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Hyper-branched phosphonated polyethyleneimine composite for the removal of samarium(III) ions from aqueous solutions: effect of process parameters

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ABSTRACT

Recovering rare-earth elements from hydro-ecosystems, particularly from water, is currently a critical priority. In this study, a synthesized extractant called phosphonated polyethyleneimine (PPEI) was characterized and used in the sorption of samarium ions Sm(III). The batch process allowed for the study of various parameters, including contact time, pH, temperature, and concentration of solutions, on the sorption of samarium by PPEI. The extraction efficiency of samarium ions exceeded 87% at an equilibrium time of 40 min and a maximum pH of 4.1. The sorption kinetics of Sm(III) were found to be in accordance with the pseudo-second-order model, and the sorption isotherms were modeled using different models, including Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich. The most suitable model was found to be Langmuir, which predicts an adsorption capacity of 20.96 mg/g. The values of $\Delta H°$, $\Delta S°$, and $\Delta G°$ were calculated from the sorption data as a function of temperature, and the results indicated that the sorption of Sm(III) on PPEI was endothermic and spontaneous. A desorption study showed that the best eluent was sulfuric acid, with an elution efficiency of 97%. Finally, a regeneration study was performed to evaluate the potential for reuse of the PPEI composite for other applications. Overall, the results suggest that PPEI is a promising extractant for wastewater treatment.

Keywords: Hyper-branched material; Phosphonated polyethyleneimine; Radionuclides; Samarium; Sorption

1. Introduction

Rare-earth elements were classified as essential elements in the last decades due to the spectacular growth of their worldwide consumption [1,2]. They are generally used in many fields of industry such as electronics, environmental protection, new energy industry and military defense [3–6]. They are essential to the development of high-tech industries and are increasingly used in chemical engineering, nuclear energy, optical, magnetic, luminescent materials and radio pharmacy [1,6–8]. However, their release into the environment at concentrations above the permitted limit value leads to the pollution of aquatic ecosystems, wastewater, soils and living organisms [3,8].

The chemical element of interest is samarium, which belongs to the lanthanide family; it is mainly used in the manufacture of cobalt-alloyed permanent magnets, which exhibit the strongest known magnetization, radio pharmacy and is also considered a good thermal neutron sensor [5,9,10]. Electronically, ceramic capacitors use a dielectric based on samarium oxides, optically, samarium is added to glass, and its oxidation allows strong infrared adsorption

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[1,11,12]. Due to the specific applications of samarium in various fields of technology, this metal has become an industrial material of exceptional importance. Samarium exists as seven isotopes in nature, its existence causes a harmful effect on the environment, and soluble salts of samarium are toxic if absorbed through the skin, swallowed or inhaled. They can cause skin, eye and respiratory tract irritation [9]. Therefore, limiting them in the environment is an important preventive measure against harmful exposure [8,13]. In this context, several technologies and methods have been developed for the removal or recovery of the maximum amount of rare earths and in particular lanthanides, such as liquid–liquid extraction, chemical precipitation, membrane separation, electrochemical deposition, ion exchange and adsorption [2,9,10,14]. However, the majority of these processes are confronted with technical, economical and health difficulties due to the selectivity, the time required for extraction, and the large amount of hazardous chemicals used [9]. The most accurate possible search for pollutants such as aromatic hydrocarbons [15,16], metals [17,18] and dyes [19] in complex matrices therefore requires an effective and robust extraction method that specifically recovers these compounds. Solid-phase extraction is a promising and attractive process because of its simplicity, efficiency, flexibility, high enrichment factor and environmental friendliness, hence the use of different materials for metal extraction [4,6,9]. Among these materials, a class of branched polymers has been spectacularly successful in the field of separation and treatment of metal pollution, for example: hyper-branched materials based on polyethyleneimine.

Hyper-branched polyethyleneimines (PEI) are a class of polymers of the empirical formula $(CH_2–CH_2–NH)_n$ that comprise a primary (dendrite end), secondary (junction) and tertiary (fork) amino group, with a stochastic distribution of dendrites. They are highly resistant to temperature and hydrolysis, and are defined by the average molecular weight and distribution of their amino groups [20–22]. Recently, advances in the development of materials synthesis processes have allowed researchers to focus their efforts on improving physicochemical properties, and porosity, exchange capacity, stability and selectivity. The most effective chelating materials are characterized by reactive P, N and O functional groups capable of coordinating with metal ions [21,23,24]. Several investigations have been published to study the extraction properties of metal ions (actinides and lanthanides) by various organophosphorus materials [5,20–22]. Also, considering the increasing interest in the use of solid organophosphorus derivatives in solid-state extraction [5,20–23], it was agreed in the present research to functionalize a hyper-branched polyethyleneimine polymer with a phosphine oxide group by the addition of tris(hydroxymethyl)phosphine (THMP).

Furthermore, the main objective is the determination of the conditions for an efficient extraction of samarium ions by phosphonated polyethyleneimine (PPEI). Different parameters were examined, such as the initial pH of the aqueous solution, ionic strength and temperature. Sorption kinetics and isotherms were described based on the experimental results obtained from contact time studies, and the initial Sm(III) ion concentration. Finally, a regeneration study of PPEI was performed for possible reuse.

2. Materials and methods

2.1. Reagents

The phosphonated hyper-branched material used in this study is a polymer synthesized from PEI Lupasol/(BASF) WF (Fig. 1): $(CH_2CH_2NH)_n$ average molecular weight 25,000 ($NH_2/NH/N$ = 1/1.20/0.76). Tetrakis(hydroxymethyl) phosphonium chloride ($[P(CH_2OH)_4]Cl$, THPC) and hydrogen peroxide (33%, w/w) H_2O_2 were purchased from Sigma-Aldrich.

The present study was carried out on the extraction of samarium from the solution prepared from the samarium nitrate salt, $Sm(NO_3)_3·6H_2O$ (Fluka). The pH of the samarium solutions was adjusted by adding dilute solutions of sodium hydroxide NaOH (Sigma-Aldrich) or nitric acid HNO_3 (Cheminova). For the study of the effect of salt, different salts were employed: potassium thiocyanate KSCN, potassium chloride KCl, potassium cyanide KCN and sodium acetate CH_3COONa supplied by the company Prolabo. Also, sodium chloride NaCl and sodium sulfate Na_2SO_4 obtained from Fluka.

For UV-Visible analysis, Arsenazo(III) (N′-[2-[2-(2-aminoethylamino)ethylamino]ethyl]ethane-1,2-diamine, M = 776.36 g/mol) was used as a complexing agent supplied by Sigma-Aldrich and a commercial buffer solution pH = 4 was obtained by Prolabo. For the desorption study, three acids were used: sulfuric acid H_2SO_4 (Fluka), hydrochloric acid HCl (Sigma), and nitric acid HNO_3 (Cheminova). All chemical reagents used were of analytical grade and distilled water was used throughout the process of this study.

