



Removal of nickel ions from aqueous solution by low energy-consuming sorption process involving thermosensitive copolymers with phosphonic acid groups

Alain Graillot^{a,b}, Denis Bouyer^{a,*}, Sophie Monge^b, Jean-Jacques Robin^b, Catherine Faur^a

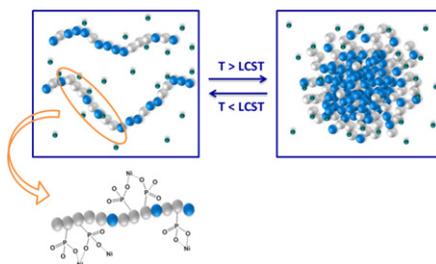
^a Institut Européen des Membranes-IEM (UMR 5635 CNRS-ENSCM-UM2) - Equipe Genie des Procédés Membranaires, Université Montpellier II cc047, Place Eugene Bataillon, 34095 Montpellier Cedex 5, France

^b Institut Charles Gerhardt Montpellier (UMR 5253 CNRS-UM2-ENSCM-UM1) - Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier II cc1702, Place Eugene Bataillon, 34095 Montpellier Cedex 5, France

HIGHLIGHTS

- Synthesis of low LCST statistical copolymer (thermosensitive/complexing).
- Investigation of sorption efficiency for (Ni²⁺ ions) in various operating conditions.
- High sorption efficiency comparing to similar thermosensitive polymer with sorption properties.
- Link between the copolymer architecture and the sorption capacity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 August 2012
 Received in revised form 11 October 2012
 Accepted 17 October 2012
 Available online 6 November 2012

Keywords:

Metal ions
 Thermosensitive copolymers
 Complexation
 Water treatment
 Phosphonic acid

ABSTRACT

In order to remove metal ions from wastewaters, thermosensitive copolymers bearing sorption properties toward metal cations were prepared by free radical copolymerization between the *N*-*n*-propylacrylamide (NnPAAm) and the (dimethoxyphosphoryl)methyl 2-methylacrylate (MAPC1), followed by a hydrolysis of the phosphonated esters into phosphonic diacid groups (*h*MAPC1). The thermosensitivity and the sorption abilities of the resulting poly(NnPAAm-*stat-h*MAPC1) copolymers were studied. Lower Critical Solution Temperatures (LCST) of these copolymers ranged from 22 °C to 26 °C, depending on the molar ratio of phosphonated monomers and were lower than those obtained with usual poly(*N*-isopropylacrylamide)-based polymers. The influence of both the temperature and the pH on the sorption properties of the copolymers was evaluated for Ni²⁺ cations. The most interesting results were obtained for temperatures around the LCST, *i.e.* when the proximity of the complexing groups favored the sorption of metallic cations. Concerning the pH effect, the maximum sorption capacity was obtained at pH 7, *i.e.* in the absence of competition between the sorption of H⁺ and Ni²⁺ ions on the phosphonic acid groups. The influence of the molar ratio of metal ions and phosphonate moieties was also studied and different sorption mechanisms were proposed.

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1. Introduction

During the last decades, thermosensitive polymers and copolymers have been widely studied because of their change of physical properties triggered by temperature stimulus. Indeed,

thermosensitive polymers are uncommon as they are soluble in water at low temperature and become non-soluble when increasing the temperature. The change of physical state occurs at the Lower Critical Solution Temperature (LCST) and depends on the chemical structure of the polymer. In such kinds of materials, the change of solubility is linked to the competition between polymer–water and polymer–polymer interactions. Below the LCST, the presence of hydrogen bonds between polymer and water as well as the formation of solvation cages explain the solubility

* Corresponding author. Tel.: +33 467 143 897; fax: +33 467 149 119.
 E-mail address: Denis.Bouyer@iemm.univ-montp2.fr (D. Bouyer).

of the polymer. Increasing the temperature above the LCST makes the hydrogen bonds break, favors the polymer–polymer interactions and leads to the loss of the solubility. Therefore this polymer is hydrophilic at a temperature below the LCST and become hydrophobic above it. Besides, thermosensitivity can be associated to many other properties, leading to a wide range of applications, such as drug delivery [1–3], surface coating [4,5], films and membranes [6–8], actuators [9,10] or water treatment [11–15]. Referring to water treatment, many polymers have been used for the removal of metallic pollution [13,16–20] and some works have described the synthesis of thermosensitive polymers with sorption properties [11,12,14,15,21–24]. In these previous works, poly(*N*-isopropylacrylamide) *p*(NiPAM), with a LCST of 32 °C [3], is usually used as thermosensitive moiety and the sorption properties are given by monomers bearing complexing groups.

A wide range of complexing groups enables the sorption of metallic cations onto a polymer; among all possibilities, a special interest was given to phosphonated groups since some authors have pointed out their good sorption properties [14,24–28] for metallic cations such as Ca²⁺, Cu²⁺ and Ni²⁺, for instance. When complexing groups are associated to a thermosensitive moiety, such copolymers combine sorption abilities and insolubility above the LCST. The LCST of the *p*(NiPAM) is equal to 32 °C but this value significantly increases when it is associated with hydrophilic monomers. For instance, poly(NiPAM)-based copolymers containing 10% (molar) of phosphonic acid groups have a LCST close to 45 °C, *i.e.* more than 10 °C higher than the LCST of poly(NiPAM) [15]. Indeed, the hydrophilic groups promote the polymer–water interactions, leading to widen the solubility domain of the copolymer and therefore to an increase of the LCST.

