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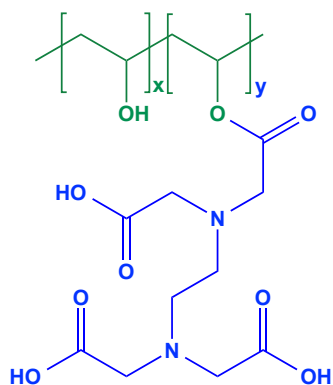
Complexation properties of water-soluble poly(vinyl alcohol) (PVA)-based acidic chelating polymers

Julien Muller, Xianyu Ding, Amine Geneste, Jerzy Zajac, Benedicte Prelot,*

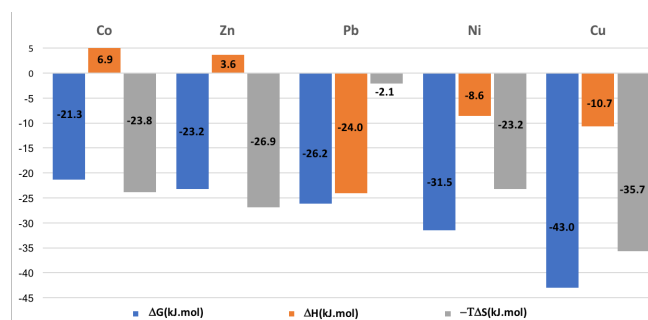
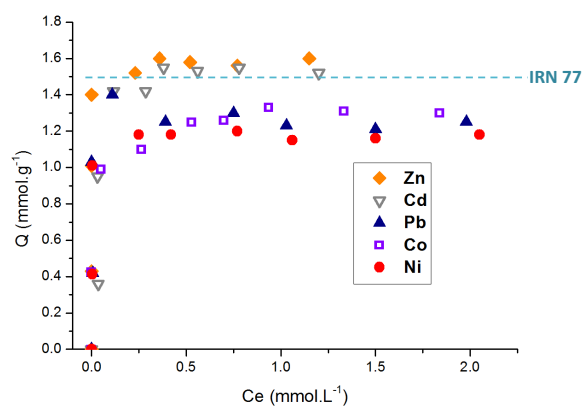
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GRAPHICAL ABSTRACT



Co(II), Ni(II), Zn(II), Pb(II), Cd(II), Cu(II)



Complexation properties of water-soluble poly(vinyl alcohol) (PVA)-based acidic chelating polymers

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Complexation properties of water-soluble poly(vinyl alcohol) (PVA)-based acidic chelating polymers

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HIGHLIGHTS

- EDTA chemical groups grafted on PVA for metal removal
- Functional poly(vinyl alcohol) (PVA) used as efficient sorbent for Co(II), Ni(II), Pb(II), Cd(II), Zn(II) and Cu(II)
- Range of selectivity of modified PVA evidenced using Isothermal Titration Calorimetry
- Preserved performances for traces and in multicomponent effluent
- Chelating polymers suitable for practical applications such as PEUF processes

Abstract

Water-soluble polymers are attractive materials for pollutants removal thanks to their ability to easily interact with soluble metal cations. In the present contribution, the chemical modification of biocompatible and non-toxic poly(vinyl alcohol) (PVA) was achieved with ethylene diamine tetraacetic acid (EDTA) groups, thus leading to new water-soluble polymers, named PVA(EDTA). Modification was carried out using Mitsunobu's reaction as an original pathway to obtain statistical copolymers with different EDTA functionalization rates in the PVA chains. Preliminary study about the variation of EDTA rate and chain length permitted determining the optimal polymeric structures. Then, sorption properties of heavy metal (*i.e.* Co(II), Ni(II), Zn(II), Pb(II), Cd(II), Cu(II)) on structures containing 15% of chelating agent were determined by performing thorough adsorption isotherms or determining removal percentage, at a high or low concentration, respectively. Additionally, the performances of the polymers were tested in a more complex effluent constituted by previous pollutants in the presence of Ca(II) and Mn(II) cations. We demonstrated that water-soluble PVA(EDTA) led to a great improvement of sorption properties in comparison with PVA. Indeed, results obtained showed high sorption capacities for Pb(II), Ni(II), Zn(II), and good selectivity towards some cations, in consistency with EDTA-metal complex formation constants. Isotherm Titration Calorimetry measurements allowed evidencing the complexation stoichiometry, and determining the interaction constant and the enthalpy. This study highlighted the interest of modifying basic commercial polymers with chelating agents for further applications based on Polymer Enhanced Ultrafiltration (PEUF) process.

Keywords: functional poly(vinyl alcohol), EDTA, metallic cation sorption, isothermal titration calorimetry, water treatment

1. Introduction

The progressive explosion of population growth, industrialization, and urbanization results in a crisis with regards to the accessibility of clean and potable water. Pollutants contained in uncontrolled discharge of wastewater from industrial and agricultural activities may be chemical contaminants such as heavy metals, organic and inorganic particles, toxins, pharmaceuticals, and hormones or other hazardous substances [1, 2]. Sustainability of global, clean and safe water supply is one of the main environmental challenges. Eliminating these types of pollutants to improve water quality requires environmental friendly treatment technologies, and led researchers worldwide coming up with developments aimed at removing impurities from wastewater. Additionally, nuclear industry produces large amounts of radionuclide and heavy metal wastes, and, in the case of nuclear incident or decommissioning processes, large volumes quantities of effluent containing several types of metal have to be treated.

Different strategies could be applied, such as ion exchange [3-9] chemical precipitation [10, 11], or membrane processes [4, 12, 13]. Chemical precipitation is one of the most useful strategies despite the limited recovery. Processes based on ions exchangers, such as resins, are simple and robust but suffered from some drawbacks including limited selectivity or deterioration under radioactivity [9]. Membrane processes are a very promising approach when coupled with water-soluble polymers bearing chelating agents. This method is well known and called polymer enhanced ultrafiltration (PEUF) [14] and is used to separate a great variety of metal ions from aqueous streams [15-18]. In PEUF processes, a water-soluble polymer is first introduced into the effluent to bind the targeted metal cations *via* strong interactions. In a second step, the solution containing pollutants flows through an ultrafiltration (UF) membrane containing pore sizes smaller than those of the

polymer/cations complexes. The main characteristic of the polymers used is their high solubility in water. Additionally, these polymers must be chemically stable and have a high affinity towards targeted metal cations together with a low affinity towards the UF membrane.

Different functional polymers were already successfully employed in PEUF processes [19-21], thus achieving selective separation and recovery of heavy metals with low energy requirements. Purification processes mainly involved acidic species. Acidic polymers including sulfonic [22, 23], phosphonic [24, 25] and carboxylic acids [26, 27] displayed great metal ion removal capacities. Depending on their acidity constant (K_a) and the pH of the aqueous solution to be treated, they may behave as polyelectrolyte or polychelator towards metallic pollution [28-32]. Sulfonic acids have always interacted as polyelectrolytes due to their negative pK_a [33]. Phosphonic acids are diacids, meaning that they exhibit two dissociation constants ($pK_{a1} = 2-3$ and $pK_{a2} = 6-7$) [34, 35]. Thus, as a function of the pH media, they could behave as polychelators or polyelectrolytes. Finally, carboxylic acids have a weak acidity ($pK_a \approx 4-5$) and behave either as a polychelator when the acid is not dissociated ($pH < pK_a$) or a polyelectrolyte when it is dissociated ($pH > pK_a$) [30, 36]. Therefore, carboxylic acids seem to be the most appropriate acidic functions for effluent treatment since they behave as polychelators in a wide range of pH involving a great selectivity towards cations. For instance, poly(acrylic acid) (PAA) was successfully employed to treat effluents containing Co(II) or Ni(II) metal ions [30, 37, 38]. PAA was also involved with poly(maleic acid) for the removal of chromium (III) [39]. Poly(methacrylic acid) was considered to bind different cations [40]. Additionally, carboxylic acid based biopolymers proved to be of interest in PEUF processes [16, 41, 42]. In general, carboxylic acids exhibited high selectivity towards heavy metals [26, 43, 44].

In this context, the present contribution deals with the synthesis and sorption properties of innovative water-soluble carboxylic acid-based poly(vinyl alcohol) (PVA) for the treatment of aqueous effluents. PVA was chosen because it is a commercial and low-cost polymer, which is additionally biodegradable and non-toxic. It has been notably already reported in the literature as chelating agent, due to the presence of one hydroxyl group per monomeric unit. PVA was, for instance, used in PEUF processes for the removal of chromium (III) [39], mercury (II) or arsenic (III) [45]. Thermosensitive copolymers based on cross-linked PVA and NiPAAm were also successfully employed as a solid phase extractor for Cu(II), Ni(II), and Cd(II) ions removal, in the presence of dodecyltrimethylammonium chloride (DTAC) as the extractant to complex with ions [46]. In another contribution, Dambies *et al.* [47] compared the efficiency of poly(vinyl alcohol), polyacrylic acid (PAA) and sulfonated-PVA for the complexation of Co(II) coupled with PEUF process. The best performances were obtained with sulfonated-PVA between pH 3 and 6. This last example highlighted the interest of modifying commercial PVA in order to produce new polymeric structures able to improve chelation properties. In this paper, PVA was modified with the introduction of ethylenediamine tetraacetic acid (EDTA) moieties thus producing PVA(EDTA) polymers in order to enhance the removal efficiency. EDTA is an aminopolycarboxylic acid, which is well known in the literature for the complexation of metallic cations [48, 49]. Then, sorption properties of the resulting functionalized polymers towards different metals were evaluated in single or multi component solutions. The first part of this study dealt with the selection of the most promising PVA(EDTA) combining good sorption properties and filterability. Then, we evaluated the selected PVA(EDTA) in the context of nuclear effluent, by choosing Ni(II) and Co(II) as cations as they were found in nuclear effluents in trace amounts. Secondly, sorption of heavy metals (*i.e.* Zn(II), Cd(II), Pb(II), Cu(II)) found

at higher concentration in wastewaters was evaluated. Selectivity of the PVA(EDTA) was also considered. Finally, simulation of a real effluent (also called simili) at fixed concentrations was studied. Therefore, this paper reports results obtained with some selected systems that deserved to attract the attention of the research community.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) ($M_n = 20000 \text{ g.mol}^{-1}$; average molecular weight: 11000-31000 g.mol^{-1} , Alfa Aesar), poly(vinyl alcohol) ($M_n = 90000 \text{ g.mol}^{-1}$; average molecular weight: 88000-97000 g.mol^{-1} , Alfa Aesar), ethylenediaminetetraacetic acid (Aldrich, 99%), diethyl azodicarboxylate (Alfa Aesar, 97%), triphenylphosphine (Aldrich, 99%), cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2, 6\text{H}_2\text{O}$) (Aldrich, 99%), nickel (II) nitrate ($\text{Ni}(\text{NO}_3)_2$) (Aldrich, 99%), lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$) (Aldrich, 99%), cadmium (II) nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2, 4\text{H}_2\text{O}$) (Aldrich, 99%), zinc (II) nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2, 6\text{H}_2\text{O}$) (Aldrich, 98%), manganese (II) nitrate ($\text{Mn}(\text{NO}_3)_2, 4\text{H}_2\text{O}$) (Aldrich, 97%), calcium (II) carbonate (CaCO_3) (Aldrich, 99%), tartaric acid (Aldrich, 99.5%), and ethylenediamine (Aldrich, 99.9%) were used without further purification. All solutions and other chemicals were purchased at the highest available purity and were used as received. Water was deionized and purified with a Millipore Super Q system (resistivity of 18.2 $\text{M}\Omega$). Dialysis membranes were purchased from Spectrum Laboratories with a MWCO equal to 2000 Da.

