAPC1 content in the feed.

Table 1 also points the fact that all copolymers were obtained with mean molecular weights of 64,000–80,000 g mol⁻¹ and similar polydispersities. Such properties are directly linked to the polymerization technique used. Finally, ³¹P NMR spectrometry enabled proof that all phosphonated groups on copolymers were only phosphonic diacid groups.

Thermosensitivity of poly(N*n*PAAm-*stat*-*h*MAPC1)

Energy consumption of processes using thermosensitive polymers is driven by the LCST of the copolymer used to remove the metallic pollution. The impact on the thermosensitivity of the molar ratio of hydrolyzed *h*MAPC1 was evaluated. Thermoresponsive behaviour of the copolymers is the result of the difference of solubility of acrylamide groups with temperature. Below the LCST, copolymer–water interactions are favourable and the copolymer is soluble. For temperatures higher than the LCST, copolymer–copolymer interactions become more stable than the copolymer–water interactions, leading to insolubility. Poly(N*n*PAAm) homopolymer exhibited a LCST value of 22 °C, therefore 10 °C lower than the LCST of poly(N*i*PAAm) usually found in literature (Figure 2).

Influence of the hydrolyzed *h*MAPC1 ratio in the copolymer was showed in Figure 2. Because phosphonic diacid groups are hydrophilic groups, higher *h*MAPC1 ratio would induce strongest copolymer–water interactions and thus higher LCST values. Thereby, Table 2 shows LCST values varying from 22 °C for poly(N*n*PAAm) to 25.6 °C

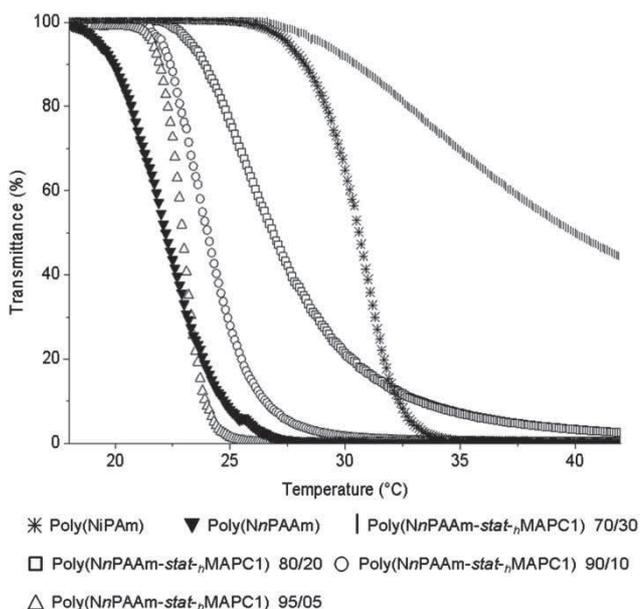


Figure 2 | Evolution of LCST with the _nMAPC1 ratio in the copolymer.

for poly(NnPAAm-*stat*_nMAPC1) 80/20. Due to its high content of hydrophilic phosphonic diacid groups, poly(NnPAAm-*stat*_nMAPC1) 70/30 did not show appropriate thermoresponsive behaviour for the targeted application. As a result, poly(NnPAAm-*stat*_nMAPC1) 90/10 showing

LCST value of 23.4 °C appeared as the best copolymers conciliating a low LCST value with a significant amount of sorption groups.

Sorption experiments

The sorption capacities of the copolymer poly(NnPAAm-*stat*_nMAPC1) 90/10 towards Ni²⁺ ions were measured at different pH and temperature and for a Ni metal ion concentration of 20 mg L⁻¹. Additionally, as sorption properties are the results of interactions between the phosphonic diacid sorption groups (P) and the Ni²⁺ cation (Ni), the influence of the Ni/P ratio on the sorption properties was also evaluated. The Ni/P ratio represents the amount of Ni cation introduced (Ni) divided by the amount of phosphonic diacid sorption groups (P).

Influence of the temperature

Study of the sorption capacities of the copolymer as a function of the temperature was carried out in order to estimate the optimal temperature for the use of such copolymers in a wastewater treatment process. Results are presented in Figure 3(a). Experiments were carried out at pH = 7. A maximal sorption capacity of 72% was attained at 20 °C. This value significantly decreases for lower and higher

Table 2 | Polymers and copolymers LCST values

	Poly(NnPAAm)	Poly(NnPAAm- <i>stat</i> _n MAPC1) 95/05	Poly(NnPAAm- <i>stat</i> _n MAPC1) 90/10	Poly(NnPAAm- <i>stat</i> _n MAPC1) 80/20	Poly(NnPAAm- <i>stat</i> _n MAPC1) 70/30	Poly(NiPAAm)
LCST value	22.0 ± 2 °C	22.8 ± 1 °C	23.4 ± 1.5 °C	25.6 ± 2 °C	–	31.2 ± 2 °C