In the water treatment area, such copolymers offer many opportunities for two main reasons: (i) the complexing properties given by the phosphonated groups allow eliminating a metallic pollution from wastewater and (ii) the thermosensitivity gives advantages for separating the insoluble copolymer–metal complexes from the treated water by simple and cheap processes. Nevertheless, such a solution is compromised by the high LCST of *p*(NiPAM)-based copolymers which implies significant energy costs to heat the water above the LCST and to reach the insolubility domain. To the best of our knowledge, NiPAM has been the only one monomer used to synthesize thermosensitive and complexing copolymers, meaning that the research of new copolymers having a lower LCST value has never been investigated whereas it could be very useful to reduce the energy consumption of water treatment processes.

In this work, new thermosensitive copolymers bearing phosphonated groups were synthesized; such copolymers with low LCST close to ambient temperature and complexing properties allowed the removal of specific metallic pollution from water. The complexing properties were given by hydrolyzed (dimethoxyphosphoryl)methyl 2-methylacrylate (*h*MAPC1) monomer and the thermoresponsive properties were obtained thanks to the polymerization of the *N*-*n*-propylacrylamide (NnPAAM) monomer. The LCST of the copolymers were controlled by the molar ratio of each monomer in the copolymer. The first part of this work focuses on the determination of the thermosensitivity behavior of the copolymer as a function of the *h*MAPC1 content. A second part deals with the sorption properties when the removal of nickel cations is targeted. The influence of temperature (from 10 °C to 40 °C), pH (between 3 and 7) and molar ratio between Ni²⁺ metal cations and phosphonated moieties was then studied so as to suggest a sorption mechanism depending on operating conditions and to highlight the most probable coordination modes involved in the sorption phenomena. In the best operating conditions studied here, poly(NnPAAM-*stat-h*MAPC1) sorption capacity reach 0.6 mmol g⁻¹, significantly higher than the sorption properties of similar phosphorus containing thermosensitive copolymers found

in the literature (0.2 mmol g_{poly}⁻¹ for APPA-NIPAM copolymer [15], and less than 0.1 mmol g_{poly}⁻¹ for NiPA-co-MEP copolymers [14]).

2. Experimental

2.1. Materials

Polymeric sorbents used in this study are statistical poly(NnPAAM-*stat-h*MAPC1) copolymers obtained from the free radical polymerization of NnPAAM and MAPC1 followed by an hydrolysis of the phosphonated ester into phosphonic acid (Fig. A.1, Appendix A). The NnPAAM/*h*MAPC1 molar ratio in the copolymers synthesized varied from 95/05 to 70/30 in order to select the best compromise between sorption properties and low energy consumption. All details concerning the copolymers synthesis and their main characteristics are given in Appendix A.

2.2. Methods

2.2.1. Thermosensitive behavior

Thermosensitivity of the poly(NnPAAM-*stat-h*MAPC1) was determined by following the transmittance of the polymer aqueous solution during a gradual increase of the temperature. The measurement of the transmittance was carried out on copolymer aqueous solutions (5 g L⁻¹) with a PerkinElmer Lambda 35 UV-Visible spectrometer equipped with a Peltier temperature programmer PTP-1 + 1. A wavelength of 500 nm was selected. Temperature ramp was 0.1 °C min⁻¹ between 15 °C and 50 °C. The thermosensitivity was characterized by a sudden slope change in the transmittance curve. The LCST values of the copolymers thus corresponded to the minimum of the derivative curves.

2.2.2. Determination of copolymer particle size

All particle size measurements have been achieved by dynamic light scattering (DLS) with a zeta-sizer Nano-ZS from Malvern Instruments on solutions containing 5 g L⁻¹ of copolymer. The temperature increase was regulated by the zeta-sizer: temperature ramp was 2 °C min⁻¹ and the measurements were performed after a stabilization period of 5 min.

2.2.3. Evaluation of sorption abilities

Sorption experiments were carried out as described in Appendix B. The amount of Ni²⁺ ions trapped by the copolymer was determined by measuring the concentration of Ni cations in the solution before and after sorption experiments. The metal ion concentration was determined by Atomic Sorption Spectroscopy. Experiments were carried out during 24 h to reach equilibrium and the temperature was controlled by a 6 L Fisher Bioblock Scientific Cryothermostated bath. The sorption capacity was studied between 10 °C and 40 °C in order to focus on the influence of the temperature; the influence of the pH on the sorption ability was investigated between pH 3 and 7 by addition of hydrochloric acid in the metal containing solution. The influence of the molar ratio between Ni²⁺ metal cations and phosphonated moieties was studied by changing the copolymer concentration.

2.2.4. Sorption properties of poly(NnPAAM-*stat-h*MAPC1)

Sorption properties of Ni²⁺ onto poly(NnPAAM-*stat-h*MAPC1) were performed with the same methods used for the sorption experiments. The Ni²⁺ concentration in the solution was determined at regular time-steps by Atomic Sorption Spectroscopy. The sorption experiments were used to monitor the sorption dynamics and find out the required time to reach equilibrium. The sorption capacity at time *t* (*Q_t*, mg g⁻¹) could then be calculated from a mass balance equation, where (*C_t*, mg L⁻¹) is the concentration of

Ni^{2+} in solution at time t , V and C_0 are the volume and the initial concentration of the Ni^{2+} solution, and m is the total mass of the poly($\text{NnPAAm-stat-hMAPC1}$):

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

At equilibrium, Eq. (1) could also be used to calculate equilibrium sorption capacity (Q_e , mg g^{-1}) from the measurement of equilibrium concentration of Ni^{2+} in solution (C_e , mg L^{-1}). The order of the sorption kinetics process can then be determined by plotting the variation of $\log(Q_e - Q_t)$ versus t (pseudo-first-order) and t/Q_t versus t (pseudo-second-order) (cf. Eq. (2) and (3)). The first-order k_1 (h^{-1}) and second order k_{II} ($\text{g}(\text{mg h})^{-1}$) could also be calculated according to the Lagergren model [29,30]:

$$\log(Q_e - Q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (2)$$

$$\frac{t}{Q_t} = \frac{1}{k_{II} q_e^2} + \frac{t}{Q_e} \quad (3)$$

In both Eq. (2) and (3), q_e is the theoretical equilibrium sorption capacity calculated by the kinetic model.