2.2. Methods

Sorption studies were carried out by mixing metal and polymer solutions in 30 mL Nalgene® reactors. Their respective concentrations were different depending on the

studied parameters, and were detailed for the various sets of experiments. An initial solution of polymer (2.5 g.L⁻¹) was poured into each tube. The dilution of the stock solution of a given cation or given cations was performed by weighing directly each Nalgene[®] tube so as to obtain about 10 mL at a fixed initial concentration of the cation(s) to be removed. The real final concentration of polymer was 0.5 g.L⁻¹. For the whole sorption isotherm, the initial concentration of nickel, cobalt, zinc, cadmium, lead, and copper varied from 0.2 to 3 mmol.L⁻¹. Then, the tubes were left slowly stirring overnight on a continuous rotary shaker at 25 °C. An equilibration time of 14 hours was sufficient to reach the sorption equilibrium. The amount of metal cations retained per mass unit of polymers was determined based on the solution depletion method by using the following equation:

$$\Gamma = \frac{(C_0 - C_e) \cdot V_0}{m_p}$$

where C_0 and C_e are the metal concentrations in the initial solution (before sorption) and in the equilibrium bulk phase (after attaining sorption equilibrium), respectively; V_0 denotes the volume of the solution, and m_p is the mass of polymer used. The equilibrium concentrations of metallic cations (namely Co(II), Ni(II), Zn(II), Cd(II), Pb(II)) at a high concentration were measured using an ionic chromatography analyzer (Shimadzu HPLC) equipped with a CDD-6A conductivity detector operating at 40 °C. A Shim-Pack IC-C1 column (with an IC-GC1 pre-column) was used. The mobile phase was composed of 4 mmol.L⁻¹ of tartaric acid and 1.5 mmol.L⁻¹ of ethylenediamine (EDA). The flow rate of eluent was 1.5 mL.min⁻¹. For the determination of low concentrations or metal traces and the study under competitive conditions, polarography experiments were carried out to compare sorption of Co(II) mixed with Ni(II), or to analyze the combination of Zn(II), Cd(II), Pb(II), and Cu(II). Owing to the voltammetry instrument (797 VA Computrace Metrohm equipment), it

was then possible to analyze these complex solutions in pure water as well as in the presence of highly concentrated recomposed effluent, without interferences of the concentrated effluent on the analytical conditions. Electrolytes had to be added in the media in order to allow the detection of the cations. In the case of the determination of Co(II) and Ni(II) concentration, the electrolyte was composed of ammonium chloride (1 M), ammonia (2 M) and dimethylglycine (0.1 M). For the monitoring of Zn(II), Cd(II), Pb(II) and Cu(II) concentrations, the electrolyte was composed of potassium chloride (1.5 M), acetic acid (0.5 M) and 30% sodium hydroxide. Finally, same experiments were carried out with an appropriate mixture of metal cations in an aqueous medium also containing manganese (II) nitrate (10 mM) and calcium (II) carbonate (1 mM) to simulate the existing effluent. Depending on the investigated systems and parameters, different concentrations of polymer and cations were selected and were indicated in the corresponding parts. In order to focus on the sorption efficiency of EDTA groups, the polymer concentration was generally related to the ratio of EDTA, and the metal concentration was adjusted to the concentration of EDTA grafted groups.

Filterability experiments were carried out by measuring the cobalt concentrations in solution at regular time-steps by Atomic Absorption Spectroscopy (AAAnalyst 400, Perkin Elmer). PVA1(EDTA) ($200 \text{ mg}\cdot\text{L}^{-1}$) was first solubilized in water and was added in large excess to a Co(II) solution (2 mL of $1\cdot 10^{-4} \text{ M Co(NO}_3)_2, 6\text{H}_2\text{O}$). The mixture (500 mL) was allowed to stir at room temperature during three hours before a dead-end filtration on a ceramic membrane. Filtration was stopped when 75 mL of permeate was recovered (15% of the initial volume). Atomic absorption spectroscopy analyses permitted the determination of the quantity of cobalt (II) in the permeate after filtration for the three PVA1(EDTA) polymers considered.

Thermodynamic data on metal/EDTA interaction were obtained from titration microcalorimetry experiments at 25 °C. By using a TAM III Thermostat, the measured heat flow was directly related with the extent of reaction taking place within the calorimetric cell. In the present work, the nanocalorimeter device including measurement and reference cells with a heat sink was placed in a heat exchanger with Peltier coolers. The temperature was controlled with a 0.1 °C accuracy. The setup contained a calorimetric cell and a syringe pump, which allowed the reagents to be introduced into the cell at given time periods and quantities. The homogeneity of the solution or suspension was ensured by a gold stirrer directly placed in the calorimetric cell (90 rpm). Measurements were made in the heat flow mode. The procedure started with filling up the calorimetric cell with 800 µL of the solution containing PVA1(EDTA)_{15%}. The stock solution of cation to be adsorbed was placed in the syringe. When the thermal equilibrium had been reached, small amounts (10 µL) of the stock solution were injected into the measuring cell. Injection speed was 10 s, and stabilization after each injection time was set at 45 minutes. A blank test for the dilution of each metal cation solution was also carried out in the same way in order to remove the thermal influence of the dilution of metallic cations solutions. Raw data were analyzed using ITC software NanoAnalyze by considering an interaction model with one independent site reaction, between the EDTA group and the cation.

Concerning the filterability studies, PVA(EDTA) polymer solution was first prepared at a given concentration (200 mg.L⁻¹) and was added to a 0.1 mM solution of Co(NO₃)₂·6H₂O to obtain a polymer/metal molar ratio equal to 1. The mixture was stirred at room temperature during 3 hours at 250 rpm. Filtration was achieved using ceramic membrane (Aldrich, MWCO = 20 kDa) using a transmembrane pressure equal to 0.5

bar. Filtration was stopped when 75 mL of permeate was obtained, which represented 15% of the full solution (500 mL).

2.3. Synthetic procedure

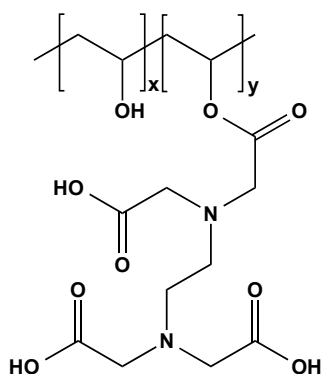
Synthesis of poly(vinyl alcohol) (PVA) grafted with ethylenediaminetetraacetic acid (EDTA)

Grafting onto PVA1 was achieved according to the procedure detailed in a previous paper [50] (see typical procedure in the Supporting Information).

3. Results and discussion

3.1. Synthesis and preliminary study of PVA(EDTA)

New functional polymers based on poly(vinyl alcohol) were prepared by modification of PVA with ethylenediaminetetraacetic acid (EDTA) groups (Scheme 1). This chelating agent was chosen owing to its ability to selectively complex metal cations thereby allowing its use for the decontamination of aqueous effluents.



Scheme 1. Chemical structure of poly(vinyl alcohol) (PVA) modified by ethylenediaminetetraacetic acid (EDTA) (PVA(EDTA)).

The modification of PVA chains was achieved using Mitsunobu's reaction between EDTA molecules and PVA chains by substitution on the alcohol groups [50]. This reaction was carried out on two commercial PVA of different chain lengths, with

molecular weights equal to either 20000 g.mol⁻¹ or 90000 g.mol⁻¹. PVA reacted with ethylenediaminetetraacetic acid in dimethylsulfoxide (DMSO) in the presence of diethyl azodicarboxylate and triphenylphosphine. The obtained solution was allowed to be stirred at different temperatures (20, 30 or 40 °C) overnight, thus leading to different functionalization rates (Table 1), as determined by ¹H NMR (for the calculation of functionalization rate, see supporting information). Labeling of the different polymers was done as follow: in the PVAx(EDTA)_y% formula, x was 1 or 2 depending on the PVA molecular weight, equal to 20000 and 90000 g.mol⁻¹, respectively, and y represented the percentage of functionalization of the PVA with EDTA. It was evidenced that the functionalization rate was higher when the temperature increased. Working at 20, 30, and 40 °C led to rates equal to 5, 11 and 15%, respectively. Additionally, grafting rate did not increase at temperatures higher than 40 °C. The PVA molecular weight did not have an influence on the functionalization rate. Indeed, similar rates were obtained under the same experimental conditions whatever the molecular weight of the PVA (20000 or 90000 g.mol⁻¹), notably with 15% of grafting at 40 °C. Modified polymers were obtained with a yield equal to 90%.

Table 1
Main characteristics of the PVA and PVA(EDTA) used in this study.

Polymer	Reaction temp. (°C)	M _n ^a (g.mol ⁻¹)	Functional. degree ^b (%)	M _n ^{NMR} ^b (g.mol ⁻¹)	Metal removal (%) ^c	
					Ni(II)	Co(II)
PVA1	--	20000	--	--	0	0
PVA2	--	90000	--	--	0	0
PVA1(EDTA) ₅ %	20	--	5	26200	99	98
PVA1(EDTA) ₁₀ %	30	--	11	33700	45	39
PVA1(EDTA) ₁₅ %	40	--	15	38700	50	35
PVA2(EDTA) ₁₅ %	40	--	15	154700	44	32

^a molecular weight of commercial polymers, ^b determined by ¹H NMR in D₂O, ^c determined by polarography with a EDTA/metal (II) equal to 1/1 (mol/mol).

A preliminary study of the different PVA(EDTA) synthesized was achieved in order to select the best candidate for further experiments. So, sorption properties and

filterability were considered as a function of the PVA molecular weight (20000 and 90000 g.mol⁻¹) and of the functionalization rate (5, 11 and 15%) as these parameters could further affect properties. It is also important to mention that unmodified PVA1 and PVA2 showed no sorption ability towards Ni(II) and Co(II) ions.