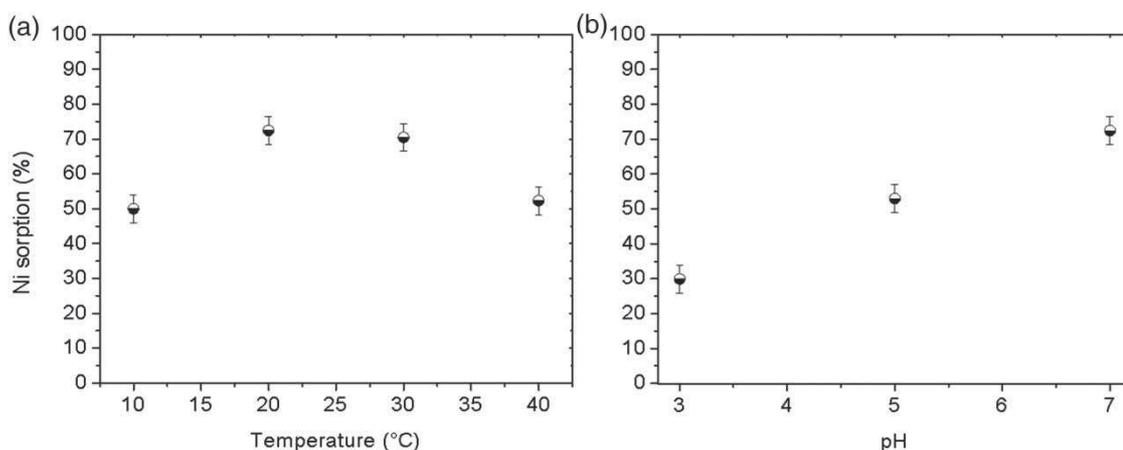


Figure 3 | Influence of temperature (a) and pH (b) on sorption properties of poly(NnPAAm-*stat*_nMAPC1) 90/10.

temperatures. Below the LCST, a temperature increase may enhance the diffusion of metal cations to the sorption sites of the copolymer, leading to better sorption properties. Above the LCST values, the temperature increase induced the insolubility of the polymer. The higher the temperature the more retracted is the copolymer and the less the sorption sites are accessible. Sorption properties were thus significantly reduced. As a result, best sorption properties were observed for a temperature of 20 °C, just below the LCST.

Influence of the pH

It is known that modifying the pH of the solution has a crucial influence on the sorption capacities of metal ions (Nonaka *et al.* 2004). This pH dependence was observed for the poly(NnPAAm-*stat*-*h*MAPC1) 90/10, as shown in Figure 3(b). More than 70% of initial Ni metal cations were sorbed at pH = 7 and this value decreased to 30% at pH = 3. So, sorption properties were significantly reduced when decreasing the solution pH. This result may be explained by the sorption competition between Ni²⁺ and H⁺ cations. Indeed, for effluents at pH = 7 and 20 mg L⁻¹ of Ni²⁺ ions, there are about 3,000 times more Ni²⁺ than H⁺ in the media, whereas at pH = 3 there are 3 times more H⁺ than Ni²⁺. Thus, sorption of Ni²⁺ metal cations on phosphonic diacid groups is less probable under acidic conditions.

Sorption rate controlled by Ni/P ratio

The use of this kind of copolymer in a wastewater purification process requires knowing the minimal amount of polymer and sorption sites needed to achieve a sufficient removal rate as well as the time needed to reach this elimination rate. Evaluation of Ni²⁺ sorption kinetics from the initial solution was evaluated as a function of the molar ratio between Ni²⁺ and phosphonic diacid sorption groups (Ni/P) at pH = 7. The Ni/P ratio was varied by changing the amount of poly(NnPAAm-*stat*-*h*MAPC1).

Figure 4 shows the results of experiments performed with Ni/P values ranging between 0.45 and 3.6. The Ni/P ratio was controlled by the concentration of copolymer in the dialysis tubular membrane. The curves representing the variation of sorbed Ni versus (i) the dry polymer mass (mmolNi_{sorbed}/g_{polymer}), and (ii) the amount of sorption sites (mmolNi_{sorbed}/mmol P) were plotted in the same figure.

