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**Abstract**

Ion separation processes using polymer-enhanced ultrafiltration (PEUF) have many advantages because they are solvent free and low energy consuming. In order to design a new free solvent process for separation of natural actinides and rare earth elements from ores, the selective sorption properties of two valuable carbamoylmethylphosphonated-based polymers regarding to Th/U/Gd mixtures were studied. This work highlighted the different selectivities between the carbamoylmethylphosphonate and carbamoylmethylphosphonic diacid functions. It showed the great interest of this kind of macromolecules for the design

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of a new process with lower environmental impact for hydrometallurgical treatments of rare earth ores.

*Keywords:* Natural actinides, Rare earth elements, Thermosensitive and flocculant polymers, Selective sorption, Th,U/Ln separation, Carbamoylmethylphosphonated polymers

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**Introduction**

Rare earth elements (REE) were discovered during the 18$^{th}$ and 19$^{th}$ centuries.[1, 2] They include the 14 lanthanides (Ln), scandium (Sc) and yttrium (Y).[3] Since the sixties and with technological advances, use of REE was gradually expanded.[4] REE have become much more important for industrials using high technology owing to their unique magnetic, phosphorescent, and catalytic properties.[5] These elements are critical for technologies involving magnets, catalytic converters, batteries, optical lenses and electronic compounds.

Rare earths are not really rare. This name was given on the basis of some assumptions made at the time of their discovery in the 18$^{th}$ century.[2] Since a long time, it has been demonstrated that REE are really quite widely distributed in minerals. REE can be found with large amounts in various minerals such as monazite and xenotime (phosphates), samarskite, euxenite and uranite (oxides), and bastnaesite (carbonate-fluorides).[6, 7, 8, 9, 10, 11, 12, 13] Although REE are mainly found in these minerals, a significant amount of natural radioelements such as thorium, uranium, and their decay products are also present in ores. These later have to be removed and recovered for their specific use in the nuclear industry or for their specific conditioning. Monazite is a phosphate based mineral containing REE as well as Th and U ($(REE,Th,U)PO_4$). Monazite is the most radioactive mineral after uraninite ($UO_2$), thorianite ($ThO_2$) and uranothorites ($(Th,U)SiO_4$) due to the large amounts of thorium and uranium (from 2% to 14% and from about 0.05% to 10% for Th and U, respectivelyy).[14, 15, 16] Thus, large amounts of thorium and uranium can be removed from monazite and may be recovered as by-products. Because thorium and uranium are of great interest for nuclear industry since they can be used as nuclear fuel, recovery processes of such by-products from REE industry were also considered.[17, 18]

Currently, after mechanical grinding then pretreatments steps, the cations present in the acidic liquor (REE(III), Th(IV), U(VI) and impurities) are separated by ion separation process such as chemical precipitation, solvent extraction, or solid phase extraction.[19] Although it was the most economical and the simplest way to implement, precipitation process was not the most efficient. Indeed, the drawback of this process is mainly due to co-precipitation phenomena (partial precipitation of untargeted cations), which made this process less selective and could induce the use of expensive successive steps to reach satisfying final purity.

Solvent extraction (SX) is currently the main method to separate REE, and allowed reaching high degree of purity of each element.[20, 17] SX consists in separating metal ions contained in the aqueous phase (liquor) by the use of an organic phase. Organic phase is a mixture of a diluent and extractant molecules with selective ligands such as carboxylic acids, amines, amides, organophosphorus, amidophosphonated or calixarenes.[21, 16, 22, 23, 24, 25, 26, 27, 28] However, even if it was proven its efficiency for many years, solvent extraction requires a large amount of aliphatic solvents such as dodecane, hydrogenated tetrapropene (THP) or kerosene. These solvents showed several risks as they are flammable and harmful for health and environment.[29, 30, 31] To avoid the use of aliphatic solvent, some processes using supercritical $CO_2$ as diluent were recently developed.[32]

Another alternative to avoid solvent was the use of sorbent materials as resins, inorganic materials and hybrid materials in solid phase extraction processes (SPE).[33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46] Organic or hybrid (inorganic-organic) materials are generally functionalized with ion exchange or solvating sites with selective complexing groups. Unfortunately, in the case of solid sorbents, the accessible complexing sites are located on porous surface only,[47] the total accessible porous volume being dependent on cation diffusion in the porosity. As a result, sorption capacity are in general low whereas sorption kinetic is slow.