3. Results and discussions

3.1. Poly($\text{NnPAAm-stat-hMAPC1}$) thermosensitivity

The energy consumption of processes using thermosensitive polymers is driven by the Lower Critical Solution Temperature of the copolymer used to remove the metallic pollution. LCST were determined by measuring the transmittance of copolymer solutions at 500 nm for reported different temperatures. The influence of the molar ratio of hydrolyzed h MAPC1 on the thermosensitivity is shown in Fig. 1 and corresponding LCST were summarized in Table 1.

Using the NnPAAm instead of NiPAAm monomer enabled to decrease the polymer LCST values by about 10°C (Table 1). Additionally, the LCST increased with the h MAPC1 content in the copolymer because of the hydrophilicity of the phosphonic diacid groups. Thereby, the LCST varied from 22°C for poly(NnPAAm) to 25.6°C for poly($\text{NnPAAm-stat-hMAPC1}$) 80/20. The poly($\text{NnPAAm-stat-hMAPC1}$) 70/30 was characterized by a higher LCST (more than 40°C) and the LCST distribution curve was strongly wider than for the other copolymers because of its high phosphonic diacid groups content. Such results considerably reduced the interest of the copolymer 70/30 for water treatment applications. However, the low LCST values of poly($\text{NnPAAm-stat-hMAPC1}$) 95/05, 90/10 and 80/20 are really promising as these copolymers imply a significant cost reduction to the process using similar polymers. Until now, temperatures higher than 35°C were needed to reach the insolubility domain of the polymers in which the separation step is achieved. With poly($\text{NnPAAm-stat-hMAPC1}$), this domain is reached below 30°C . Such differences of temperature might appear really important if large volumes of water are considered. Therefore, the sorption properties were only determined for poly($\text{NnPAAm-stat-hMAPC1}$) 95/05, 90/10 and 80/20 as only these three polymers show interesting LCST values.

3.2. Poly($\text{NnPAAm-stat-hMAPC1}$) sorption abilities for Ni metal cations

3.2.1. Sorption kinetic

Kinetic experiments were carried out in order to determine the time needed to reach the sorption equilibrium. The kinetic curve (Fig. 2) was obtained using 0.1 g of poly($\text{NnPAAm-stat-hMAPC1}$) 80/20 and 100 mL of a solution containing 20 mg L^{-1} (0.34 mmol L^{-1}) of Ni^{2+} . The pH of the solution was equal to 7

Table 1
LCST values of the thermosensitive homopolymers and copolymers.

LCST value	22.0 ± 2 °C	22.8 ± 1 °C	23.4 ± 1.5 °C	25.6 ± 2 °C	31.2 ± 2 °C
	Poly(NnPAAm)	Poly($\text{NnPAAm-stat-hMAPC1}$) 95/05	Poly($\text{NnPAAm-stat-hMAPC1}$) 90/10	Poly($\text{NnPAAm-stat-hMAPC1}$) 80/20	Poly($\text{NnPAAm-stat-hMAPC1}$) 70/30
					Poly(NiPAAm)

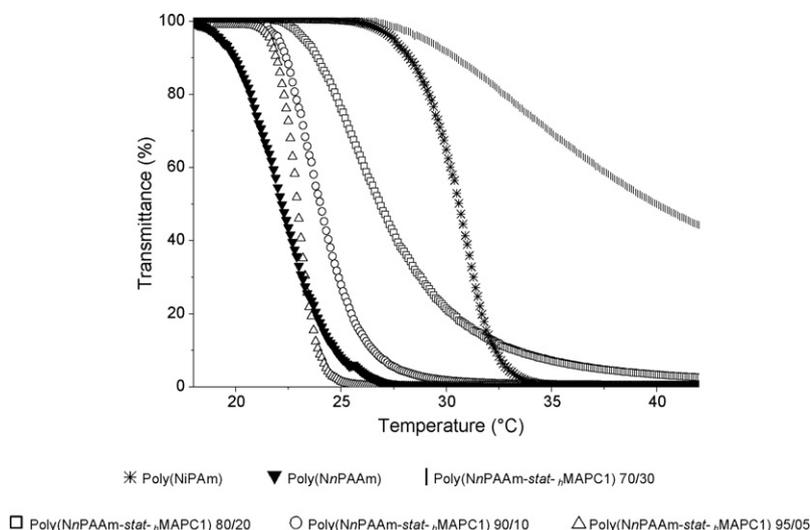


Fig. 1. Transmittance of the copolymer solutions as a function of the temperature.

and the temperature was maintained at 20 °C during the whole experiment.

As aforementioned, the sorption capacity Q_t was obtained from (i) measurement of the nickel concentration in the solution and (ii) a mass balance to calculate sorption capacity. Fig. 2 exhibits that the equilibrium was reached after 8 h, leading to a sorption capacity of 14.9 mg of Ni sorbed per gram of dry polymer. In this case, the sorption rate, which represents the number of complexed Ni ions divided by the total number of Ni^{2+} introduced in the solution, was higher than 70%. Hence, the whole equilibrium experiments were carried out during 24 h in order to ensure that the sorption equilibrium was reached.

