



## Lanthanum recovery from aqueous solutions by polyelectrolytes assisted ultrafiltration

Nourhen Ben Kraiem, Dorra Jellouli Ennigrou\*, Khira Zlaoui, Karima Horchani-Naifer

Physical Chemistry Laboratory of Mineral Materials and their Applications, National Center for Research in Materials Sciences, Technopark Borj Cedria, P.O. Box: 73-8027 Soliman, Tunisia, Tel. (+216) 79 32 52 50/(+216) 79 32 52 80; emails: [nourhenbenkraiem@gmail.com](mailto:nourhenbenkraiem@gmail.com) (N.B. Kraiem), [ennigrou2@gmail.com](mailto:ennigrou2@gmail.com) (D.J. Ennigrou), [khira.zlaoui@gmail.com](mailto:khira.zlaoui@gmail.com) (K. Zlaoui), [karima\\_horchani@yahoo.com](mailto:karima_horchani@yahoo.com) (K. Horchani-Naifer)

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### ABSTRACT

The increased use of rare earth elements in varied commercial applications has led to the release of these elements into the environment. These rare earth elements have adverse effects on aquatic and terrestrial organisms as well as on humans. The aim of this work is to evaluate the lanthanum(III) recovery by ultrafiltration assisted by complexation with poly(sodium 4-styrenesulfonate, PSS) as chelating agent. The ultrafiltration studies were carried out using a tangential cell system, equipped with a regenerated cellulose membrane with molecular weight cutoff of 10 kDa. The influence of several parameters such as transmembrane pressure, PSS concentration, and pH have been optimized to improve the retention of La(III) ions. Experimental results indicated that the La(III) retention increases with the increase of transmembrane pressure and PSS concentration. Rejection of La(III) ions using ultrafiltration membrane was widely influenced by solution pH. A pronounced increase on the removal efficiency occurs for a pH about 6. This behavior can be explained based on the sorbent surface chemistry (deprotonation with increasing pH) and aqueous phase chemistry. A better retention was observed at  $10^{-4}$  mol L<sup>-1</sup> PSS concentration and 2.5 bar transmembrane pressure. The photoluminescence measurements were performed to study the complexation behavior between lanthanum ions and three polyelectrolytes (PSS, polyvinyl alcohol, and polyethylenimine).

*Keywords:* Lanthanum(III) ions; Poly(sodium 4-styrenesulfonate); Polyelectrolyte-enhanced ultrafiltration; Recovery efficiency; Fluorescence spectroscopy

### 1. Introduction

Lanthanum has become an important contaminant in aquatic environments. Therefore, there is a growing need to develop simple methods able to separate and recover lanthanum traces from wastewaters.

Lanthanum is one of the most abundant rare earth elements (REEs), it has an important physical and chemical effects. It is widely used in the field of chemical engineering, luminescence [1,2], catalysis [3], nuclear energy, metallurgy microelectronics [4], therapeutic applications, and magnetism

[3]. The use of lanthanum in various research activities and manufacturing has contaminated the environment [4].

The high demand and poor resources base of lanthanides reinforce the development of new ways to recover these elements from wastewaters and aquatic systems [2]. The presence of lanthanides in rivers, wastewater, and effluents are typically in ultra-trace concentrations [5].

Feng et al. [1] have shown that lanthanum exposure decreases the abilities of learning and memory. It is found in other studies [2] that the long-term exposure of low dose lanthanides also would cause a significant negative impact

\* Corresponding author.

on the people's brain living in lanthanide area. The toxic effects of lanthanum upon release into aquatic environments has been previously reviewed by Balusamy et al. [3].

According to Yamaguchi [6], lanthanides can be separated by conventional solvent extraction technique. Many others such as Campbell and Buxton [7] and Kim et al. [8] use chromatography and co-precipitation to affect the removal or the separation of lanthanides. However, all these methods have some disadvantages, such as high consumption of reagent and energy, low selectivity, high operational cost, and generation of secondary metabolites [9].

In order to effectively recover the REEs ions from aqueous media, various methods including chemical precipitation [10], electrochemical treatment [11], extraction [12], and adsorption [13] have been applied. To our best knowledge, few reports have been published so far regarding the recovery of REEs using the polyelectrolyte assisted-ultrafiltration process (PAUF) technique [14–19], compared to other elements such as heavy metals and dyes [20–24].