Since the last decade, low energy consuming processes have emerged such as polymer enhanced ultrafiltration or polymer assisted ultrafiltration (PEUF/PAUF) associating a sorption step on a hydrosoluble polymer with a separation step by

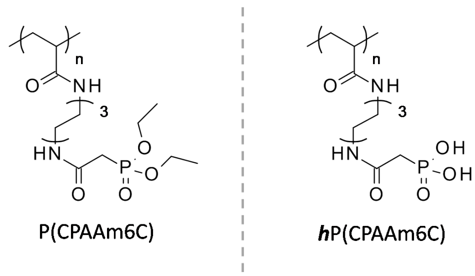


Figure 1: Chemical structures of the poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate) (P(CPAAm6C))[51] and the poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonicdiacid) (***h***P(CPAAm6C))[53]

filtration.[48, 49, 50] The use of hydrosoluble sorbent allows making accessible all complexing sites. In recent years, Graillot *et al.* developed thermosensitive polymer enhanced filtration (TEF) process for wastewaters treatment.[48] TEF enables an easier filtration step through thermosensitive polymers. In order to design new process of lanthanides recovery from electronic waste, two hydrosoluble phosphonated based polymers were developed for PEUF like process: the poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate) (P(CPAAm6C)) and the poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonic diacid) (***h***P(CPAAm6C) (Fig. 1).[51, 52, 53, 54] Several works demonstrated that phosphonate and carbamoylphosphonated ligands had selective properties for actinides +IV and +VI respectively.[55, 56, 57, 26, 58]

This paper deals with the phase separation of P(CPAAm6C) and ***h***P(CPAAm6C) in acidic media and their selective sorption properties regarding to Gd(III)/Th(IV)/U(VI) solutions. In order to reduce the environmental impact of separation process, polymer enhanced filtration process is planned for thorium and uranium separation from REE.

## 1. Material and methods

### *1.1. Chemicals*

#### *1.1.1. Hydrosoluble polymeric sorbent*

Poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate) (P(CPAAm6C)) was synthesized according to the procedure detailed in a previous paper, [51] whereas poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonic diacid (***h***P(CPAAm6C)) was obtained from P(CPAAm6C) hydrolysis as already described.[52] In supplementary materials are presented the structural characterization of P(CPAAm6C) and ***h***P(CPAAm6C).

### *1.1.2. Gd(III)/Th(IV)/U(VI) synthetic solutions*

**Caution!** Thorium and uranium are $\alpha$-emitting radioelements; precautions should be followed for handling these nuclear matters.

Crystallized gadolinium(III) nitrate hexahydrate ($Gd(NO_3)_3 \cdot 6H_2O$, Aldrich, metal basis trace, 99.99%), thorium nitrate ($Th(NO_3)_4$) and uranyl nitrate ($UO_2(NO_3)_2$) commercial standard solutions (10000 mg·L$^{-1}$ in 4% $HNO_3$) were used for the preparation of synthetic solutions.

In order to model mineral leachates, synthetic mixtures containing 0.82 mol% Gd, 0.10 mol% Th and 0.04 mol% U solution were used.[59, 6, 7] Gadolinium was chosen as representative of all lanthanide elements. Solutions were prepared in mQ water (resistivity $\leq$ 18.2 MΩ·cm) and pH was adjusted to 1 by slow drop addition of concentrated $HNO_3$ (68.0 - 70.0 %, Alfa Aesar).

### *1.2. Cloud point (CP) measurements*

Thermosensitivity of the polymers was determined from the change in the transmittance value through the polymer solution with temperature. The measurement of the transmittance was carried out using a 5 g·L$^{-1}$ polymer solution with a Perkin Elmer Lambda 35 UV-Visible spectrometer equipped with a Peltier temperature programmer PTP-1+1. A wavelength of $\lambda$ = 500 nm was selected for the analysis. The temperature ramp was fixed at 0.1 °C·min$^{-1}$ between 20 °C and 50 °C. The thermosensitivity was characterized by a sudden slope change in the transmittance curve. The cloud point (CP) values of the polymer thus corresponded to the minimum of the derivative curves.

