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Synthesis and study of sorption properties of polyvinyl alcohol (PVA)-based hybrid materials

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Abstract

The present contribution aims at reporting the synthesis and the preliminary evaluation of hybrid materials combining polyvinyl alcohol (PVA) functionalized with ethylenediaminetetraacetic acid (EDTA) as complexing groups, and alumina that, together, were able to efficiently complex and remove metallic cations from aqueous effluents. For such purpose, well-defined PVA homopolymers bearing an azide (PVA-N₃) or an alkyne function (PVA-alkyne) were functionalized *via* chemical modification by either phosphoric acid (PPVA-N₃), to promote adhesion to alumina, or ethylenediaminetetraacetic acid (PVA(EDTA)-alkyne), able to efficiently complex metallic cations. Modified PVA chains were coupled by Huisgen reaction using copper catalysis (CuAAC) leading to the formation of bifunctional diblock copolymers. Then, hybrid materials were produced *via* the grafting of PVA-based copolymers onto alumina particles. Finally, the sorption capacity of these materials towards Co(II), Ni(II) and Sr(II) was determined to evaluate their removal efficiency. Such hybrid materials could be efficiently used in the context of nuclear effluents treatment.

Keywords: functionalized polyvinyl alcohol; hybrid materials; water treatment

1. Introduction

Despite environmental legislation and regulations, the release of pollutants in aqueous media is continuously growing. For heavy metals, their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment, with raising concerns over their potential effects on human health and the environment [1-5]. For instance, metals such as lead, cadmium, nickel or copper are carcinogen and can induce kidney and neuronal diseases [6-8]. As a result, environmental regulations have been established and various strategies were developed for the uptake of heavy metal from wastewater. Conventional methods such as ion exchange [9-12], chemical precipitation [13, 14], adsorption onto activated carbon [15, 16] and membrane processes [17, 18] have proved to be efficient but, depending on the processes, several limitations may happen. The main drawbacks of the precipitation technology are the large volume of the ultimate wastes generated and the relatively high costs treatments and storage. Concerning ion exchange, the selectivity of resins towards metallic cations is sometimes limited in the presence of organic residues or in competitive conditions with strong influence of the salinity, and they might be damaged under irradiation [19]. Phosphonated-based thermosensitive polymers were also considered [20-25]. The advantage of such materials was that they were soluble below their lower critical solution temperature (LCST), leading to a rapid and efficient complexation. Additionally, they became insoluble above their LCST, allowing an easy filtration step. Other researches focused on chelating agents [26, 27] to enhance metal uptake taking in consideration capacity, selectivity, or affinity. In particular, carboxylic acid has proved to be a valuable complexing group. Interactions with metal ions occur by interaction between the oxygen atoms of the carboxylic acid and the metallic ions, finally leading to the formation of coordination bonds. Ethylenediaminetetraacetic acid (EDTA) and derivatives were widely used to remove heavy metal on an important pH range [28]. For exemple, glycidyl methacrylate-based polymer resins functionalized with diethylenetriaminetetraacetic acids efficiently removed Mg(II) and Ca(II) [29].

Organic-inorganic hybrid materials have attracted much attention in recent years because of their advantageous combination of organic and inorganic moieties [30]. Indeed, in such materials, different organic groups are combined with thermally

stable and robust inorganic moiety, leading to strong binding affinities and high metal ion adsorption capacities toward appropriate metal cations [31]. They are generally prepared *via* covalent binding of specific organic groups onto inorganic substrates thanks to the hydroxyl groups on the surface, therefore used as anchoring points. Such type of materials were already used for various applications including flame retardancy [32, 33], corrosion protection [34], light emitting diodes [35] or solar cells [36]. Wastewater decontamination application was also considered [37, 38]. Numerous studies focused on the sorption of heavy metal cations onto modified mesoporous silica (MCM-41 or SBA-15) [39, 40]. The functionalization of mesoporous silica SBA-15 with 1-furoyl thiourea urea allowed efficient removal of Hg(II) from aqueous media *via* the thiourea derivative [41]. Other functional groups than sulfur-containing chelating agents showed good metal ion removal properties and were considered as efficient for wastewater treatment. Ethylenediaminetetraacetic acid functionalized mesoporous silica (EDTA-SBA-15) was synthesized and used to efficiently remove Co(II), Ni(II), Cu(II) [42], and Pb(II) [43]. Chitosan-silica hybrid adsorbents functionalized with ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) were efficiently employed to complex rare earths [44].

Compared to silica [45], alumina oxides were rarely considered in hybrid materials for water treatment whereas they are of interest since alumina particles are among the most used inorganic substrate to graft organic groups. The grafting strategy followed in the framework of the present work consisted in making polymeric chains interact chemically with hydroxyl groups on the inorganic surface [46, 47]. Several anchoring groups including phosphonic/phosphoric acids can lead to strong and covalent bonds. In the literature, three main kinds of phosphorus-based organic layers can be immobilized onto alumina surfaces: alkylphosphonic acids [48], phenylphosphonic acids [49], and phosphonic acid-based polymers [50].

The purpose of the present contribution is to develop innovative alumina oxide-based hybrid materials that will be involved in a decontamination process offering a realistic and cost-efficient solution for the removal of some radionuclide cations, and leading to small amounts of ultimate solid waste. The choice of alumina as a support was also motivated by a procedure of waste treatment employed in nuclear industry where the low- and intermediate-level short-lived waste is melted at high temperatures and solidified into a synthetic rock matrix [51]. In such processes,

mineral oxide particles may play a role of adjuvants during the melting stage necessary to diminish the overall energy consumption. The experimental and modeling studies indicated that the surface of alpha-alumina was inherently hydroxylated and contained numerous isolated aluminol groups [52, 53]. The use of a high-purity and nonporous alpha-alumina powder is thus appropriate for the purpose of polymer grafting. To achieve that goal, appropriate functionalized polymers will be grafted onto solid particles with adequate sizes. Polymeric chains will contain numerous groups for selective sequestration (complexation) of radionuclide cations. In the ideal case, the uptake of cationic species by the coated particles will gradually lead to the compensation of initial negative charge. For the future applied process, this should promote the contact between hydrophobized and destabilized particles, which will stick together to form flocs, thus favoring the separation step by filtration. Functionalized polymer will derive from polyvinyl alcohol (PVA) as the latter showed biodegradability and non-toxicity. PVA-based diblock copolymers will be prepared by coupling two PVA homopolymers, either functionalized with phosphoric or EDTA groups. The interest of using diblock copolymers is that the first segment will be devoted to the establishment of interactions with alumina whereas the second one will be exclusively available for the sorption of metallic cations. The bifunctional copolymers will be grafted onto alumina particles using phosphoric acid groups whereas the second block bearing EDTA will be responsible for metal complexation. Sorption tests on Co(II), Ni(II), and Sr(II) have been investigated to assess the potential use of these novel materials.