2.2. Apparatus

The sorption of samarium ions by the PPEI was studied by the batch method. A multi-poste magnetic stirrer (Wise-Stir MS-MP8 Model) was employed for all sorption experiments, except for the temperature effect where a magnetic stirrer (RCT Basic IKAMAG Stirrer with ETS-D5 Temperature Controller) was used. For the separation of the liquid and solid phases, a centrifuge (Sigma 2-6) was employed. The mass of the PPEI sorbent was measured using an analytical balance (Ohaus Pioneer) and all pH measurements were performed with a WTW-3310 Set 2 digital pH meter.

The determination of the samarium concentration in solution was performed by a UV-Visible spectrophotometer (Analytik Jena SPECORD 210 PLUS). Microanalyses were performed on the automatic elemental analyzer (Thermo Quest NA 2500, Thermo Finnigan) (C, H, N and P). Infrared spectra were obtained with KBr and recorded between 4,000 and 500 cm⁻¹ using Fourier-transform infrared

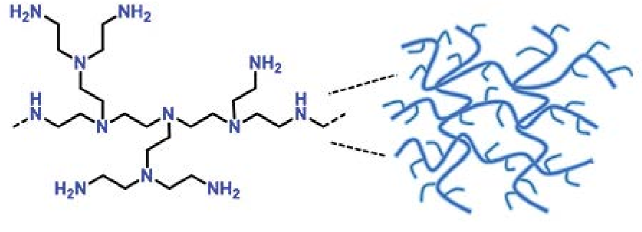

Fig. 1. Chemical structures of branched polyethyleneimine.

spectrophotometer (Perkin Elmer 684 IR spectrophotometer). The surface characteristics and grain morphology of the PPEI were analyzed using a Hitachi-SEM (TM1000) scanning electron microscope (15 kV).

2.3. Synthesis of PPEI sorbent

According to the literature studies, THMP must be prepared just before the reaction with the THPC [25,26]. The primary and/or secondary amine functions of polyethyleneimine (PEI) react with tris(hydroxymethyl)phosphine to produce phosphine, which has been converted by hydrogen peroxide to phosphine oxide.

Under argon, a solution was prepared with 50 g of tetrakis(hydroxymethyl)phosphonium chloride salt in 500 mL of water, cooled to 0°C. An aqueous solution of NaOH was then added progressively with stirring (11.5 g in 100 mL of water) to obtain tris(hydroxymethyl)phosphine.

Next, a fresh solution of THMP (80 mmol) was added to 58 g of polyethyleneimine (Lupasol WF, MW = 25,000 g/mol) dissolved in a mixture of 200 mL of water and 800 mL of ethanol. The resulting synthesis product was stirred and heated to reflux for 4 h.

The synthesis mixture was then stirred in air for 48 h, treated with hydrogen peroxide (5%) and the precipitate was then washed with distilled water to remove unreacted reagents. Finally, the PPEI was washed three times with distilled water and ethanol. After drying, the solid was pulverized again before use to give a yellow-orange powder.

The synthesis of PPEI is presented in Fig. 2, with the polyethyleneimine intercalated with a phosphonated group by reaction with tris(hydroxymethyl)phosphine. The steps are as follows:

2.4. Sorption–desorption studies

Sorption of samarium ions by PPEI grains was studied by solid-phase extraction from aqueous media in a batch system. A mass of 0.0300 g of the solid PPEI was added to 5 mL of a solution containing metal ions Sm(III), in a stoppered glass vial (25 mL) and the mixture was stirred for an appropriate time at ambient temperature (20°C ± 1°C). Next, the aqueous phases were separated from the chelating PPEI by centrifugation and analyzed by UV-Visible spectrophotometer at a wavelength of 653 nm using the Arsenazo(III) method described in the literature [1,27].

Kinetic studies on the removal of Sm(III) ions were carried out, for an initial concentration of 0.5 mmol/L at ambient temperature. The effect of contact time on sorption was studied up to 60 min, while other parameters, such as sorbent dosage, stirring speed (Ø) and pH were maintained constant. The effect of initial pH on the sorption of Sm(III) ions by PPEI was studied in the range of 1–8. The pH was adjusted by adding appropriate amounts of HNO_3 or NaOH solutions (0.01 mol/L). The temperature effect was studied for a range of 10°C–60°C using a magnetic stirrer with a temperature controller, under a stirring speed of 300 rpm. All data reported are based on the average of three replicate measurements.

The transformation of the experimental results into analytical responses is done in the following terms:

The percentage of samarium ions that were adsorbed on the PPEI (i.e., extraction yield, E%) was determined by comparing its concentrations before and after extraction Eq. (1) [28]:

$$E(\%) = 100 \times \frac{C_i \times C_e}{C_i} \tag{1}$$

The amount of samarium ions uptaken at time t, q_t (mg/g), was calculated by Eq. (2) [1,28]:

$$q_t(\text{mg/g}) = \frac{C_i - C_t}{w} \times V \times M \tag{2}$$

where C_i, C_t and C_e are the metal ion concentrations at the initial, time t and equilibrium, respectively; V (L) is the volume of the solution; M (g/mol) is the molar mass of samarium ion and W is the mass of the sorbent (g).

After saturation of PPEI with samarium ions, it could be regenerated for further extraction using chloride, sulfuric

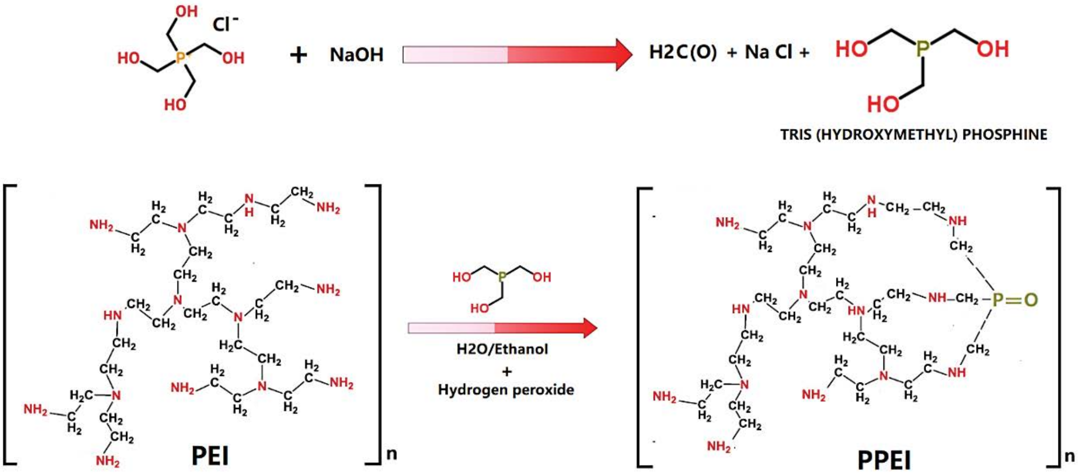

Fig. 2. Schematic illustration of the synthesis process of PPEI.

