Sorption properties of a new thermosensitive copolymeric sorbent bearing phosphonic acid moieties in multi-component solution of cationic species

Alain Graillot a,b, Denis Bouyer a, Sophie Monge b, Jean-Jacques Robin b, Pierre Loison a, Catherine Faur a,*

a Institut Européen des Membranes–IEM (UMR 5635 CNRS-ENSCM-UM2) – Equipe Genie des Procedes Membranaires, Universite Montpellier II 5247, Place Eugene Bataillon, 34095 Montpellier Cedex 5, France
b Institut Charles Gerhardt Montpellier (UMR 5253 CNRS-UM2-ENSCM-UM1) – Equipe Ingenierie et Architectures Macromoleculaires, Universite Montpellier II cc1702, Place Eugene Bataillon, 34095 Montpellier Cedex 5, France

HIGHLIGHTS

• Influence of cation valence on sorption properties on functionalized copolymer.
• Investigation of sorption mechanisms depending on the operating conditions.
• Sorption selectivity in multi-component systems.
• Role of Al3+ cation on sorption properties in multi-component system.

GRAPHICAL ABSTRACT

ABSTRACT

In this paper, original thermosensitive copolymers bearing phosphonic acid groups, namely the poly(N-n-propylacrylamide-stat-2-(methacryloyloxy)methylphosphonic acid) (P(NnPAAm-stat-2MAPC1)) were synthesized, and their sorption properties for three divalent cations (Ni2+, Ca2+, Cd2+) and one trivalent cation (Al3+) have been investigated. The sorption experiments were performed with increasing relative amount of cationic pollution compared to the amount of sorption sites (Cm/P ratio) in mono and multi-component solutions to investigate the sorption mechanisms. Cm/P proved to strongly affect the sorption capacity and high capacities were obtained for all cations at highest Cm/P ratios, reaching one mole of sorbed per phosphonated moiety. For divalent cations, sorption mechanisms were likely to be described by electrostatic interactions only, whereas for aluminum trivalent cation the sorption not only resulted from electrostatic interactions also but from the formation of coordination binding. The selectivity of the phosphonic acid moieties for aluminum cations was demonstrated, highlighting the interest of P(NnPAAm-stat-3MAPC1) for their use for the treatment of metallic pollution from wastewater.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In the last decades, a wide spectrum of processes has been developed to eliminate the metallic pollution from wastewater. The most common processes are based on lime precipitation, electrolytic methods or ion-exchange resins but the evolution of standards for the metallic pollution in wastewater drove the
scientific community either to improve these usual methods or to find out original solutions to remove metallic pollution from wastewater. Among all of these processes, a special interest has been given to polymeric sorbents. Their main advantage for the treatment of metallic pollution is that a polymer can be specifically built to remove a targeted metal, i.e. the selectivity of the process is greatly improved compared to the common processes, such as precipitation for instance. It has been shown in literature that the wide range of sorption chemical moieties (alcohol, carboxylic acid, sulfonic acid, phosphonic acid, amidoxime, crown ether, etc.) [11] enables to synthesize a broad spectrum of functionalized polymers, which have therefore specific sorption properties for a wide range of elements (transition metals, lanthanides, rare earth elements, etc.). Within these functional moieties, a special interest was given in this work to phosphonic acid groups since they allow the sorption of a lot of metallic cations in aqueous solution (Ag⁺, Ni²⁺, Ca²⁺, Cu²⁺, Pb²⁺, Co²⁺, Cr³⁺, etc.) [2–7]. The physical state (soluble, insoluble) and properties (thermal, mechanical or chemical properties) of such functionalized polymers can be adapted to the purification process and also to the separation technique (decantation, filtration, etc.). In this respect, it is possible to build (i) insoluble polymer sorbents (polymer beads [8], gels [9,10], membranes [11,12], polymeric networks [13], fibers [14,15], etc.) or (ii) water soluble polymers. On the one hand, insoluble polymer sorbents are of great interest for wastewater treatment since they can be easily removed from the water after metal sorption. On the other hand, water-soluble polymeric sorbents ease the sorption step since the sorption groups are directly in contact with the metallic pollution in water due to polymer hydrophilicity [3]. As they combined both advantages, thermosensitive polymeric sorbents are therefore particularly attractive. At temperature lower than the Lower Critical Solution Temperature (LCST), the thermosensitive polymeric sorbent is soluble in water; that is, the sorption of the metallic cations is favored in solution. Above the LCST, the polymeric sorbent becomes non-soluble, making the polymer–water separation more favorable. For these reasons, many researchers have highlighted the advantages to use thermosensitive polymeric sorbents for the elimination of metallic pollution in wastewater [3,5,16–18]. Among all the thermosensitive polymeric sorbent used, a special interest was given in our previous works [5,16] to poly(N-n-propylacrylamide-stat-2-(methacryloyloxy)methylphosphonic acid) (P(NnPAAm-stat-nMAPC1)) copolymers as they combined low LCST values and good sorption properties due to the presence of phosphonic acid moieties on the polymer chains. These studies, focusing on the elimination of Ni²⁺ cations from synthetic effluents, highlighted the link between the sorption capacity and the temperature, the pH and the moles of Ni vs the moles of sorption sites (Ni/P ratio). Additionally, it was shown that the Ni²⁺ sorbed under the LCST were not released above the LCST, once the copolymer–metal complex switched from soluble to non-soluble state in water.