Moreover, the comparison between the experimental data and Lagergren kinetic models exhibit that the pseudo second-order model is more relevant than the pseudo-first model to describe the sorption process. Indeed, the agreement between the pseudo-first-order model and the experimental data is good only during the first 6 h whereas the pseudo-second-order model fit well the experimental data during the whole sorption process (Fig. 2). Such a trend has already been reported in the literature in previous papers [29,30]. Thus, the pseudo-second-order kinetic parameters have been determined (k_{II} and q_e) for the Nickel sorption onto poly(NnPAAm-stat-hMAPC1) (Table 2).

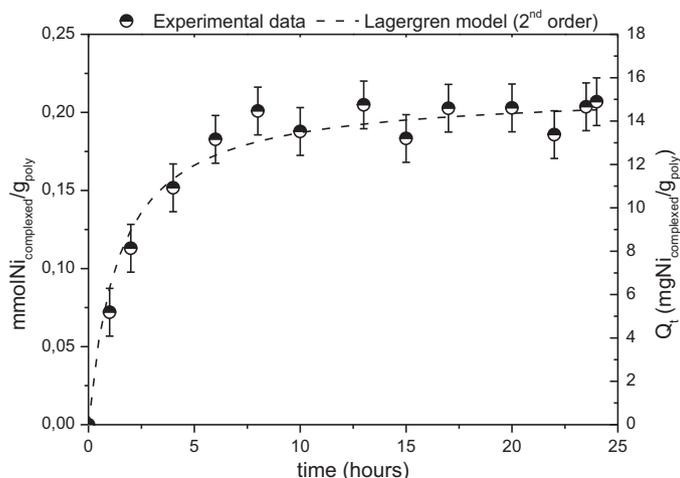


Fig. 2. Sorption kinetic obtained with poly(NnPAAm-stat-hMAPC1) 80/20.

Table 2

Pseudo-second-order kinetic parameters for the sorption of Ni^{2+} onto poly(NnPAAm-stat-hMAPC1) – Lagergren pseudo-second-order model.

Experimental Q_e (mg g^{-1})	14.9
Lagergren pseudo-second-order model	
k_{II} [$\text{g}(\text{mg h})^{-1}$]	0.0455
Calculated $q_{e,II}$ (mg g^{-1})	15.38
R^2	0.990

3.2.2. Sorption abilities as a function of the pH

Since phosphonic diacid groups were used in this work, the sorption properties were expected to depend on the pH. Indeed, phosphonic diacid groups are characterized by two dissociation constants that have been determined by pH titration in the case of poly(NnPAAm-stat-hMAPC1) 80/20, 90/10 and 95/05: mean values obtained are $\text{pK}_{a1} = 2.13$ and $\text{pK}_{a2} = 7.06$ (Table C.1, Appendix C). Such dissociation constants indicate that the dissociated nature of the complexing groups is linked to the pH in acidic medium, as expressed in Eq. (4) and (5).



The mole fraction of dissociated phosphonic diacid groups as a function of the pH can be inferred from these dissociation constant. Resulting regression curves (Fig. C.1) show different ratios of the predominant forms of the dissociated groups as function of the pH. At pH 7, there is about 50% of ($\text{R} - \text{PO}_3^{2-}$) and 50% of ($\text{R} - \text{PO}_3\text{H}^-$) whereas at pH 3, there is 85% of ($\text{R} - \text{PO}_3\text{H}^-$) and 15% of ($\text{R} - \text{PO}_3\text{H}_2$). Such variations affect the sorption properties. So, it was interesting to investigate the influence of the solution pH on the sorption capacities of poly(NnPAAm-stat-hMAPC1) copolymers (Fig. 3a).

The results clearly exhibit that the sorption capacity decreased with decreasing the pH. Between pH 7 and 5, the sorption capacities were reduced by 30% for the poly(NnPAAm-stat-hMAPC1) 90/10 and 95/05 and by 20% for the poly(NnPAAm-stat-hMAPC1) 80/20. Such significant decreases of the sorption capacities were explained by the decreasing amount of ($\text{R} - \text{PO}_3^{2-}$) in the solution between pH 7 and 5. Moreover, decreasing the pH from 5 to 3 emphasized the trend: the decrease of the sorption properties were close to 45% for poly(NnPAAm-stat-hMAPC1) 80/20 and to 60–65% for both poly(NnPAAm-stat-hMAPC1) 90/10 and 95/05. Such gaps in sorption properties between pH 5 and pH 3 could first be explained by the protonation of the ($\text{R} - \text{PO}_3\text{H}^-$) into ($\text{R} - \text{PO}_3\text{H}_2$) as shown in