Concerning the influence of the polymer molecular weight, the retention values for Co(II) and Ni(II) were determined on functionalized PVA1 ($M_n = 20000 \text{ g.mol}^{-1}$) and PVA2 ($M_n = 90000 \text{ g.mol}^{-1}$) grafted with 15% of EDTA groups, in a single-component solution in water and at low concentration using polarography as an analytical tool. The polymer concentration was fixed in the range of 26-70 mg.L⁻¹ depending on the functionalization degree, whereas the initial cation concentration was adjusted at 0.17 mM so as to get an initial metal/EDTA molar ratio equal to 1. First, sorption results showed that Co(II) percentage removal was smaller compared to Ni(II) for both PVA1(EDTA)_{15%} and PVA2(EDTA)_{15%}. This indicated a lower affinity between Co(II) and PVA(EDTA)_{15%}. In addition, better sorption properties were observed for polymer with a lower molecular weight. This was slightly more pronounced for Ni(II) sorption experiments, with 50% sorption for PVA1(EDTA)_{15%} against 44% for PVA2(EDTA)_{15%}. This was probably due to a better mobility in solution with the smaller polymer. Indeed, EDTA groups were more accessible and as a result more cations were retained. Additionally, water solubility of longer polymer was probably weaker, thus limiting metal cation sorption properties. In the case of Co(II), sorption rates were quite similar, with 34 and 32% for PVA1(EDTA)_{15%} and PVA2(EDTA)_{15%}, respectively. This demonstrated the weak affinity between the Co(II) and the polymers. To conclude, best Ni(II) and Co(II) sorption results were obtained for PVA1(EDTA). The latter was thus selected to study the influence of the functionalization rate.

As already mentioned, varying the temperature allowed modulating the EDTA grafting rate. So, three different polymers PVA1(EDTA)_{5%}, PVA1(EDTA)_{10%}, and PVA1(EDTA)_{15%} were prepared at different temperatures with experimental grafting rates very close to the theoretical ones equal to 5, 11, and 15%, respectively. Once again, Ni(II) and Co(II) sorption measurements were carried out at a low concentration (0.17 mM) in a single-component solution in water with a polymer concentration—corresponding to a metal/EDTA molar ratio equal to 1. Sorption measurements showed that the decrease of EDTA grafting rate in the PVA backbone led to an increase of the quantity of metal cation retained. Indeed, PVA1(EDTA)_{5%} showed greater sorption capacities, in comparison with PVA1(EDTA)_{10%} and PVA1(EDTA)_{15%}. Co(II) and Ni(II) were totally removed in the presence of PVA1(EDTA)_{5%} copolymer corresponding to an adsorption of one cation per one EDTA site. The lower adsorption of PVA1(EDTA)_{10%} and PVA1(EDTA)_{15%} could be explained by a possible steric hindrance with a higher complexing group content as complexation of nickel or cobalt is known to involve several carboxylic acid moieties. The highest the grafting rate was, the closest the EDTA groups were, thereby preventing an efficient complexation of metallic cations. Finally, same tests were achieved using polymer equimass conditions for each experiment (*i.e.* 100 mg of polymer and 2 mL of cobalt (II) nitrate hexahydrate solution at 0.1 mmol.L⁻¹, in a total of 500 mL aqueous solution). In this particular case, best results were obtained with PVA1(EDTA)_{15%} yielding 93% sorption, whereas PVA1(EDTA)_{10%} and PVA1(EDTA)_{5%} led to 86 and 74% sorption, respectively. This result was expected since there were more EDTA sites for the same mass of polymer, and EDTA/metal molar ratio were equal to 0.95, 1.63, and 1.93 for PVA1(EDTA)_{5%}, PVA1(EDTA)_{10%} and PVA1(EDTA)_{15%}, respectively.

To conclude, considering EDTA/metal molar ratio, PVA1(EDTA)_{5%} appeared to be the most interesting material in term of sorption efficiency. As polymers will be used in a polymer enhanced ultrafiltration process, it was also important to study the filterability of the different functionalized PVA. Experiments were carried out with cobalt (II) nitrate to be in the most disadvantageous conditions as Co(II) proved to have less affinity for PVA1(EDTA) polymers than Ni(II) ions. PVA1(EDTA) solubilized in water was added in a large excess to a Co(II) solution. After stirring to ensure the whole sorption, the mixture was filtered as described in the experimental part. The quantity of cobalt (II) in the permeate after filtration for the three PVA1(EDTA) polymers considered was measured to evaluate the resulting percentage removal shown in Fig. 1. Best results were obtained in the case of PVA1(EDTA)_{15%} with 86% of cobalt eliminated. As expected, PVA1(EDTA)_{5%} was the less efficient as its molecular weight was the lowest (Table 1).

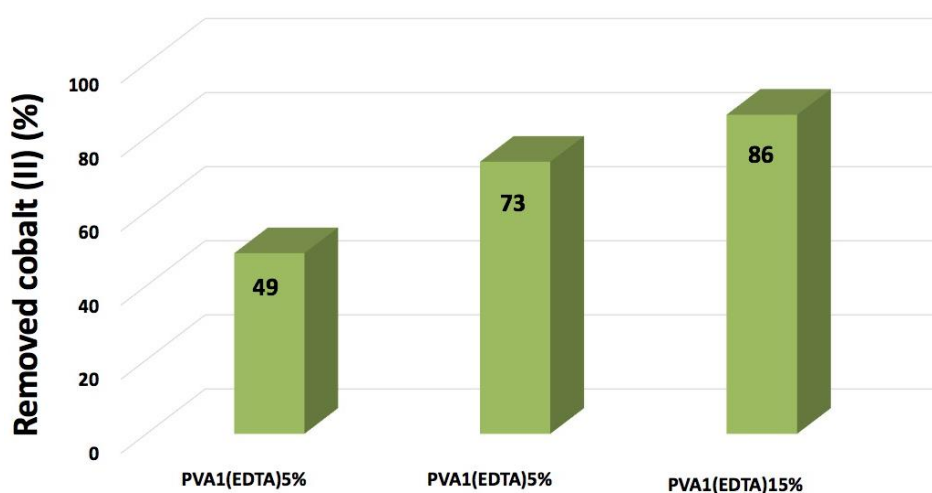


Fig. 1. Percentage of cobalt (II) ions retained onto PVA1(EDTA) with different EDTA grafting rates as determined by monitoring the concentration of Co(II) in the permeate by absorption spectroscopy after filtration. Conditions: PVA1(EDTA): 200 mg, Co(NO₃), 6H₂O 1.10⁻⁴ M: 2 mL in a 500 mL global volume of aqueous solution.

To conclude, from all results obtained, PVA1(EDTA)_{15%} was selected as it represented the best compromise between high sorption efficiency and good filterability. So, further experiments were carried out using PVA1(EDTA)_{15%}. First of all, the sorption efficiency was evaluated using sorption isotherms to estimate in the first case the removal capacity with respect to Co(II) and Ni(II) found in a decontamination process, and in the second case, the retention of the selected heavy metals, *i.e.* Cd(II), Pb(II), Zn(II), and Cu(II).

Evaluation of the sorption efficiency of PVA1(EDTA)_{15%}

To clearly evaluate the sorption capacity of the prepared PVA1(EDTA)_{15%}, complete sorption measurements have been investigated for Co(II), Ni(II), Zn(II), Cd(II) and Pb(II) and the efficiency results have been compared. Fig. 2 shows the sorption isotherms of PVA1(EDTA)_{15%} in single-component solutions in pure water. The sorption isotherm of Cu(II) was not determined since its concentration could not be measured in similar conditions.

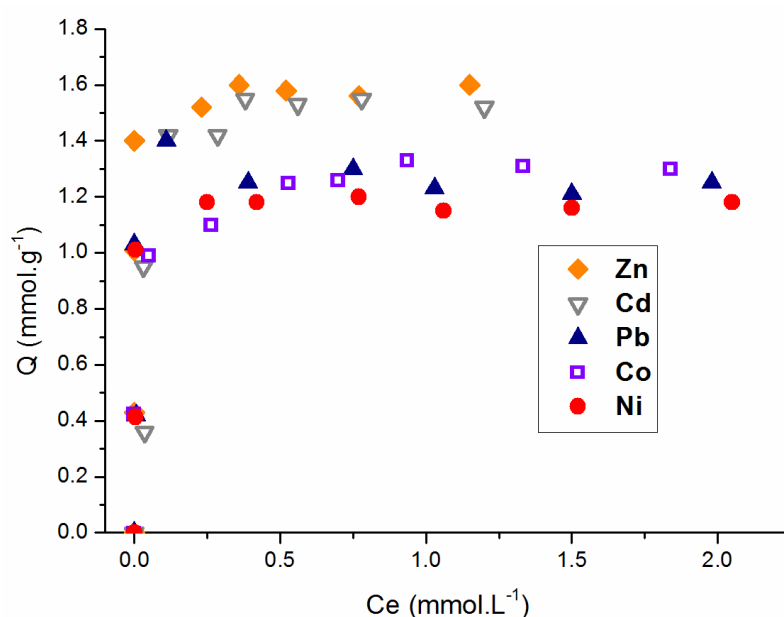


Fig. 2. Sorption properties of PVA1(EDTA)_{15%} at 298 K. Isotherms for Co(II), Ni(II), Pb(II), Cd(II), Zn(II) uptake by the polymer (0.5 g L⁻¹) from single-component aqueous solutions.

For Zn, Cd, Pb, Co and Ni, in the first part of the isotherms, the amounts adsorbed rapidly increased for equilibrium concentrations lower than 0.25 mmol.L⁻¹. The quasi-vertical initial portion indicated the strong affinity of cations towards PVA1(EDTA)_{15%}. The second part corresponded to a pseudo-plateau region where the adsorption capacity was fairly stable and was attributed to the saturation of the sorption sites. The maximum sorption quantities varied from 1.2 to 1.5 mmol.g⁻¹ (Table 2).

Table 2

Sorption properties of PVA1(EDTA)_{15%} towards studied metal cations. Q_{\max} was estimated at the pseudo plateau of the sorption isotherm.

Metal cation	Q_{\max} (mmol.g⁻¹)	Metal/EDTA ratio
Ni(II)	1.18	0.5
Co(II)	1.22	0.5
Zn(II)	1.58	0.6
Cd(II)	1.55	0.6
Pb(II)	1.28	0.5
Cu(II)	nd*	nd

* not determined

The PVA1(EDTA)_{15%} exhibited high sorption capacity. The efficiency was similar to those reported for resins commonly used in water or in nuclear waste treatment. In particular, this maximum adsorbed amount was only slightly lower than the one obtained for IRN 77 (1.5 mmol.g⁻¹) [51]. These values of sorption efficiency were higher than the one reported for functionalized support. In the case of the functionalization of cellulose, and chitosan (or relative materials) with a large variety of grafted groups, the performance was rather low. Table 3 reports here the sorption efficiency of various EDTA grafted materials (silica particles, electrospun nanofibers, magnetic adsorbent, etc). They all exhibited relatively low sorption performances.

Only in particular cases, with the examples of cyclodextrins or using magnetic adsorbent, results were reported similar to what has been obtained here.

The values of sorption capacity were consistent with the amount of EDTA groups grafted on PVA chains, showing that the complexation phenomenon was based on the EDTA functions. The ratio of metal to EDTA was ranging from 0.5 to 0.6, with around 0.5 for Pb(II), Co(II) and Ni(II), and 0.6 for Zn(II) and Cd(II). This means that one cation was in interaction with two (or 1.7 for Zn(II) and Cd(II)) EDTA groups in PVA1(EDTA)_{15%}.

Table 3

Sorption properties concerning EDTA grafted materials and reported maximum sorption capacity.