Nevertheless, our previous work only focused on the sorption of a specific cation (Ni²⁺) onto P(NnPAAm-stat-nMAPC1) copolymer in various conditions of Ni/P ratio but no special attention was given to the sorption mechanisms. Actually, to date, two different theories are described in the literature to tempt explaining the sorption of metallic cations onto phosphonic acid groups: (i) ion exchange [4,19–21] and (ii) complexation [6,22]. However, the predominance of one mechanism on the other is still unclear and to our knowledge no detailed work was carried out until now to determine which sorption mechanism is predominant when different experimental conditions are used.

In this contribution, we demonstrated for the first time that the sorption of cationic species on phosphonic acid is due to both ion exchange and/or complexation, notably depending on the metallic cation and its concentration. This was shown investigating (i) the influence of the cation on the sorption properties, (ii) the sorption mechanisms involved between the phosphonic acid groups and different cations and (iii) the selectivity of the phosphonic acid as a function of cationic species. More concretely, the sorption properties of P(NnPAAm-stat-nMAPC1) copolymeric sorbent were evaluated for diverent cations (Ca²⁺, Ni²⁺ and Cd²⁺) and for a trivalent cation (Al³⁺) in mono and multi-component solutions and for various operating conditions. Results allowed to discuss the sorption mechanisms involved between phosphonic acid groups and cations having different valences and also to conclude on the affinity of these functional groups.

2. Experimental

2.1. Materials

2.1.1. Thermosensitive polymeric sorbent

All P(NnPAAm-stat-nMAPC1) copolymers used in this study have been synthesized by free radical polymerization between (dimethoxyphosphoryl)methyl 2-methylacrylate (MAPC1, Specific Polymers,[86242-61-7]-SP41-003) and N-n-propylacrylamide (NnPAAm, Specific Polymers,[25999-13-7]-SP43-0-002) using AIBN as radical initiator. The copolymerization procedures as well as the hydrolysis of the phosphoryated ester into phosphonic acid groups of the MAPC1) moieties were described in a previous paper [16]. Chemical structure and architecture of P(NnPAAm-stat-nMAPC1) is reported in Fig. 1.

Copolymers with different NnPAAm/nMAPC1 molar ratios (80/20, 90/10 and 95/05) were used. The amount of sorption groups per gram of copolymer (mmol P/gpoly) was calculated using 1H NMR spectroscopy. The signals of nMAPC1 at 4.0–4.3 ppm corresponding to the hydrogens of the CH₂ in α of the phosphorus atom were compared with those of NnPAAm at 1.2–1.8 ppm attributed to the hydrogen of the methyl group. P(NnPAAm-stat-nMAPC1) 80/20, 90/10 and 95/05 contained 1.45 mmol, 0.67 mmol and 0.37 mmol of phosphonic acid sorption moieties per gram of copolymer, respectively.