2. Experimental

2.1. Materials

Ethylenediaminetetraacetic acid (Aldrich, 99%), urea (Aldrich), ethylenediaminetetraacetic acid disodium salt dihydrate (Aldrich, 97%), aluminium oxide α -phase (Alfa Aesar, 99.9%), phosphoric acid (Aldrich, 99%), diethyl azodicarboxylate (Alfa Aesar, 97%), triphenylphosphine (Aldrich, 99%), copper (I) bromide (Aldrich, 98%), N,N,N',N'',N''-pentamethyldiethylenetriamine (Aldrich, 99%), cobalt (II) nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99%), nickel nitrate $\text{Ni}(\text{NO}_3)_2$ (Aldrich, 99%), and strontium nitrate $\text{Sr}(\text{NO}_3)_2$ (Aldrich, 99%) were used as received. All solvents and others chemicals were purchased from Alfa Aesar or Sigma-Aldrich at the highest available purity. Water was deionized and purified with a Millipore Super Q system (resistivity of 18.2 M Ω). Dialysis membranes (MWCO 1000 Da) were purchased from Spectrum Laboratories.

2.2. Methods

Molar mass distribution of polymers was determined by size exclusion chromatography (SEC) using a PL-GPC50 Plus equipped with a RI refractive index detector. Polar Gel M was used at 50 °C with a dimethylacetamide (DMAc) flow rate (+0.1% LiCl weight) equal to 0.8 mL.min⁻¹, calibrated with PMMA standards. ¹H NMR spectra (δ , ppm) were recorded on a Bruker DRX 200 (200 MHz) spectrometer with tetramethylsilane (TMS) as an internal standard and CDCl_3 , D_2O or $\text{DMSO-}d_6$ as deuterated solvents. Solid-state ³¹P NMR spectra were recorded on a Bruker DRX 600 (600 MHz) spectrometer with a K_2HPO_4 probe. Spectra were analyzed using a deconvolution method using OnePulse ¹H decoupled software. 2D DOSY NMR spectra were recorded on a Bruker Advance 3 (600 MHz) at 20 °C. The deuterated solvent was $\text{DMSO-}d_6$. Chemical shifts (δ , ppm) were referenced to the peak of residual non-deuterated solvent at 2.5 ppm. The software was Topspin 2.1 using the exponential method with a logarithmic scale. Infrared spectra (ν_{max} , cm⁻¹) were recorded on a Perkin Elmer precisely Spectrum 100 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) was performed using an Al K α (1486.6 eV) source

and an ESCALAB 250 (Thermo Electron) as analyzer. Calibration of the energy scale was performed using the C-C bond of the C_{1s} carbon at 284.8 eV. Elementary analyses were carried out using ICP-AES (Solaize, France). The phosphorus content was evaluated after mineralization in acid media.

Sorption measurements were carried out using 30 mL Nalgene[®] reactors in which hybrid materials and metal solution at a given concentration were stirred slowly overnight at 25 °C. A 250 mg sample of hybrid material was poured into each tube. The preparation of the solution for sorption was performed by direct weighing in each Nalgene[®] tube water and stock solution so as to obtain about 10 mL of the appropriate solution. The initial concentration of cobalt, strontium and nickel 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. A time of 14 hours was used to reach the sorption equilibrium. The hybrid material was separated from equilibrium solution by sedimentation and filtration of the supernatant using 0.22µm filter. The amount of cations retained per unit mass of polymer was calculated using the following equation:

$$Q = \frac{(C_0 - C_e) \cdot V_0}{m_s}$$

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 solution, and m_s is the mass of material. The equilibrium concentrations of metallic cations were measured with 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 used was a solution composed of tartaric acid (4 mmol.L⁻¹) and ethylenediamine (EDA) (1.5 mmol.L⁻¹).

2.3. Syntheses

Synthesis of PVA-N₃ and PVA-alkyne

Functionalized PVA (PVA-N₃ and PVA-alkyne) syntheses were reported in a previous work [54].

Typical procedure for the synthesis of PVA(EDTA)-alkyne

A solution of PVA-alkyne (500 mg in 10 mL of DMSO, 11.4 mmol in hydroxyl groups, 1 eq.) was added to a mixture containing triphenylphosphine (3.28 g, 12.5 mmol, 1.1 eq.) and ethylenediaminetetraacetic acid (3.65 g, 12.5 mmol, 1.1 eq.) in 50 mL of dimethylsulfoxide (DMSO) at 120 °C. Then, diethyl azodicarboxylate (4.35 g, 25 mmol, 2.2 eq.) was added dropwise during two hours at room temperature. The obtained solution was then allowed to stir at room temperature overnight. Reactional medium was transferred into a dialysis tubing (MWCO \approx 1000 Da) and dialyzed against DMSO during two days in order to remove all organic components excepted the functionalized polymer. Last dialysis was carried out with water in order to remove all the DMSO (540 mg, **yield: 85 %**). $^1\text{H NMR } \delta_{\text{H}}$ (200 MHz; D_2O , Me_4Si): 1.4-2.2 ($\text{CH}_2\text{-CH}$, $\text{C}\equiv\text{CH}$), 3.1-4.2 ($\text{CH}_2\text{-CH}$, $\text{C}(\text{O})\text{CH}_2\text{N}$, $\text{N-CH}_2\text{-CH}_2\text{-N}$, $\text{NCH}_2\text{-COOH}$), 5.3-5.4 (CH-O-CO); 2D diffusion ordered (DOSY) NMR ($\text{DMSO-}d_6$): $-10.4 \text{ m}^2 \text{ s}^{-1}$; IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 1395 (C=O acid), 1625 (C=O acid), 1729 (C=O ester); Elementary analysis: O (29%), N (2.5%).

Typical procedure for the synthesis of PPVA-N₃ by phosphorylation reaction

Urea (5.45 g, 0.09 mol) was dissolved in DMF (20 mL) and the resulting solution was heated at 130 °C. A phosphoric acid solution (9.1 g in 40 mL of DMF) and then PVA-N₃ (2 g, 45.4 mmol) were added. The mixture was allowed to stir at 130 °C during 90 minutes under nitrogen. The product was purified by dialysis method against water during several days (2.1 g, **yield: 87 %**). $^1\text{H NMR } \delta_{\text{H}}$ (200 MHz; D_2O , Me_4Si): 1.3-2.1 ($\text{CH}_2\text{-CH}$), 3.6-4.2 (CH-OH), 4.3-4.6 ($\text{CH}_2\text{-N}_3$, $\text{CH-OP}(\text{O})(\text{OH})_2$), 4.5 (CH-O-P), 7.2-7.3 (aromatic CH); 2D diffusion ordered (DOSY) NMR ($\text{DMSO-}d_6$): $-10.2 \text{ m}^2 \text{ s}^{-1}$; Elementary analysis: P (4.8%); C (44%), O (30%).