### *1.3. Dynamic light scattering (DLS)*

Dynamic light scattering (DLS) measurements were recorded on a Malvern Zetasizer Nano Series equipped with a He-Ne laser ($\lambda$ = 632.8 nm). Samples were introduced into the cells (pathway: 10 mm) after filtration through 0.45 $\mu$m PTFE microfilters to determine the hydrodynamic radius of polymer objects in aqueous solutions. The correlation function was analyzed via the general purpose method (NNLS) to obtain the distribution of diffusion coefficients ($D$) of the solutes. For the dynamic study, the Stokes-Einstein equation allowed obtaining the apparent equivalent hydrodynamic radius ($R_H$) from the Contin's method as described in Eq. 1:

$$R_H = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot D} \tag{1}$$

where $T$ is the sample temperature sample (K), $k_b$ is the Boltzmann constant ($1.38 \cdot 10^{-23}$ $m^2 \cdot kg \cdot s^{-2} \cdot K^{-1}$), $\eta$ is the viscosity of the fluid ($kg \cdot m^{-1} \cdot s^{-1}$) and $D$ is the translational diffusion coefficient at infinite dilution ($m^2 \cdot s^{-1}$).

### *1.4. Sorption experiments*

Sorption experiments were carried out using a dialysis tubular membrane as described in previous papers.[52, 53] A 2 kDa membrane cut-off was chosen to keep the polymer solution in the membrane tube, which was dipped in cation solutions (see Supplementary Material). The solution was stirred during the sorption experiment using magnetic stirring at room temperature (approx. 20°C).

The concentrations of cations were checked before and after experiment in the bulk solution. When thermodynamic equilibrium was reached, the concentration of free ions in dialysis were considered to equal the concentration in the bulk, *i.e.* $C_{e,bulk} = C_{e,dial} = C_e$. The initial concentration of cation $C_0$ (mmol·L$^{-1}$) was considered in the total volume of experiment and was calculated from Eq. 2:

$$C_0 = \frac{C_{bulk} \times V_{bulk}}{V_{bulk} + V_{dial}} \tag{2}$$

where $C_{bulk}$ (mmol·L$^{-1}$) and $V_{bulk}$ (L) are the concentration and volume of the bulk solution (out of dialysis), respectively. $V_{dial}$ (L) is the volume of solution contained in dialysis membrane.

After 24 h of stirring (optimized from kinetic experiments), the elemental concentrations in solution at equilibrium, $C_e$ (mmol·L$^1$) were measured and the sorption capacity at equilibrium, $Q_e$ (mmol·L$^1$) was determined from the mass balance (Eq. 3).

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (3)$$

where $C_0$ (mmol·$L^1$) is the initial concentration of the metal, m (g) is the mass of polymer and V (L) is the total volume of solution.

Elemental concentrations were determined in solution by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) with a Spectro Arcos ICP spectrometer. The spectrometer was calibrated with 0; 0.5; 1; 5; 10 and 15 mg·$L^{-1}$ standard solutions (prepared by dilution of 1000 commercial standards of Gd, Th and U). All samples were diluted in 4% $HNO_3$ to be within this reference range.

## 2. Results and discussions

### *2.1. Phase separation properties of polymers*

Previous work showed that the P(CPAAm6C) exhibited thermosensitive behavior which resulted in a difference of solubility with the temperature as

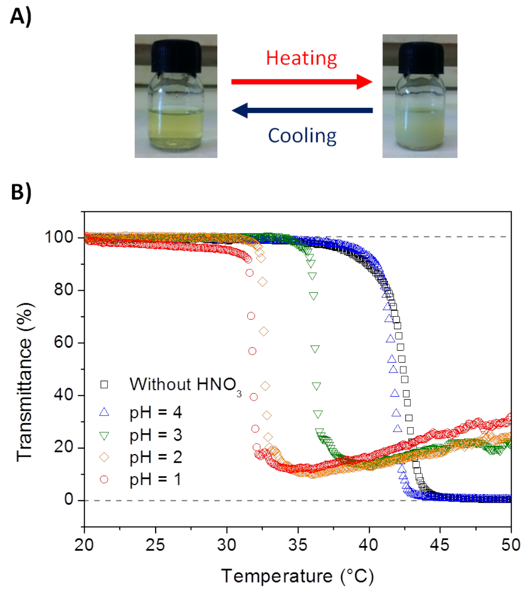


Figure 2: Thermosensitive behavior of P(CPAAm6C) in solution **(A)** photo obtained below (left) and above (right) the cloud point (CP). **(B)** Variation of the transmittance *vs.* the temperature for several pH values.