and nitric acids. Desorption of Sm(III) was performed by mixing 0. 0300 g of PPEI loaded with Sm(III) ions with 5.0 mL of acidic solutions (HCl, HNO_3 and H_2SO_4) at a 1 mol/L, and stirring them at 300 rpm for 1 h at ambient temperature (20°C ± 1°C). The final concentrations of Sm(III) in the aqueous phase were analyzed by UV-Vis spectrophotometer. All reported data are based on the average of three replicate measurements. The most efficient eluent was defined using Eq. (3) [21]:

$$\text{Elution Yields} = \frac{C_{\text{Elut}}}{C_i - C_e} \times V \tag{3}$$

where C_{Elut} is the concentration of Sm(III) (mol/L) after acid treatment.

3. Results and discussions

Polyethyleneimine belongs to the hyper-branched cationic polymers, with their structures always consisting of an amine nitrogen and two methylene groups [20,21,29]. They have the highest charge density per weight or per molecule and have a very high retention capacity on polar surfaces. In addition, modified polyethyleneimines materials can selectively separate heavy metals [29,30]. A novel polyethyleneimine-based extractant "PPEI" has been synthesized for the removal of samarium ions from aqueous solutions, having two functional groups, amine and phosphine oxide, due to the high affinity and good coordination of these groups towards metals [21,22].

3.1. PPEI characterization

This novel phosphonated polymer is stable in all pH ranges, is inert and resistant to most oxidizing reagents such as HNO_3 and H_2SO_4 up to a concentration of 5 mol/L and is not soluble in all common solvents. The structure and purity of the hyper-branched PPEI were identified and characterized by various physico-chemical techniques, namely Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and elemental microanalysis. FTIR spectroscopy offers detailed information on each molecular bond as the absorption/transmission spectra represent the fingerprint of a material with absorption peaks generated by vibrational transitions of atomic bonds. The absorption spectra of the PPEI in the frequency range between 500 and 4,000 cm^{-1} are presented in Fig. 3.

Fig. 3 shows that the characteristic polyethylenimine peaks at 3,367 cm^{-1} (–N–H stretch), 2,958 and 2,845 cm^{-1} (–C–H stretch), 1,661 cm^{-1} (–N–H bend), and 1,042 cm^{-1} (–C–N stretch) appeared in the spectrum of the PPEI [29]. The appearance of bands at 1,138 cm^{-1} (P=O), 1,334 cm^{-1} (C–P) and 1,042 cm^{-1} (C–N) confirm the existence of phosphorus groups on the PPEI [4,21,31]. Based on the results obtained from the CHNP analysis (%) of the PPEI composite (C: 52.17; H: 10.58; N: 28.35 and P: 5.85) the proposed monomer was $(C_{23}H_{58}N_{10}PO)_n$ which has the theoretical elemental analysis C: 52.97; H: 11.13; N: 26.87 and P: 5.95. SEM analysis was then carried out to determine the topographic and structural properties of PPEI.

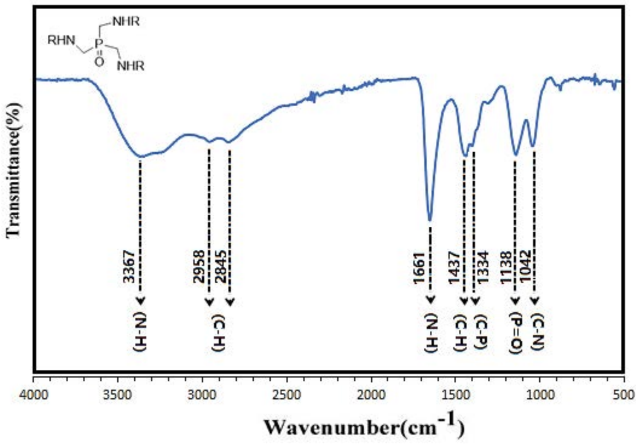

Fig. 3. Fourier-transform infrared spectra of PPEI composite.

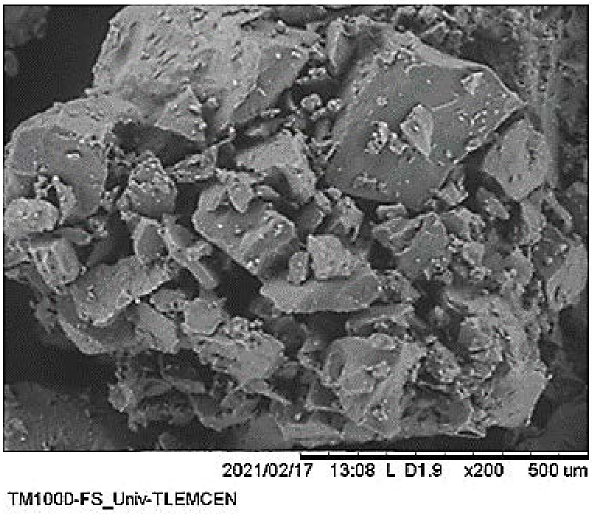

Fig. 4. Scanning electron micrographs of PPEI composite.

From Fig. 4, the hyper-branched composite exhibits a rough and ill-defined surface structure, with the presence of many small irregular particles and a uniform pore distribution. These properties would facilitate the diffusion of metals during sorption, increasing the adsorption capacity of metals and reducing the equilibrium time.

3.2. Sorption of Sm(III) ions by PPEI

3.2.1. pH effect

pH is one of the most important factors affecting the process of sorption of metal ions from aqueous systems by the batch method. The pH of the solution controls the surface charge of the sorbent and the ionization of the sorbate in solution. Based on the CHEAQS v. L 20.1 software (A Program for Calculating Chemical Equilibria in Aquatic Systems), the predominant Sm(III) species were determined as a function of pH (Fig. 5).

This study reveals seven types of extractable species in the medium for $(Sm(NO_3)_3)$ with a pH between 1 and 14.

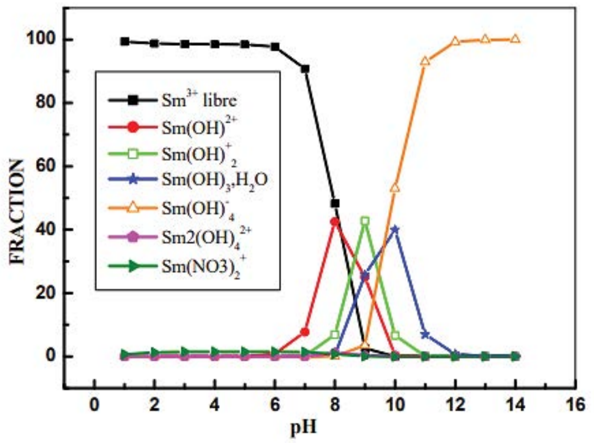

Fig. 5. Samarium species at different pH values in nitrate media (CHEAQS, database) concentration of $Sm(NO_3)_3$ = 0.5 mmol/L and temperature of 20°C.

