



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,*}

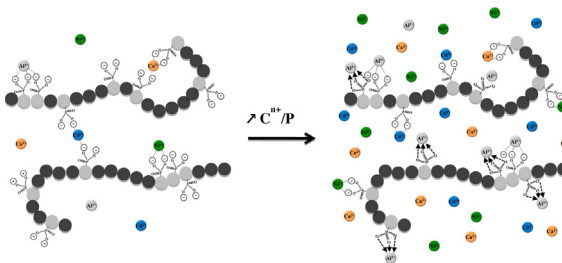
^a Institut Européen des Membranes-IEM (UMR 5635 CNRS-ENSCM-UM2) – Equipe Genie des Procédés Membranaires, Université Montpellier II cc047, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

^b Institut Charles Gerhardt Montpellier (UMR 5253 CNRS-UM2-ENSCM-UM1) – Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier II cc1702, Place Eugène 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



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ABSTRACT

In this paper, original thermosensitive copolymers bearing phosphonic acid groups, namely the poly(*N*-*n*-propylacrylamide-*stat*-2-(methacryloyloxy)methylphosphonic acid) (P(*Nn*PAAm-*stat*-*n*MAPC1)) 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 (C^{n+}/P ratio) in mono and multi-component solutions to investigate the sorption mechanisms. C^{n+}/P proved to strongly affect the sorption capacity and high capacities were obtained for all cations at highest C^{n+}/P ratios, reaching one mole of C_{sorbed}^{n+} 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 but also from the formation of coordination binding. The selectivity of the phosphonic acid moieties for aluminum cations was demonstrated, highlighting the interest of P(*Nn*PAAm-*stat*-*n*MAPC1) for their use for the treatment of metallic pollution from wastewater.

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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

* Corresponding authors. Tel.: +33 467143897; fax: +33 467149119.
E-mail addresses: denis.bouyer@um2.fr (D. Bouyer),
Catherine.Faur@iemm.univ-montp2.fr (C. Faur).

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.) [1] 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^+ , Ni^{2+} , Ca^{2+} , Cu^{2+} , Pb^{2+} , Co^{2+} , Cr^{3+} , 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 polymeric 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(*Nn*PAAm-*stat*-*h*MAPC1)) 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 Ni^{2+} 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 Ni^{2+} 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 (Ni^{2+}) onto P(*Nn*PAAm-*stat*-*h*MAPC1) 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

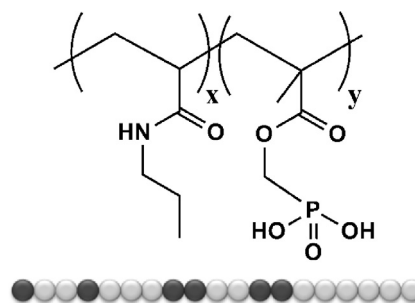


Fig. 1. Chemical structure of P(*Nn*PAAm-*stat*-*h*MAPC1) polymeric sorbent and its architecture (○: *Nn*PAAm, ●: *h*MAPC1).

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(*Nn*PAAm-*stat*-*h*MAPC1) copolymeric sorbent were evaluated for divalent cations (Ca^{2+} , Ni^{2+} and Cd^{2+}) and for a trivalent cation (Al^{3+}) 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(*Nn*PAAm-*stat*-*h*MAPC1) 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 (*Nn*PAAm, Specific Polymers, [25999-13-7]-SP43-0-002) using AIBN as radical initiator. The copolymerization procedures as well as the hydrolysis of the phosphonated ester into phosphonic acid groups of the P(MAPC1) moieties were described in a previous paper [16]. Chemical structure and architecture of P(*Nn*PAAm-*stat*-*h*MAPC1) is reported in Fig. 1.

Copolymers with different *Nn*PAAm/*h*MAPC1 molar ratios (80/20, 90/10 and 95/05) were used. The amount of sorption groups per gram of copolymer ($\text{mmol}_P/\text{g}_{\text{poly}}$) was calculated using ^1H NMR spectroscopy. The signals of *h*MAPC1 at 4.0–4.3 ppm corresponding to the hydrogens of the CH_2 in α of the phosphorus atom were compared with those of *Nn*PAAm at 1.2–1.8 ppm attributed to the hydrogen of the methyl group. P(*Nn*PAAm-*stat*-*h*MAPC1) 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 ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Fisher Scientific, 97%), calcium(II) chloride tetrahydrate ($\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, VWR 99%), cadmium(II) chloride hydrate ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$, Fisher Scientific, 98%) and aluminum(III) nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 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

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