PAUF represents a good alternative to remove REEs elements from aqueous solutions [15,25,26], due to its simplicity, low-energy requirement, and a high removal efficiency [16,27,28].

In the process, water-soluble polymeric ligands are able to bind lanthanide ions to form macromolecular complexes [29–31].

In this study, PAUF process presents the advantages of being able to separate ions or concentrate them, without affecting the other components of the solution, by bringing chemical affinity mechanisms into play. In fact, PAUF process separates larger volumes of solution than with NF, it improves liquid–liquid extraction and ion exchange, and allows the regeneration of complexing agent for reuse [32].

The aim of this work is to examine the applicability of PAUF for the removal of lanthanum from aqueous solution using the poly(sodium 4-styrenesulfonate, PSS). The complexation of La(III) ions in the presence of PSS are investigated by fluorescence studies. The effects of applied pressure, polyelectrolyte concentration, and pH on the removal of lanthanum are studied.

The influence of polymer nature on technical viability of the proposed reactive process of lanthanum recovery. Photoluminescence measurements were performed to study the fluorescent properties of the different mixture La-PE. In this way, two others types of polymers (PVA and PEI) have been tested for the study of the complexation

behavior between lanthanum ions and polyelectrolytes and is to compare its recovery performance to that obtained with PSS.

## 2. Experimental section

### 2.1. Reagents and chemical analysis

Three polyelectrolytes are used as chelating agents such as: poly(sodium 4-styrenesulfonate, PSS), polyethylenimine (PEI), and polyvinyl alcohol (PVA) with an average molecular weight, respectively, 70, 25, and 15 kDa.

The chemical structure of these polyelectrolytes is shown in Fig. 1.

Lanthanum oxide ( $\text{La}_2\text{O}_3$ , Ventron 99.99 percentage) is used to prepare the synthetic solution of La(III). Sodium hydroxide and chlorid acid are used for pH adjustments.

All the chemicals were of analytical grade and are provided by Sigma-Aldrich, (Germany).

For the solution preparation, ultrapure water is produced by Milli-Q gardient unit (Millipore).

The analysis of lanthanum ions concentrations in feed and permeate solutions are made using the inductivity couple plasma optical emission spectrometer (ICP–OES) (optima 7300 V). Each sample is analyzed three times to get an average concentration value.

Fluorescence spectra are measured with a Perkin Elmer LS-55 spectrophotometer (Germany) with a 150 W xenon lamp as excitation source and a R928 photomultiplier for detection. The sample is illuminated with the wavelength of 240 nm and the emission spectra recorded from 200 to 700 nm. The recording of the signals produced is carried out by computer using the FL Winlab software supplied with the spectrofluorometer. All the experiments were performed at ambient temperature and all spectra are corrected for the instrument responses.

The pH meter (Metrohm 654, Switzerland, certificate of calibration from the firm, and calibrated periodically by an approved center), equipped with a calibrated glass electrode and reference standards, was used for measuring pH solutions.

### 2.2. Ultrafiltration process

A tangential cell system (LabScale TFF, Millipore, USA) is used for ultrafiltration experiments. A stainless-steel

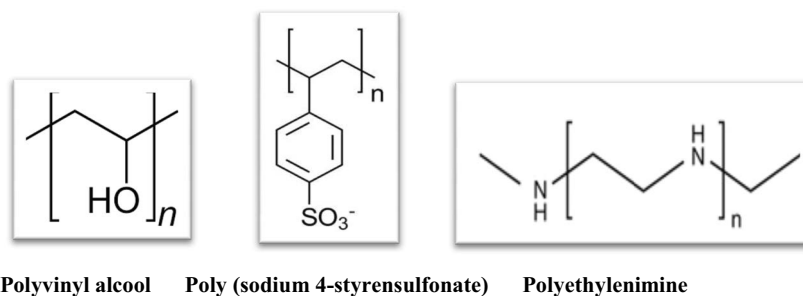


Fig. 1. Chemical structures.

cross-flow cell, with a 500 mL feed tank, is equipped with a plate cellulose membrane module; nominal molecular weight cutoff (MWCO) of 10 kDa and surface membrane area of 50 cm<sup>2</sup> (PTGC OMS 10, Millipore system, USA).