shown in Fig. 2A.[51] This property was due to the temperature dependency of polymer-water and polymer-polymer interactions. Below the cloud point, polymer-water interactions were favored and the P(CPAAm6C) was soluble in aqueous solution. For temperatures higher than the cloud point, polymer-polymer interactions became more stable than the polymer-water interactions, leading to a phase separation of P(CPAAm6C). The variation of the transmittance *vs.* the temperature $\theta$ was plotted in Fig. 2B for solutions containing P(CPAAm6C) without acid and for several pH values (4, 3, 2 and 1) adjusted by addition of $HNO_3$. P(CPAAm6C) in water exhibited a CP value of 42 °C but a decrease of pH by an addition of $HNO_3$ led to a sharp decline of the CP down to 32 °C at pH = 1. Also, others important differences were observed. In the case of polymer solution without acid and at pH = 4, the transmittance decreased to reach 0 and remained null until temperature reached 50 °C. However, for pH values equal to 3, 2 and 1, the transmittance did not reach 0% but increased again after being at 15%. This was due to the strong sedimentation, which occurred during the measurement when temperature was higher than the CP. It was confirmed by the simple visual observation of spectrophotometric cuvettes for pH = 1, 2 and 3. In order to understand the different behaviors, DLS measurements were performed at CP + 10 °C (Fig. 3).

For $\theta <$ CP, the polymer was soluble and hydrodynamic radius $R_H$ were below 30 nm (see Supplementary Material). After heating, the phase separation led to an increase of particle size when temperature was above the CP. The $R_H$ of P(CPAAm6C) without nitric acid addition at $\theta =$ CP + 10°C was about 171 nm while at pH = 1, the $R_H$ value was more than 11 times higher (about 1940

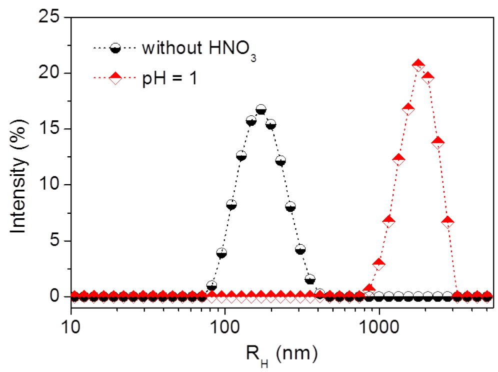


Figure 3: Dynamic light scattering measurements at $\theta$ = CP + 10 °C for P(CPAAm6C) 5 g·L$^{-1}$ without nitric acid ($\theta$ = 52 °C) and at pH = 1 ($\theta$ = 42 °C).

nm). These results explained the stability of polymer particles above the CP value. Indeed, the sedimentation velocity varied as a function of the size and thus, the smaller the particles, the lower the sedimentation velocity was.[60]

In contrast, ***h***P(CPAAm6C) did not exhibit thermosensitive properties due to hydrophilic phosphonic diacid moiety borne by each subunit. However, it showed flocculation properties when it complexed lanthanides.[53] This property was also of interest to develop an easy separation step.

*2.2. Selective sorption in Gd/Th/U mixed solutions*

*2.2.1. Sorption with P(CPAAm6C)*

Previous works demonstrated the P(CPAAm6C) selectively with the preferred complexation of Gd(III) ions in the presence of Ni(II) in nitric conditions.[52] Infrared spectroscopy confirmed that the sorption occured by solvation mechanism from the P=O and C=O oxygens of the carbamoylmethylphosphonate function (*cmp*). In order to study the selective sorption behavior of the P(CPAAm6C) towards actinides and lanthanides, sorption experiments were performed in mixture containing 86 mol% of Gd(III), 10 mol% of Th(IV) and 4 mol% of U(VI). The molar ratio of each cations was chosen in accordance with an averaged stoichiometry determined in natural monazite minerals. In this work, the pH was fixed to 1 by addition of $HNO_3$ to model the solutions after the dissolution process.