2.2. Synthetic effluents

The synthetic effluents were prepared by dissolution of salts in deionized water. Nickel(II) chloride hexahydrate (NiCl₂·6H₂O, Fisher Scientific, 97%), calcium(II) chloride tetrahydrate (CaCl₂·4H₂O, VWR 99%), cadmium(II) chloride hydrate (CdCl₂·H₂O, Fisher Scientific, 98%) and aluminum(III) nitrate nonahydrate (Al(NO₃)₃·9H₂O, Fisher Scientific, 98%) salts have been used as received. The concentrations of metal cations of all synthetic effluents were checked by Atomic Sorption Spectroscopy with a Perkin Elmer AAnalyst 400, an AutoPrep 50 dilutor and a S10 Auto-sampler. Calibration curves were obtained by automatic
dilution of a standard solution (100 mg L⁻¹). In order to limit the cationic species in solution and to avoid bias in the determination of the sorption properties, the pH of the synthetic effluents was not adjusted and only depended on the amount of salts introduced in solution.

3. Methods

3.1. Sorption experiments

Sorption experiments were carried out using a dialysis tubular membrane as already described in a previous paper [5]. The amount of metallic cations trapped by the copolymer was determined by measuring the concentration of the metal cations in the synthetic effluent before and after sorption experiments. The latter were carried out at 20 °C during 24 h and the temperature was controlled by a 6 Liter Fisher Bioblock Scientific Cryothermostat bath. The sorption properties were only attributed to the interactions between the cationic species and the phosphonic acid moieties. Indeed, it was checked that P(NnPAAm) thermosensitive homopolymers did not have any sorption properties.

3.1.1. Sorption kinetics

Sorption kinetic experiments were performed by measuring the cation concentrations in solutions at regular time-steps by Atomic Sorption Spectroscopy. For each sorption kinetic, six experiments were conducted in parallel in order to avoid bias when samples were collected. Half of these experiments was launched with 12 h delay; thus the sorption kinetics were followed during 24 h without intermission.

3.1.2. Isothermal sorption experiments

3.1.2.1. Mono-component experiments. The ratio between the relative amount of cationic pollution and the amount of phosphonic acid sorption groups (C<sup>n+</sup>/P ratio) was obtained by changing either the copolymer concentration in the tubular dialysis membrane from 1.25 g L⁻¹ to 10 g L⁻¹ (corresponding to 0.42 mmol<sub>P</sub> L⁻¹ to 14.5 mmol<sub>P</sub> L⁻¹ depending on the copolymer used) or the cation concentration in the effluent. The pH of the effluents was followed during the sorption experiments.

3.1.2.2. Multi-components experiments. For these experiments, synthetic solutions containing equimolar amount of the targeted cations (Ni<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup> and Al<sup>3+</sup>) were prepared.

3.1.2.3. Two steps sorption experiments. These experiments were performed in order to estimate the sorption properties of a copolymer already loaded with cationic species. The first sorption step was made as previously described for mono-component experiments. Second sorption step was achieved by taking out the dialysis tubular membrane from the first sorption bath and then immersing it in a second sorption bath containing cationic species in the same concentration as the one used in the first sorption step.

4. Results and discussion

4.1. Sorption kinetics

Sorption kinetics experiments were achieved at 20 °C for Ni<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup> and Al<sup>3+</sup> in order (i) to highlight the influence of the cation on the sorption kinetics and (ii) to evaluate the time needed to reach the equilibrium. Sorption experiments were performed with molar concentrations of metal ions that corresponded to C<sup>n+</sup>/P ratios equal to 0.5 (Fig. 2a) and 5 (Fig. 2b). At low C<sup>n+</sup>/P ratio (0.5), the amount of cations was in excess compared to the amount of phosphonic acid sorption, unlike at high C<sup>n+</sup>/P ratio (5).

The results obtained at lowest C<sup>n+</sup>/P ratio (Fig. 2a) were very similar whatever the cation: the sorption equilibrium was reached after about 8 h and varied from 0.24 and 0.3 mmol<sub>sorbed</sub> / mmol<sub>P</sub>. At highest C<sup>n+</sup>/P ratio (Fig. 2b), the amount of cations sorbed per sorption were comprised between 0.8 and 1.05 mmol<sub>sorbed</sub> / mmol<sub>P</sub> at equilibrium, which was reached after 13 h in each case. Sorption experiments were also conducted during 24 h.