Material	Cations	Maximum sorption capacity	Reference
EDTA-modified chitosan	Co(II)	63.0 mg.g ⁻¹	[52]
	Ni(II)	71.0 mg.g ⁻¹	
DTPA-modified chitosan	Co(II)	49.1 mg.g ⁻¹	[52]
	Ni(II)	53.1 mg.g ⁻¹	
EDTA-modified silica gel	Co(II)	60 mg.g ⁻¹	[53]
Electrospun polyacrylonitrile nanofibers modified with EDTA	Cd(II)	32.68 mg.g ⁻¹	[54]
EDTA-functionalized chitosan magnetic adsorbent	Pb(II)	210 mg.g ⁻¹ (1 mmol.g ⁻¹)	[55]
		for highly optimized conditions:	
L-lysine and EDTA resins	Cu(II)	0.860 mmol.g ⁻¹	[56]
	Cd(II)	0.558 mmol.g ⁻¹	
	Pb(II)	0.520 mmol.g ⁻¹	
	Zn(II)	0.570 mmol.g ⁻¹	
	Ni(II)	0.316 mmol.g ⁻¹	
Chitosan-EDTA-β-cyclodextrin polymer	Co(II)	0.558 mmol.g ⁻¹	[57]
	Pb(II)	0.803 mmol.g ⁻¹	
EDTA-cross-linked- β-cyclodextrin	Cd(II)	1.258 mmol.g ⁻¹	[58]
	Cu(II)	1.241 mmol.g ⁻¹	
	Cd(II)	1.106 mmol.g ⁻¹	

The observed sharp increase was due to the high affinity of these cations for EDTA, as demonstrated by the high formation constants for the metal with EDTA, with log K_f values in the range of 16.5 to 18.4 [59] (Table 4). The curves profile suggested that high affinities were obtained. These results observed from adsorption isotherm confirmed that PVA1(EDTA)_{15%} exhibited good sorption efficiency towards different

divalent metallic cations in the single component system, at relatively high concentrations.

Nevertheless, the real effluents to treat are more complex, and contain various species to be removed [60]. In such multicomponent systems, heavy metals are present simultaneously and at lower concentrations. Therefore, the following part of this manuscript describes the sorption efficiency of the present systems for the removal of targeted cations at a concentration lower than the one studied when building up the complete isotherms in water, in single component systems and in multicomponent systems where cations were mixed. The removal efficiency test will then be carried out in simulated recomposed effluents to evaluate the use of such systems for practical uses. The observed selectivity will be correlated with the thermodynamic quantities obtained based on direct calorimetric measurements using Isotherm Titration Calorimetry (ITC).

Table 4
Formation constant of the EDTA complex (Pb(II), Cu(II), Cd(II), Zn(II), Co(II) and Ni(II)) [59].

Metal cations	Cd(II)	Pb(II)	Zn(II)	Cu(II)	Co(II)	Ni(II)
Formation constant	16.5	18	16.5	18.78	16.45	18.4

Sorption properties of PVA1(EDTA)_{15%} for Ni(II) and Co(II) at low concentration in the context of nuclear effluent purification

In the context of nuclear plants, the removal of radionuclides is of great importance. Among the critical metals, nickel and cobalt, notably its activated ⁶⁰Co radioisotope, are found at low concentrations, 1 mM and 20 nM, respectively [61]. As a result, a concentration within the order of nanomol per liter was chosen to study the sorption of these cations.

Adsorption in water

The concentration investigated to determine the sorption isotherm was in the 10^{-4} M range using ionic chromatography. In the following part of this study, lower metal concentrations (10^{-6} M) were explored using polarography. Thanks to the specificity of the analytical tool, it was also possible to evaluate the concentration of several cations in a mixture, thus shedding more light of the possible selectivity. In the preliminary tests, in order to reveal the various contributions of the interaction of the PVA(EDTA) with various cations, the PVA alone was tested for its removal efficiency. It was observed by using Co(II) and Ni(II) isothermal titration calorimetry that interactions of PVA with these cations could be neglected (data not shown here). This confirmed that the metal sorption of PVA was limited and rather to be neglected when compared to the functionalized polymer, and that modification strongly enhanced removal capacities.

Fig. 3 illustrates the removal properties of PVA1(EDTA)_{15%} for Co(II) and Ni(II) with a concentration of EDTA adjusted at 0.17 μ M. Sorption properties were first studied in water with single-component solutions of metal cations and with a mixture of both cations in water. Experiments were carried out for a four- or two-fold excess of EDTA, and in equimolar properties for metal and EDTA. In the case of Ni(II) alone in water, with a four-fold excess of EDTA, PVA1(EDTA)_{15%} was highly efficient for the Ni(II) complexation with retention values going up to 96%. When the amount of EDTA decreased (M/EDTA ratio equal to 1/2 or 1/1), the efficiency decreased. For the 1/1 ratio, the sorption was only 50 % of the removed cations. For Co(II), the adsorption capacity was reduced, below 50% irrespective to the proportions, and it dropped to 35 % in equimolar conditions of EDTA and cation. Under these experimental conditions, it again appeared that PVA(EDTA) was slightly less effective for Co(II) in comparison with Ni(II).

Thereafter, competitive medium composed of Co(II) + Ni(II) mixture were prepared and sorption performances of each ion were investigated. The same amounts of metal/PVA1(EDTA)_{15%} as for the single-component solutions were used. The total concentrations corresponded to the sum of all metal cation concentrations with each metal in equimolar ratio. In excess of EDTA (1/4 cations/EDTA ratio), the efficiency of the mixture was similar to the one observed in the single solution. The removal of Ni(II) was not modified by the presence of Co(II) that was less retained compared to Ni(II). When the amount of cations increased (cations/EDTA =1/1), the sorption decreased. The removal performance was divided by 2 for Ni(II), and by 4 for Co(II), which indicated a selective complexation of Ni(II) in line with a better affinity of PVA1(EDTA)_{15%} for Ni(II).

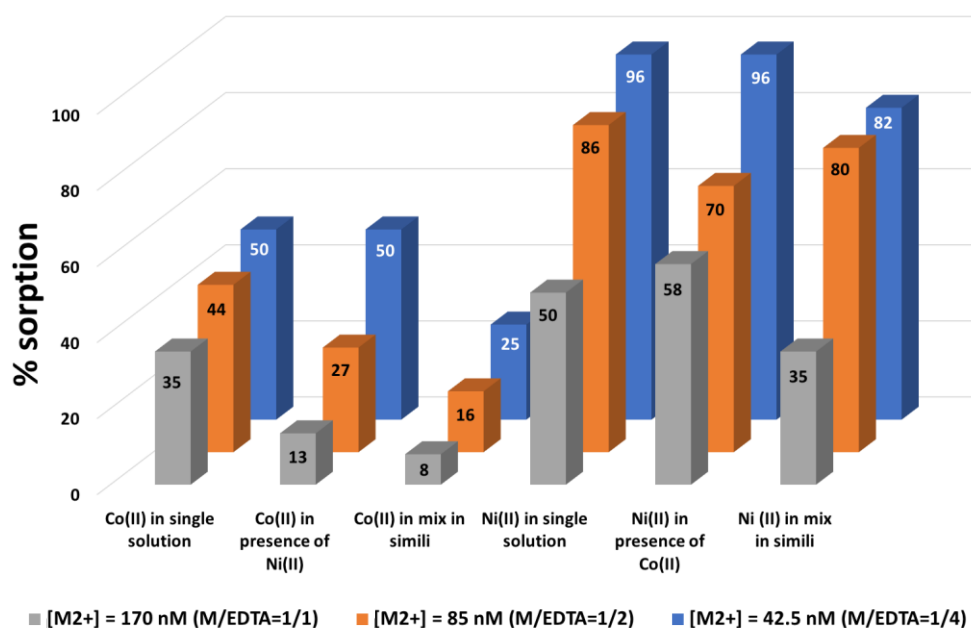


Fig. 3. Sorption efficiency of PVA1(EDTA)_{15%} for Co(II), and Ni(II) evaluated for low concentration. The polymer concentration was 40 mg.L⁻¹. The cation concentration was adjusted according to the amount of EDTA (170 nM). Different proportions of metal/EDTA were tested, with 1/4, 1/2 and 1/1, corresponding to a cation concentration [M²⁺] being equal to 42.5, 85 or 170 nM respectively. The figure describes the uptake by the polymer from i) single-component aqueous solutions, ii) cations mixture in aqueous solutions, and iii) cations mixture in the simulated effluent.

Adsorption in recomposed effluent

In order to investigate the practical uses of such systems, experiments were also conducted in a multicomponent effluent simulating the real effluent. The recomposed solvent had the following composition: 10 mmol.L⁻¹ of Mn(NO₃)₂.4H₂O and 1 mmol.L⁻¹ of CaCO₃, whereas the concentration of radionuclides was in the nanomolar range (42 to 170 nmol.L⁻¹). The solution to be treated contained the mixture of cations, in equimolar proportions. The results are also shown in Fig. 3. The sorption of Ni(II) was only slightly affected by the presence of the ions contained in the recomposed effluent. The decrease of efficiency was comprised between 10 and 15 %. The effect of the simuli and the presence of Ca(II) and Mn(II) were insignificant for Ni(II) removal. Otherwise, the effect was more pronounced for Co(II) as the sorption efficiency was divided by two in this particular case. Nevertheless, in both cases, PVA1(EDTA)_{15%} polymers selectively complexed these cations in accordance with the EDTA-metal complex formation constants. The difference between the various formation constants [59] for Ca(II) (log K_f = 10.65), Mn(II) (log K_f = 13.89), Co(II) (log K_f = 16.45) and Ni(II) (log K_f = 18.4) was high enough to explain the great selectivity towards them. Concerning Co(II), the obtained results reflected the weaker affinity already noticed. Sorption quantities were lower than those monitored in pure water, thus proving the competitive sorption between Ca(II), Mn(II) and the targeted metal cations. The lower difference in the EDTA complex formation constants between the metals, *i.e.* log K_f (Co(II)) = 16.45) with Ca(II) and Mn(II), could justify these lower variations in Co(II) metal removal when compared with Ni(II).