The transmembrane pressure is monitored by the pressure control valve to give a pressure in the range 1–3 bar. The feed flow rate is controlled by a speed peristaltic pump. The stirrer speed is set at 2 m s<sup>-1</sup> for good homogeneity of the solution. A cooling coil, fed with tap water, is used in the feed tank to keep the temperature of the feed solution at 25°C ± 1°C. A schematic of the experimental ultrafiltration system is shown in Fig. 2.

The membrane is rinsed with ultrapure water after each experiment and permeates flux are measured to evaluate the filtration efficiency.

Analyzed samples are taken at the inlet (feed solution) and at the outlet of the system (permeate).

The pH of solutions was adjusted by adding either 0.1 M hydrochloric acid or 0.1 M sodium hydroxide solutions.

### 2.3. Theoretical basis

Permeate flux ( $J_v$ ) was calculated using Eq. (1):

$$J_v = \frac{V_p}{S \times t} \quad (1)$$

where ( $J_v$ ) is the permeate flux (L m<sup>-2</sup> h<sup>-1</sup>),  $V_p$  is the volume of the permeate,  $S$  is the effective membrane area, and  $t$  is the time.

The pure water flux through the membrane ( $J_w$ ) is usually expressed with Darcy's law following Eq. (2):

$$J_w = L_p^0 \Delta P = \frac{\Delta P}{\eta^0 R_m} \quad (2)$$

where  $J_w$  is the pure water flux,  $L_p^0$  is the permeability of solvent. It depends of the solvent viscosity  $\eta$  and morphological characteristics of membrane (porosity, specific surface, etc),  $\Delta P$  is the transmembrane pressure, and  $R_m$  the hydraulic membrane resistance (m<sup>-1</sup>).

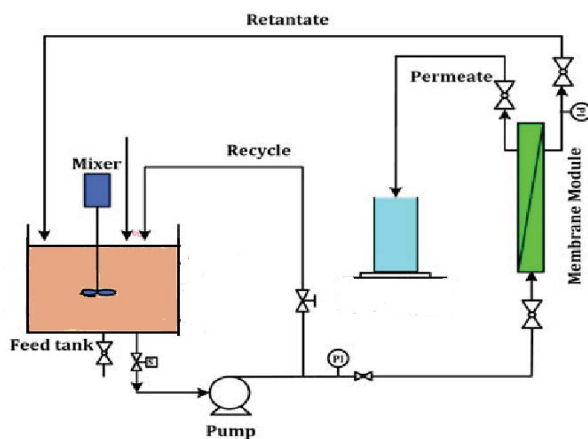


Fig. 2. Schematic diagram of the UF experimental setup.

$$J_v = \frac{\Delta P}{\eta \times R_{tot}} = L_p \Delta P \quad (3)$$

where  $R_{tot}$  is the total resistance during ultrafiltration. The calculation of  $R_m$  and  $R_{tot}$  values can be made using the above equations and flux data, Eqs. (2) and (3).

To evaluate the filtration efficiency in removing lanthanum ions from the permeate solution, the observed retention is defined in Eq. (4):

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (4)$$

where  $C_p$  and  $C_f$  are, respectively, the concentrations of the lanthanum ions in the permeate and the feed solution.

## 3. Results and discussions

### 3.1. Membrane performance

Before the experiments, permeability  $L_p^0$  solvent (ultrapure water) was measured to characterize the membrane. Flux is proportional to transmembrane pressure, as it could be defined by Eq. (2). According to Fig. 3, the  $L_p^0$  value was 33.69 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, which is in the range of ultrafiltration membranes. The resulting membrane resistance  $R_m$  has a value of 11.07 × 10<sup>12</sup> m<sup>-1</sup>.

The permeability of the lanthanum solution ( $L_p = 22.60$  Lm<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>) was obtained using Eq. (3), it implies that the presence of lanthanum ions solution does not generate significant additive resistance, generally manifested when solutes were filtered by the membrane.

