# A Novel Phosphonated Polyethyleneimine Composite for The Removal of Thorium(Iv) and Uranium(Vi) Ions from Aqueous Solutions: Kinetic, Isotherm, and Thermodynamic Studies

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**ABSTRACT:** *Hyperbranched polymers are one of the most promising, cost-effective and important materials sorbents for wastewater treatment. In this study, a newly synthesized hyperbranched polyethylene-methylene phosphine oxide (PEMPO) was characterized and applied for individual retrieval of Thorium (IV) and Uranium (VI). The impact of the different adsorption parameters, namely interactions contact time, the measure of pH, ionic force, metallic concentration, temperature additionally to metal adsorption kinetics, was studied using a batch adsorption process. Experimental results displayed that PEMPO had a bigger metal ion adsorption capacity for uranium (VI) than for thorium (IV) and $pH_{int}$ significantly affected the extraction yield, with an optimum yield at 5.8 for Urannium (VI) and 3.6 for Thorium (IV). Moreover, the sorption kinetics exhibited successful adherence to a pseudo $2^{nd}$ order. Langmuir's pattern isotherm was well fitted to the adsorption equilibrium measurements for both metals compared to Temkin, Freundlich, and Dubinin Radushkevich isotherms. The sorption capacities of Uranium (VI) and Thorium (IV) ions were 200.1 and 28.6 mg $g^{-1}$ respectively. Also, the addition of (KCl, KSCN) increased the extraction capacity, which showed the existence of a synergistic ionic force for the removal process. Thermodynamic analysis showed that the adsorption mechanism for both metals showed an endothermic nature and progressively became more spontaneous as the degree of freedom increased. The outcomes of desorption study indicated that the best eluents for the recovery of thorium and uranium ions were sulphuric acid and hydrochloric acid, respectively. After three cycles, the PEMPO resin can be regenerated for reuse, with a desorption efficiency still above 85%. These results concluded that PEMPO could potentially be applied for the extraction of metals from water.*

**KEYWORDS:** *Actinide; Hyperbranched phosphonated polyethylenimine; Isotherm, Kinetic; Thorium(IV); Uranium(VI).*

**INTRODUCTION**

Mineral resources are essential for energy production and manufacturing industries, and their development is therefore a strategic issue for nuclear industry development. The difficulty is particularly acute where resources are not rich enough to justify conventional processes [1, 2]. These minerals, such as uranium and thorium, are non-renewable, have been consumed extensively in recent times worldwide and some are being depleted [3]. To ensure their availability in the future, more efficient and less costly extraction and recovery methods need to be developed [4] as these substances are commonly used in various industries and are often associated with rare earths, leading to mining difficulties and, among other things, numerous contaminations [4, 5]. Furthermore, these nuclear industrial activities generate very diverse and complex wastewater containing pollutants that can have dangerous consequences for humans and ecosystems [2, 6, 7]. Because of their high toxicity, exposure to these radioactive metals is a problem for human health and environmental contamination, and it is therefore necessary to eliminate them from the ecosystem [8]. Therefore, finding a way to treat water contaminated with metals, including actinides has taken on a major environmental challenge. Generally, and in wastewater metal ions able to be removed by chemical, physical, and biological ways such as precipitation, flocculation, adsorption, coagulation, electrochemical techniques and technical membrane [2, 4, 9]. A lot of research has been conducted on the removal of radioactive ions, such as actinides (thorium and uranium), from effluents [10-13]. However, most of these techniques have disadvantages in terms of cost and technical constraints related to the long extraction time, low selectivity and large quantities of hazardous chemicals used [8, 14]. Of all these techniques, adsorption is the most cost-effective in terms of technical performance, practicability and environmental safety [2, 6].