Typical procedure for the synthesis of PPVA-b-PVA(EDTA) by Huisgen coupling reaction between PPVA-N₃ and PVA(EDTA)-alkyne

A mixture of Cu(I)Br (86 mg, 0.6 mmol), PPVA-N₃ (0.6 g, 0.2 mol), PVA(EDTA)-alkyne (0.72 g, 0.24 mmol), N,N,N',N'',N''-pentamethyldiethylenetriamine (104 mg, 0.12 mmol), and DMSO (15 mL) was put into a Schlenk tube under nitrogen bubbling for 20 minutes. The tube was then heated at 50 °C under nitrogen for 7 days. The solution was filtered through a short column of silica gel in order to remove catalytic

complex. The solvent was removed *via* cryodistillation. The final PPVA-*b*-PVA(EDTA) diblock copolymer was purified by dialysis against hydrochloric acid solution (pH = 2) until the elimination of all remaining copper and then against water (900 mg, **yield: 70 %**). ^1H NMR δ_{H} (200 MHz; DMSO- d_6 , Me $_4$ Si): 1.0-2.0 (CH $_2$ -CH), 3.2-4.0 (CH $_2$ -CH, C(O)CH $_2$ N, N-CH $_2$ -CH $_2$ -N, NCH $_2$ -COOH, CH-OH), 4.3-5.2 (CH $_2$ -N_{triazole}, CH-OP(O)(OH) $_2$, CH-O-CO), 7.1-7.25 (aromatic CH); 2D diffusion ordered (DOSY) NMR (DMSO- d_6): $-10.5\text{ m}^2\text{ s}^{-1}$; Solid-state ^{31}P NMR (δ , ppm): -2 (P(O)(OH) $_2$); SEC (DMAc): $M_n = 25200\text{ g}\cdot\text{mol}^{-1}$, $\mathcal{D} = 1.35$.

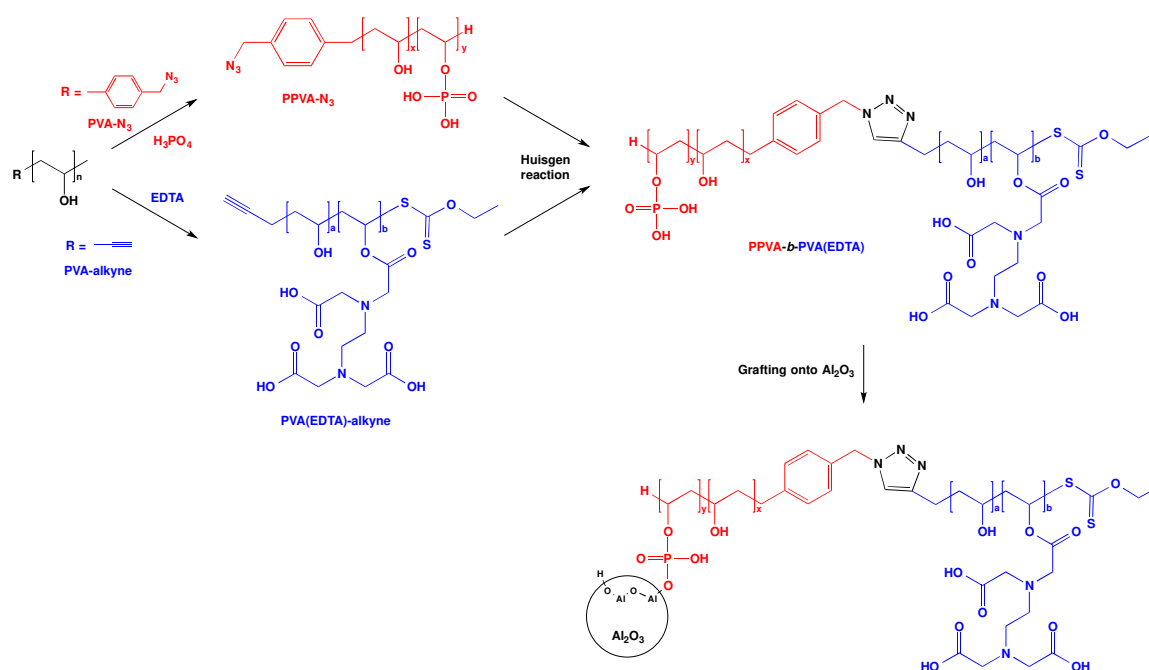
*Typical procedure for the grafting of PPVA-*b*-PVA(EDTA) onto alumina particles*

PPVA(5%)-*b*-PVA(EDTA)(6%) copolymers (160 mg, 0.032 mmol) was solubilized in ultrapure water (100 mL). A dispersion of alumina particles (1 g in 50 mL of water) was added after 10 minutes of sonication. The mixture was allowed to stir at 20 or 90 °C during 3 days. The resulting powder was then washed 5 times with water, and the solid was then recovered by freeze-drying (750 mg, **yield: 74 %**). Solid-state ^{31}P NMR (δ , ppm): -20 - +5 (P(O)). TGA (800 °C): 2.1%. DRIFT $\nu_{\text{max}}/\text{cm}^{-1}$: 1100 (P=O), 1730 (C=O), 2800 (C-H), 3100-3500 (OH).

3. Results and discussion

3.1. Functionalization of PVA homopolymers

The synthesis of polyvinyl alcohol-based hybrid materials was achieved according to the general reactional pathway shown in Scheme 1. The first step dealt with the synthesis of functionalized homopolymers of polyvinyl alcohol (PVA) bearing either an azide group or an alkyne function, namely PVA-N₃ or PVA-alkyne, respectively, obtained with controlled molecular weights and end-groups, according to previously reported procedures [54]. These polymers were obtained from poly(vinyl acetate) (PVAc) corresponding derivatives, which were quantitatively hydrolyzed into PVA [54]. Each PVA homopolymer was then appropriately functionalized, with carboxylic acid or phosphonic acid groups, which permitted the complexation of metallic cations and promoted adhesion onto alumina particles, respectively.



Scheme 1. General reactional pathway leading to PVA-based hybrid materials.