Fig. 3 depicts also the variation of La(III) retention vs. transmembrane pressure at 10<sup>-3</sup> mol L<sup>-1</sup> lanthanum concentration. It shows that the retention rate of lanthanum does not exceed 18%. The Lanthanum retention in the water remained practically constant at the value of 18%. Therefore, the observed retention may be due to the electrostatic repulsion.

In fact, membranes in contact with an aqueous solution acquire an electric charge by dissociation of surface

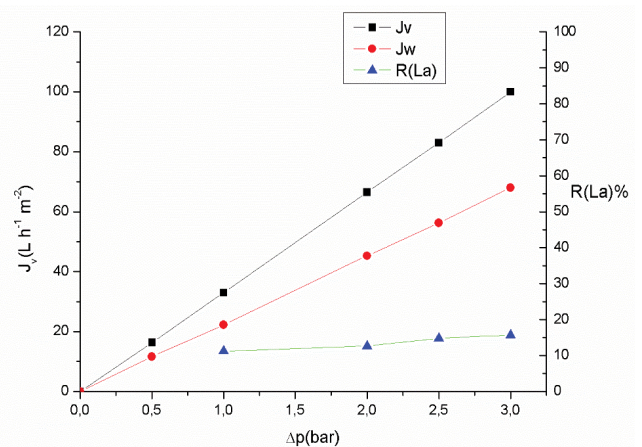


Fig. 3. Lanthanum retention and permeates flux of water, lanthanum solution as a function of transmembrane pressure, [La<sup>3+</sup>] = 10<sup>-3</sup> mol L<sup>-1</sup>.

functional groups, adsorption of ions, and ionized solutes from the solution. The electrostatic interaction can take place on the surface of the membrane or through the pore [33]. In this way, the addition of the complexing agent significantly improves the retention of lanthanides ions on the surface of the membrane.

### 3.2. Ultrafiltration of PSS solution

The variation of the permeate flux according to the transmembrane pressure at different PSS concentrations is represented in Fig. 4. The permeate flux increases when transmembrane pressure increases from 0.5 to 3 bar and decreases when the PSS concentrations increases from  $10^{-6}$  to  $10^{-4}$  mol L<sup>-1</sup>. The line segments passing through the origin has shown a minor effect of osmotic pressure and concentration polarization.  $J_v$  vs.  $\Delta P$  for different PSS concentrations studied are compared to pure water line and describes that the Darcy Law cannot be applied for permeate fluxes. In fact, the flux decline is essentially due to several factors such as concentration polarization, membrane clogging, adsorption of polyelectrolyte, and solvent viscosity [31].

### 3.3. Photoluminescence

Fluorescence spectroscopy was used to study the complexation behavior of lanthanum ions with PSS [34]. The emission spectrum of PSS solution and mixtures of PSS-La, under excitation at 240 nm is represented in Fig. 5.

The emission spectrum of the PSS solution indicates a large band at 376 nm. After adding La(III) ions to the PSS solution, the emission intensity of the polymer is weaker and shift beyond the high wavelength due to the absorbed energy by La(III) ions and the energy transfer [35].

On the other hand, the emission spectrum of the PSS-La solution before and after the ultrafiltration process shows a significant intensity decreasing and width at half height increases which indicates a new harmonic around 400 nm and confirms the good retention of La(III) ions by PEUF technique [38].

### 3.4. Effect of transmembrane pressure and PSS concentration

The experiments were carried out to study the effect of transmembrane pressure on permeate flux for different PSS concentrations. Fig. 6 shows the variation of permeate flux vs. transmembrane pressure at  $10^{-3}$  mol L<sup>-1</sup> La(III). It reports that the permeate flux increases when the transmembrane pressure increases in the range of 0.5–3 bar.

However, the permeate flux decreases with the growth of the PSS concentration from  $10^{-6}$  to  $10^{-4}$  mol L<sup>-1</sup>. The decline of permeate flux could be attributed to the concentration polarization which is the accumulation of solute particles on the membrane surface forming a growing gel layer, thereby decreasing the effective driving force [37].

