



Thermosensitive polymer Enhanced Filtration (TEF) process: An innovative process for heavy metals removal and recovery from industrial wastewaters



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ARTICLE INFO

Article history:

Received 16 June 2014

Received in revised form 13 November 2014

Accepted 17 November 2014

Available online 29 November 2014

Keywords:

Heavy metals

Thermosensitive copolymers

Sorption

Filtration

Water treatment

Phosphonic acid

ABSTRACT

This study reports on a new process for the removal and recovery of metal elements from wastewaters, associating a sorption step on a thermosensitive copolymer bearing phosphonic acid moieties, namely the poly(*N*-*n*-propylacrylamide-*stat*-hydrolyzed (dimethoxyphosphoryl)methyl 2-methylacrylate) (P(*Nn*PAAm-*stat*-*n*MAPC1)), with a separation step by filtration. The phosphonic acid groups enable high sorption capacities for multi-component solutions (Ca²⁺, Ni²⁺, Cd²⁺, Al³⁺), while the thermosensitive behavior of the polymer allows, for temperatures higher than its LCST (25.6 °C), to get copolymer–cations non soluble particles. In the presence of aluminum, which was shown to have simultaneous coagulation and neutralization actions, these particles form aggregates of mean diameter 27–63 μm easily removed by conventional filtration (pore diameter >10 μm), leading to a lower energetic separation process compared with the well-known Polymer Enhanced Ultrafiltration (PEUF) Process. To recover metal ions and regenerate the thermosensitive copolymer sorbent, an acidic (H₂SO₄) regeneration step was studied. A decrease of the regeneration solution pH from 4 to 1 led to 100% desorption when the pH was set to 1. Such low pH conditions simultaneously allowed (i) a decrease of the copolymer LCST down to 19.5 °C, and (ii) to reach the isoelectric point of copolymer particles to finally lead to the formation of regenerated copolymer particles which could be recovered by filtration and reused in additional sorption–filtration cycles without any loss of sorption capacities.

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1. Introduction

In the last decades, heavy metal pollution contained in aqueous effluents never stopped increasing due to the considerable development of industries like mine extraction, batteries production or textile industry. Such an increase of the metallic pollution is of special concern since heavy metals are persistent, tend to accumulate in the environment and can lead to serious diseases as lung and kidney problems, cancers or severe damage in the central nervous system [4]. Facing this problem, many works have been conducted in order to develop new methods for heavy metals removal

from wastewaters. Most recent ones are either based on separation as lime precipitation [4,2] or coagulation–flocculation [1], electro-dialysis [18], electrocoagulation [9,13] or electrodeposition [10], or on sorption involving adsorption (Bhattacharyya and Sen Gupta 2008) [11,12], ion exchange, [23,8,5] or complexation [8,5,15,16]. In this last field, the most common treatment methods consist in (i) coupling sorption on water-soluble polymers with ultrafiltration in a process called Polymer Enhanced Ultrafiltration (PEUF) [17] or (ii) sorbing onto insoluble polymeric resins in a process named Solid Phase Extraction (SPE) (Beauvais and Alexandratos 1998). In the PEUF process, the hydrophilicity of water-soluble polymeric sorbents enables a direct contact of the functional groups with the metal elements present in water [21]. However, the soluble polymer–metal complexes need to be removed from the treated effluent by an energy consuming ultrafiltration separation (pore diameters 10–100 nm), which limits the use of PEUF

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processes. In the case of SPE, water-insoluble materials can be easily removed from the treated water after metal sorption but the insolubility of the material implies slow sorption kinetics and low sorption capacities since the metallic cations must diffuse through the material prior its sorption [14]. In this context, the innovative process reported in the present paper consists in combining advantages of both PEUF and STE water treatment processes by using thermosensitive polymeric sorbents coupled with a conventional filtration separation step. Such polymeric materials are of great interest for two reasons. First, at temperatures lower than the Lower Critical Solution Temperature (LCST), the thermosensitive polymeric sorbent is soluble in water leading to a favored sorption of the metallic cations in solution compared with SPE. Secondly, above the LCST, the polymeric sorbent becomes non-soluble giving the possibility to use an easy handling and low energy-consuming filtration separation rather than the ultrafiltration.

New copolymer materials synthesized to develop this original process were poly(*N-n*-propylacrylamide-*stat*-hydrolyzed (dimethoxyphosphoryl)methyl 2-methylacrylate) P(*Nn*PAAm-*stat-h*MAPC1) statistical thermosensitive copolymers. In previous works, high sorption properties have been demonstrated for the removal of aluminum, nickel and cadmium from wastewaters [5,6,7]. In this contribution, we now focus on the separation and the regeneration steps following the sorption of metal ions frequently encountered in real industrial wastewaters, to design a low energy-consuming process enabling the simultaneous recovery of the metal elements and the polymeric sorbent.