4.2. Influence of C<sup>n+</sup>/P ratio on sorption equilibrium

Fig. 2 exhibited that the sorption capacity at equilibrium strongly depended on C<sup>n+</sup>/P ratio between 0.5 and 5. Consequently, this parameter was investigated in more details in this section. The sorption properties were evaluated for a wide range of C<sup>n+</sup>/P ratios ranged between 0 and 22 for three divalent cations (Ni<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>) and one trivalent cation (Al<sup>3+</sup>):

Fig. 3 reports the moles of cation sorbed per mole of sorption groups (i) for C<sup>n+</sup>/P ratios between 0 and 22 (Fig. 3a) and (ii) with a focus between 0 and 6 (Fig. 3b). Overall, the curves relative to each cation followed the same trend: the amount of cation sorbed per sorption site increased from 0 to 1 when increasing C<sup>n+</sup>/P. Note that standard deviations relative to the results obtained at the highest ΣC<sup>n+</sup>/P are high due to analytical factor; hence the absolute values of these last points should be considered carefully. As
**demonstrated in our previous paper for Ni^{2+} cations [5], different coordination modes could be considered due to the copolymer statistical architecture (Fig. 1): coordination modes involving one and two phosphonated moieties per Ni cation were considered depending on Ni/P (Fig. 4). At low Ni/P ratio, two phosphonated moieties were involved in sorption of one Ni cation whereas at higher Ni/P ratio, it was shown that one Ni cation was sorbed on one phosphonated moiety.**

Fig. 3 exhibits that the curves relative to other cations used in this study (Ca^{2+}, Cd^{2+}, Al^{3+}) followed the same trend, suggesting that the same coordination modes could explain their sorption on the copolymer. For C^{2+}/P ratios lower than 2.5, metal sorption mainly occurred on neighboring sites and therefore A, A' and A'' coordination modes (Fig. 4) are the most relevant. This assumption implies that a non-negligible amount of sorption sites were not involved in the sorption at low C^{2+}/P ratios as they were isolated in the copolymer chains. When increasing C^{2+}/P, the sorption mechanisms switched to other coordination modes, which involved an average of one phosphonated sorption groups per cation (B, C, D, D' and D'' coordination modes).

Even though the same coordination modes could explain the sorption of these four cations, the sorption capacity at different C^{2+}/P ratios was different for Ca^{2+}. The maximum capacities corresponding to one metal sorbed per sorption moiety was reached at C^{2+}/P between 5 and 7 for Ni^{2+}, Cd^{2+} and Al^{3+} whereas it was reached only at C^{2+}/P = 10 for Ca^{2+}. This difference could be displayed by a lower affinity of calcium cations for the phosphonic acid sorption groups compared to the other cations, especially at highest C^{2+}/P ratios.

### 4.3. pH during the sorption process

Different sorption mechanisms may explain (i) the coordination modes involved between phosphonic acid and the cations and (ii) the differences observed in the case of Ca^{2+}. These sorption mechanisms are of two kinds: (i) cation exchange and (ii) complexation. Ion exchange processes involve attraction of cations by the negative charges of the functional groups. Resulting functional groups–cations interactions are relatively weak, also reversible and allow ion exchange. To maintain the electronegativity, the negative charges of the functional groups are always balanced by an equivalent amount of cationic species. Furthermore, complexation process results from the formation of coordination bonds between one cation and an organic ligand which bears electron

**Fig. 4.** Representation of the most probable coordination modes involved in the sorption of cations on P(NiPAAm-stat-MAPC1) copolymer for different conditions of C^{2+}/P ratios.
donor groups that can be either basic (−NH₂, −OH, etc.) or acidic (−COOH, −PO₃H₂, −SO₃H₂, etc.). When two or more coordination bonds are involved in the cation sorption, the functional groups are defined as chelates or chelating agents. One sorption mechanism can prevail on the other, depending on the nature of the functional groups, but both are most often involved in the sorption process. In order to determine which sorption mechanism prevail in these experiments, the pH has been measured during the sorption process to determine the moles of H⁺ released per mole of phosphonic moieties and compared to the moles of cations sorbed per sorption site. Table 1 summarizes the sorption and release values obtained for C²⁺/P equal to 0.5 and 5 at equilibrium.