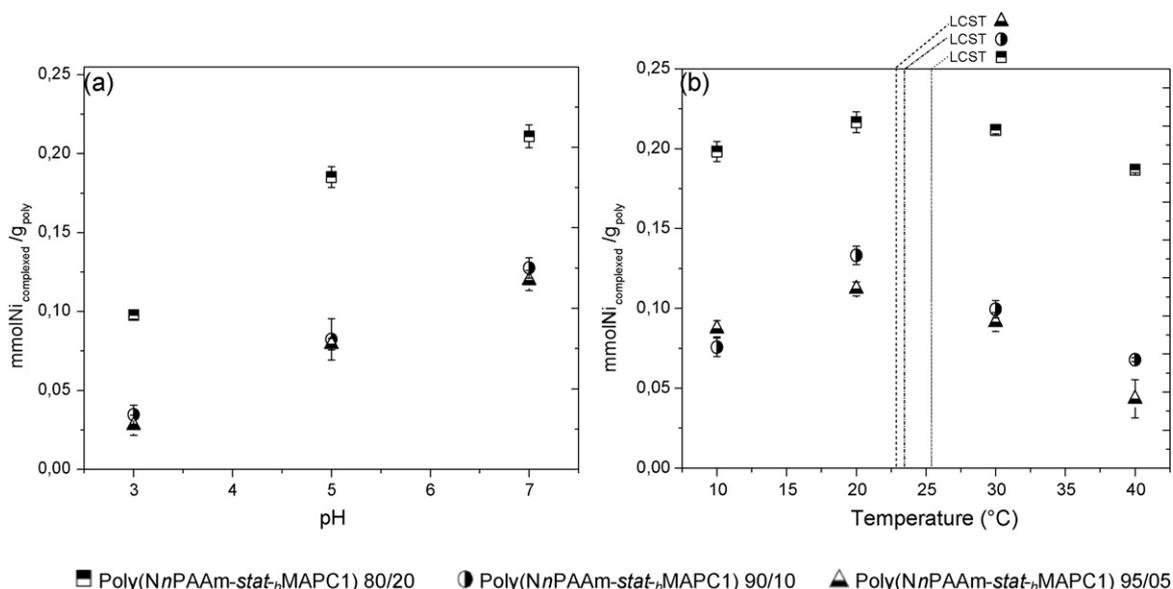


Fig. 3. Sorption properties as a function of the pH (a) and the temperature (b).

Fig. C.1. Additionally, a sorption competition between Ni²⁺ and H⁺ cations can also explain the decrease of the sorption properties when decreasing the pH. Indeed, at pH 5 and for Ni²⁺ concentration of 20 mg L⁻¹, the molar ratio between Ni²⁺ and H⁺ ions was close to 30/1, whereas this ratio decreased to 1/3 at pH 3. Such competition phenomenon between H⁺ and Ni²⁺ sorption was assumed by a pH change before and after the sorption experiments. Indeed, the initial solution pH at 5 and 3 increased respectively to pH 7 and 4 at the end of the experiment which proved that H⁺ was sorbed on the copolymer. Thus, sorption of Ni²⁺ on phosphonic diacid groups was less probable under strong acidic condition.

3.2.3. Sorption abilities as a function of the temperature

Since the physical states of poly(NnPAAm-stat_nMAPC1) copolymers are temperature dependent, meaning that a drastic change of solubility is expected at the LCST, the copolymer sorption capacity for Ni²⁺ was determined at different temperatures. Both Ni concentration (20 mg L⁻¹) and pH (pH 7) were kept constant in order to estimate the optimal temperature. The results are reported in Fig. 3b, for poly(NnPAAm-stat_nMAPC1) 80/20, 90/10 and 95/05. The sorption properties of all copolymers exhibited similar trends: on the one hand, in the temperature range of polymer solubility, the higher Ni sorption capacities were obtained just before the LCST in all cases. On the other hand, when the temperature is significantly higher than the LCST, a decrease of the sorption properties was observed: the sorption properties were reduced by 15, 45 and 65% between 20 °C and 40 °C for the copolymers poly(NnPAAm-stat_nMAPC1) 80/20, 90/10 and 95/05, respectively.

Such variation of sorption properties with the temperature was linked (i) to the physical state of the copolymer in solution before and after the LCST and (ii) to the change of the copolymer chains conformation in solution at temperatures above the LCST. The change of the copolymer chains organization in water was highlighted by the determination of the copolymer particle size. Measurements were carried out by DLS in the whole range of temperature for the poly(NnPAAm-stat_nMAPC1) 80/20 and for various concentrations of Ni²⁺ leading to different Ni/P ratios (the Ni/P ratio represents the molar ratio between the quantity of Ni²⁺ introduced in solution divided by the amount of phosphonic diacid groups) (Fig. 4). Three trends were identified as a function of the temperature: (i) at a temperature lower than the LCST, particle sizes were close to 150 nm and remained constant between 15 °C and

25 °C; (ii) around the LCST and in a narrow range of temperature (between 25 °C and 30 °C), a sudden increase of the particle sizes was observed (from 150 nm to 400 nm); finally (iii) between 30 °C and 50 °C, a slight decrease was observed leading to particle sizes equal of 350 nm. According to the sorption results, a temperature-dependent conformation was suggested as illustrated in Fig. 4.

(i) At a temperature lower than the LCST, copolymer chains are dispersed in the solution and the particle sizes corresponded to the hydrodynamic volume of the copolymer chains in solution. Then sorption results observed in this case (Fig. 3b) correspond to the sorption capacities of the copolymer chains when each chain is considered one independently to the others.

(ii) Around the LCST, the thermosensitive moieties of the copolymer promote polymer–polymer interaction and lead to the aggregation of the polymer chains, in agreement with the increase of the particle size. Nevertheless, segment of polymer chains which are rich in phosphonated moieties are more hydrophilic and remain soluble at this temperature. Resulting particles are then likely to

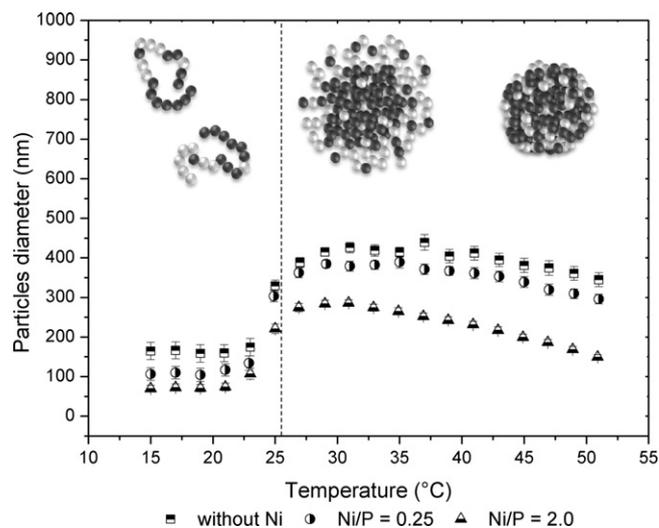


Fig. 4. Poly(NnPAAm-stat_nMAPC1) 80/20 particle size evolution with the temperature.

be composed of a core that mainly contains the thermosensitive moieties and a shell rich in phosphonated moieties (Fig. 4). This assumption was also consistent with the fact that the sorption capacities were not degraded by the copolymer insolubility as the sorption sites of the copolymers remained in the particle shell, accessible for the metallic cations. Finally, the fact that the complexing groups moved closer one to each other on the surface of the particles ease the sorption of metallic pollution and explained the improvement of the sorption capacity.