Polymers are one of the most effective and widely used of the many available methods for removing metal ions. Polyethyleneimine (PEI), a polyamine, appears to be a better candidate for actinide adsorption, but cannot be used directly as it is water-soluble [15, 16]. It is renowned for its metal coordination properties and in its cross-linked form has applications ranging from medicine to wastewater treatment and trace metal recovery [17, 18]. Recently, the preparation of new hyper-branched composites with mixed donor atoms (N, O, P, S) have taken a particular interest because they display high-performance metal selectivity [18-20]. These chelating polymers are founded on the Lewis acid-base principle, where, the chelating group can be considered like a Lewis base, however, the metal ions as Lewis-acids [21, 22]. One such material is an interesting resin, phosphonated polyethyleneimine, which has a significant quantity of secondary, ternary amines, and (P=O) groups [19-21].

This study focused on the synthesis of a chelating insoluble polymer for use as a sorbent to remove metal pollution. Therefore, the objective was the synthesis of a new hyper-branched material, polyethylene methylene phosphine oxide (PEMPO), which was prepared from polyethyleneimine by reaction with tri(hydroxymethyl)phosphine. Infrared Spectroscopy (FTIR) was employed to characterize it, Scanning Electron Microscopy (SEM), elemental analysis, Thermogravimetric Analysis (TGA), and the (BET) Brunauer Emmett Teller surface analyses. In addition, the performance of this sorbent for extracting Thorium (IV) and Uranium (VI) ions in acetate and nitrate media respectively was evaluated. For this purpose, different factors on the batch adsorption such as stirring speed, the kinetics, pH, initial metal's concentration and the thermal conditions were studied and improved. The results obtained allowed the identification of the most appropriate adsorption isotherm models such as Langmuir, Freundlich, Temkin and D/R and kinetic models (pseudo 1$^{st}$ and pseudo 2$^{nd}$ order and the phenomenon of intraparticle diffusion. Thermodynamic parameters were calculated for each metallic ion.

Further studies were also conducted on the regeneration of the phosphonated polyethyleneimine composite for reuse.

## EXPERIMENTAL SECTION

### Reagents

Hyperbranched phosphonated polyethyleneimine is an organophosphorus extractant based on polyethyleneimine (PEI) (Lupasol WF marketed by BASF) which has been utilized during the extraction process of two actinides, Thorium (IV) and Uranium (VI), for which two salts have been used: Uranyl acetate $UO_2(CH_3COO)_2.2H_2O$, from Merck and thorium nitrate Th $(NO_3)_4.4H_2O$, from Fluka. Chemical structure of the branched PEI was presented in Fig. 1. The initial pH levels of the sample solutions were modified using dilute $(HNO_3)$ and (NaOH) solutions produced by Sigma-Aldrich. Sodium chloride NaCl (Panreac), potassium chloride KCl, potassium cyanide KCN, potassium thiocyanate KSCN (Prolabo), sodium sulphate $Na_2SO_4$ (Fluka) were applied to study the effect of salt. For desorption, three acids were used: hydrochloric acid, HCl, 37% (Organics), nitric acid $HNO_3$ (Cheminova) and sulphuric acid $H_2SO_4$, 95%, (Fluka). The two actinides Uranium (VI) and Thorium (IV) were analysed by UV-Visible using the complexing agent Arzenazo (III) (M= 776.36 g mol$^{-1}$) supplied by Sigma-Aldrich. It was prepared in absolute ethanol (Riedel de Haen). During this study, the various chemical solutions utilized were obtained using a commercial chemical reagents and deionized water.
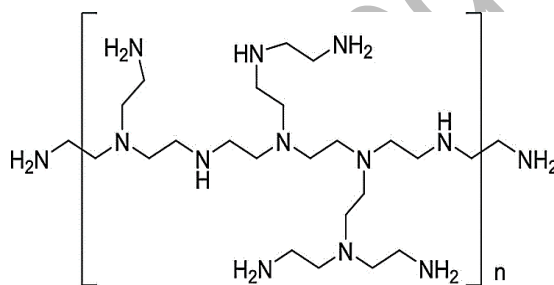