Chemical modification of PVA-alkyne was carried out using either ethylenediamine tetraacetate dianhydride (EDTAD), or ethylenediaminetetraacetic acid (EDTA) in order to introduce chelating moieties. The choice of these reagents was motivated by the common use of the carboxylic acid functional groups for the selective complexation

of metallic cations [55]. Functionalization was not easy to achieve, as highest functionality was required while avoiding cross-linking. Different experimental procedures were tested. Reaction of EDTAD onto PVA at 60 °C in diluted DMSO (homogeneous medium) or diluted DMF (heterogeneous medium) led to cross-linking, resulting products being insoluble in common solvents. Same problem was observed using Steglich esterification with EDTA. Best results were obtained when EDTA reacted with alcohol groups of PVA-alkyne following the Mitsunobu's reaction [56] in DMSO in the presence of triphenylphosphine. Only 1.1 equivalent of EDTA was used with respect to PVA hydroxyl groups to avoid cross-linking. It is important to notice that even if the experimental conditions minimized the likelihood that one EDTA molecule functionalized multiple alcohol moieties (which was confirmed by the remaining solubility of PVA(EDTA)-alkyne after functionalization), this possibility could not be totally excluded as EDTA includes four carboxylic acid functions. The functionalized PVA(EDTA)-alkyne was recovered with 85% yield. Characterization by ^1H NMR in deuterated water (Fig. 1) showed characteristic signals of EDTA in comparison with the starting PVA-alkyne material. Only ^1H NMR spectrum corresponding to PVA(EDTA)-alkyne(15%) is shown as all spectra were identical. In particular, signal at 5.3-5.4 ppm was attributed to the protons of the CH in α -position of the EDTA (labeled (4)). Other EDTA protons were found between 3.1 and 4.2 ppm, overlapping with the CH of the PVA monomeric unit.

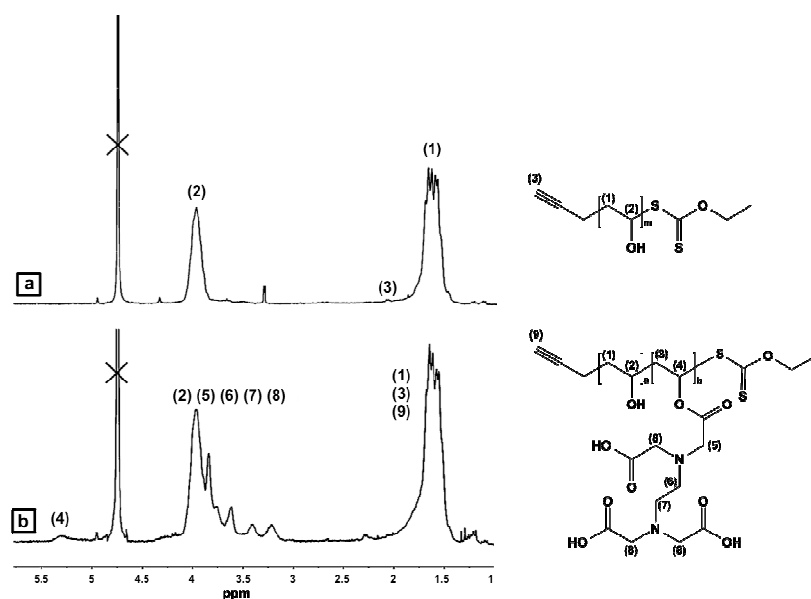


Fig. 1. ^1H NMR spectra of (a) PVA-alkyne, and (b) PVA(EDTA)-alkyne(15%) in deuterated water.

The determination of the level of functionalization was carried out using ^1H NMR by comparing the signal of the CH (4) of the EDTA at 5.3-5.4 ppm with the one at 1.4-2.2 ppm attributed to the methylene of the main chain ($\text{CH}_2\text{-CH}$) of the PVA polymer. It was demonstrated that the efficiency of the reaction was temperature dependent. Indeed, for PVA(EDTA)-alkyne homopolymer, the increase of the temperature resulted in the increase of the degree of functionalization, from 5 to 15 % for reaction temperature going from 20 to 40 °C (Table 1). Then, the substitution rates remained similar at higher temperature. It has to be mentioned that both ^1H NMR and elementary analysis led to similar results. To conclude, functionalization of PVA-alkyne with EDTA without cross-linking reaction was very challenging. Best results were obtained using Mitsunobu reaction. Highest degree of functionalization was equal to 14.5% while greatly minimizing cross-linking reactions at the same time.

Table 1

Characteristics of functionalized PVA-based homopolymers.

Polymer	Reaction temp. (°C)	Degree of functionalization (%)			M_n^a (g.mol ⁻¹)	\bar{D}^a
		^1H NMR ^b	Element. analysis	^{31}P solid state NMR		
PVA-alkyne	-	-	-	-	7500	1.30
PVA(EDTA)-alkyne(6%)	20	5	6.5	-	11500	1.32
PVA(EDTA)-alkyne(10%)	30	8.8	9.3	-	14100	1.35
PVA(EDTA)-alkyne(15%)	40	14.7	14.5	-	17200	1.35
PVA-N₃	-	-	-	-	7800	1.25
PPVA-N ₃ (5%)	115	5.5	-	-	9000	1.32
PPVA-N ₃ (7.5%)	120	7.5	-	-	10500	1.27
PPVA-N ₃ (10%)	125	9.5	9	10	11000	1.30
PPVA-N ₃ (14%)	130	13.5	12.4	14.5	13600	1.34

^a PMMA-calibrated size exclusion chromatography in dimethylacetamide as eluent; ^b ^1H NMR (200 MHz) in deuterated water.

The polyvinyl alcohol homopolymer bearing the azide group as chain-end (PVA-N₃) was used for the introduction of phosphorus-based functions that will be further grafted onto alumina surface. PVA-N₃ was phosphorylated by substitution of alcohol groups with phosphoric acid functions. The phosphorylation reaction was carried out in dimethylformamide using phosphoric acid and urea [57]. Comparison of ^1H NMR spectra before and after PVA-N₃ phosphorylation (Fig. 2) showed the appearance of

new signals, especially at 4.5 ppm, attributed to the proton in α of the phosphoric acid unit.

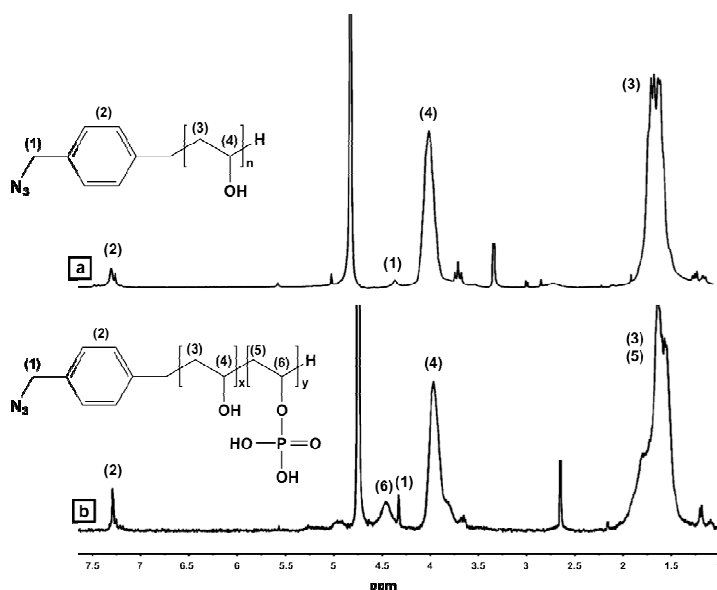


Fig. 2. ^1H NMR spectra of PVA- N_3 before (a) and after (b) phosphorylation reaction in deuterated water.