(iii) At high temperatures (close to 40 °C), a shrinkage of the copolymer particles was more pronounced and led to a reduction of the particle size. Indeed, a temperature increase promotes the polymer–polymer interactions, leading to a contracted state of the particles. In addition, Takeshita et al. [21] exhibited that at high temperature, the copolymer shrinkage could induce a water expulsion; hence the reduction of the complexing properties was in good agreement with the loss of accessibility to the complexing sites in the shrunk particles.

It was then verified that in the presence of nickel cations in the solution, the variation of the particle size with temperature increase followed the same trend (Fig. 4): Ni²⁺ were added to the copolymer solution in order to reach low and high Ni/P ratios (0.25 and 2 respectively). It was observed that in excess of nickel cations in the solution (Ni/P=2), the particle size was divided by more than two (Fig. 4) whereas particles sizes obtained with Ni/P=0.25 were close to those obtained in the absence of Ni. Such results imply that the complexing sites, and thus the polymer chains, have moved closer to enable the sorption of metallic cations. As a consequence, interaction of one metallic cation with more than one complexing groups can thus be foreseen. Such a conformation change of the copolymer chains into water as function of the temperature is finally consistent with the aforementioned sorption results.

3.2.4. Influence of Ni/P ratio

To clarify the difference of sorption mechanisms between phosphonic diacid groups and nickel ions *versus* the Ni/P molar ratio, the sorption properties of the copolymers for the Ni ions were evaluated for increasing Ni/P molar ratios. The amount of copolymer used per experiment was ranged between 100 mg and 12.5 mg whereas the Ni²⁺ concentration was kept constant to 20 mg L⁻¹ (0.34 mmol L⁻¹). This method enabled to study a wide range of Ni/P ratios between 0.2 and 5.6. An additional experiment was carried out with a Ni²⁺ concentration of 60 mg L⁻¹ and 25 mg of copolymer in order to reach a Ni/P ratio of 7.9. All experiments were carried out in the best operating conditions previously identified, namely at 20 °C and pH 7.

Fig. 5a reports the variation of the molar amount of Ni sorbed per mole of complexing site *versus* the Ni/P ratio and Fig. 5b represents the percentage of Ni sorbed at the end of each experiment. For Ni/P ratios ranging from 0 to 1, the amount of Ni sorbed per complexing sites did not significantly change and remained around 0.2 mol Ni sorbed per mol sites corresponding to 1 nickel cation sorbed every 5 complexing sites in the whole copolymer chains. Since the number of complexing sites was kept constant when increasing the Ni/P ratio from 0 to 1, the resulting sorption rate sharply decreased from 70% to 20% in the same Ni/P range.

Over a Ni/P ratio of 1, the simulation of sorption capacities using the same hypothesis of 1 Ni cation sorbed every 5 complexing sites leads to underestimating the sorption capacities, as highlighted in Fig. 5. This surprising result indicates that the number of Ni ions sorbed on the complexing site was increased with the Ni/P ratio; from 0.2 at Ni/P = 1 to 1 at Ni/P = 7.9. This change confirms the fact that the complexing mechanisms depend on the Ni/P ratio: for Ni/P lower than unity, five sites were necessary to complex one Ni cation whereas for Ni/P higher than 5.6, one Ni was fixed per complexing site in the whole copolymer chains. This improvement of

complexing properties led to an unexpected constant sorption efficiency (higher than 20%) at high Ni/P ratios (Fig. 5b), even when the number of Ni ions was more than 8 times higher than the number of phosphonated complexing sites.

All the experimental results finally converged and allowed to suggest specific sorption mechanisms coupled to the variation of Ni/P ratio and to the changes of solubility and chains conformations in water.

3.3. Coordination modes

Since the amount of Ni ions sorbed per complexing site increased from 1 per 5 to 1 per 1 when the Ni/P ratio increased from 0.2 to 7.9, it was meaningful to investigate the possible coordination modes involved in the sorption mechanisms and to link them with the experimental results obtained at increasing Ni/P ratios and various temperatures. Starting from the different coordination modes proposed by Popa et al. describing the interaction between polymer-grafted phosphonates and different cations [31], our strategy consisted to propose different interaction mechanisms by taking into account our experimental results (Fig. 6).

Coordination mode A involves two phosphonated groups per metal ion. Modes B and C involve only one phosphonated group per metal ion (with a slight difference in the coordination mode) and mode D involve two phosphonated groups for two metal ions. Modes A' and A'' and modes D' and D'' involves intra- or inter-chain interactions, implying two phosphonated groups per metal ion and two phosphonated groups for two metal ions, respectively.