The effect of PSS concentration on lanthanum retention is represented in Fig. 7. The lanthanum retention increases with increasing PSS concentrations. A better retention is obtained at  $10^{-4}$  mol L<sup>-1</sup> PSS concentration and attain 90%

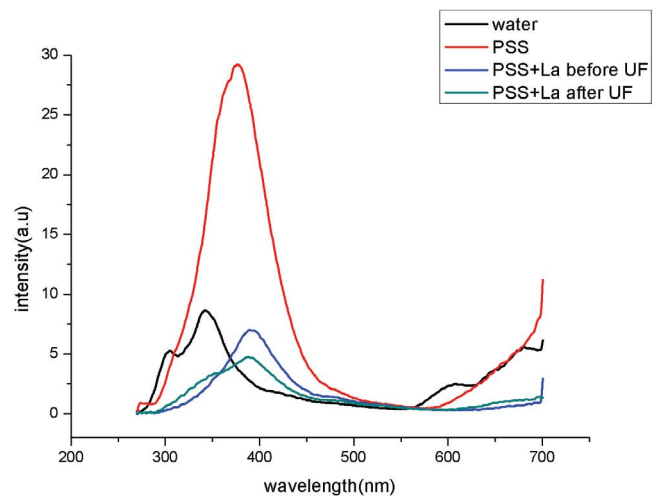


Fig. 5. Emission spectra ( $\lambda_{exc} = 240$  nm) of PSS-La before UF and PSS-La after UF,  $[La^{3+}]_{feed} = 10^{-3}$  mol L<sup>-1</sup>,  $[PSS] = 10^{-4}$  mol L<sup>-1</sup>, and pH = 5.

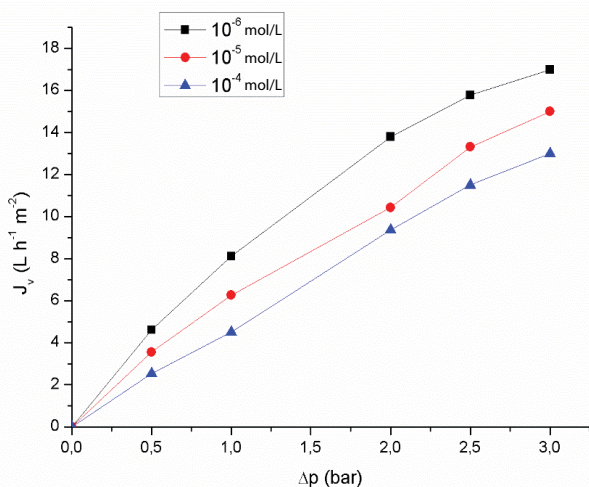


Fig. 4. Permeate flux as a function of transmembrane pressure at different PSS concentrations.

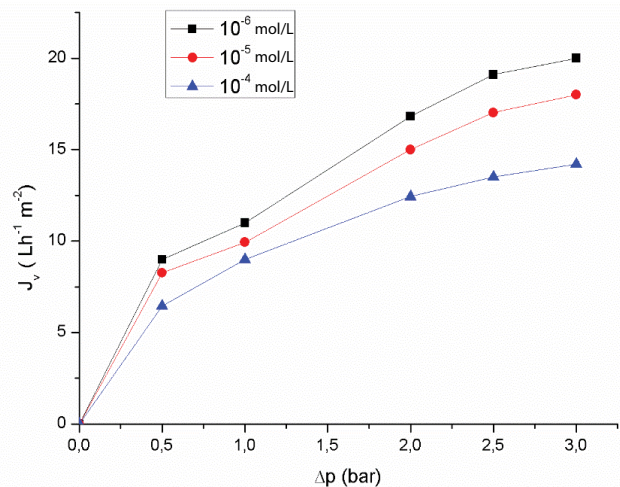


Fig. 6. Permeate flux as a function of transmembrane pressure at different PSS Concentrations,  $[La^{3+}] = 10^{-3}$  mol L<sup>-1</sup>.



rate retention at 2.5 bar. Beyond this pressure, La(III) retention decreases which explained by the occurrence of clogging phenomena and membrane fouling. The retention of La(III) increases with the increasing of the PSS concentration. The phenomenon may be explained as follows: with the improvement of the amount of PSS, the number of complex sites increases, and leading to the result that the retention of La(III) increased.

Considering from both transmembrane pressure and PSS concentration effects, the optimum values were chosen to be 2.5 bars and  $10^{-4}$  mol L<sup>-1</sup>, respectively.