2. Materials and methods

2.1. Materials

2.1.1. Thermosensitive polymeric sorbent

(*Nn*PAAm-*stat-h*MAPC1) copolymers used in this study were synthesized by free radical polymerization using (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) as monomers and azobisisobutyronitrile (AIBN, Aldrich) as radical initiator. The copolymerization procedure as well as the hydrolysis of the phosphonated ester into phosphonic acid groups of the P(MAPC1) moieties were described in a previous paper [7]. Synthesis and chemical structure of P(*Nn*PAAm-*stat-h*MAPC1) is reminded in Appendix A (Fig. A.1). Copolymers used in this study contained *Nn*PAAm/*h*MAPC1 molar ratio equal to 80/20. The amount of sorption phosphonic acid 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 contained 1.45 mmol of phosphonic acid sorption moieties per gram of copolymer. The experimental molecular weight determined by size exclusion chromatography in *N,N*-dimethylacetamide, with 0.1 wt% of lithium chloride at 50 °C, was equal to 45,000 g/mol.

2.1.2. 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

AAAnalyst 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 all this study, C^{n+}/P ratio is defined as the molar ratio between the amount of cationic species in the mono-component solution compared to the amount of phosphonic acid borne by the copolymer. For multi-component solution, $\Sigma\text{C}^{n+}/\text{P}$ represents the global C^{n+}/P ratio, *i.e.* $\Sigma\text{C}^{n+}/\text{P} = \text{Ni}^{2+}/\text{P} + \text{Ca}^{2+}/\text{P} + \text{Cd}^{2+}/\text{P} + \text{Al}^{3+}/\text{P}$.

2.2. Methods

2.2.1. Determination of thermosensitive behavior

Thermosensitivity of the P(*Nn*PAAm-*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 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 $0.1 \text{ }^\circ\text{C min}^{-1}$ between 15 °C and 50 °C. The thermosensitivity was characterized by as 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

Two methods have been used for the determination of copolymer particle sizes in water depending on the size range. For particles sizes lower than 1 μm , measurements have been achieved by dynamic light scattering (DLS) with a zeta-sizer Nano-ZS from Malvern Instruments on solutions containing 1 g L^{-1} of copolymer. For particle size measurements achieved as a function of the temperature, the latter was regulated by the zeta-sizer: temperature ramp was $2 \text{ }^\circ\text{C min}^{-1}$ and the measurements were performed after a stabilization period of 5 min. For particles sizes higher than 1 μm , particle diameter distributions were obtained with a Cilas 920 granulometer on solutions containing 1 g L^{-1} of copolymer mechanically stirred (100 rpm) during 10 min at 40 °C.

2.2.3. Zeta-potential (ζ) measurements

All zeta-potential measurements have been achieved by measuring the electrophoretic mobility of 1 g L^{-1} copolymer solutions with a zeta-sizer Nano-ZS from Malvern Instruments. The variation of C^{n+}/P and $\Sigma\text{C}^{n+}/\text{P}$ ratios was obtained by dissolving different amounts of cationic salts in the copolymer solution.

2.2.4. Evaluation of water-copolymer separation

The sedimentation behavior of the copolymer in water has been determined in mono-component and multi-component solutions containing Ni^{2+} , Ca^{2+} , Cd^{2+} , Al^{3+} cations with various $\Sigma\text{C}^{n+}/\text{P}$ ratios. The $\Sigma\text{C}^{n+}/\text{P}$ ratio was adjusted by modifying the cationic concentration in the effluent while the copolymer concentration was kept constant for all separation tests (1 g L^{-1}). Separation was observed after mechanical stirring (100 rpm) at 40 °C during 10 min. Afterwards, the polymeric aggregates were recovered by filtration on filter paper (pore size: 16 μm , 11485218 Fisher Scientific) under atmospheric pressure. The efficiency of the separation was determined by Chemical Oxygen Demand (COD) measurements before and after filtration as explained in the Supplementary information (Appendix C). Such method was relevant since the copolymer was the only organic component in the solutions which explains the linear evolution of the COD as function of the copolymer concentration (Appendix C Fig. C.1).

2.2.5. Sorption and desorption experiments

2.2.5.1. Sorption experiments. Sorption experiments were carried out using a tubular ester cellulose dialysis membrane, stable at

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