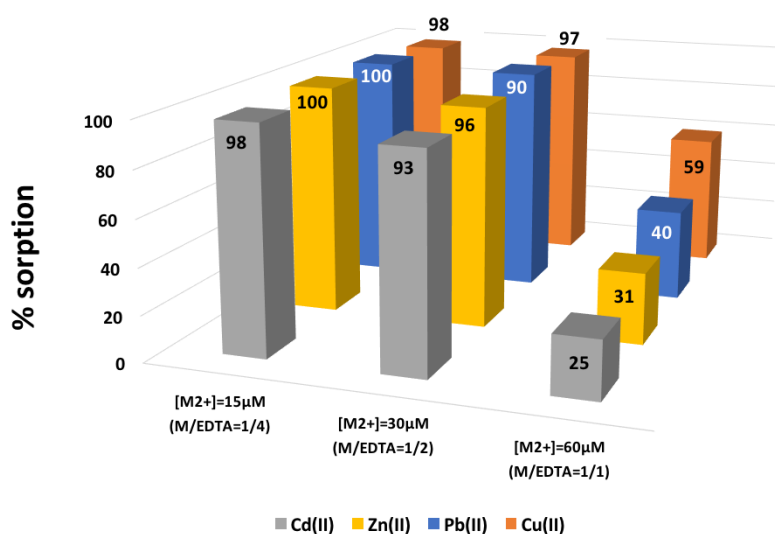
Sorption properties of PVA1(EDTA)_{15%} for Zn(II), Cd(II), Pb(II) and Cu(II) at higher concentration in the context of heavy metal pollution

Similar approach was followed for solutions containing Cd(II), Zn(II), Pb(II) and Cu(II), or mixture of these four cations. In order to optimize the cation detection for heavy metal removal, the concentration of introduced ions was in the micromolar range (15-60 $\mu\text{mol.L}^{-1}$). Beforehand, in order to reveal the various contributions of the interaction of the PVA(EDTA) with cations, the PVA alone was tested for its removal efficiency. It has been observed, by using polarography for Zn(II), Cd(II), Pb(II) and Cu(II), that sorption of PVA with cations could be neglected (data not shown here). This confirmed the enhanced removal capacities due to the functionalization of the PVA. Fig. 4 illustrates the removal properties of PVA1(EDTA)_{15%} for Cd(II), Zn(II), Pb(II) and Cu(II), in the single component system (Fig. 4 a) and in mixture of cations in water (Fig. 4 b).

Sorption experiments in single component solutions for a four- or two-fold excess of polymer led to a very efficient metal complexation, with retention values going up to 93%. When polymer (*i.e.* EDTA in polymer) and metal cations were introduced in equimolar proportions, the histogram bars evidenced different retention behavior depending on the metallic cation. Best results were achieved for Pb(II) and Cu(II) with the removal of 40 and 58% of metal, respectively, whereas the sorption was 25 or 31% for Cd(II) and Zn(II), respectively. Thereafter, a competitive medium composed of Pb(II) + Zn(II) + Cu(II) + Cd(II) mixture was prepared and sorption performances of each ion was investigated. The same metal/PVA1(EDTA)_{15%} ratios as for single-component solutions were used. The total concentrations corresponded to the sum of all metal cation concentrations with the metals being mixed up in equimolar ratios. Sorption with a polymer excess (for 1/4 and 1/2 cations/EDTA ratios) led to a similar tendency when compared to with the single-component solutions. Indeed, retention

values obtained for each metal were higher than 97%, excepted for Cd with the 1/2 ratio. In the case of an equimolar mixture (1/1 and global concentration equal to 60 μM), Cu(II) ions were effectively removed (96% removed) whereas Cd(II) and Zn(II) were not retained by the PVA1(EDTA)_{15%} polymer. Concerning lead sorption, only

(a)



(b)

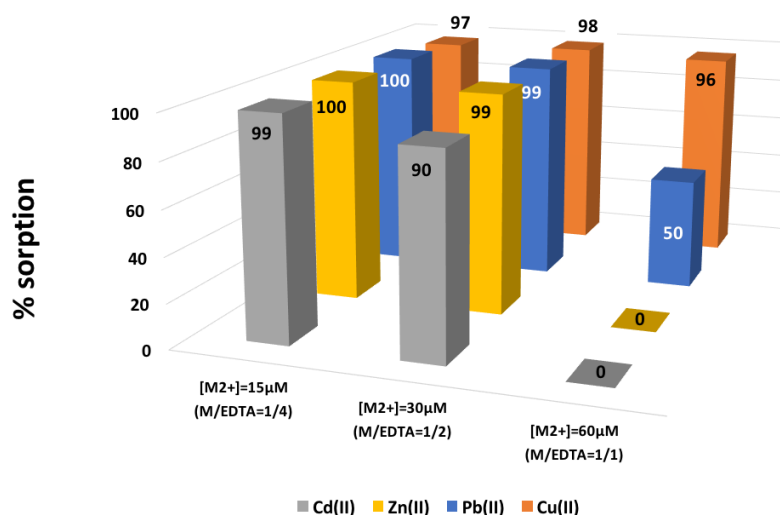


Fig. 4. Sorption efficiency of PVA1(EDTA)_{15%} for Pb(II), Cu(II), Cd(II), Zn(II) evaluated for low concentrations. The polymer concentration was 1.5 g.L⁻¹. The cation concentration was adjusted according to the amount of EDTA (60 μM). Different proportions of metal/EDTA were tested, with 1/4, 1/2 and 1/1, corresponding to a cation concentration [M²⁺] equal to 15, 30 or 60 μM , respectively. (a) the uptake by the polymer from single-component aqueous solutions, (b) the uptake from a cation mixture in aqueous solutions; for the mixture, the [M²⁺] concentration corresponded to the sum of Pb(II), Cu(II), Cd(II) and Zn(II) species, in equimolar conditions.

half of the cations were taken up. This evidenced a selective complexation of mainly Cu(II) and Pb(II) to a less extent. In all cases, when the amount of cation increased, the efficiency globally decreased, but the selectivity between the various cations was enhanced.

Finally, the sorption was tested in recomposed effluents involving Ca(II) and Mn(II) cations present in a significantly greater ratio (between 16 and 125 000 times more concentrated) to induce strong competitive effect (Fig. 5). For the mixture of the four cations, namely Zn(II), Cd(II), Pb(II) and Cu(II), the sorption efficiency of Cu(II) was hardly modified.

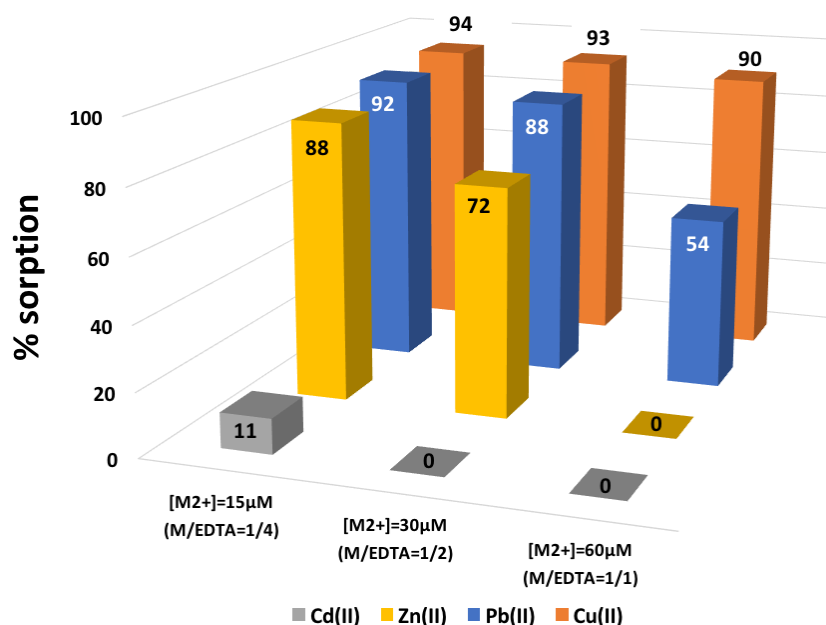


Fig. 5. Sorption efficiency of PVA1(EDTA)_{15%} for Pb(II), Cu(II), Cd(II), Zn(II) evaluated for low concentration in a recomposed multicomponent effluent. The polymer concentration was 35 mg.L⁻¹. The cation concentration was adjusted according to the amount of EDTA (60 μmol.L⁻¹). Different proportions of metal/EDTA ratio were tested, with 1/4, 1/2 and 1/1, corresponding to a total cation concentration [M²⁺] equal to 15, 30 or 60 μM respectively. The [M²⁺] corresponded to the sum of Pb(II), Cu(II), Cd(II), and Zn(II) concentrations, added in equimolar quantities.

The highest modification was observed for the 1/1 metal/EDTA ratio, with 96% retention in water and 90% for the simili. This tendency was similar for Pb(II). The presence of Ca(II) and Mn(II) did not affect the sorption of PVA1(EDTA)_{15%} towards

Pb(II), Cu(II) even if they were present in much lower quantities compared to Ca(II) and Mn(II) from the recomposed effluents. On the contrary, the sorption efficiency of Cd(II) was strongly impacted by the presence of Ca(II) and Mn(II). For the 1/4 ratio, the sorption was 90 % in water, whereas it dropped to 11% in the simili. For 1/2 and 1/1, there was no sorption in the simili. In the case of Zn(II), a small decrease was observed, especially for the 1/2 ratio. Differences in sorption efficiency between considered cations in the simili could be explained by the differences in the thermodynamic constants. Indeed, PVA1(EDTA)_{15%} polymers selectively complexed the cations in accordance with EDTA-metal complex formation constants. The difference between the various formation constants [59] for Ca(II) (log K_f = 10.65), Mn(II) (log K_f = 13.89) on the one hand, Pb(II) (log K_f = 18), and Cu(II) (log K_f = 18.78) on the other hand was high enough to explain the great selectivity towards them. Concerning Zn(II) and Cd(II), the obtained results reflected the weaker affinity already previously observed. Sorption quantities were lower than in pure water proving the competitive sorption between Ca(II), Mn(II) and the targeted metal cations. The lower difference in the EDTA complex formation constants between metals (log K_f (Zn(II)) = 16.5, log K_f (Cd(II)) = 16.5) compared with those of Ca(II) and Mn(II) could justify these smaller variations in heavy metal removal. Despite the large excess of Ca(II) and Mn(II), the sorption of targeted metal cations was satisfying and demonstrated the selectivity of PVA1(EDTA)_{15%} towards some cations.

To conclude, all cations of the present study (Ni(II), Pb(II), and Cu(II) cations) showed a great affinity towards PVA1(EDTA)_{15%} whereas affinity was lower for other cations. Thereafter, these tendencies were all confronted with the formation constants of the cation/EDTA complex (Table 4) [59]. The observed range of selectivity was clearly correlated with these constants. The EDTA complexes formed with Ni(II), Cu(II) and Pb(II) were more stable in comparison with those obtained with Co(II), Zn(II) and

Cd(II), which could explain the selectivity behavior of PVA1(EDTA)_{15%} towards Ni(II), Cu(II) and Pb(II). Additionally, selectivity was improved when the amount of cations increased for a given amount of EDTA. Nevertheless, it was important to consider that these constants corresponded to the interaction between cations and EDTA alone. These ranges of affinity were further confirmed by thermodynamics direct measurements of the thermodynamic parameter of the complexation reaction of PVA(EDTA). Finally, besides the good sorption properties, it is also important to mention that it is possible to desorb the metallic cations from the polymer, as already mentioned in the literature for carboxylic acid groups [32]. Indeed, it was notably shown that quantitative desorption was efficiently achieved using hydrochloric acid [62]. Additionally, ester linkage was stable at pH 2 [63]. These points are of great interest as they open the way to the PVA(EDTA) reutilization in a new cycle of decontamination.