### 3.5. pH effect on La(III) retention by PEUF

The pH of the feed solution is a key parameter affecting the performance of PEUF through its influence on lanthanum-polymer interactions. However, the pH may also cause precipitation of the polymer and cause aggregation phenomena. In order to determine the effect of pH on Lanthanum ion retention efficiency, the experiments were performed with fixed La and PSS concentrations respectively  $10^{-4}$  and  $10^{-3}$  mol L<sup>-1</sup> and transmembrane pressure of 2.5 bar under varied pH solutions.

Fig. 8 shows that when the pH varied from 1 to 6, the lanthanum retention increases and attain a maximum retention 90% beyond pH 6. The explanation of this behaviour is that the increase in pH leads to an increase in the dissociation of SO<sub>3</sub><sup>-</sup>Na groups in PSS, which favors the formation of La-PSS complexes.

The retention increases drastically with increasing pH, that is, from 10% to 90%. A variation in pH will often affects such aspects as conformation of the polymer and the distribution of lanthanide species in the feed [38], thereby affecting metal rejection and water flux in PEUF as well.

At low pH, it also affects the conformation of the water soluble polymers in the aqueous phase, and this in turn influences the rejection of the macromolecules during UF. The PSS chains with dissociated sulfonate groups will be less extended and more compact as the inter- or intra-molecular repulsive force diminishes [39–42]. Consequently, the macromolecules will be able to penetrate the UF membrane

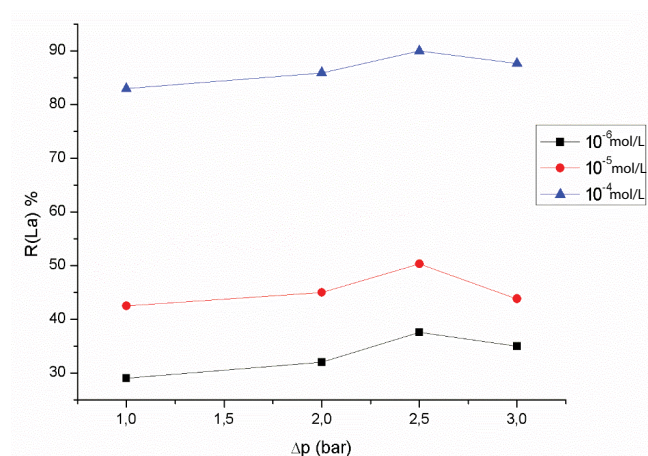


Fig. 7. Lanthanum retention as a function of transmembrane pressure at different PSS concentrations, [La<sup>3+</sup>] =  $10^{-3}$  mol L<sup>-1</sup>.

more easily [43], resulting in a reduction in polymer retention by the membrane and thus a reduction in the La(III) retention as well [44].

In addition, the majority of the sulfonate groups are protonated, affinity toward La ions is poor and the stability of the complex is low. At pH beyond an isoelectric point, the membrane is negatively charged. Associated with a pH solution, sulfonate groups of polymer start dissociating and the presence of sulfonate groups (SO<sub>3</sub><sup>-</sup>) becomes more important. The electrical charges existing in the molecules lead to the apparition of intramolecular and intermolecular repulsion forces.

When the pH increases up to 5, lanthanum ions disappears and lets place to the formation of Lanthanum hydroxides. This form can be retained by membranes and La retention increases consequently.

### 3.6. Competition test

In the fluorimetric methods for identification or determination of substances, based on Ln(III) ions and their complexes as sensitizers, the excited Ln(III) ions are obtained mainly through intramolecular energy transfer from the ligand to Ln(III) ion. Sensitized luminescence of lanthanide ions is a complex process which has already been described in a few review papers [45–48].

Photoluminescence measurements were performed to study the fluorescent properties of the different mixtures polyelectrolytes–lanthanum(III) ions. The emission spectra of PVA-La, PEI-La, and PSS-La before ultrafiltration are shown in Fig. 9.