Several experiments were carried out in a pH range of 1–8 since the majority species is Sm(III) and to avoid precipitate formation. The results are presented in Fig. 6, which shows that the extraction depends on the variation of the pH of the aqueous solution; when the pH of the solution varies from 1 to 4, the extraction yield increases from 10 to over 87%. This is due to the favorable conditions for the complex formation of samarium with the PPEI composite.

In acidic media, the extraction yield was very low, which can be explained by the competition between samarium ions and the protons of the acidic medium H^+ fixed on the heteroatoms O, N and P of PPEI functional groups. This protonation of these heteroatoms will render them inaccessible to samarium ions. Deprotonation during the pH increase makes the approach of samarium ions favorable. This is attributed to the presence of a free lone pair of electrons on nitrogen and deprotonated oxygen atoms, which are suitable ligands for coordination with the samarium ions [23,31]. The same pH ranges have been obtained with other sorbents for the sorption of Sm(III) [4,6,10–12,32,33]. At higher pH, the uptake of Sm(III) decreases slightly as the ions lead to more stable hydroxide complexes in the aqueous phase like $Sm(OH)_4^-$, $Sm(OH)^{2+}$, $Sm(OH)_2^+$, etc [4,11,12,34].

3.2.2. Kinetic study

Sorption kinetic studies are important to (i) determine the time required to reach equilibrium, (ii) derive predictive models and (iii) understand the influence of variables on solute sorption. The kinetic study was carried out at ambient temperature at pH 4.1, as shown in Fig. 7. The sorption capacity has increased considerably over time with a more or less rapid adsorption rate. The equilibrium time in which the PPEI composite attains 50% saturation with Sm(III) (half time $t_{1/2}$ is ≤5 min). Indeed, the kinetic curve of the sorption efficiency is divided into two stages with the first one considered fast from 0 to 40 min. This is related to the availability of more active sites on the surface of the PPEI composite and the higher driving force of samarium(III), allowing it to overcome external resistance to mass transfer. While the active sites with higher affinity are occupied first, Sm(III) ions easily penetrate the accessible porous sites and bind to the functional groups of the PPEI [29,31].

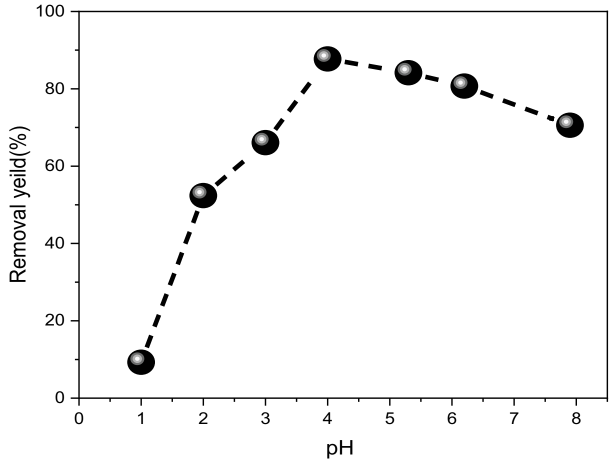

Fig. 6. Removal yield of samarium ions by the PPEI composite as a function of initial pH (w = 0.030 g, V = 5 mL, Ø = 300 rpm, $[Sm^{+3}]_0$ = 0.5 mmol/L).

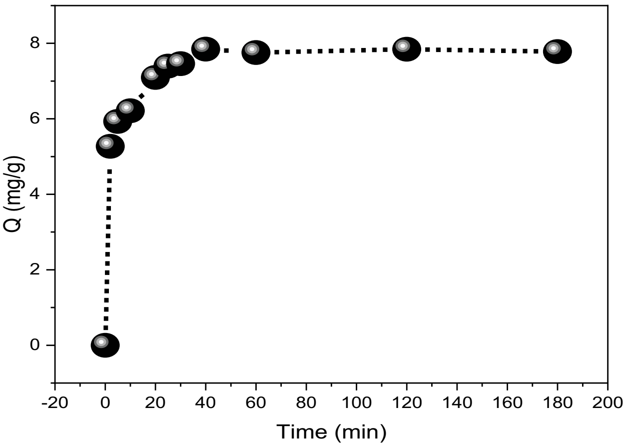

Fig. 7. Influence of contact time on the sorption capacity of Sm(III) onto PPEI. ($[Sm^{+3}]_0$ = 0.5 mmol/L, w = 0.03 g, V = 5 mL, Ø = 300 rpm, T = 20°C ± 1°C, pH = 4.1).

On the other hand, the second one is slow from 40 to 120 min, explained by an equilibrium of sorption and desorption, which could be due to the fact that some Sm(III) ions will be impeded from diffusing and propagating in the deeper pores and also to the existence of different sorption mechanisms [35].

Consequently, the contact time of 40 min was maintained for all subsequent experiments to ensure the invariance of this parameter. The contact time, necessary to achieve maximum sorption on PPEI composite, was lower than many sorbents reported in the literature: equilibrium time at 60 min [4,11,14,34], 90 min [2,36], 120 min [10], 180 min [5], 240 min [37,38], and 1440 min [1,7,32].

Furthermore, the kinetic parameters and sorption mechanisms of samarium ions on the PPEI sorbent were estimated using kinetic, pseudo-first-order, pseudo-second-order, and diffusion models [39]. The pseudo-first-order model, given by Lagergren [40], is based on the relationship between the amounts of solute bound to the material surface as a function of time. The pseudo-first-order kinetic model is more suitable for lower concentrations of solute. The linear form of the equation is expressed in Eq. (4) [11,28]:

$$\ln\left(q_e - q_t\right) = \ln\left(q_e\right) - k_1 t \tag{4}$$

The pseudo-second-order model (by Ho and McKay [41]), which is based on the sorption capacity of the solid phase, was also used. The rate of the pseudo-second-order reaction is dependent on the amount of solute adsorbed on the sorbent surface and the amount adsorbed at equilibrium. The rate equation for the pseudo-second-order chemisorption kinetics is represented as follows [11,28,35]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

The nature of the rate-limiting step in a batch system can also be assessed from the properties of the solute and the sorbent. The diffusional model, called the Morris–Weber model [37], shows that the sorption capacity q_t is a linear function of the square root of time ($\sqrt{t}$), and is applied to study the diffusion of metal ions in the pores of the material. Its mathematical expression is represented in Eq. (6) [2,28]:

$$q_t = k_{\text{id}} \times \sqrt{t} + C \tag{6}$$

where q_e, q_t: quantities adsorbed of samarium on the PPEI at equilibrium and at a time t, respectively (mg/g); k_1: the first-order sorption rate constant (min^{-1}); k_2: the pseudo-second-order sorption rate constant (g/mg·min); and k_{id}: the intraparticle diffusion rate constant (mg/g·min$^{0.5}$).