The level of functionalization was determined by comparison of this signal with the signal at 3.6-4.2 ppm attributed to the CH of the main chain of the PVA units. This rate also depended on the reaction temperature. An increase by 15 $^\circ\text{C}$ (115 to 130 $^\circ\text{C}$) of the temperature led to the increase of the degree of functionalization, going from 5.5 to 13.5%. In order to confirm results obtained by ^1H NMR, solid-state ^{31}P NMR and elemental analysis were also carried out on PPVA- N_3 (10%) (Fig. 3 and Table 1).

In the ^{31}P NMR analysis, K_2HPO_4 salts and PPVA- N_3 were mixed up in equimolar amounts (related to phosphorus) and the resulting mixture was analyzed. Area of both species was similar, confirming the functionalization found by ^1H NMR (9.5 and 10% by ^1H NMR and solid-state ^{31}P NMR, respectively). As ^{31}P NMR peaks slightly overlapped, we also achieved elementary analyses in phosphorus to confirm the experimental values of the degree of functionalization. These analyses were in accordance with NMR techniques as they gave a phosphorylation rate equal to 9%. Comparable results were obtained irrespective of the characterization method employed.

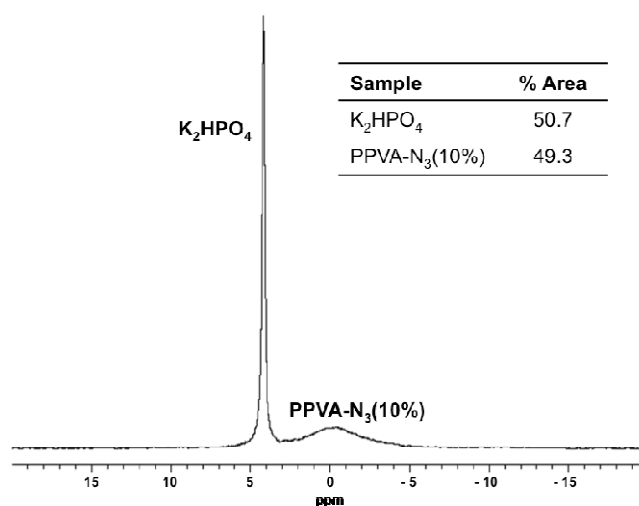


Fig. 3. Solid-state ^{31}P NMR spectrum of PPVA-N₃(10%) and K₂HPO₄ salt mixture.

To conclude, several PPVA-N₃ with various phosphorylation rates were obtained for the various temperature conditions used. The control of phosphorylation was a key point to tune accurately the grafting process.

3.2. Synthesis of PPVA-*b*-PVA(EDTA) copolymers by Huisgen reaction

Both homopolymers were coupled by Huisgen reaction to give PPVA-*b*-PVA(EDTA) diblock copolymers. The latter combined the behavior of selective complexation of cations and the property of grafting onto alumina thanks to the PVA(EDTA) and PPVA blocks, respectively. The diblock architecture is of great interest as functional groups are adjacent which will lead to enhanced adhesion of phosphoric acid onto alumina particles for PPVA block, and optimized complexation of cations for PVA(EDTA) block, as more than one complexing group is often involved in the complexation mechanism. PPVA-*b*-PVA(EDTA) diblock copolymers were prepared from both PPVA-N₃ and PVA(EDTA)-alkyne homopolymers using the Huisgen reaction, following an efficient experimental procedure previously reported in our group [54]. Copper (I) bromide and N,N,N',N'',N''-pentamethyldiethylenetriamine were used as catalyst for cycloaddition. As EDTA could complex with copper, we used a large excess of copper (I) bromide to ensure the success of the coupling reaction. The reaction was achieved at moderated temperature and resulting PPVA-*b*-PVA(EDTA) copolymers were purified by dialysis using hydrochloric acid solution (pH = 2), and then water (yield: 70%). Acidic medium was used to remove all copper

(copper (I) was oxidized to copper (II) by exposition to air at the end of the reaction) that could be sorbed onto EDTA moieties from the copolymers [58]. Once all copper removed, dialysis against water was achieved until pH of the copolymer remained constant (pH around 4). Several copolymers were prepared with various phosphorus and EDTA quantities (Table 2).

Table 2

Characteristics of functionalized PVA-based copolymers.

Polymer	Reaction temp. (°C)	M_n^a (g.mol ⁻¹)	\mathcal{D}^a
PPVA(14%)-PVA(EDTA)(6%)	50	21000	1.28
PPVA(7.5%)-PVA(EDTA)(6%)	50	19500	1.30
PPVA(5%)-PVA(EDTA)(6%)	50	20000	1.34
PPVA(7.5%)-PVA(EDTA)(15%)	50	25200	1.35
PPVA(14%)-PVA(EDTA)(15%)	50	27600	1.40

^a PMMA-calibrated size exclusion chromatography in dimethylacetamide as eluent.

The obtained products were characterized by size exclusion chromatography (SEC). The comparison between the starting homopolymers and the resulting PPVA(14%)-*b*-PVA(EDTA)(15%) copolymer (Fig. 4) clearly demonstrated that the molecular weight increased after the coupling. Additionally, monomodal signal was observed for the diblock copolymer, indicating that no side reaction occurred and that the reaction was successful. Finally, dispersity (\mathcal{D}) of the copolymers obtained after Huisgen reaction were relatively low ($1.28 \leq \mathcal{D} \leq 1.40$).

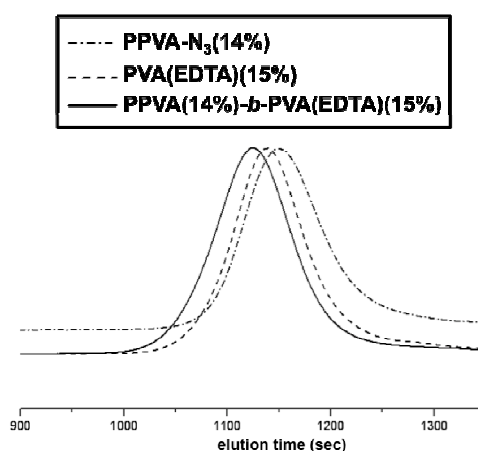


Fig. 4. Size exclusion chromatograms of PPVA-N₃(14%), PVA(EDTA)(15%), and the resulting PPVA(14%)-*b*-PVA(EDTA)(15%) after the coupling reaction. (baseline was not normalized to ensure a better reading of the figure).