The sorption capacities $Q_e(Gd)$, $Q_e(Th)$ and $Q_e(U)$ with P(CPAAm6C) chains *vs.* the global concentration of free cations $\sum C_e(cation)$ were determined

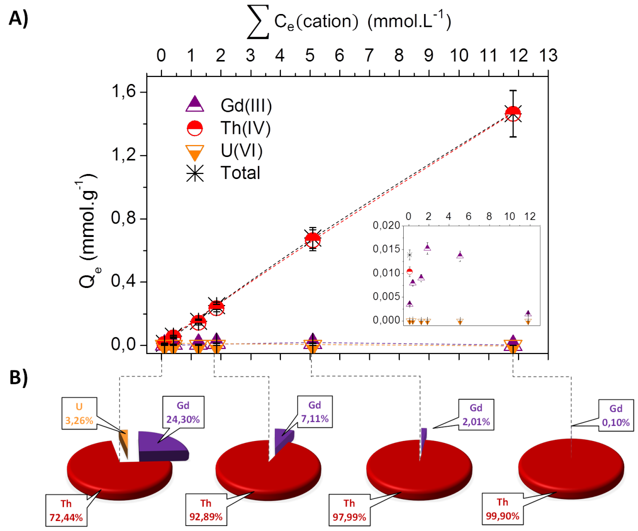


Figure 4: Selective sorption of the P(CPAAm6C) obtained for Gd/Th/U mixtures: **(A)** sorption capacity of each cation $Q_e(cation)$ in (mmol·g$^{-1}$) vs. total concentration of cations at equilibrium (mmol·L$^{-1}$) and **(B)** partition diagram of each sorbed cation on the P(CPAAm6C). **Initial operating conditions:** 50 mg of P(CPAAm6C), pH = 1, mixture containing 86 mol%, 10 mol% and 4 mol% of Gd(III), Th(IV) and U(VI), at room temperature.

at equilibrium (Fig. 4A).

Sorption results showed that $Q_e(Th)$ increased continuously from $1.04\times10^{-2}$ to 1.46 mmol·g$^{-1}$ when increasing $\sum C_e(cation)$ from $9.56\times10^{-2}$ to 11.82 mmol·L$^{-1}$. Simultaneously $Q_e(Gd)$ increased from $3.50\times10^{-3}$ to $1.53\times10^{-2}$ mmol·g$^{-1}$ when $\sum C_e(cation)$ ranged from $9.56\times10^{-2}$ to 1.76 mmol·L$^{-1}$ and then decreased until 0.10 mmol·g$^{-1}$. The $Q_e(U)$ value remained null, which demonstrated no affinity of the P(CPAAm6C) for uranium. Thus, in the range of this study, $Q_e(Th)$ was higher whatever the $\sum C_e(cation)$ values. $Q_e(Th)$ was approximately equal to $Q_e(total)$ and the maximum capacity was not reached because no plateau was observed. Hence, the maximum capacity $Q_{max}(Th)$ should be higher than 1.6 mmol·g$^{-1}$ while $Q_{max}(Gd)$ previously determined was about 0.6 mmol·g$^{-1}$.[52]

From sorption data, the distribution of each cation $\chi_{sorb}(i)$ on polymer chain was determined ($\chi_{sorb}(i) = Q_e(i)/\sum Q_e$). As shown in Fig. 4B, the distribution of thorium $\chi_{sorb}(Th)$ on the polymers chains increased from 72.5 mol% to 99.9 mol% between the lowest and highest concentrations while $\chi_{sorb}(Gd)$ and $\chi_{sorb}(U)$ both decreased to reach 0.10 and 0 mol% respectively.

Selectivities are generally characterized by a separation factor (SF) between two ions in di-component solutions. But since the initial solution contained three different cations with non-equimolar distributions, it was chosen in this work to quantify the selectivity using a selectivity index $S_i$ determined from the initial concentrations and sorption capacities of each metals and defined by the Eq. 4:

| Polymer | $\sum C_e(cation)$ (mmol·L$^{-1}$) | $S_{Gd}$ | $S_{Th}$ | $S_U$ |
|---|---|---|---|---|
| P(CPAAm6C) | 9.56×10$^{-2}$ | 0.28 | 7.2 | 0.82 |
| | 1.96 | 0.082 | 9.3 | 0.00 |
| | 5.09 | 0.023 | 9.8 | 0.00 |
| | 11.82 | 0.0012 | 10 | 0.00 |
| ***h***P(CPAAm6C) | 1.92×10$^{-2}$ | 0.90 | 0.75 | 3.8 |
| | 1.58 | 0.78 | 0.64 | 6.7 |
| | 4.46 | 0.41 | 0.59 | 14 |
| | 11.18 | 0.028 | 0.056 | 24 |