***Fig. 1: Structure of branched polyethyleneimine (PEI).***

### Apparatus

The sorption experiments were performed using a multi-station magnetic stirrer (WiseStir). The magnetic stirrer (Kika Werke TC-2) was exceptionally used utilizing a controller's temperature to explore the temperature effect. Measurements of pH were Executed using a potentiometer with a collective pH electrode (AD1030, Adwa). The aqueous solutions containing the two metals Thorium and Uranium were analysed with a UV-visible spectrophotometer (Perkin-Elmer, Lambda 800). The morphology of the PEMPO material was characterized using a HITACHI SEM scanning electron microscope (TM-1000). Nitrogen adsorption desorption experiments were performed at 77 K to establish their exposed area and pore dimension distribution according to the BJH model using a Micromeritics analyser (BET, 3 Flex Version 5.00). The recording of IR spectra was conducted using a Perkin-Elmer FTIR 1000 spectrometer on KBr disks between 4000-400 cm$^{-1}$. The Analys Thermogravimetric recorded of the samples was carried out using a high-resolution TGA (T.A. Instruments Q Series Q 600 SDT) from 33 to 700 °C under heating velocity of 5 ° C min$^{-1}$ under a rate of flow of 60 ml min$^{-1}$ of nitrogen atmosphere. Microanalysis was performed on the ThermoQuest NA 2500 automatic elemental analyser (C, H, N and P) (ThermoFinnigan). All solid samples were dried at 60 °C before analysis.

### Synthesis of the PEMPO resin

Polyethylenimine functionalized by methylene phosphine oxide group resin "PEMPO" was developed to remove metal ions, due to phosphine oxide's high affinity for metal ions [19, 20, 23]. Tri(hydroxymethyl)phosphine, which is unstable and highly oxidisable, is therefore prepared just before the reaction from tetra(hydroxymethyl)phosphonium chloride salt according to the literature [24]. Tri(hydroxymethyl) phosphine reacts with the functional groups of primary secondary amines of polyethyleneimine (PEI) leading to phosphines. This phosphine was oxidised to phosphine oxide by hydrogen peroxide. This wholly phosphonated "PEMPO" was synthesised in two steps (Fig. 2).

First, a solution was prepared in an argon atmosphere using 25 g of (tetra-hydroxyl-methyl) phosphonium chloride salt and 250 mL of cooled water (0 °C). Aqueous solution (100 mL) of 5,76 g of NaOH was then added under stirring (5 minutes). In the second step, under argon, fresh Tri(hydroxymethyl) phosphine solution was added to 29.2 g f polyethylenimine (Lupasol-WF) solubilized within a blend of a volume water equal to 100 mL and 400 mL volume of ethanol and was stirred and refluxed 2 hours. After, the mixture was mixed in air for 20 hours. The orange resin was washed with hydrogen peroxide (5%) to complete phosphine oxidation. The resulting phosphonated polyethyleneimine (PEMPO) resin was filtered then rinsed several times with bi-distilled water and was subsequently desiccated using a void. Finally, the PEMPO solid was pulverised again provide a yellowish powder. Samples were preconditioned at 80°C for 30 minutes to remove any trace of moisture.
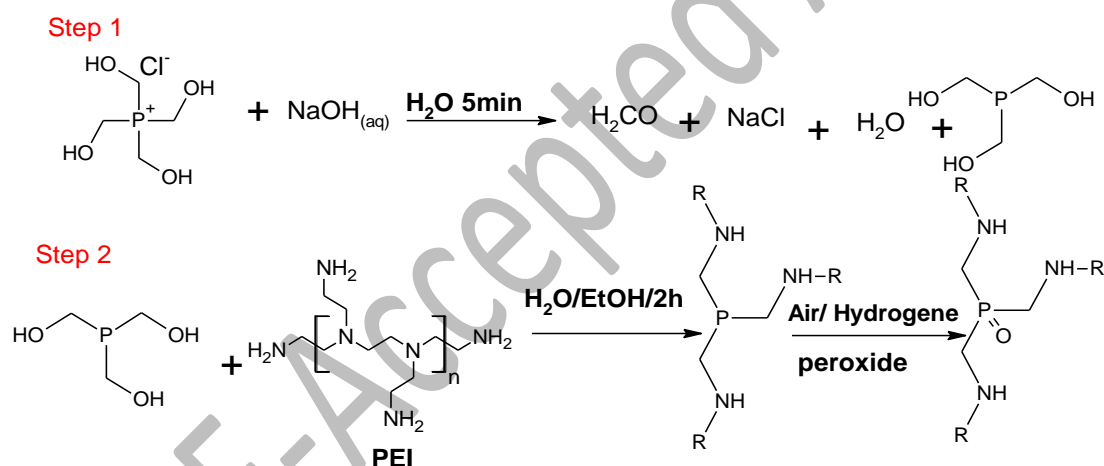