Thermodynamic study

This part deals with the study of the interactions existing between PVA1(EDTA)_{15%} and some selected metallic cations. The aim of this analysis was to obtain more information about the complexation phenomenon between the modified functionalized polymer and the ion to be removed, in comparison with the EDTA alone. The thermodynamic parameters of the interaction between PVA1(EDTA)_{15%} and various cations were investigated using direct calorimetric measurement carried out under conditions as close as possible to the ones used for the sorption tests described in the previous sections. In particular the free ionic strength and the unadjusted pH conditions were applied in line with the procedures used in industrial applications. The raw data thermograms obtained for Cobalt and Lead are displayed in Fig. 6, which represents the results obtained for the calorimetric titration of Co(II) or

Pb(II) stock solutions injected into pure water (dilution experiments), together with the sorption experiments with the use of PVA1(EDTA)_{15%}. The successive injections of the stock solution into the calorimetric cell resulted in a raw heat flow record representing several thermal peaks equally spaced as a function of time. For dilution experiments, the intensity of the peak was small compared to the signal obtained in the presence of PVA1(EDTA)_{15%}, being in the range of 100 to 500 nW. In this second case, the thermograms clearly showed initially intense and clearly defined peaks. The rapid return to a stable baseline was an indirect indication that the kinetics was fast. This evidenced the good accessibility of the cation to the sorption sites. For Co(II) sorption, the first peaks were endothermic (3 mW) whereas they were exothermic for Pb(II) (14 mW). The heat flow decreased after 8-9 injections and then, after passing through an inflexion point, the heat flow peak leveled off and became negligible.

The integration of the areas under these thermal peaks should lead to the determination of the complete thermodynamic balance together with the binding constant, the reaction enthalpy (both leading to the entropy calculation), and the binding stoichiometry. These thermal peaks were further processed and integrated by using the NanoAnalyze™ Software offered by TA Instruments. The dilution correction terms to be subtracted from the sorption measurements were considered using experiments carried out in water using similar conditions (dilution experiments). The so-obtained heats of injection were plotted as a function of the metal-to-ligand molar ratio. The experimental heat values were fitted to independent site binding models (NanoAnalyze™), thus leading to the determination of the equilibrium dissociation constants for all systems. Best fitting curves corresponding to Co(II) and Pb(II) are shown in Fig. 7 with the corresponding dissociation constant K_d .

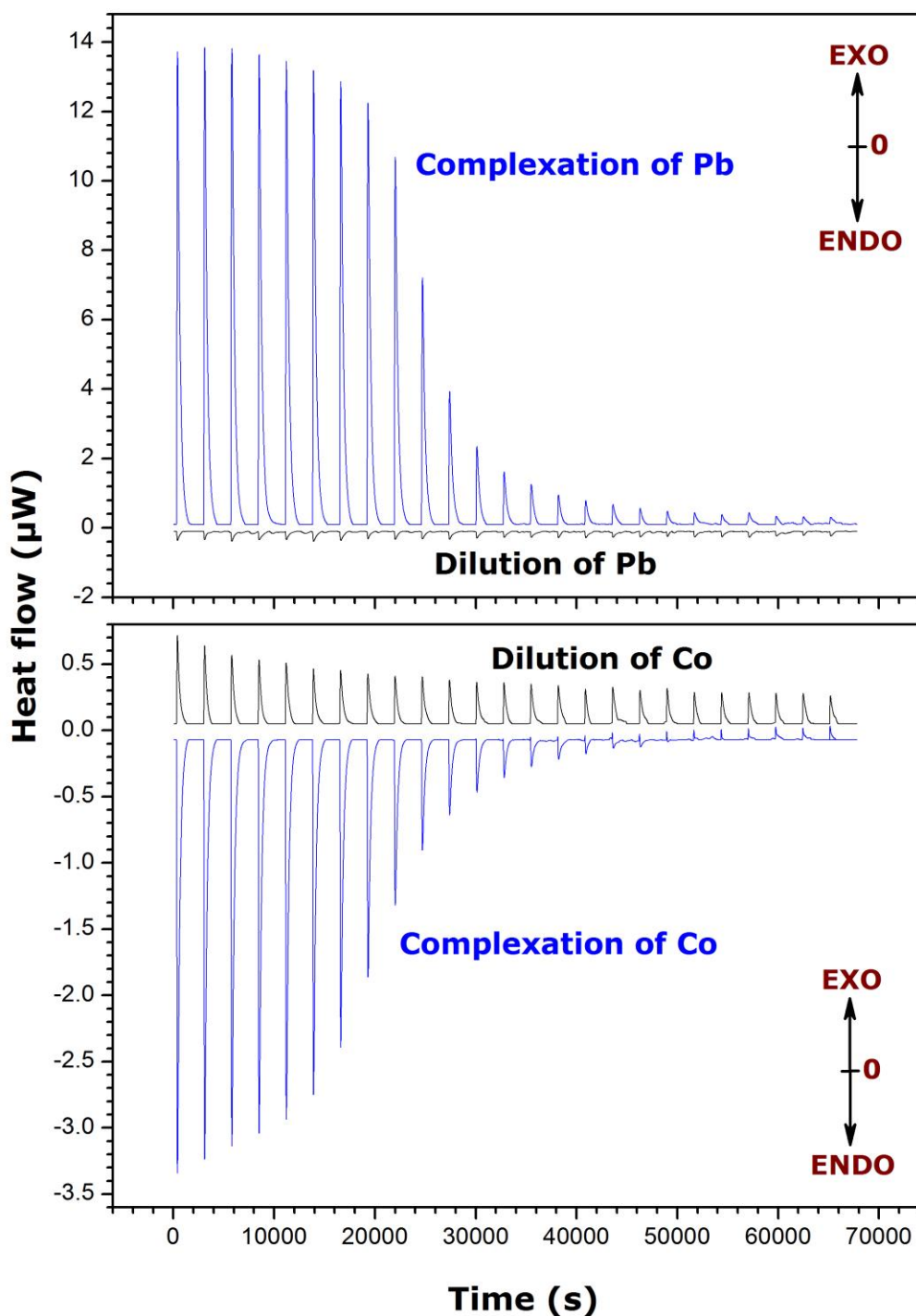


Fig. 6. Processed thermal profiles for dilution of cobalt- (bottom) or lead- (top) containing aqueous solutions and metal ion retention onto PVA1(EDTA)_{15%} from single-solute aqueous solutions at 298 K under the unadjusted pH condition: records of 25 successive injections of the 10 μL aliquots of a 20 $\text{mmol}\cdot\text{L}^{-1}$ $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ or $\text{Pb}(\text{NO}_3)_2$ stock solution into a 1 mL glass ampoule containing initially 800 μL of ultrapure water (dilution experiment) or 800 μL of ultrapure water and PVA1(EDTA)_{15%} at a 2.5 $\text{g}\cdot\text{L}^{-1}$ concentration (binding experiment). An injection time of 10 s and an equilibration time of 45 min between 2 successive injections were set up. Peak Analyzer procedures available in OriginPro software were applied to subtract the baseline. Both the dilution and the adsorption profiles have been plotted by using the same heat-flow scale (y-axis).

Table 5 summarizes the thermodynamic parameters for the Co(II), Ni(II), Zn(II), Cu(II) and Pb(II) sorption onto PVA1(EDTA)_{15%} as calculated from the fit of the ITC curves. Due to the low affinity of Cd(II) with PVA1(EDTA)_{15%}, it was impossible to evaluate the corresponding thermodynamic parameters. For other cations, the dissociation constant K_d was the lowest for Co(II) (3.74), and the highest for Cu(II) (7.53). These values were four times smaller than the ones given in the literature for EDTA [59]. This evidenced the influence of the polymer chain on the strength of interaction with various cations. The constants were smaller, but as seen before, the sorption in competitive conditions was still suitable for practical applications. Furthermore, the tendency in the formation constant of PVA1(EDTA)_{15%} with the cations followed the order: Co(II) < Zn(II) < Pb(II) < Cu(II) < Ni(II), similar to the tendency in the formation constant of the EDTA complex, namely Co(II) \approx Zn(II) < Pb(II) < Cu(II), < Ni(II) [59].

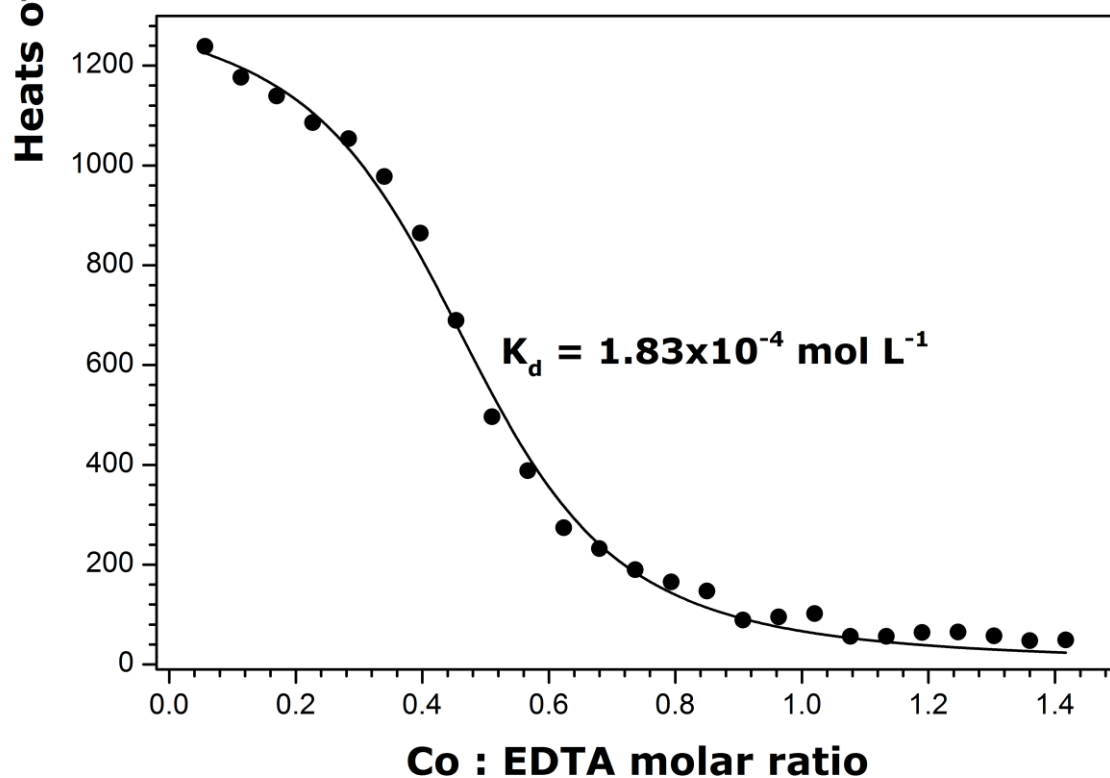
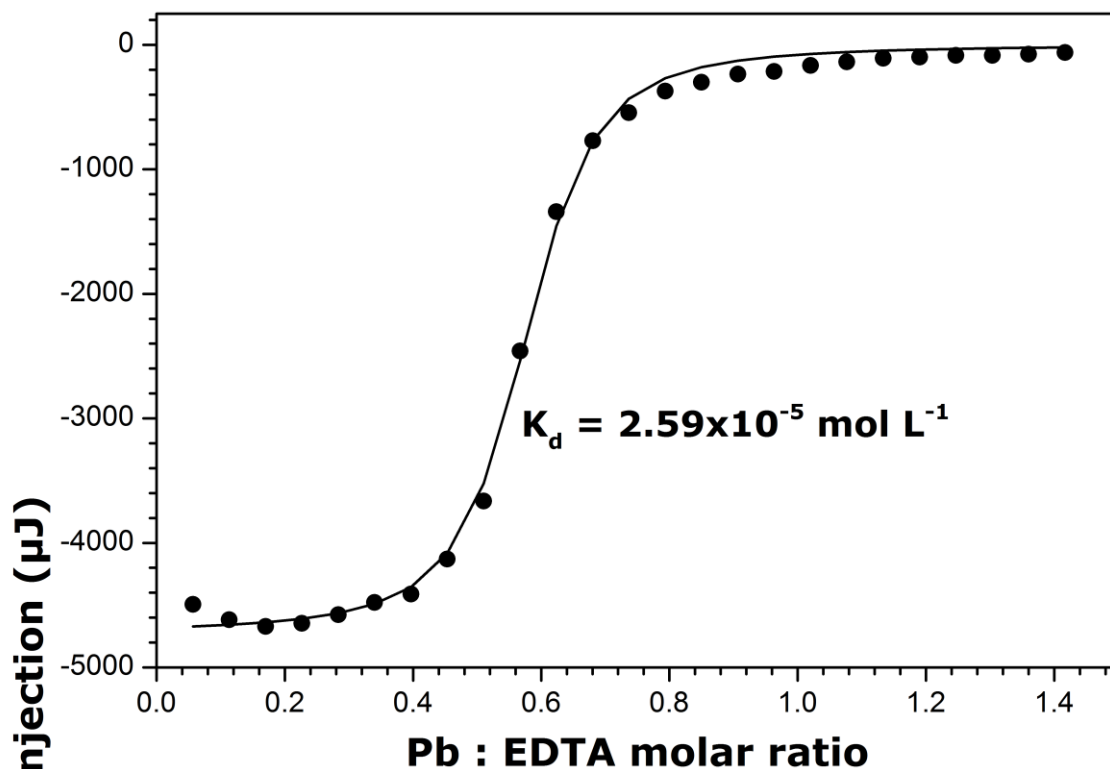