For Ni/P ratios lower than 1, the coordination modes A, A' and A'' were the most representatives. These coordination modes imply sorption efficiency equal to 1:2, significantly higher than the sorption ratio of 1:5 obtained at low Ni/P ratio in this study. Theoretical sorption efficiency of 1:2 would be globally reached only if each Ni cation could access two neighboring sites (Fig. 6b). This could be possible with block architecture of the polymer chains where the whole phosphonated sites would be adjacent and form a homogeneous linear chain. In our study, the use of a statistical copolymer did not enable such configuration, but promote the presence of isolated phosphonated sites randomly dispersed along the copolymer chain. Such architecture therefore leads to reduction in the global sorption efficiency because the probability that two phosphonated groups would be adjacent becomes lower than for block architecture. Consequently, in this range of Ni/P ratio, a substantial number of complexing groups in the copolymer would remain free of metal sorption because of their position in the chain. The sorption efficiency observed in this condition can then be attributed to coordination modes A, A' and A'', taking into account that a significant number of the complexing sites cannot be involved in the sorption process for Ni/P ratios lower than unity.

For Ni/P ratio above unity, the chemical potential of Ni increased in the vicinity of the copolymer, leading to enhance the driving force for mass transfer of Ni cations from the aqueous solution to the sorption sites. The Ni cations are thus pushed to the complexing sites, promoting their sorption on the complexing sites. Once the driving force exceeded a critical value, corresponding to a Ni/P ratio close to one, the increase in the sorption properties described in Fig. 5 would imply a shift of the sorption equilibrium, leading to a modification of the sorption mechanisms. In this respect, different coordination modes B, C, D, D' and D'' (Fig. 6) can be involved to explain the increase in the sorption capacity from 0.2 to 1 mmolNi_{complexed}/mmolP. Indeed, a strong driving force for Ni transfer could force the free sites (sites that were not involved in the complexation at low Ni/P ratio due to their position in the polymer chain) to interact with Ni cations, thus leading to the other coordination modes B, C, D, D' and D''. Those new coordination modes become more and more favorable with increasing the driving force;

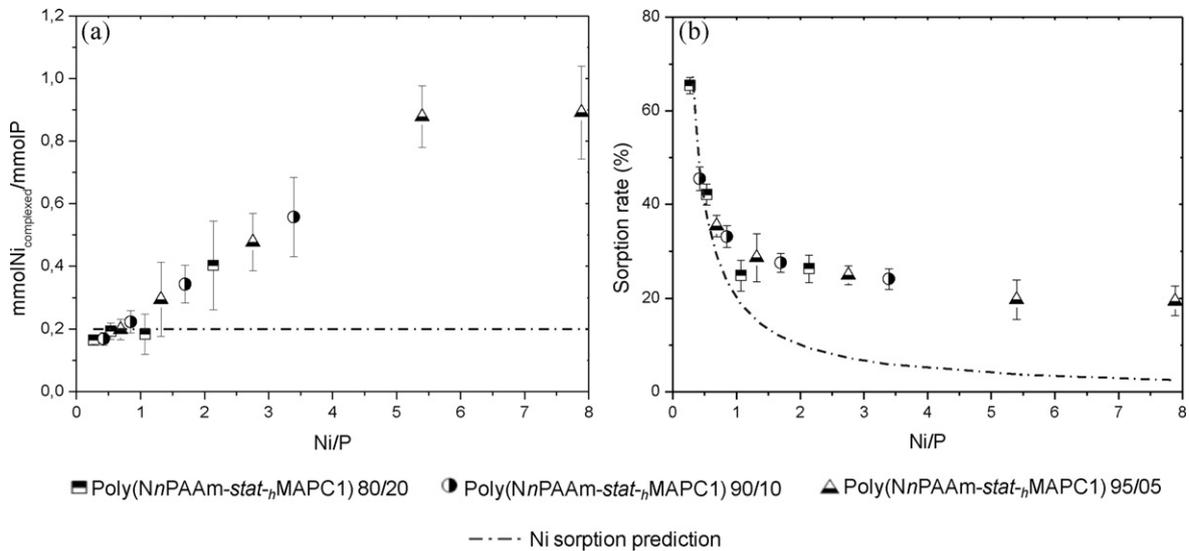


Fig. 5. Sorption capacities (a) and rates (b) of poly(NnPAAm-stat-hMAPC1) as a function of the Ni/P ratio.

hence the following modification of coordination modes becomes realistic: A into D, A' into D' and A'' into D''. Finally, the mix of these coordination modes would lead to sorption efficiency of 1:1 and explain the gradual increase in the global sorption efficiency when increasing the Ni/P ratio (Fig. 5).

Additionally, the coordination modes presented in Fig. 6 also explain (i) the differences of sorption properties observed between

10 °C and 20 °C (Fig. 3b) and (ii) the reduction of the particle size when increasing the Ni/P ratio (Fig. 4). Below the LCST and for a Ni/P ratio lower than unity, the sorption capacity was shown to decrease with decreasing temperature from 20 °C to 10 °C (Fig. 3), therefore A, A' and A'' coordination modes are the most representative. Moreover, another phenomenon can be involved in the decrease of sorption properties between 20 °C and 10 °C: at 10 °C,