4.3.1. Divalent cations

For divalent cations (Ni²⁺, Ca²⁺ and Cd²⁺), Table 1 shows that the amount of released H⁺ was nearly two times higher than the amount of cations sorbed on the copolymer, whatever C²⁺/P ratio. This result suggests that ion exchange is the most probable sorption mechanism since the sorption of divalent cations was regulated by charge conservation. Also, the divalent cations would be preferentially sorbed on adjacent phosphonic moieties at low C²⁺/P ratio whereas isolated sorption moieties would remain free of sorption [5]. Indeed, as shown in Fig. 5a–c, adjacent sorption moieties concentrate the local charge density and therefore promote the sorption of divalent cations on the contrary to isolated sorption moieties, which are characterized by a lower local charge density.

At low C²⁺/P ratio, the coordination modes involving two sorption sites per cation (A, A’ and A’’ coordination modes, Fig. 4) are therefore directly explained by the electrostatic interactions. At high C²⁺/P ratio, electrostatic interactions are also consistent with the modification of the coordination modes from one cation sorbed for two sorption sites to one cation sorbed per site. Indeed, in a first time, the sorption would also result on electrostatic interactions on adjacent moieties as proposed in Fig. 5d. Then, at higher C²⁺/P ratios, the higher cation concentration gradient would favor the sorption on sites that remained free (Fig. 5e) and would lead to an average of one cation sorbed per site (Fig. 5f), corresponding to B, C, D, D’ and D” coordination modes.

Also, the sorption mechanism mainly based on electrostatic interaction is consistent with the lower affinity of Ca²⁺ for the phosphonic acid moieties. The lower calcium electronegativity (χ = 1.0) compared to those of nickel (χ = 1.9) and cadmium (χ = 1.69) implies a lower tendency of Ca to attract electrons than to other divalent cations. Hence, the sorption of calcium on isolated phosphonic acid moieties occurred at higher C²⁺/P values in comparison with the other divalent cations (Fig. 3).

4.3.2. Trivalent cations

At low C³⁺/P ratio (0.5) and for trivalent Al³⁺ cations, electrostatic interactions were also involved in the sorption mechanisms as the amount of H⁺ released in solution was three times higher than the amount of Al³⁺ sorbed on the copolymer. But a different trend was observed at higher C³⁺/P ratio (5): the amount of released H⁺ was only two times higher than the amount of sorbed Al³⁺. This result was in agreement with the maximum capacity of two H⁺ released per phosphonic acid site, meaning that at high C³⁺/P ratio, all phosphonic moieties were involved in the sorption process. But, in this case, the principle of charge conservation was not checked as the sorption of one Al³⁺ (three positive charges) came with the release of only two H⁺ (two positive charges). That is, another kind of interactions was probably involved in the sorption mechanism.

One reason could be proposed to explain these results but it was not perfectly convincing: at the beginning of the sorption experiments, the pH was contained between 4.0 and 4.5 and therefore aluminum was decomposed in various forms, i.e. 10% of Al(OH)₃²⁺, 5% of Al(OH)₂²⁺ and 85% of Al³⁺. The sorption of divalent Al(OH)₂²⁺ and monovalent Al(OH)₂⁺ species could occur without charge conservation issues, as illustrated in Fig. 6a. But, at the end of the experiments, the sorption of 1 mmol_{Al}^{3+}/mmol_{P} from a mono-component solution of Al³⁺ still implied a default of charge.
conservation, which could not only be explained by electrostatic interactions. Consequently, the formation of coordination bonds could happen between the phosphonic acid groups and Al$^{3+}$ cations as illustrated in Fig. 6b. The existence of both electrostatic interactions and coordination bond formation to describe the sorption mechanisms could be explained by the acidity of the phosphonic acid moieties. Indeed the latter is contained between the acidity of sulfonic acid and the one of carboxylic acid and both have different sorption mechanisms [23,24]: the sorption properties of sulfonic acid are mainly due to electrostatic interactions because of their strong acidity whereas the sorption properties of carboxylic acid preferentially result from coordination bonds. Additionally, the pH of solutions containing Al$^{3+}$ was lower (from pH = 4.0–4.5 to 2.9–3.0) than the pH of solutions containing divalent cations (from pH = 6.5–6.0 to 3.3–3.0), which might also have an impact on the sorption mechanisms. Lower pH values imply a lower ionization of the functional groups (–OH rather than –O–) and therefore promote complexation rather than electrostatic interactions.