The efficiency of the Huisgen reaction between PPVA-N₃ and PVA(EDTA)-alkyne was investigated using 2D diffusion ordered (DOSY) NMR in deuterated DMSO. ¹H NMR spectrum (Fig. 5 (top)) showed signals corresponding to both homopolymers, especially at 3.2-4.0 ppm, and 4.3-5.2 ppm/7.1-7.25 ppm, which corresponded to protons attributed to EDTA and phosphoric acid based blocks, respectively. Additionally, results obtained on PPVA(14%)-*b*-PVA(EDTA)(15%) (Fig. 5 (bottom)) evidenced that the ¹H NMR signals of PPVA and PVA(EDTA) moieties had the same diffusion coefficient (-10.5 m² s⁻¹). This was consistent with an efficient coupling of PPVA-N₃ and PVA(EDTA)-alkyne. As expected [54], diffusion coefficients of the homopolymers were lower: -10.2 m² s⁻¹ and -10.4 m² s⁻¹ for PPVA-N₃ and PVA(EDTA)-alkyne, respectively. Spectrum of the copolymer showed that there was no residual free homopolymers. The two other copolymers showed similar results with a diffusion coefficient lower than their respective homopolymers (Table 3).

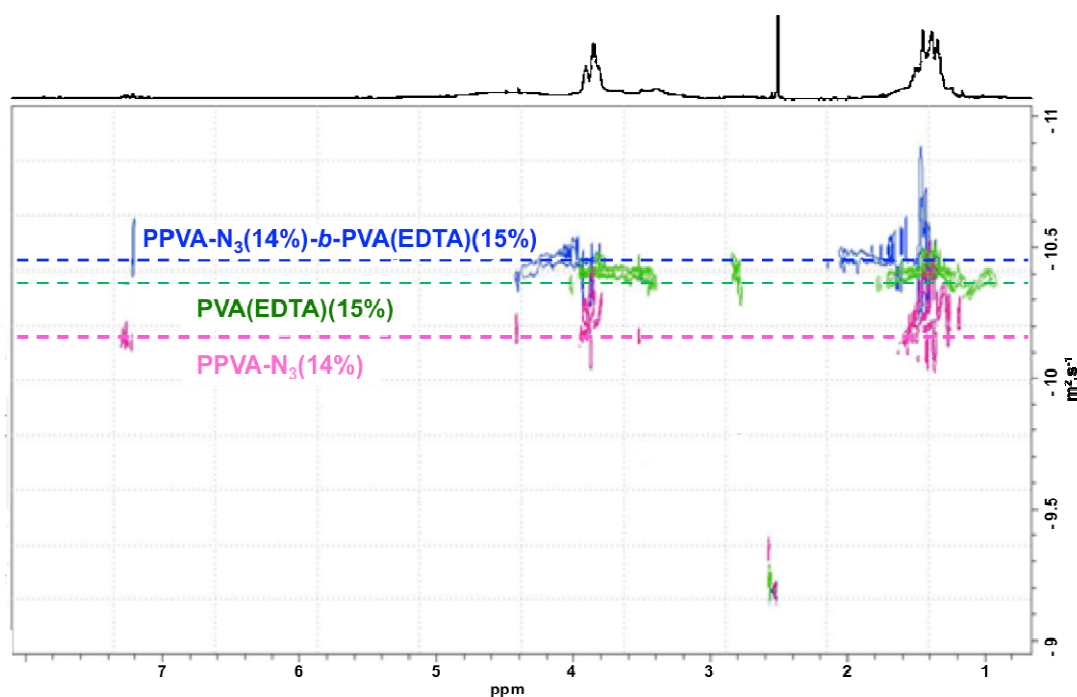


Fig. 5. (top): ¹H NMR spectrum of PPVA(14%)-*b*-PVA(EDTA)(15%) in DMSO-*d*₆ ; (bottom): Diffusion Ordered NMR spectroscopy (DOSY) of the PPVA(14%)-*b*-PVA(EDTA)(15%), PVA(EDTA)(15%), and PPVA-N₃(14%) in DMSO-*d*₆.

To conclude, SEC and DOSY NMR analyses proved the efficient synthesis of different pure block copolymers. Such PPVA-*b*-PVA(EDTA) structures were then used to be grafted onto alumina particles to obtain hybrid materials.

Table 3

Diffusion coefficients of the different homo- and copolymers synthesized.

Homopolymer	Diffusion coefficient (m ² s ⁻¹)	Copolymer	Diffusion coefficient (m ² s ⁻¹)
PPVA-N ₃ (5%)	- 10.1	PPVA(14%)-PVA(EDTA)(6%)	- 10.4
PPVA-N ₃ (7.5%)	- 10.1	PPVA(7.5%)-PVA(EDTA)(6%)	- 10.3
PPVA-N ₃ (14%)	- 10.2	PPVA(5%)-PVA(EDTA)(6%)	- 10.3
PVA(EDTA)(6%)	- 10.3	PPVA(7.5%)-PVA(EDTA)(15%)	- 10.5
PVA(EDTA)(15%)	- 10.4	PPVA(14%)-PVA(EDTA)(15%)	- 10.5

3.3. Grafting of PPVA-*b*-PVA(EDTA) copolymers onto alumina particles

For this purpose, a suspension of alumina was directly mixed with a solution of appropriate copolymer in aqueous media. Alumina support used for the grafting process was spherical non-porous particles (particle size from 100 nm to 20 μm), with a low specific surface (6 m²/g). This means that few active sites were available for the grafting reaction, probably leading to low loading density. On the other hand, the absence of porosity was preferred to favor the accessibility for the polymers to be grafted, whereas smaller alumina particles were not investigated to ensure proper separation of particle for future applied processes. The crude material was washed to remove the copolymer in solution. Carbon organic total (COT) analyses were carried out on the supernatants and confirmed the loss of free copolymers in solution after the complete washing procedure. Several characterization methods were carried out to check the success of the grafting process of PPVA-*b*-PVA(EDTA) copolymers onto alumina including X-ray photoelectron spectroscopy (XPS), diffuse reflectance infrared Fourier transform (DRIFT) and thermogravimetric analysis (TGA). XPS analyses performed on PPVA(7.5%)-*b*-PVA(EDTA)(15%) grafted onto alumina particles (Fig. 6) showed signals attributed to phosphorus and nitrogen attesting the presence of PPVA and of PVA(EDTA), respectively.

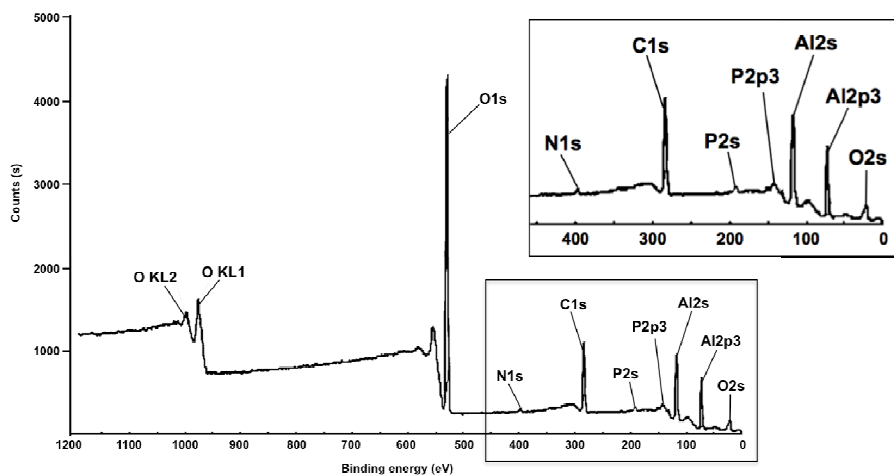


Fig. 6. X-ray photoelectron spectroscopy spectrum of PPVA(7.5%)-*b*-PVA(EDTA)(15%) hybrid material.