The plots of the sorption of Sm(III) ions using the pseudo-second-order, and intraparticle models are shown in Fig. 8. The equations and linear forms presented below in Table 1 describe the kinetic parameters of the samarium extraction process by PPEI composite. It was observed that the equilibrium sorption capacity was close to the experimental value. The best correlation is obtained with the pseudo-second-order equation ($R^2 > 0.9999$).

The sorption of samarium ions by the PPEI extractant was shown to be in agreement with the pseudo-second-order model. This implies that the rate controlling step in the sorption process is the chemisorptive forces [4,28] between ions Sm(III) in the solution phase and the active cites (N, O and P) on the PPEI composite.

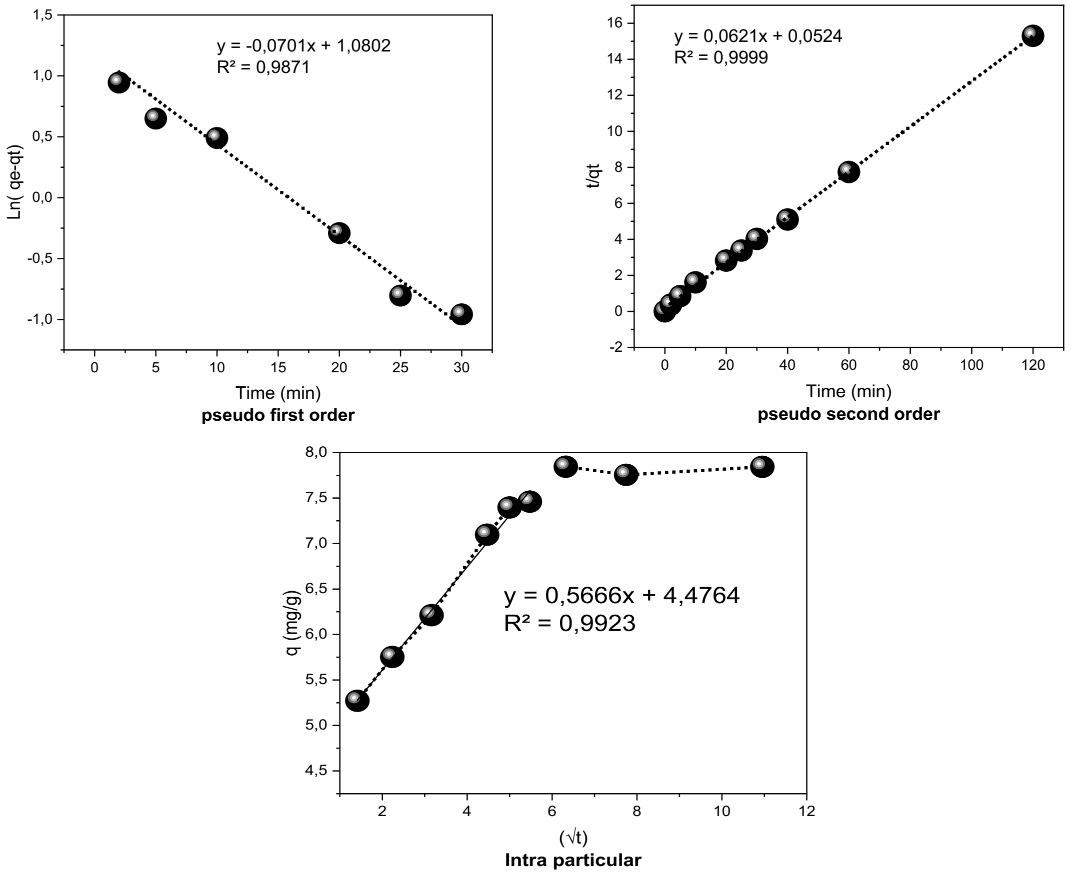

Fig. 8. Pseudo-first-order and pseudo-second-order and the intraparticle plots of Sm(III) sorption kinetics onto PPEI (w = 0.03 g, V = 5 mL, Ø = 300 rpm, T = 20°C ± 1°C).

Table 1
Parameters of pseudo-first-order and pseudo-second-order and intraparticle diffusion models for the sorption of samarium by PPEI

Metal	$q_{e(\exp)}$	Pseudo-first-order	Pseudo-second-order	Intraparticle diffusion
Sm(III)	7.84 mg/g	$k_1 = 0.0744$ $q_e = 3.25$ mg/g $R^2 = 0.9871$	$k_2 = 0.0806$ $q_e = 7.94$ mg/g $R^2 = 0.9999$	$k_{id} = 0.6986$ $C = 4.4764$ $R^2 = 0.9923$

For the intraparticle diffusion results (Weber–Morris model), the curve does not pass through the origin indicating that intraparticle diffusion is not the limiting step. Thus, the curve is divided into two steps, the first one concerns the diffusion of samarium ions by microporous and the second one by macroporous [23,42–45].

3.2.3. Adsorption isotherms

The optimization of all parameters influencing the adsorption process is very important to achieve maximum adsorption efficiency. One of the significant effects of the adsorption process is the initial concentration of the metal studied. The extraction efficiencies of samarium sorption on the PPEI composite are shown in Fig. 9 as a function of the initial concentration of Sm(III) ions in the aqueous medium.

According to the results obtained in Fig. 9, the sorption capacity increases with increasing initial Sm(III) ions concentration onto PPEI composite, which proves that the sorption mechanism of samarium ions occurred on the surface and in the porous structure of the adsorbent. The maximum sorption capacity was 18.47 mg/g. This result indicates that PPEI is an effective sorbent in the treatment of diluted metal solutions in batch processes. For comparison, this sorption capacity is also considerably higher than some other sorbent materials reported in the literature (Table 4).

However, the relationship between the magnitude of sorption and the equilibrium concentration of the contaminant (C_e) is known as the sorption isotherm, which is highly indicative of the mechanism and nature of the sorption process. In the literature, several scientists have developed a number of models for sorption, for example: Langmuir, Freundlich, Dubinin–Radushkevich and Temkin. The calculated isotherm parameters can be used for the development of full-scale sorption processes.