To check the relevance of this assumption and to investigate the selective behavior of the copolymers, the sorption competition between the divalent and trivalent cations was studied.

### 4.4. Sorption competition and selectivity

#### 4.4.1. Multi-component sorption experiments

Additional experiments were carried out with synthetic effluents in order to evaluate the competitive sorption on the phosphonic acid moieties. Equimolar mixtures of the four cations were prepared (25 mol% of each cation in the initial solution). The global cationic concentration was adjusted to reach a global C$^{n+}$/P ratio ranging from 0.44 to 4.62. As this global C$^{n+}$/P ratio takes into consideration all the cationic species in solution, it is called $\sum$C$^{n+}$/P later in this study.

Fig. 7 represents the distribution of the cationic species sorbed on the copolymer at equilibrium, with increasing $\sum$C$^{n+}$/P ratios. At the lowest $\sum$C$^{n+}$/P ratio, the distribution of the cations sorbed on the copolymer is almost the same than the one of the initial synthetic solutions. At higher $\sum$C$^{n+}$/P ratios, the distribution was modified and the aluminum was preferentially sorbed on the copolymer: the mole fraction of sorbed aluminum reached 53% at $\sum$C$^{n+}$/P of 0.85, 67% at $\sum$C$^{n+}$/P of 1.70, 69% at $\sum$C$^{n+}$/P of 2.75, 81% at $\sum$C$^{n+}$/P of 3.60 and almost 100% at $\sum$C$^{n+}$/P of 4.62. In the same time, the proportion of sorbed Ca$^{2+}$ decreased when increasing the $\sum$C$^{n+}$/P ratio from 22% at $\sum$C$^{n+}$/P of 0.44 to 4% at $\sum$C$^{n+}$/P of 1.70 and less than 0.5% when $\sum$C$^{n+}$/P exceeded 3.60. The proportion of Ni$^{2+}$ and Cd$^{2+}$ decreased with the same order of magnitude when increasing the $\sum$C$^{n+}$/P ratio, but less than for Ca$^{2+}$: from 22% and 30% for Ni$^{2+}$ and Cd$^{2+}$ respectively at $\sum$C$^{n+}$/P = 0.44 until 1% at $\sum$C$^{n+}$/P = 4.62.

These results suggest that, at low $\sum$C$^{n+}$/P, the large number of sorption sites compared to the global amount of cations did not allow distinguishing the sorption affinity of all cations on the copolymer. Increasing the $\sum$C$^{n+}$/P ratio led to the increase of the Al$^{3+}$ proportion sorbed on the copolymer. The affinity between the copolymer and both Ni$^{2+}$ and Cd$^{2+}$ was similar and much greater than the one of Ca$^{2+}$. Consequently, the affinity of the phosphonic acid groups for the divalent cations could be classified as follows: Ni$^{2+} >$ Cd$^{2+} >$ Ca$^{2+}$, in agreement with the electro-negativity of the cations (1.91, 1.69 and 1.00, for Ni$^{2+}$, Cd$^{2+}$ and Ca$^{2+}$, respectively). The increasing amount of Al$^{3+}$ sorbed on the copolymer observed when increasing the $\sum$C$^{n+}$/P indicates that phosphonic acid had greater affinity for the trivalent cation than for divalent ones; that in agreement with the different interaction mechanisms proposed to describe the sorption of these cations.