DRIFT measurements have been performed (Fig. 7) to detect organic species on alumina, comparing spectra of pure alumina particles, PPVA(7.5%)-*b*-PVA(EDTA)(15%) copolymer, and the resulting hybrid material. Only the aluminol band was observed at 3100-3500 cm^{-1} on alumina spectrum. The PPVA(7.5%)-*b*-PVA(EDTA)(15%) spectrum exhibited C=O bond at 1730 cm^{-1} , C-H at 2800 cm^{-1} , P=O at 1300 cm^{-1} , P-O at 1100 cm^{-1} and O-H at 3000-3400 cm^{-1} . Finally, the presence of both organic and inorganic moieties was detected on the hybrid material spectrum, despite the weak signal intensity. Band corresponding to the aluminol groups and several bands attributed to organic layer including C-H (2800 cm^{-1}), C=O (1730 cm^{-1}) and P=O (1300 cm^{-1}) were observed, demonstrating the successful grafting of the PPVA-*b*-PVA(EDTA) copolymers onto alumina particles. It is important to notice that same experiment with PVA(EDTA) was carried out and demonstrated that the grafting process was only due to the phosphoric acid group since DRIFT spectrum of $\alpha\text{-Al}_2\text{O}_3$ was recovered in this particular case.

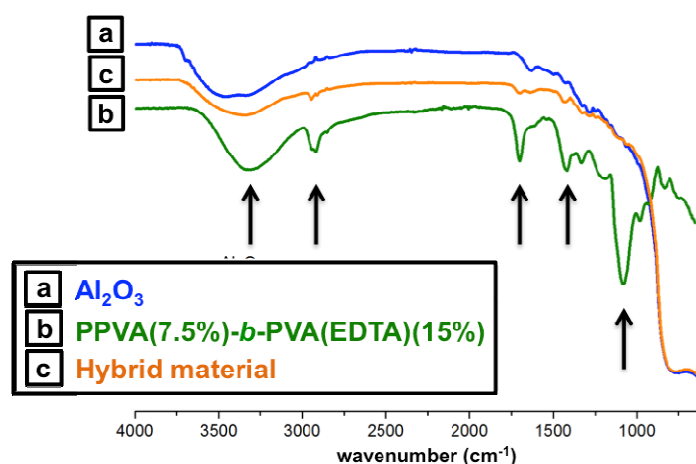


Fig. 7. DRIFT spectra of α - Al_2O_3 (a), PVA(7.5%)-*b*-PVA(EDTA)(15%) (b), and Al_2O_3 -PPVA(7.5%)-*b*-PVA(EDTA)(15%) hybrid material (c).

TGA analyses have also been performed for PPVA-*b*-PVA(EDTA)(15%) copolymers with various phosphorus quantities, *i.e.* 5%, 7.5% and 14%. It is important to notice that hybrid materials were first prepared at 20 °C from pure copolymers. Then, resulting materials were washed with water, and freeze-drying was finally carried out to ensure that all solvents were completely removed. As a consequence, TGA mass losses could be only conclusively assigned to polymer mass loss. Obtained results showed low mass losses those were consistent with the low specific surface of the α - Al_2O_3 . The results indicated mass losses of 1, 1.25 and 1.4% for PPVA(14%)-*b*-PVA(EDTA)(15%), PPVA(5%)-*b*-PVA(EDTA)(15%), and PPVA(7.5%)-*b*-PVA(EDTA)(15%), respectively (Table 4). The highest grafting rate was obtained for the intermediate phosphorus content (7.5%), which was the optimal phosphorus rate. Polymers with less phosphorus occupied less binding sites. For a given surface, alumina was thus covered with more polymer chains. Consequently, a lower mass loss was obtained when passing from 7.5% to 14%, as shown for PPVA(14%)-*b*-PVA(EDTA)(15%) copolymers compared to PPVA(7.5%)-*b*-PVA(EDTA)(15%). In contrast, PPVA(5%)-*b*-PVA(EDTA)(15%) copolymers contained less phosphorus compared to PPVA(7.5%)-*b*-PVA(EDTA)(15%). For the 7.5% ratio, better grafting properties were obtained compared to PPVA(5%)-*b*-PVA(EDTA)(15%). This was due to a better water solubility of PPVA(7.5%)-*b*-PVA(EDTA)(15%) allowing better functionalization. The 7.5% phosphorus content was the best compromise between

the minimal quantity of phosphorus needed for the grafting and too high phosphorus content leading to a sterically hindered material.

Hybrid materials were also prepared at 90 °C to study the influence of the temperature onto the grafting properties. The weight losses of resulting materials prepared with the copolymers containing various phosphorus contents (Table 4) demonstrated that the increase of the temperature slightly improved the grafting process. Indeed, a raise of the temperature led to an increase of the polymer chain mobility allowing a better accessibility to active sites of alumina. Same trend was obtained as at 20 °C as the results evidenced that the highest degree of functionalization was obtained with a phosphorus content of 7.5%.

Table 4

Weight losses determined from TGA experimental data measured on alumina grafted with various PPVA-*b*-PVA(EDTA) copolymers and prepared at various temperatures.

Polymer	Reaction temp. (°C)	Weight losses (%)
PPVA(14%)-PVA(EDTA)(15%)	20	1
PPVA(7.5%)-PVA(EDTA)(15%)	20	1.4
PPVA(5%)-PVA(EDTA)(15%)	20	1.25
PPVA(14%)-PVA(EDTA)(15%)	90	1.7
PPVA(7.5%)-PVA(EDTA)(15%)	90	2.4
PPVA(5%)-PVA(EDTA)(15%)	90	2.1

Scanning electron microscopy experiments were also performed and confirmed the relatively low grafting rate as no significant difference was observed between alumina and alumina grafted with diblock copolymers. As a result, complexation study was achieved using hybrid material exhibiting highest degree of functionalization, which appeared as the most promising material.