Table 1: Selectivity index $S_i$ in Gd: 86 mol%, Th: 10 mol% and U: 4 mol% at pH = 1 for various $\sum C_e(cation)$ in the case of P(CPAAm6C) and ***h***P(CPAAm6C).

$$S_i = \frac{\chi_{sorb}(i)}{\chi_{ini}(i)} = \frac{Q_e(i) \times \sum C_0}{\sum Q_e \times C_0(i)} \tag{4}$$

where $\chi_{sorb}(i)$ is the molar distribution of a cation $i$ on the polymer after sorption and $\chi_{ini}(i)$ is the initial distribution in solution. For $S_i = 1$, the distribution of sorbed cations is the same than the one of the solution which meant that there is no significant selectivity *i.e.* there is not any cation favored. On the reverse, for $S_i > 1$, the cation $i$ is selectively sorbed.

Calculated $S_i$ are listed in table 1 for $\sum C_e(cation)$ equal to 9.56×10$^{-2}$, 1.96, 5.09 and 11.8 mmol·L$^{-1}$.

The $S_{Th}$ value was higher than 1 in all range of the study and increased with $\sum C_e(cation)$. In contrast, $S_{Gd}$ and $S_U$ remained lower than 1 and tended toward 0 at higher cation concentrations. Although the Gd(III) was in a large excess (86 mol%) compared to others, the $S_{Th}$ remained the highest value even in very small amounts and clearly highlighted the high selectivity of P(CPAAm6C) for Th(IV) in these conditions.

*2.2.2. Sorption with hP(CPAAm6C)*

To compare the properties of ***h***P(CPAAm6C) and P(CPAAm6C), the same initial conditions than that used in part 2.2.1. Previous work has demonstrated that the ***h****cmp* site allowed to obtain a better $Q_{max}(Gd)$ value in Gd(III)/Ni(II) mixture and both solvation and ion-exchange mechanisms were involved.[53]

Sorption capacities $Q_e(i)$ and cation partition sorbed on ***h***P(CPAAm6C) ($\chi_{sorb}(i)$) when contacting with Gd/Th/U mixtures are represented in Fig. 5A and B, respectively.

Results showed that $Q_e(U)$ continuously increased from $2.85\times10^{-2}$ to 2.63 mmol·g$^{-1}$ when increasing the $\sum C_e(cation)$ from $1.92\times10^{-2}$ to 11.20 mmol·L$^{-1}$. However, in the same range of $\sum C_e(cation)$, $Q_e(Gd)$ increased from $1.41\times10^{-1}$

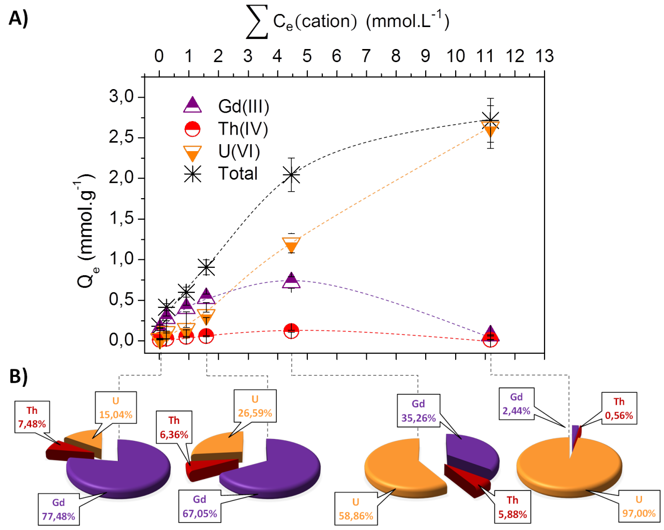


Figure 5: Selective sorption of the ***h***P(CPAAm6C) obtained for Gd/Th/U mixtures: **(A)** sorption capacity of each cation $Q_e(cation)$ in (mmol·g$^{-1}$) vs. total concentration of cations at equilibrium (mmol·L$^{-1}$) and **(B)** partition diagram of each sorbed cation on ***h***P(CPAAm6C). **Initial operating conditions:** 50 mg of P(CPAAm6C), pH = 1, mixture containing 86 mol%, 10 mol% and 4 mol% of Gd(III), Th(IV) and U(VI), at room temperature.