Consequently, a special attention was given to the total amount of cations sorbed per site (mmolC$^{n+}$/P sorbed / mmolP) when increasing $\sum$C$^{n+}$/P ratio (Fig. 7). For $\sum$C$^{n+}$/P ranging from 0.44 to 2.75, all the cationic species were sorbed and the total sorption capacity increased from 0.29 to 0.58 mmolC$^{n+}$/P sorbed / mmolP, in agreement with the results shown in Fig. 3. However, at $\sum$C$^{n+}$/P $\geq$ 3.60, the total sorption capacity decreased to 0.45 mmolC$^{n+}$/P sorbed / mmolP. Such a decrease could not be attributed to the pH of these solutions since it remained almost constant for all solutions (from pH = 4.4 at $\sum$C$^{n+}$/P = 0.85 to pH = 4.1 at $\sum$C$^{n+}$/P = 4.6). However, this decrease was correlated to the high affinity of phosphonic acid groups for Al$^{3+}$ cations. Indeed, the sorption capacity value obtained for $\sum$C$^{n+}$/P = 4.6 was the same than the one corresponding to a mono-component solution of Al$^{3+}$ with an Al$^{3+}$/P ratio equal to 1.15 (Fig. 3), meaning that the multi-component sorption of Al$^{3+}$ is so favored at high $\sum$C$^{n+}$/P ratio that the copolymer sorption capacity is similar to that obtained for mono-component solutions of Al$^{3+}$.

#### 4.4.2. Sorption of cations on loaded copolymers

To confirm the link between the sorption mechanisms and C$^{n+}$/P ratio and more specifically to better understand the specific interactions between the phosphonic acid groups and Al$^{3+}$, new sorption experiments have been carried out. In a first step, sorption experiment was achieved between the copolymer and a first cation (named C$^{1+}_{1}$) until equilibrium; then in a second step, the same copolymer was put into contact with a second cation (named C$^{2+}_{2}$). In Fig. 8, the first column corresponds to the amount of cation C$^{1+}_{1}$.
sorbed in the first sorption step. The four other columns show (i) the amount of $\text{C}_n^{\text{a}+}$ sorbed in the second sorption step and (ii) the amount of $\text{C}_1^{\text{b}+}$ that was still sorbed after the sorption of $\text{C}_2^{\text{a}+}$. The initial cationic molar concentration was the same in all cases. As in Fig. 3, the ordinate represents the total mole number of cations sorbed per mole of phosphonic acid moieties. Fig. 8a–d represents the results obtained at $\text{C}^{\text{a}+}/P$ ratio of 0.5 and Fig. 8e–h correspond to a targeted $\text{C}^{\text{a}+}/P$ of 5. The total mole number of cations sorbed per mole of phosphonic acid moieties reached 0.3–0.4 when $\text{C}^{\text{a}+}/P = 0.5$ whereas it increased to 0.8 and almost unity when $\text{C}^{\text{a}+}/P = 5$. When $\text{C}^{\text{a}+}/P = 0.5$, a significant number of sorption sites remained free from cations after the first sorption step, whereas at $\text{C}^{\text{a}+}/P = 5$ almost all sorption sites were saturated at the end of the first sorption step.

At lowest $\text{C}^{\text{a}+}/P$ ratio, Fig. 8a–d shows that the sorption of the second cation $\text{C}_2^{\text{a}+}$ (second step) did not lead to a significant release of the sorbed cation $\text{C}_1^{\text{b}+}$ already sorbed during the first step. Similar results were obtained for all cation couples, suggesting that the sorption of the second cation $\text{C}_2^{\text{a}+}$ occurred on free sorption sites, i.e. sites that have not been involved during the first sorption step. On the contrary, when the copolymer was previously saturated at

---

**Fig. 7.** Repartition of the cationic species sorbed on P[NiPAAm-stat-g-MAPC1] copolymers starting from equimolar synthetic effluent of the four cations (Ni, Ca, Cd, Al) for different $\sum_{\text{C}^{\text{a}+}}/P$ ratios.