The maximum removal was reached at low Ni/P values when there is an excess of sorption groups versus Ni²⁺ metal

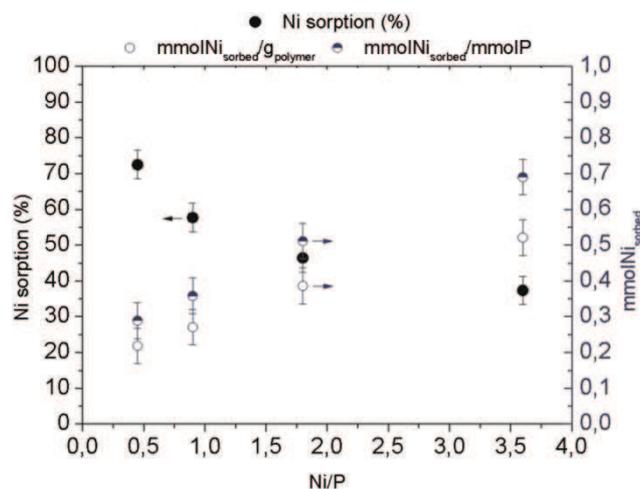


Figure 4 | Sorption properties versus Ni/P ratio of poly(NnPAAm-*stat*-*h*MAPC1) 90/10.

ions (about twice the number of sorption groups than Ni²⁺ ions). In this case, the sorption was efficient (72%) but only 28% of the sorption sites were involved (mmolNi_{sorbed}/mmolP = 0.28). When increasing the Ni/P ratio, the removal efficiency was shown to decrease, as expected, since the number of sorption sites was strongly reduced (Ni/P = 3.6). Thereby, the sorption efficiency was significantly improved and an increasing number of phosphonic diacid sorption sites were involved (mmolNi_{sorbed}/mmolP = 0.7). Such results suggest that for low Ni/P ratios, the concentration gradient between the outer solution and the solution in the tubular membrane rapidly decreased, inducing a reduction of the driving force for diffusion of Ni ions. On the contrary, for high Ni/P ratio, the amount of Ni²⁺ metal ions remained sufficiently high in the solution despite the sorption by phosphonic diacid sites, hence keeping high the driving force for ions diffusion. In such a case, much more sorption sites were involved in the Ni²⁺ ions retention.

In addition, the sorption kinetics of Ni²⁺ ions on phosphonic diacid sites was determined for Ni/P ratios of 0.45 and 3.6 during 24 hours. The system reached an equilibrium after approximately 9 hours in both cases, therefore the curves were reported in Figure 5 for the first 9 hours to focus on the first kinetic period.

For low Ni/P ratio, the reduction of the driving force for Ni ions transfer was very fast; indeed more than 50% of the initial Ni²⁺ was sorbed within 2 hours. When the equilibrium was reached, around 30% of the sorption sites were involved in the sorption. Furthermore, for higher Ni/P ratios, the decrease of the concentration gradient was slower as expected since the amount of sorption sites was

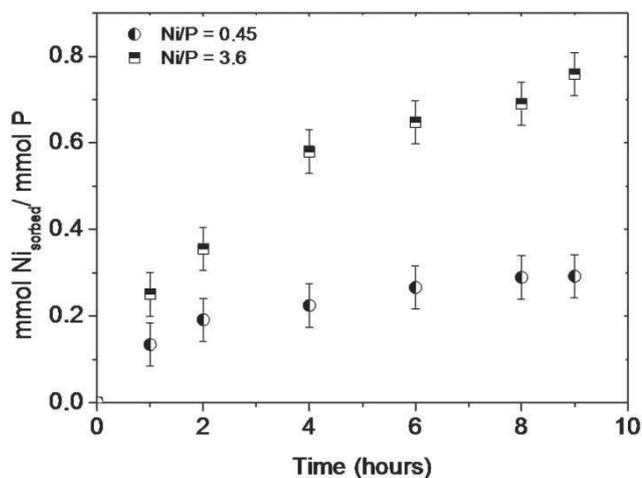


Figure 5 | Sorption kinetics as a function of Ni/P ratio of poly(NnPAAm-stat-nMAPC1) 90/10.

lower. In this case, the driving force for Ni ions transfer remained high, promoting the phosphonic diacid sites to fix more Ni metal cation ($\text{mmol Ni} / \text{mmol P} = 0.7$ after 9 hours). As a summary, these results clearly exhibited that the driving force for Ni ions diffusion controlled the sorption process.

CONCLUSIONS

Metallic cation polymeric sorbents with LCST around 23°C have been synthesized. Compared to NiPAm based copolymers, such LCST values would significantly decrease the energy consumption from an industrial point of view. An efficiency of 70% Ni^{2+} removal was reached by sorption on a polymeric sorbent containing 10 mol% of phosphonic diacid groups. The best sorption efficiency was reached for a temperature just lower than the LCST. Above this temperature, the insolubility of the copolymer significantly decreased the sorption ability of the copolymer. Best sorption results were observed at $\text{pH} = 7$. For lower pH, increasing amount of H^+ cations in the solution explained the decrease of the sorption properties. Sorption properties also appeared to be controlled by the driving force for Ni transfer. The minimal amount of copolymer needed for the elimination of metal ions thus depended on the initial Ni/P ratio. For low Ni/P ratios, high elimination rate can be reached quickly but less than only 30% of the sorption capacity of the copolymer is used. On the contrary, for high Ni/P ratios, copolymer sorption capacity was higher but low elimination rate could be reached in such a case.

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