Fig. 7. ITC heat data corresponding to successive injections of a Co- or Pb-containing stock solution into a PVA1(EDTA)_{15%} aqueous solution placed in the calorimetric cell at 298 K; the solute concentrations, respectively, in the syringe and in the cell are as follows: 20 mol L⁻¹ Co(II) or Pb(II) and PVA-EDTA 2.5 g/L. The dissociation constants (K_d) obtained by fitting the heat experimental values (filled circles) to the independent site binding model (solid lines) are indicated.

This means that the EDTA complexation properties were not modified when EDTA was grafted on the polymer chain. The stoichiometry n was between 0.47 and 0.63, indicating that 2 EDTA were necessary to complex one cation, with the only exception of Zn for which 1.6 EDTA per cation were enough. These observations were in a full agreement with those inferred from the analysis of the adsorption isotherms.

Table 5

Thermodynamic parameters for the heavy metal sorption onto PVA1(EDTA)_{15%} as calculated from the fit of the ITC data.

Cation	K_d	n	ΔG (kJ.mol⁻¹)	ΔH (kJ.mol⁻¹)	$-T \Delta S$ (kJ.mol⁻¹)
Co(II)	3.74	0.47	-21.3	6.9	-23.8
Ni(II)	5.52	0.46	-31.5	-8.6	-23.2
Zn(II)	4.07	0.63	-23.2	3.6	-26.9
Cd(II)	nd*	nd	nd	nd	nd
Pb(II)	4.59	0.56	-26.2	-24.0	-2.1
Cu(II)	7.53	0.49	-43	-10.7	-35.7

* not determined

The complete thermodynamic balance is finally shown in Fig. 8 for Co(II), Ni(II), Zn(II), Pb(II), and Cu(II). The Gibbs free energy, ΔG , was negative in all cases, pointing out the spontaneous character of the phenomena studied here, as generally reported in other studies on grafted and functional polymers such as bifunctional graft copolymer composed of vinyl imidazole and acrylic acid [64], PVA-polyelectrolyte membranes [65], polymers based on divinyl ether and acrylamido-2-methyl-1-propan sulfonic acid [66], on amylopectin grafted with acrylamide and acrylic acid [67].

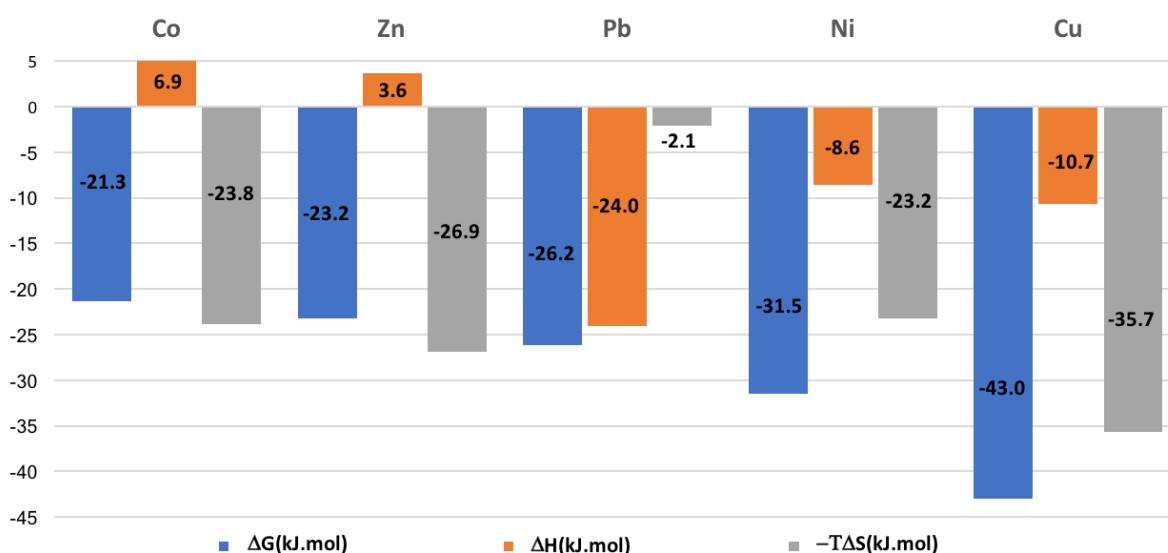


Fig. 8. Thermodynamic parameters for the metal ion binding to PVA1(EDTA)_{15%}: Co(II), Ni(II), Zn(II), Pb(II), and Cu(II).

The ΔG (and K_d) values were higher for Ni(II) than those for Co(II), indicating that Ni(II) would be more easily removed under competitive conditions in the presence of Co(II). In the Cu, Zn and Pb series, the ΔG was the highest for Cu(II), and the smallest for Zn(II). The lower constant was explained by the slightly less exothermic enthalpies of formation and the consequently less strong chelate effects expressed by lower (but still positive) entropies [68].

Concerning the enthalpy contributions, ΔH was negative (exothermic phenomenon) for Ni(II), Pb(II) and Cu(II), and positive (endothermic phenomenon) for Zn(II) and Co(II). Depending on the system studied, ΔH was negative [65, 66, 69, 70] indicating that the reaction was enthalpically favorable, but some endothermic contribution was also observed [64]. Finally, the entropic contribution was positive ($\Delta S < 0$) for all cations. It was very small for lead, and the highest for copper, with the following order: $\text{Cu} > \text{Zn} > \text{Co} \approx \text{Ni} > \text{Pb}$. Even though Cu usually exhibited the highest entropy, the general tendency varied depending on the system studied. In the literature, the following orders were reported: $\text{Cu} > \text{Pb}$ for PVA-polyelectrolyte membranes [65], Cu

> Zn > Ni > Pb > Co for biopolymer sericin containing small polypeptides [69], and Cu>Ni>Zn for amylopectin-*graft*-poly[(*N,N*-dimethylacrylamide)-*co*-(acrylic acid)] [67]. Sometimes the inverse range was observed: Ni > Zn > Co for bifunctional graft copolymer composed of vinyl imidazole and acrylic acid [64] or Pb>Cu for tea waste modified by poly(vinyl alcohol) [70].

At this stage of the work, the described tendencies were not completely understood. There were few exhaustive studies on thermodynamics and systematic comparison of cation on grafted polymers using real direct calorimetric measurements. As described by Wang [66], positive ΔS indicated the increased randomness at the polymer/solution interface during the sorption of metal ions onto grafted EDTA. The enthalpic outcome ΔH contained both metal ion-EDTA interaction together with the partial dehydration of the ion. For Co(II) and Ni(II), the hydration enthalpies were similar [71], and the difference of the observed enthalpy balance between the two cations is still unexplained. In the case of Pb(II), the entropic effect was very small probably due to the low number of water molecules in the hydration sphere, with 6 for this cation, and between 9.6 and 10.4 for the others [71]. This explained the high hydration enthalpy contribution in the case of lead. Other cations also displayed similar hydration enthalpy and entropy. In the present case, it seemed that the enthalpy, ΔH , was overcompensated by endothermic dehydration in the case of Co(II) and Zn(II). Positive values of the reaction enthalpy demonstrated the thermodynamic stability of the complexes to be strongly dependent on the entropy change [72].

The results obtained in the present study helped to explain the differences in sorption properties observed between the cations and gave first insight into the driving forces involved. The differences in the affinity between PVA1(EDTA)_{15%} and metal cations

could be attributed to the differences in the binding energy involved in the complexation phenomenon but also to the hydration and mobility effects.