Fluorescence spectra of the different polyelectrolytes with La(III) and without La(III) (La(III)+PE/PE) were recorded at excitation wavelength 240 nm. The emission spectrum of the PSS solution and the PVA solution indicates a large band at 376 and 337 nm respectively. While, PEI revealed weak emission may be due to photo induced electron transfer (PET) near 350 nm [49]. Upon addition

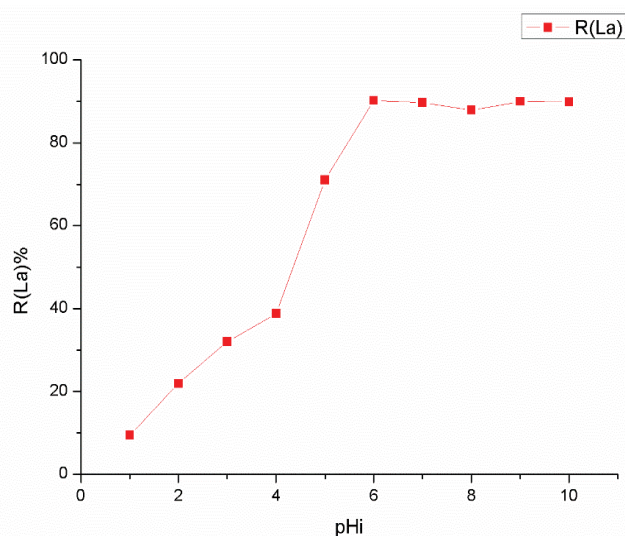


Fig. 8. Lanthanum retention as a function of pH, [La<sup>3+</sup>] =  $10^{-3}$  mol L<sup>-1</sup>, [PSS] =  $10^{-4}$  mol L<sup>-1</sup>, and ΔP = 2.5 bars.

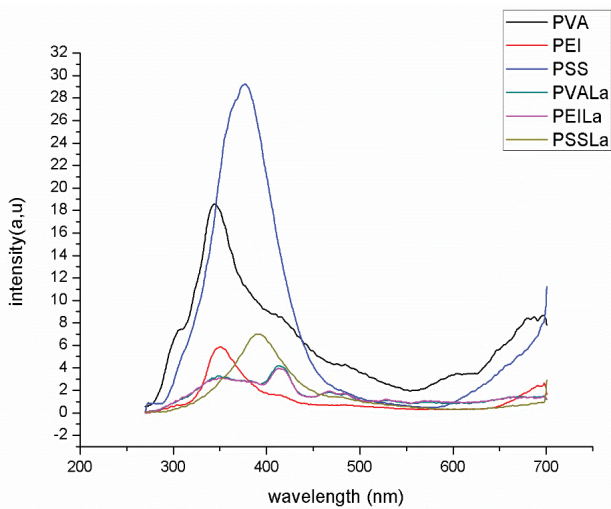


Fig. 9. Emission spectra ( $\lambda_{exc} = 240 \text{ nm}$ ) of PSS-La, PEI-La, and PVA-La before UF, ( $[La^{3+}]_{feed} = 10^{-3} \text{ mol L}^{-1}$ ,  $[PSS] = [PEI] = [PVA] = 10^{-4} \text{ mol L}^{-1}$ ).

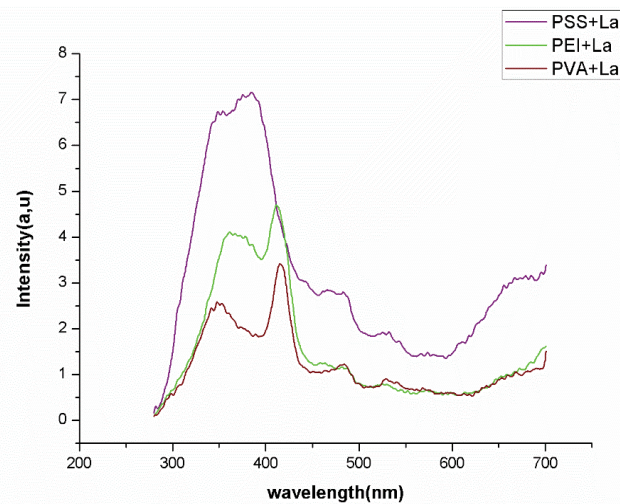


Fig. 10. Emission spectra ( $\lambda_{exc} = 240 \text{ nm}$ ) of PSS-La, PEI-La, and PVA-La after UF, ( $[La^{3+}]_{feed} = 10^{-3} \text{ mol L}^{-1}$ ,  $[PSS] = [PEI] = [PVA] = 10^{-4} \text{ mol L}^{-1}$ ).

of  $La^{3+}$  ions to solutions of polyelectrolyte, a significant decreasing fluorescence was observed, a change in maximum intensity with a bath chromic shift 350 to 410 nm.