3.4. Study of Co(II), Ni(II), and Sr(II) complexation by PVA- based hybrid materials

The obtained hybrid materials were evaluated for the complexation of metallic cations. We focused on PPVA(7.5%)-*b*-PVA(EDTA)(15%) prepared at 90 °C as it combined an optimized phosphorus content and the highest number of EDTA complexing groups. The advantage of these new materials for heavy metal removal

was evaluated using three different cations: cobalt (II), nickel (II), or strontium (II). The latter were chosen as it was known, in the literature, that EDTA chelating groups efficiently complex these potentially radioactive metal ions [59]. The ion solutions were mixed with the Al_2O_3 -PPVA(7.5%)-*b*-PVA(EDTA)(15%) hybrid material. In order to explore the use of such materials in waste treatment process employed in nuclear industry, their sorption properties were evaluated in single-component solutions of cobalt, nickel and strontium usually present in contaminated effluents. The sorption isotherms of Co(II) and Ni(II) are displayed on Fig. 8, and compared with the sorption efficiency of commercial Amberlite resin (IRN77) commonly used in nuclear water treatment unit.

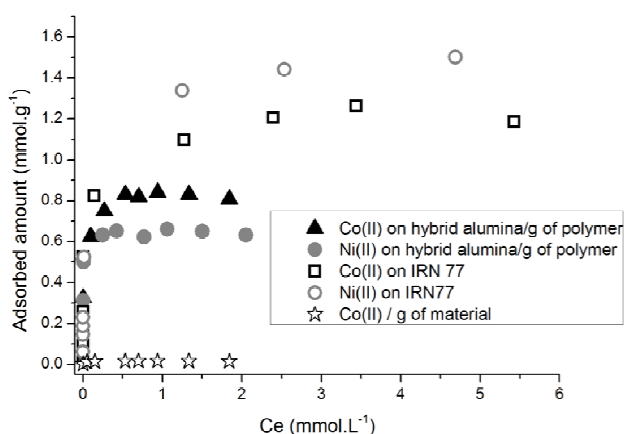


Fig. 8. Adsorption isotherm of Co(II) (squares), and Ni(II) (circles) from single-component onto PPVA(7.5%)-*b*-PVA(EDTA)(15%) hybrid materials at 25 °C. C_e is the metal concentration in the equilibrium bulk phase after attaining sorption equilibrium; Q is the adsorbed amount (adsorbate per unit mass of polymer or mass of adsorbent).

For hybrid material, results of sorption are firstly expressed in adsorbate per unit mass of polymer, and then for Co(II), expressed in adsorbate per unit mass of adsorbent. For our material, the initial portion of the curve exhibited a sharp increase even for low equilibrium concentrations that indicated very strong affinity of both cations towards hybrid material. This affinity is similar for the IRN 77 resin. The second part at higher concentrations corresponded to a plateau region showing the saturation of the adsorbing sites. The summary of the sorption capacity is reported in Table 5. The maximum sorption quantity is 0.80 mmol.g^{-1} for cobalt and 0.65 mmol.g^{-1} for Ni(II).

Table 5 Sorption properties of hybrid Al₂O₃-PPVA(7.5%)-PVA(EDTA)(15%) material toward divalent metallic cations.

Metallic cation	Q _{max} ^a	Eq. Metal/EDTA ^a
Co(II)	0.80	0.5
Ni(II)	0.65	0.4
Sr(II)	0.09	0.05

^a Evaluated from the plateau on the isotherm

From the maximum of sorption and the amount of EDTA, the number of metal sorbed per EDTA has been calculated (Table 5). For cobalt, it corresponded to 0.5 equivalent of Co(II) fixed for one equivalent of EDTA. This indicated that two EDTA groups were needed to sorb one Co(II). This means that half of the incorporated EDTA are available for sorption. This value is lower than the expected interaction between EDTA and such metallic cations. This could be due to the lowered diffusion of ions within the layer of PPVA-*b*- PVA(EDTA) grafted onto silica, and / or to the distribution of EDTA on the copolymer, that could decrease their accessibility. Quite similar results were obtained for Ni(II) with a ratio of 0.4 Ni(II) / EDTA. Nevertheless, the efficiency for Ni(II) removal seems slightly lower, which can not be explained at the moment. On the contrary, the uptake of Sr(II) ions was negligible with a maximum sorption quantity below 0.1 mmol.g⁻¹ (isotherm not shown). This is explained by the lower complexation constant of Sr(II) with EDTA. This behavior demonstrated the selectivity of the hybrid material towards specific ions with high adsorption capacity for Co(II) and Ni(II). It has to be mentioned that materials prepared with only PPVA were also tested, but no sorption were observed. This confirmed that the complexation was only due to EDTA groups of PVA(EDTA) block of the hybrid materials. Nevertheless, the calculation of the sorption capacity taking into account the total mass of the materials resulted in removal efficiency equal to 0.017 mmol.g⁻¹. When compared with the performance of ion exchange resins, PPVA(7.5%)-*b*-PVA(EDTA)(14%) unfortunately showed a smaller retention than the one determined for IRN 77 with a maximum sorption capacity between 1.2 and 1.4 mmol.g⁻¹ for Co(II) and Ni(II), respectively. This was due to the low specific surface area of alumina, leading to a small amount of EDTA available for complexation. This also means that the performances of the present hybrid materials cannot compete with those of resins.

Preliminary sorption results showed that the Al_2O_3 -PPVA(7.5%)-*b*-PVA(EDTA)(14%) hybrid materials were able to complex Co(II) and Ni(II) in a sufficient manner. On the contrary, sorption of Sr(II) was low. Even if these hybrid materials were less efficient than classical ion exchange resins in terms of sorption capacity, their selectivity based on specific cation complexation is of high interest whenever used in very dilute multicomponent solutions. This provides an interesting opportunity to develop Al_2O_3 -PPVA-*b*-PVA(EDTA) hybrid materials.

4. Conclusions

The objective of the present contribution was to develop of innovative hybrid materials resulting from grafting of functionalized PVA-based diblock copolymers onto alumina particles for the removal of divalent cations in wastewater effluents. To achieve that goal, PVA homopolymers were modified by either phosphoric acid groups or EDTA to afford PPVA-N₃ and PVA(EDTA)-alkyne, respectively. The obtained structures were characterized by ¹H and ³¹P NMR, and elementary analysis, which notably allowed evidencing that the degree of functionalization was temperature-dependent. Then, PPVA-N₃ and PVA(EDTA)-alkyne moieties were successfully coupled using Huisgen reaction catalyzed with copper. The produced copolymers were grafted onto alumina in aqueous media using different experimental conditions, especially different temperatures. Hybrid materials were fully characterized by X-ray photoelectron spectroscopy, solid-state ³¹P NMR, diffuse reflectance infrared Fourier transform and thermogravimetric analysis. Obtained results permitted to show that the grafting was effective. Finally, preliminary sorption tests confirmed that PVA-based hybrid materials exhibited high capacity combined with strong affinity towards Co(II) or Ni(II) cations. Low sorption of Sr(II) was in accordance with a possible selectivity of the PVA-base hybrid materials. Concerning further separation step, it is reasonable to assume that good cation complexation will destabilize particles which will stick together to form flocs, thus favoring the separation step by filtration.

Conflicts of interest

There are no conflicts to declare.

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GRAPHICAL ABSTRACT

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