The Langmuir model [46] is a mathematical model that consists of maximum adsorption by a monolayer covering of the sorbent surface, the adsorption energy is constant regardless of the covering rate and the adsorption sites are homogeneous. Its mathematical formula is expressed in Eq. (7) [21,28,31]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{7}$$

Freundlich proposed adsorption on a surface with non-ideal and reversible characteristics, which is not limited to monolayer adsorption [47]. This empirical model can be adapted to multilayer adsorption, with a non-uniform distribution of heat of adsorption and affinities on the heterogeneous layer. In this context, the quantity adsorbed is the result of adsorption on all sites (each with a binding energy), considering that the strongest binding sites are occupied first, until the adsorption energy decreases exponentially at the end of the adsorption process. Its mathematical equation is expressed by Eq. (8) [31,32]:

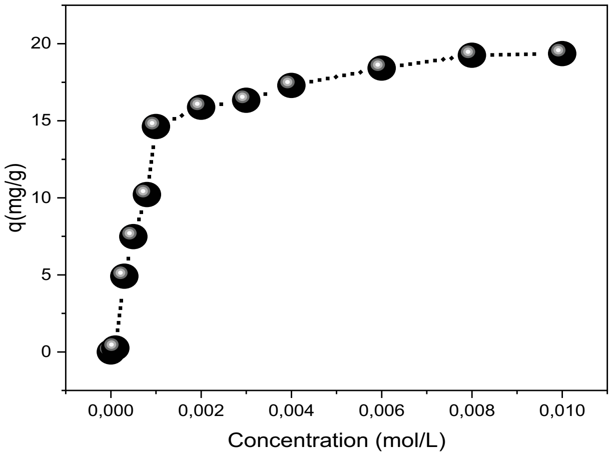

Fig. 9. Quantity adsorbed of samarium by the PPEI composite as a function of [Sm(III)] (w = 0.03 g, V = 5 mL, Ø = 300 rpm, T = 20°C ± 1°C, pH = 4.1).

$$\ln\left(q_e\right) = \ln\left(K_F\right) + \frac{1}{n}\ln\left(C_e\right) \tag{8}$$

The Dubinin–Radushkevich model [48], based on the principle that the degree of pore filling is related to the free enthalpy of adsorption, and proposes that the adsorption potential changes. It is generally applied to express the adsorption mechanism with a Gaussian energy distribution on a heterogeneous surface. The model has often successfully fitted high solute activities and the intermediate range of concentrations.

The equation is expressed in Eq. (9) [49]:

$$\ln\left(q_e\right) = \ln\left(q_{m_{\mathrm{DR}}}\right) - \left(\frac{RT}{E}\right)^2 \cdot \left(\ln\left(\frac{C_s}{C_e}\right)^2\right) \tag{9}$$

The Temkin model [50] supposes that the variance between the heat of adsorption and the degree of coverage is linear, this linearity is expressed on a uniform surface by interactions between the adsorbed molecules, and on the non-uniform surface, due to the heterogeneity of the surface. Its formula is expressed in Eq. (10) [49,51]:

$$\theta = \frac{RT}{B_T} \ln K_T \cdot C_e \tag{10}$$

where q_e, q_m: sorption capacity at equilibrium and saturation (mg/g); C_e: molar concentration at equilibrium (mg/L), C_s: solubility of the solute, K_L: Langmuir equilibrium constant in (L/mg), K_F: Freundlich constant related to the sorption capacity, n: constant related to the sorption intensity and capacity, $q_{m\text{DR}}$: maximum adsorption capacity in the micropores, R: gas constant (8.314 J/mol·K), T: absolute temperature in Kelvin, and θ: degree of coverage. B_T (J/mol) is the Temkin isotherm constant, which is the variation of adsorption energy and K_T is the equilibrium binding constant corresponding to the maximum binding energy (L/g).

The main characteristics of the sorption process can be interpreted by the corresponding calculated parameters of the isothermal equations. The obtained data are presented in Table 2.

According to the results obtained, the experimental isotherm of the sorption capacity of samarium ions is acceptably described by Langmuir, Freundlich, Dubinin–Radushkevich and Temkin models. Precisely, the Langmuir model with an R^2 close to unity most accurately described the sorption process, implying that the sorption of samarium ions by the PPEI occurs in a monolayer, with a maximum capacity equal to 20.96 mg/g. The separation factor R_L is a characteristic constant of the Langmuir isotherm, it allows to qualify the type of adsorption, if it is favorable or not [32,51], its equation is presented as follows:

$$R_L = \frac{1}{1 + bC_0} \tag{11}$$

The R_L values range from ($0 < R_L < 1$) at ambient temperature, showing favorable adsorption of samarium ions by PPEI at low concentration in the aqueous phase.

For the Dubinin–Radushkevich model, the adsorption energy is calculated as follows:

$$E_{\text{DR}} = \frac{1}{\sqrt{\beta}} \tag{12}$$

The calculation of the adsorption energy enables the determination of the interactions nature between the adsorbent and the adsorbate, which is physical based on van der Waals forces, or chemical based on ionic exchange and complex formation [28]. An adsorption process is considered physical if the calculated E_{DR} value is lower than 8 kJ/mol, and it is chemical if the E_{DR} is higher than 8 kJ/mol [43]. The calculated value of the adsorption energy of samarium ions by the PPEI is 10.31 kJ/mol greater than 8 kJ/mol, which confirms that the sorption is chemical.

3.2.4. Effect of salts addition

Aqueous discharges of hydrometallurgical and nuclear wastes generally contain large quantities of chemical compounds in many forms depending on their origin (ores) [31,52]. Therefore, the study of the effect of ions on the sorption of Sm(III) on the PPEI sorbent appears important because the modification of the ionic strength by the addition of an electrolyte influences the sorption by [31]:

- affecting interfacial potential and therefore the activity of electrolyte ions and adsorption.
- affecting the competition of the electrolyte ions and adsorbing anions for sorption sites.

A variety of sodium and/or potassium salts (chloride, nitrate, cyanide, thiocyanate, and sulfate) were added to the aqueous phase at the same concentration (1.0 mol/L) to study the effect of salt on the extraction yield. The concentration of Sm(III) was set at 0.5 mmol/L.

Fig. 10 shows that the sorption efficiency of Sm(III) is increased with the addition of KCl, $NaNO_3$, NaCl and $Na_2S_2O_3$ (synergistic effect) and decreased when the salts KSCN, KCN, Na_2SO_4 and CH_3COONa were added

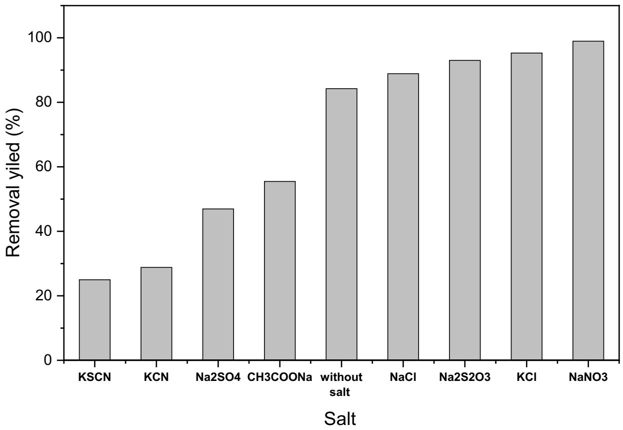

Fig. 10. Effect of salts addition on Sm(III) sorption by PPEI composite ([salt] = 1.0 mol/L, w = 0.03 g, V = 5.0 mL, Ø = 300 rpm, T = 20°C ± 1°C).