to $7.21\times10^{-1}$ mmol·g$^{-1}$ and then decreased to reach $6.62\times10^{-2}$ mmol·g$^{-1}$. The maximum $Q_e(Gd) = 7.21\times10^{-1}$ mmol·g$^{-1}$ was reached for $\sum C_e(cation) = 4.46$ mmol·L$^{-1}$. $Q_e(U)$ and $Q_e(Gd)$ crossed for a $\sum C_e(cation)$ between 1.58 and 4.46 mmol·L$^{-1}$. $Q_e(Th)$ weakly increased from $1.36\times10^{-2}$ to $1.20\times10^{-1}$ mmol·g$^{-1}$ and then decreased to reach $1.53\times10^{-2}$ mmol ·g$^{-1}$.

The saturation of polymer with cations was not reached because no plateau was observed in the range of the study. Hence, in view of the results, the maximum capacity $Q_{max}(U)$ should be higher than 2.5 mmol·g$^{-1}$.

In the same manner, from sorption data, the distribution of uranium $\chi_{sorb}(U)$ on the polymer chains increased from 15.0 mol% to 97.0 mol% between the lowest and highest concentrations while $\chi_{sorb}(Gd)$ and $\chi_{sorb}(Th)$ both decreased to reach 2.4 and 0.6 mol%, respectively.

The selectivity indexes for uranium $S_U$ (Table 1) was higher than 1 in all range of the study and increased from 3.8 to 24 with increasing the $\sum C_e$. In contrast, $S_{Gd}$ and $S_{Th}$ remained lower than 1 and they reached 0.03 and 0.06 at higher cation concentrations, respectively. Although the amount of U(VI) was the lowest (4 mol%) compared to Gd(III) (86 mol%) and Th(IV) (10 mol%) in the starting mixture, the $S_U$ value remained the highest obtained. It clearly evidenced the high selectivity of ***h***P(CPAAm6C) regarding to U(VI).

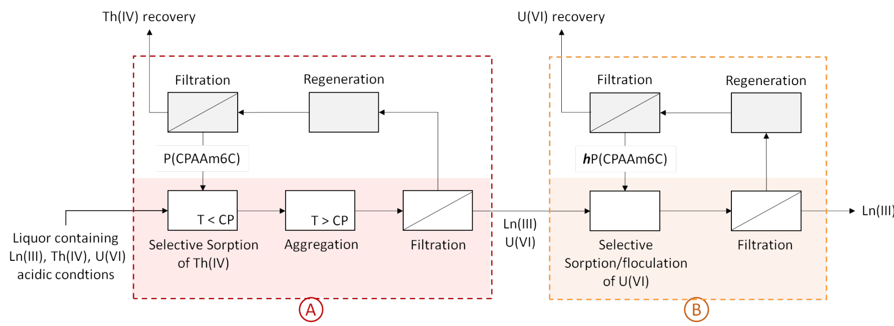


Figure 6: Schematic representation of proposed Th(IV),U(VI)/Ln(III) separation process by thermosensitive polymer enhanced filtration (TEF) and polymer enhanced filtration (PEF) applied for REE treatments.

### *2.3. Perspectives of the process coupling TEF and PEUF process units for U,Th/Ln separation*

All the results obtained in previous works and in this study concerning the phase separations and selective sorption in Gd/Th/U mixtures together allowed designing an innovative process for Th(IV),U(VI)/Ln(III) separation in REE industry (Fig. 6).

(i) *Th separation from Gd(III)/Th(IV)/U(VI) mixtures by thermosensitive polymer enhanced filtration.* The first separation unit would consist of using both selective complexation for Th(IV) and thermosensitive behavior of P(CPAAm6C). The successive sorption, aggregation and filtration steps should allow removing selectively Th(IV), and leaving uranium and gadolinium in solution. The separation by filtration will be easy thanks to the large hydrodynamic size of the particles - higher than 3800 nm in diameter - generated in acidic conditions at a temperature above the cloud point.