These observations indicate that the compound has a synergic effect. The change in emission spectra after addition of  $La(III)$  ions are due to chelation of  $La(III)$  with N and O atoms of the different polyelectrolytes [50].

From these results, we deduce that the complexation of lanthanum ions with PEI and PVA is stronger than PSS.

It can be proved by the analysis of the emission spectra of PSS-La, PEI-La, and PVA-La after UF ( $\lambda_{exc} = 240 \text{ nm}$ ) shown in Fig. 10. It depicts, that after ultrafiltration, all peaks of mixture solutions (La+PE) decrease with different intensities, the lower peak is attributed to the PVA-La(III).

#### 4. Conclusions

The polyelectrolyte enhanced ultrafiltration method was proved to be effective and efficient for processing waste solutions containing lanthanum ions using PSS with average molecular weight 70 kDa. This study permits to evaluate the influence of various operating variables to removal Lanthanum ions from feed solution.

In the absence of PSS, the lanthanum retention was low and the permeate flux increases linearly with transmembrane pressure.

By adding PSS solution, the emission intensity of the polymer decreases following the transfer of energy between PSS and  $La(III)$  ions. The emission spectrum of the PSS-La solution before and after ultrafiltration indicates a new harmonic around 400 nm and confirms the good retention of  $La(III)$  ions by PEUF technique.

The study of the variation of permeate flux as a function of the transmembrane pressure for different PSS concentrations, shows that the permeate flux increases with the transmembrane pressure and decreases with the growth of the PSS concentrations.

Experimental results indicated that the retention of lanthanum ions increases with increase in transmembrane pressure (0.5–3 bar) and increases when PSS concentration varied to  $10^{-6}$  at  $10^{-4} \text{ mol L}^{-1}$ . The maximum observed retention of  $La(III)$  was found to be 90% for  $10^{-4} \text{ mol L}^{-1}$  PSS concentration and 2.5 bar transmembrane pressure.

The  $La(III)$  ions removal efficiency for the PSS system has a maximum removal efficiency at pH of 6. The explanation of this behavior is that the increase in pH leads to an increase in the dissociation of  $SO_3Na$  groups in PSS, which favors the formation of La-PSS complexes.

The competition test uses a photoluminescence measurement to study the fluorescent properties of the different mixture La-PE. PVA and PEI have been tested for to compare its recovery performance to that obtained with PSS. This study demonstrate that the lanthanum ions complexation with PEI and PVA are stronger than PSS and also to prove the affinities of  $La(III)$  toward PVA, PSS, and PEI polyelectrolytes.

#### Symbols

$J_v$	—	Permeate flux, $Lm^{-2} h^{-1}$
$V_p$	—	Volume of the permeate, mL
$S^e$	—	Effective membrane area, $cm^2$
$t$	—	Time, h
$J_w$	—	Permeate flux of pure water, $Lm^{-2} h^{-1}$
$L_p^0$	—	Permeability of solvent, $Lm^{-2} h^{-1} bar^{-1}$
$\Delta P$	—	Transmembrane pressure, bar
$\eta_0$	—	Solvent viscosity
$R_m$	—	Hydraulic membrane resistance, $m^{-1}$
$\eta$	—	Dynamic viscosity of permeate, Pa s
$R (\%)$	—	Lanthanum retention, %
$C_p$	—	Lanthanum concentration in permeate
$C_f$	—	Lanthanum concentration in feed solution
$L_p$	—	Permeability of aqueous lanthanum solutions, $L h^{-1} m^{-2} bar^{-1}$
$[La^{3+}]$	—	Concentration of lanthanum
$[PSS]$	—	Concentration of poly (sodium 4-styrenesulfonate)

- [PEI] – Concentration of polyethylenimine  
 [PVA] – Concentration of polyvinyl alcohol

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