Table 2
Sorption isotherms parameters of Sm(III) sorption onto PPEI

Metal	Dubinin–Radushkevich	Langmuir	Freundlich	Temkin
Sm(III)	$R^2 = 0.8795$ $E = 10.31$ $\beta = 0.0047$	$R^2 = 0.9979$ $K_L = 3.493$ $q_m = 20.96$ mg/g $R_L = 0.626$	$R^2 = 0.8485$ $K_F = 18.245$ $1/n = 0.414$	$R^2 = 0.916$ $B_T = 4.030$ $\ln(K_T) = 9.75$

(negative effect). The reasons could be attributed either to the formation of non-extractable anionic species of samarium at higher free anionic concentrations (Cl^-, CN^-, NO_3^-, SCN^- and SO_4^{2-}), or by the effect of the ionic strength of the solution which can influence the activity coefficients of Sm(III) ions limiting their transfer to the PPEI sorbent. The highest extraction yield was obtained by adding $NaNO_3$, with a yield equal to 98%.

3.2.5. Temperature dependence of sorption

The influence of temperature on the adsorption efficiency of samarium ions by PPEI was studied at various temperatures: 10°C, 20°C, 30°C, 40°C, 50°C and 60°C. The results obtained are reported in Fig. 11; where the extraction efficiency of samarium ions by PPEI increased with increasing temperature, and the maximum percentage was 93% at 60°C. This result is expected; at higher temperatures, samarium ions move faster. The ions become smaller as solvation is reduced [31,53] and increased diffusion rates through the outer boundary layer and into the inner pores of the sorbent reaching the NH, N and –P(O) groups of the PPEI composite, resulting in increased sorption capacities.

The thermodynamic parameters were determined from the temperature effect data. The thermodynamic parameters enthalpy ($\Delta H°$), entropy ($\Delta S°$), and free enthalpy ($\Delta G°$) are calculated, in order to explain the mechanism of sorption of samarium ions by PPEI. Eqs. (13)–(16) are used for calculating these parameters [28,31,35]:

$$K_d = \frac{q_e}{C_e} \tag{13}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{14}$$

$$\Delta G° = -RT\ln(D) \tag{15}$$

The relation between K_d, $\Delta H°$ and $\Delta S°$ can be described by Van't Hoff correlation in Eq. 16.

$$\ln D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{16}$$

where T: temperature (K), R: gas constant (8.314 J/mol·K).

From the results of Fig. 12 and Table 3 it is evident that the value of enthalpy $\Delta H°$ is positive, which implies that the extraction process of samarium ions by the PPEI composite is endothermic. The positive $\Delta S°$ value reflects the high affinity of the PPEI composite for Sm(III) ions and suggests increased randomness at the solid-solution interface during sorption. In contrast to the values of the free enthalpy which are negative [28,43]. Furthermore, the observed decrease in negative $\Delta G°$ values with increasing temperature indicates that adsorption is more favourable at higher temperatures, indicating that the sorption process is spontaneous, and confirming the thermodynamic feasibility of the sorption process (Table 3).

3.3. Comparison of the adsorption capacity of PPEI with other materials

Three parameters were considered, contact time, pH and sorption capacity, for comparison with the literature, to evaluate the PPEI composite.

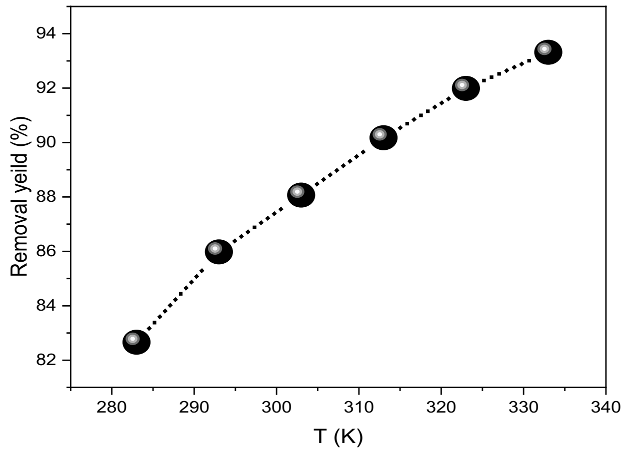

Fig. 11. Removal yield of samarium by PPEI composite as a function of temperature ($[Sm^{3+}]$ = 0.5 mmol/L, w = 0.03 g, V = 5 mL, Ø = 300 rpm, pH = 4.1).

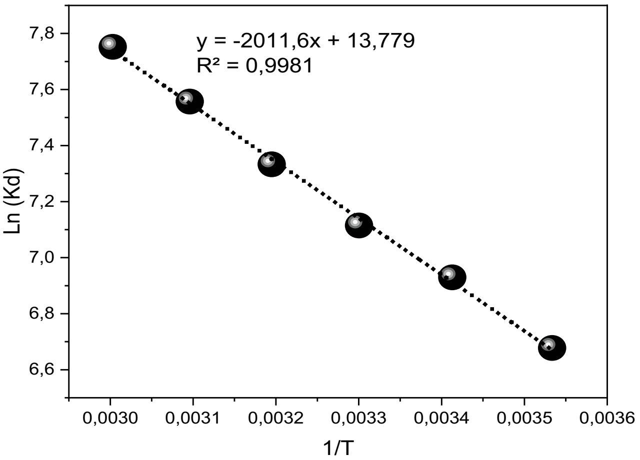

Fig. 12. ln(K_d) Sm^{+3} removal by PPEI composite as a function of 1/T ($[C]_0$ = 0.5 mmol/L, w = 0.03 g, V = 5 mL, Ø = 300 rpm pH = 4.1).