(ii) *U separation from Gd(III)/U(VI) mixtures by polymer enhanced filtration.*

The second separation unit would consist in using the selective complexation/precipitation of ***h***P(CPAAm6C) regarding to U(VI). Consecutive sorption/precipitation and filtration should allow eliminating the U(VI) from solution, leaving only trivalent lanthanides in solution. Precipitated particles with sizes higher than 3800 nm would be easily filtered by conventional filtration ($> 10$ $\mu$m) instead of ultrafiltration (commonly used in the PEUF process).

Regeneration-filtration steps have to be further studied in order to achieve both thorium and uranium species recovery and polymeric sorbent regeneration for reuse in additional sorption-filtration multi-cycles. Such developed process will represent an important evolution in separating processes, allowing the replacement of the solvent extraction or conventional SPE processes.

## Conclusions

In this work, two hydrosoluble polymeric sorbents bearing carbamoylmethylphosphonated moieties (P(CPAAm6C) and ***h***P(CPAAm6C) allowed suggesting a new solvent free sorption-separation process to perform the specific recovery of Th(IV) and U(VI) from REE. By this way, it allows to purify REE from radioelements

P(CPAAm6C) exhibited thermosensitive behavior: an increase of temperature above the CP led to the insolubility of P(CPAAm6C). In acidic conditions, the generated particles above the CP were characterized by sizes higher than 3800 nm, making them easy to separate from the solution. Although ***h***P(CPAAm6C) was not thermosensitive, it showed selective flocculation properties in the presence of targeted ions and could be easily filtered by conventional filtration (PEF) ($> 10$ $\mu$m) instead of ultrafiltration (commonly used in PEUF process).

Sorption results clearly confirmed that P(CPAAm6C) polymer had a stronger affinity for Th(IV) compared to Gd(III) and U(VI) while ***h***P(CPAAm6C) polymer showed stronger selectivity for U(VI). The saturation conditions of each polymer were not reached and higher concentrations of cations were not studied because of the limitations in terms of radioactivity in the laboratory. Other studies in concentrated solutions could be performed for the determination of $Q_{max}(Th)$ and $Q_{max}(U)$ in the case of P(CPAAm6C) and ***h***P(CPAAm6C), respectively.

In order to implement both process units, it will be necessary to study the regeneration-filtration steps for reuse in additional sorption-filtration multi-cycles. Resulting Th(IV),U(VI)/Ln(III) separation process would be an original and low energy consuming process allowing the removal and the specific recovery of thorium and uranium. It could be considered as a very valuable alternative of the solvent extraction process in REE industries.

## Conflicts of interest

There are no conflicts to declare.


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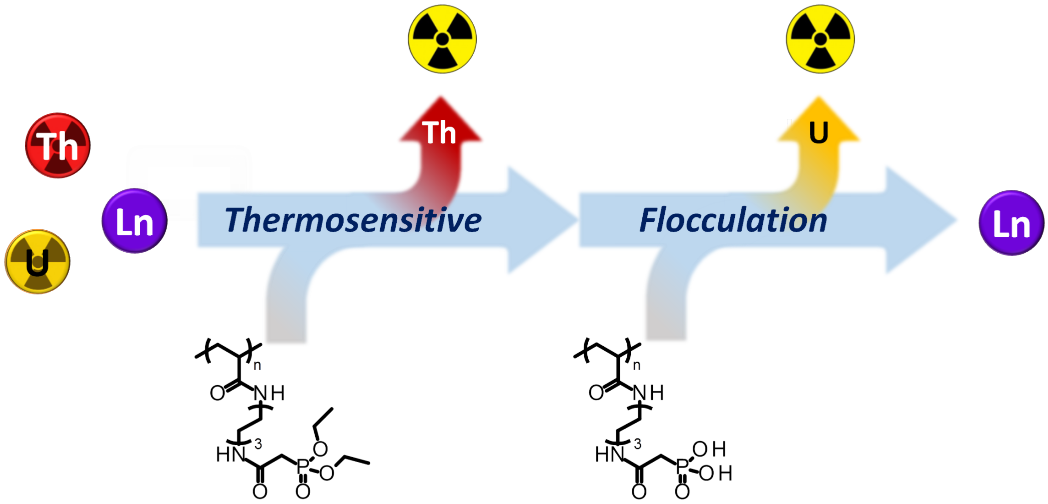
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