4. Conclusion

PVA(EDTA) copolymers have been developed and proved to be valuable sorbents for metal cation removal. The influence of polymer properties (molecular weight and EDTA content) was studied. Results indicated better sorption properties for lower molecular weight polymers due to mobility and solubility. Lower EDTA grafting rate in the PVA backbone led to a better Co(II) and Ni(II) retention. But in real conditions of filterability, the polymer with the lowest molecular weight and the highest grafting rate was preferred for further experiments. The study of PVA1(EDTA)_{15%} underlined the great sorption capacity of these copolymers for divalent cations in pure water, namely Zn(II), Cd(II), and Pb(II), Co(II), and Ni(II) to a lesser extent. Two EDTA units from the PVA backbone were necessary to complex one cation (1.7 for Zn(II) and Cd(II)). The sorption properties were also evaluated when the cations were mixed up in equimolar quantities, in particular Co(II) and Ni(II), on the one hand, and Cd(II), Zn(II), Pb(II) and Cu(II), on the other hand. Under such competitive conditions in pure water, the preferential sorption of Ni(II), and Cu(II), as well as Pb(II) to a lesser extent, was demonstrated. Retention efficiency was also evaluated under competitive conditions in a simili composed of Ca(II) and Mn(II) present at higher concentrations. The cation removal was impacted by the presence of these new competing cations but the functionalized polymer remained very efficient for sorption. Additionally, a correlation between the selectivity towards the cations and the EDTA metal-complex formation constants was established. The obtained reaction constants were four times lower for functionalized polymers, but the range order was similar for EDTA and PVA1(EDTA)_{15%}, indicating that the EDTA properties were not greatly modified. The

entropic term was probably the main contribution with a high effect of hydration, relatef to both the cation and the polymer chain.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/>

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Supporting Information

Complexation properties of new hydrosoluble poly(vinyl alcohol) (PVA)-based acidic chelating polymers

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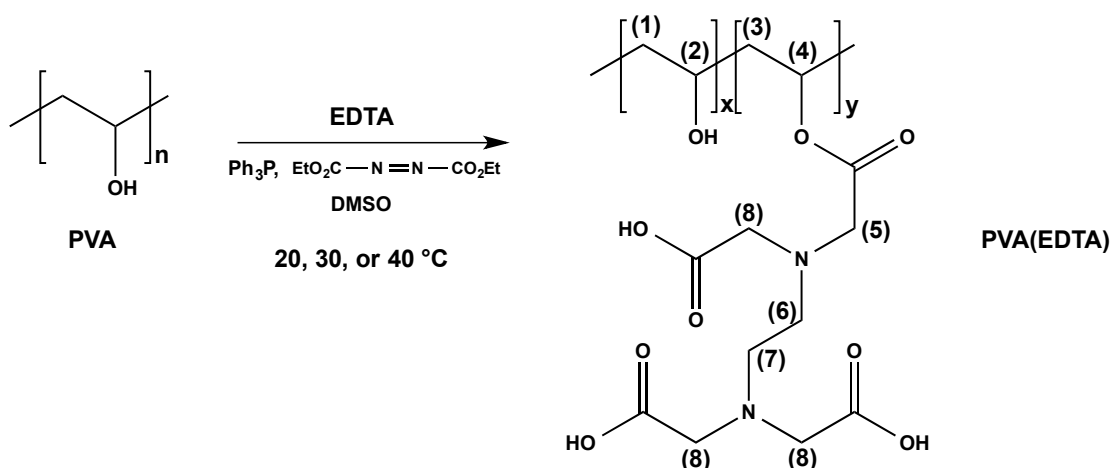
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Synthesis of poly(vinyl alcohol) (PVA) grafted with ethylenediaminetetraacetic acid (EDTA)



Methods

^1H NMR spectra (δ , ppm) were recorded on a Bruker DRX 200 (200 MHz) spectrometer with tetramethylsilane (TMS) as an internal standard and DMSO- d_6 as deuterated solvent. Infrared spectroscopy (ν_{max} , cm^{-1}) were recorded on a Perkin Elmer precisely Spectrum 100 FT-IR spectrometer.

Typical procedure for the grafting of 15% of EDTA onto PVA with $M_n = 20000 \text{ g}\cdot\text{mol}^{-1}$ (PVA1(EDTA)_{15%})

Grafting onto PVA1 was achieved according to the procedure detailed in a previous paper [49]. A solution of PVA (1.5 g in 30 mL of DMSO, $M_n = 20\,000 \text{ g}\cdot\text{mol}^{-1}$, 34.1 mmol in hydroxyl groups, 1 eq.) was added to a mixture containing triphenylphosphine (9.8 g, 37.5 mmol, 1.1 eq) and ethylenediaminetetraacetic acid (10.95 g, 37.5 mmol, 1.1 eq) in 150 mL of dimethylsulfoxide (DMSO) at 120 °C. Then, diethyl azodicarboxylate (6.5 g, 37.5 mmol, 1.1 eq), was added dropwise during two hours at room temperature. The obtained solution was then allowed to stir at 40 °C during one night. The resulted mixture was transferred into a dialysis tubing

(MWCO \approx 2000 Da) and dialyzed against DMSO during two days in order to remove all organic components excepted the functionalized PVA1(EDTA)_{15%} polymer (1.9 g, yield: 90%).

¹H NMR δ_H (200 MHz ; D₂O): 1.3-2.4 (CH₂-CH), 3.1-4.2 (CH₂-CH, C(O)CH₂N, N-CH₂-CH₂-N, N-CH₂-COOH), 5.1-5.4 (CH-O-CO); IR: ν_{\max} / cm⁻¹ 1390 (C=O acid), 1625 (C=O acid), 1730 (C=O ester), 3400 (OH).

Determination of functionalization rates

Functionalization rates were determined by ¹H NMR, comparing the signal at 1.3-2.4 ppm corresponding to the methylene of the main chain with the one at 5.1-5.4 ppm attributed to the methyne of the main chain in the α position of the EDTA grafted group.

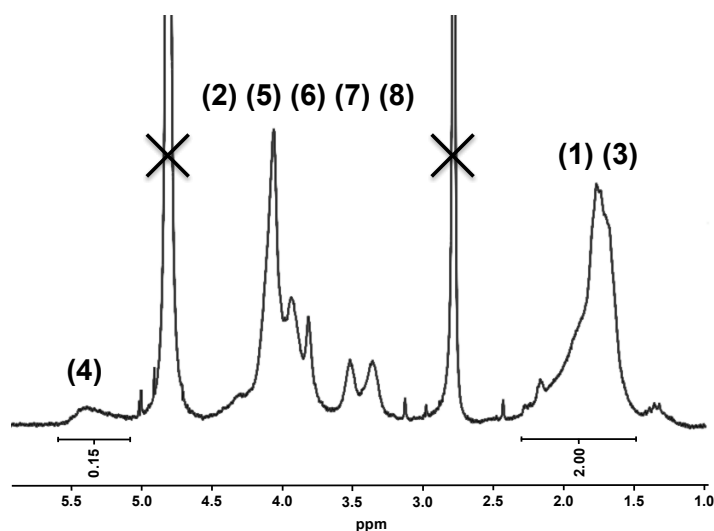


Fig. S1. ¹H NMR for PVA1(EDTA)_{15%} in CDCl₃.

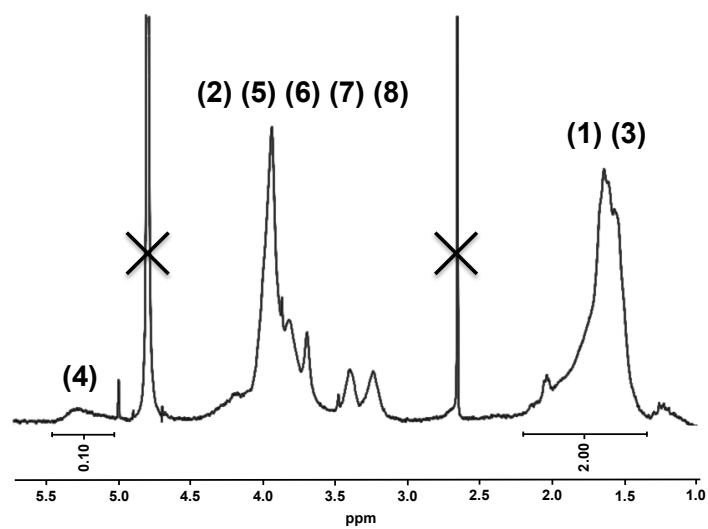


Fig. S2. ^1H NMR for PVA1(EDTA) $_{10\%}$ in CDCl_3 .

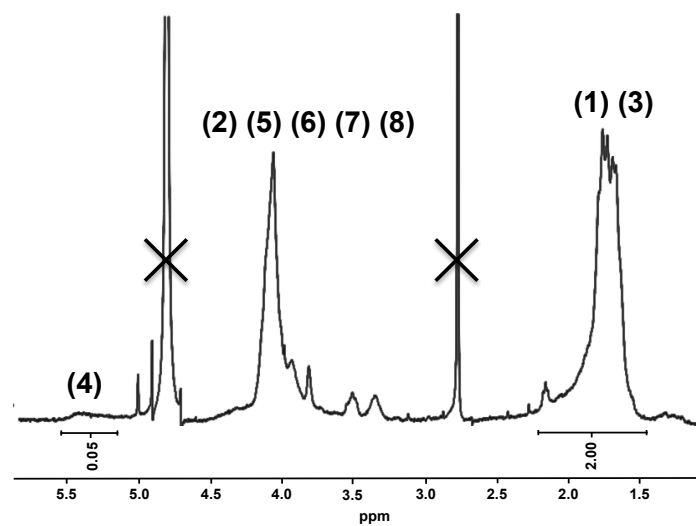


Fig. S3. ^1H NMR for PVA1(EDTA) $_{5\%}$ in CDCl_3 .

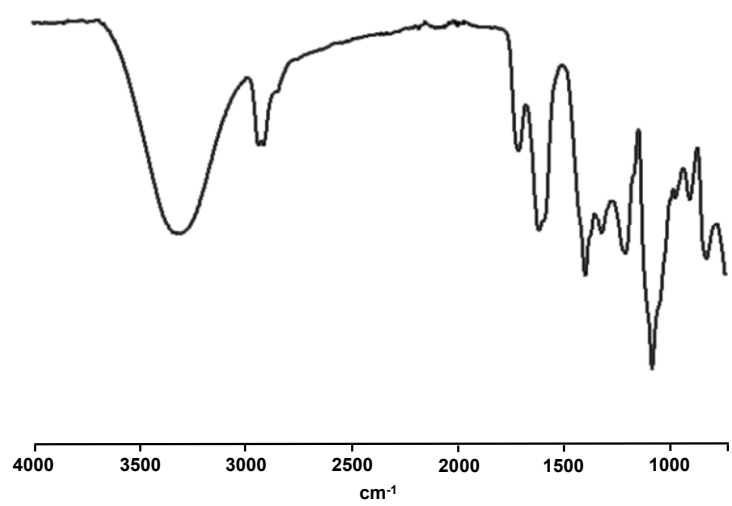


Fig. S4. Infrared spectrum for PVA1(EDTA)_{15%}.

Analytical conditions for polarography experiments

For polarography experiments, the analysis was based on the electrochemical reactions between mercury drop and metal cations present in solution. In our case, we worked in Hanging Mercury Drop Electrode (HMDE) mode limiting the consumption of mercury. The following table S1 presents the different parameters used for the measurements.

Table S1

Parameters used for polarography experiments.

Drop size	Deposition potential	Deposition time	Equilibration time	Pulse time	Voltage step time	Pulse amplitude	Voltage step
4	-0.7 V	150 s	30 s	0.04 s	0.3 s	0.05 V	0.004 V

Complexation properties of water-soluble poly(vinyl alcohol) (PVA)-based acidic chelating polymers

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Conflict of interest

There are no conflicts to declare.

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Author statement

The corresponding author is responsible for ensuring that the descriptions are accurate and agreed by all authors.

Role(s) of all authors:

Julien Muller: synthesis and characterization

Xianyu Ding: characterization

Amine Geneste: characterization

Jerzy Zajac: conceptualization

Benedicte Prelot: conceptualization, methodology, supervision

Sophie Monge: conceptualization, methodology, supervision