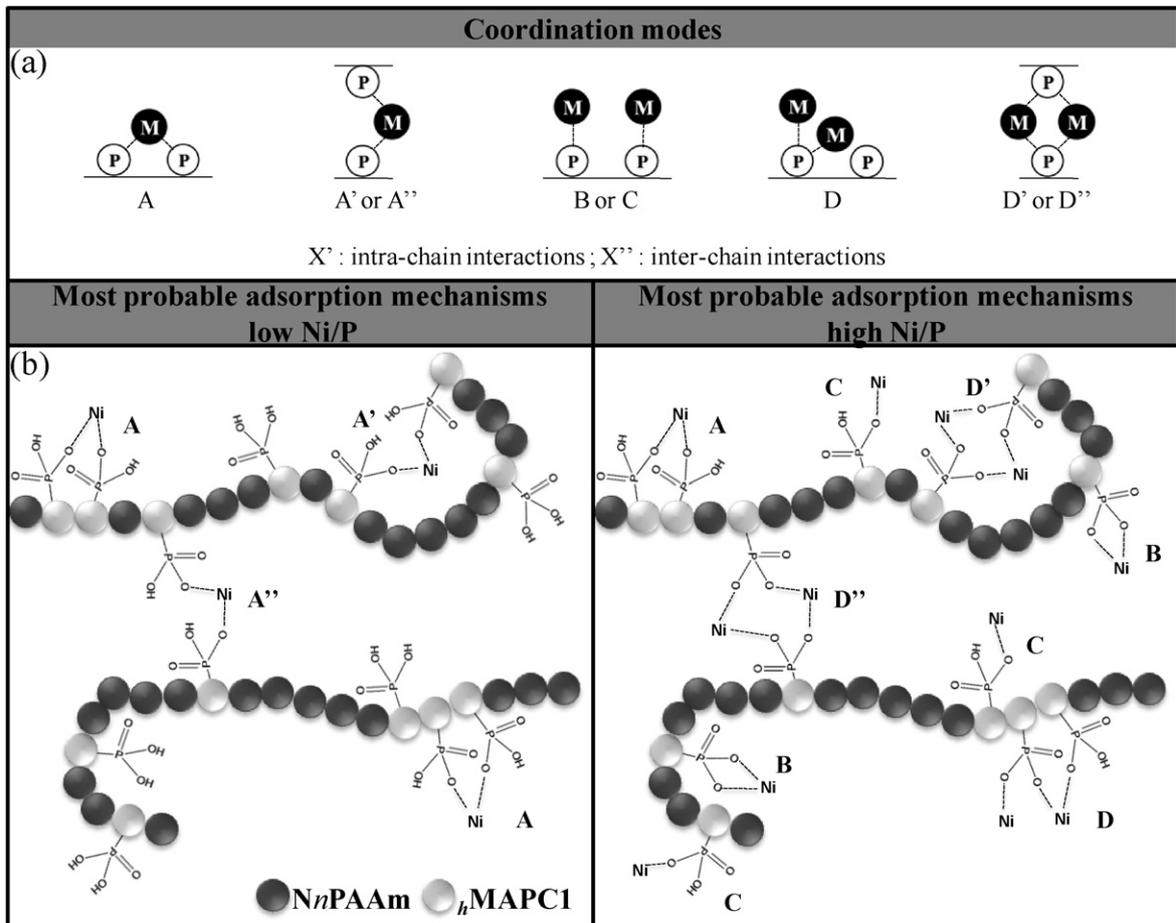


Fig. 6. Representation of the most probable adsorption mechanisms as function of Ni/P ratio.

the polymer chains are fully extended whereas at 20 °C, close to the LCST, the polymer chains will tend to (i) fold and (ii) to move closer due to interactions of thermosensitive segments because of the reduction of polymer solubility. Therefore, the conformation of polymer chains in water is more favorable at 20 °C since the proximity between complexing groups favors coordination modes A' and A'' in addition to the mode A.

Concerning the change of the particle size with the Ni/P ratio (Fig. 4), the existence of coordination modes A', A'', D' and D'' also contributes to the reduction of the particle size observed for all temperature when increasing the nickel concentration. Indeed, such coordination modes favor the intra- and inter-chain interactions, all the more since the Ni/P ratio is high.

4. Conclusion

New thermosensitive copolymers sorbents with complexing properties toward Ni cations were synthesized by free radical copolymerization for water treatment applications. The LCST of the synthesized copolymers ranged from 22 °C to 26 °C, *i.e.* significantly lower than the LCST of poly(*N*-isopropylacrylamide) p(NiPAm) currently used in the literature. Such low LCST values must provide significant cost reduction of for the separation of the insoluble copolymer–metal complexes from the treated water, and would lead to simpler and cheaper processes. The sorption properties of such copolymers toward Ni cations were evaluated in various conditions of pH, temperature and Ni/P ratio. The best sorption capacities were obtained at temperatures around the LCST and under neutral pH conditions when there was no sorption competition with H⁺ cations. At neutral pH, the evolution of the sorption capacities with the temperature was related to the polymer chain conformation: in the solubility domain, increasing the temperature push the copolymer chain to move closer and enhance the metal–polymer interaction. In the insolubility domain, the increase in the temperature led to the shrinkage of the copolymer particles, reducing the number of phosphonated sites available for complexation. Furthermore, the Ni/P ratio was shown to strongly affect the sorption properties of the copolymers. At low Ni/P (<1), an average of 1 Ni cation complexed every 5 phosphonated sites was observed. This result was explained by the statistical structure of the copolymer, since isolated phosphonated sites were dispersed in the polymer chain. At higher Ni/P (>1), the sorption capacity increased, leading to one Ni cation sorbed per phosphonated site at highest Ni/P ratio and therefore to a better sorption efficiency per gram of polymer. In the best operating conditions (pH 7, 20 °C, high Ni/P ratio), the maximal sorption capacity reached 0.6 mmol g_{poly}⁻¹ which is significantly higher than the sorption properties of the similar thermosensitive and complexing materials found in the literature. Finally, according to the sorption capacities obtained in different operating conditions (pH, T, metal vs polymer concentration), we presented in this paper different sorption mechanisms involving various coordination modes, which could be monitored in water treatment to focus on (i) the sorption efficiency and/or (ii) the polymer consumption.

Acknowledgments

The authors thank the “Agence Nationale de la Recherche” (ANR) for funding this work under the 2009 ECOTECH program and Specific Polymers Society (Montpellier, France) for supplying both monomers enabling the synthesis of the copolymers studied in this paper.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2012.10.031>.

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