Table 3
Thermodynamic parameters for the sorption of samarium on PPEI

Metal	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol)	$\Delta G°$ (kJ/mol)					
			T (°K)	283	293	303	313	323	333
Sm(III)	16.72	114.55		–15.71	–16.88	–17.92	–19.08	–20.29	–21.46

Table 4
Comparison of q_m (mg/g) of various sorbents materials for Sm(III) sorption

Sorbent	Sm(III)			References
	$q_{\max}$ (mg/g)	Time (min)	pH	
Bentonite–dolomite composites (B-D)	7.42	1,440	4.5	[1]
Pectin–activated carbon composite (Pec-AC)	21.09	90	7	[2]
Magnetic nanoparticles functionalized with a phosphonic group	23.90	60	4	[4]
Cyanex 272 impregnated XAD-7 resin	0.75	180	2.5	[5]
Bentonite modified with N-(2-hydroxyethyl)ethylenediamine	17.70	30	4	[6]
Polyacrylamide stannic molybdophosphate (PASnMoP)	15.38	1,440	3	[7]
Nano-structured samarium(III) ion-imprinted polymer	14.91	120	4	[10]
Molybdo-vanado phosphoric acid-Zr mesoporous silica SBA-15	1.83	60	4	[11]
Carbonized parachlorella	1.23	20	4	[12]
Nanoscale zero-valent iron	10.01	30	5	[13]
Mycelium of *Botryosphaeria rhodina* MAMB-05	1.04	60	5	[14]
Chelating resin “Chelex 100”	19	10	3.2	[27]
Polyacrylonitrile zirconium titanate (PANZrTi)	1.63	1,440	4.2	[32]
Fe_3O_4@SiO_2@polyaniline–graphene oxide composite	7.70	20	4	[33]
Hollow core/shell microspheres of hematite	14.48	60	7	[34]
Chelating-modified biosorbent: modified yeast cells	7.24	90	6.2	[36]
Ordered mesoporous carbon CMK-8	3.47	240	2.6	[37]
Synthetic analogue of heulandite	0.17	240	5	[38]
Diethylenetriamine-pentetic acid-magnetic nanosorbents	1.37	30	3	[54]
Phosphonated polyethyleneimine composite PPEI	20.96	40	4.1	This work

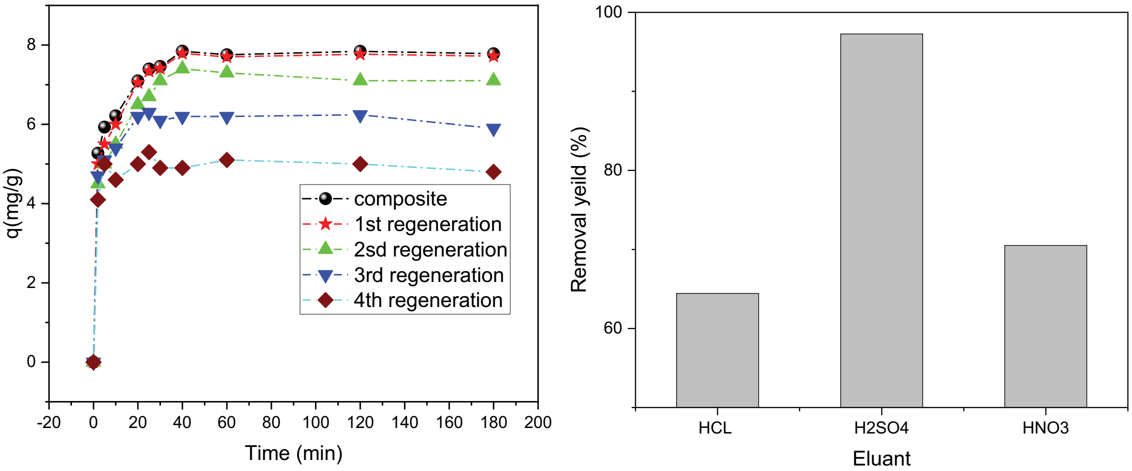

Fig. 13. Recovery percent of various solvent and number of regenerations of the composite PPEI for desorption of samarium ions (w = 0.03 g, V = 5 mL, Ø = 300 rpm, T = 20°C ± 1°C).

According to Table 4, the PPEI composite is considered to be an efficient material compared to the majority of extractants for the extraction of samarium ions in aqueous media.

3.4. Desorption study

An elution study was carried out, involving three eluting acids, hydrochloric acid HCl, sulphuric acid H_2SO_4 and nitric acid HNO_3, of a concentration of 1 mol/L. Firstly, the PPEI was saturated with a concentrated samarium solution and the elution yield was calculated by Eq. (3). To a saturated sample of the resin (0.03 g), 5 mL of the selected acid was added and held for 1 h. As shown in Fig. 13 the best eluent was the sulphuric acid H_2SO_4 with a percentage elution of over 97%. These results confirm the high affinity and bond strength between the samarium ions and PPEI.

The same results were obtained in the desorption of Sm(III) from magnetite nanoparticles functionalised with a phosphonic acid group (PA-MNPs) using sulphuric acid, which revealed higher desorption efficiencies than HCl and HNO_3 acids with a value of 78% [4]. In addition, a kinetic study was carried out to test the performance and lifetime of the composite. Fig. 13 showed the sorption of samarium by the PPEI, after its regeneration. Each sorption step of samarium solution was followed by a regeneration step. It was found that after four cycles of regeneration the amount adsorbed decreased significantly.

4. Conclusion

The extraction efficiency of samarium ions by hyper-branched phosphonated polyethyleneimine PPEI, was established as a function of the different parameters, pH, contact time, concentration effect, salt effect, temperature, and desorption. The equilibrium time was 40 min and the pseudo-second-order model was determined by a kinetic study, which means that the chemical sorption model. From the effect of the samarium ion concentration, the study of the sorption isotherms showed that the most suitable model to describe the extraction was the Langmuir model, which confirms that the extraction is conducted in a monolayer, the maximum sorption capacity of the samarium ions was 20.96 mg/g. The optimal pH of the solution is 4.1. Several salts were used to investigate this effect on the extraction yield, of which the addition of $NaNO_3$ to the solution increased the yield to 98.96%. A thermodynamic study was carried out, of which the extraction yield increases with increasing temperature, the calculated enthalpy and entropy are positive which implies that the reaction is endothermic, and the disorder increases during the reaction. On the other hand, the value of the free enthalpy is negative, which means that the sorption process is spontaneous. The phosphonated hyper-branched polyethyleneimine composite have a high adsorption capacity and rate, and it is possible to reuse them in multiple adsorption/desorption cycles, making them competitive with other technologies currently in use. From all these results, it is concluded that PPEI may be a promising material for the immobilisation and sorption of samarium.

Author statement

All authors contributed to the conception and design of the study and read and approved the final manuscript: MILOUDI Wissam: Preparation of material; data collection and analysis; Investigation; Writing – original version. OUKEBDANE Khalil: Methodology; Writing – original version; Conceptualisation; Visualisation; Validation; Writing – revision and editing. ABDERAHIM Omar: Writing – original draft; Revision and editing; Interpretation of results. DIDI Mohammed Amine: Writing – original draft; revision and editing; Formal analysis; Supervision.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability statement

Data is contained within the article.

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