**Fig. 8.** Two steps sorption experiments results obtained at low (a–d) and high (e–h) $\text{C}^{\text{a}+}/P$ ratios.
the end of the first sorption step, different cases were observed (Fig. 8e–h). Firstly, for all cations, no additional sorption of the same cation was noticed, which confirmed that all available sorption sites have been involved in the sorption process at the end of the first step. Secondly, when the cation sorbed during the first sorption step (C\textsuperscript{2+}) was a divalent cation, the sorption of the second cation C\textsuperscript{n+} occurred on sorption sites already engaged in the sorption of C\textsuperscript{2+} which implied a significant release of C\textsuperscript{2+}. Fig. 8e–h point out that the amount of cation released depended on the C\textsuperscript{n+}/C\textsuperscript{2+} couple. Hence, the most important release was observed for Ca\textsuperscript{2+} (C\textsuperscript{2+}) (between 85% and 100% of Ca\textsuperscript{2+} released at the end of the second sorption step), whatever C\textsuperscript{n+} cation. The release of cadmium and nickel during the second step was ranged from 70 to 95% and 65 to 80%, respectively, depending on C\textsuperscript{2+}. Furthermore, Fig. 8e and g confirmed that the affinity of the phosphonic group is higher for the nickel than for the cadmium.

These results confirmed (i) that ion exchange was the main mechanism involved in the sorption of divalent cations and (ii) the classification of the divalent cations based on their affinity with phosphonic acid sorption moieties: Ni\textsuperscript{2+} ≥ Cd\textsuperscript{2+} > Ca\textsuperscript{2+}. When C\textsuperscript{2+} was trivalent aluminum cation (Al\textsuperscript{3+}), the sorption of C\textsuperscript{2+} divalent cation in the second step occurred but the amount of aluminum released in the solution was relatively low (20–25% of Al\textsuperscript{3+} release depending on C\textsuperscript{2+} cation). In this case, the amount of C\textsuperscript{2+} cation sorbed in the second step finally represented 15% of the whole cations sorbed on the copolymer, whereas the other 85% corresponded to aluminum. This result was in agreement with the sorption mechanisms (ion exchange and complexation) proposed for the Al\textsuperscript{3+} sorption. Indeed, as the electrostatic interactions are known to be weaker than the coordination bonds, the aluminum released in solution probably corresponded to the one sorbed by ion exchange whereas Al\textsuperscript{3+} sorbed by complexation remained on the copolymer.

5. Conclusion

This work focused on the sorption properties of four different cations (Ni\textsuperscript{2+}, Ca\textsuperscript{2+}, Cd\textsuperscript{2+} and Al\textsuperscript{3+}) on a new P(NnPAam-stat-MAPC) thermostable polymer sorbent bearing phosphonic acid moieties and demonstrated that the sorption capacities of P(NnPAam-stat-MAPC) depend on the relative amount of cationic pollution compared to the amount of sorption sites (C\textsuperscript{n+}/P ratio). The maximal sorption capacity of the copolymer was strongly influenced by C\textsuperscript{n+}/P ratio whatever the cation. More, adjusting this ratio allowed reaching a maximal sorption capacity of 1 mmol\textsubscript{cations}/mmol\textsubscript{P}, which was significantly higher than that was observed in the literature for similar di- and trivalent cations (less than 0.2 mmol\textsubscript{cations}/mmol\textsubscript{P}) [6,7]. This work also showed that the sorption phenomena involved between phosphonic acid and cationic species depend not only on the cation valence but also on the C\textsuperscript{n+}/P ratio. Two kinds of interactions should be taken into consideration to describe the sorption of cations on P(NnPAam-stat-MAPC): electrostatic and coordination bindings. For divalent cations, the sorption mainly resulted from electrostatic interactions and the affinity of the phosphonic acid for the divalent cations was linked to the cations electro-negativities. As a result, the affinity between the phosphonic acid and the cations could be classified as follows: Al\textsuperscript{3+} > Ni\textsuperscript{2+} > Cd\textsuperscript{2+} > Ca\textsuperscript{2+}. For aluminum, simultaneous electrostatic interactions and coordination bonds were involved in the sorption mechanisms. This assumption is in agreement with the acidic force of the phosphonic acid, which is located between those of carboxylic acid (which creates coordination bonds with metals) and sulfonic acid (which mainly interacts with metals by electrostatic interactions) [23,24]. At low C\textsuperscript{n+}/P ratios, sorption mainly resulted from electrostatic interactions whereas, for high C\textsuperscript{n+}/P ratios, the formation of coordination bonds prevailed to explain the metal–polymer interactions.

Acknowledgements

The authors thank the “Agence Nationale de la Recherche” (ANR) for funding this work under the 2009 ECOTECH program (ANR COPOTERM) 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.2013.05.050.

References