*Fig. 2: Poly Ethylene Methylene Phosphine Oxide resin synthesis.*

## Sorption and desorption studies

In a closed glass reactor, at ambient temperature (22 °C) were mixed and stirred, at a speed of 300 rpm, 0.030 g PEMPO in 5 mL volume of aqueous solutions containing Thorium or Uranium. Batch sorption was undertaken at a variety of experimental factors. To assure the dependability, accuracy, reliability and reproducibility of the data obtained, all the experiments batch were conducted out twice, and arithmetic mean are given for selected data. At equilibrium, solutions were filtered, the solid phase was regenerated for further use, while 100 µL of aqueous phase was added to 100 µl of $10^{-3}$ M Arzenazo III solution and 2 mL of buffer (pH = 2.1) for U(VI) analysis and 2 mL of HCl (9 N) solution for Th(IV) analysis. The thorium and uranium complexes of arsenazo-III are highly stable, making them ideal for analytical applications. Arzenazo III reacts with the metal ions Uranium (VI) and Thorium (IV) to form green colored complexes, the wavelength of which is evaluated at $\lambda_{max}$= 655nm and $\lambda_{max}$= 665nm respectively [20, 25].

Desorption method was performed after saturation of the hyper-branched composite materiel (loaded with metal ions), mixed with 5 mL of the acid solution ($H_2SO_4$, HCl, $HNO_3$, 1 mol $L^{-1}$ ), and under magnetic stirring equal to 300 rpm for 1 hour. After phase separation, aqueous phase was analysed using UV -Visible. The percentage of Uranium and Thorium ions extracted by the hyperbranched composite PEMPO resin was calculated according to equation 1:

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

In order to describe this extraction process, another analytical response involved is the quantity sorbed, given in (mg $g^{-1}$) and its equation is the following:

$$q_t = \frac{C_i - C_t}{w} \times V \qquad (2)$$

V: Volume of aqueous solution (5 mL);

w: Mass of the PEMPO used (0.030 g).

## RESULTS AND DISCUSSION

Functionalized hyperbranched materials are recognized as the highest efficient adsorbents for the water treatment discharges. They exhibit a high capacity for recovering metal ions effectively, it's due to reactive groups with nucleophilic atoms as N, P and O that have the ability to donate electrons to the ions, to form a polymeric metal coordination complex [26, 27]. The PEI ($-NH -CH_2 -CH_2 -NH-)_n$ is a hyper-branched cationic polymer with a high proportion of primary, secondary and tertiary amino groups, which can be highly reactive functions [15, 16]. Chemically, these PEI amino groups are active and can therefore be subject to a wide range of chemical changes, giving PEI relevant and appropriate physicochemical properties [19, 20, 27].

### *Characterization of PEMPO resin*

The fonctionalization of polyethyleneimine allows for enhanced sorption performance and selectivity [27]. In this study, polyethyleneimine was phosphonated by reaction with tri(hydroxymethyl)phosphine. The Fourier transform infrared spectroscopy was applied to describe the phosphonated resine based polyethyleneimine to affirm the inclusion of the P=O chelating group in the PEMPO materiel structure (Fig. 3). The amine on the resulting phosphonated "PEMPO", was validated by the appearance of absorption bands at 3362, 2952 and 1651 cm $^{-1}$ (N-H). The occurrence of the phosphonated group on PEMPO composite was corroborated by the apparition of absorptions at 1300 cm$^{-1}$ (C-P), 1042 (C-N), 1139 (P=O) and the loss of the bond of $NH_2$ at 2910 cm$^{-1}$ [20, 28-30].
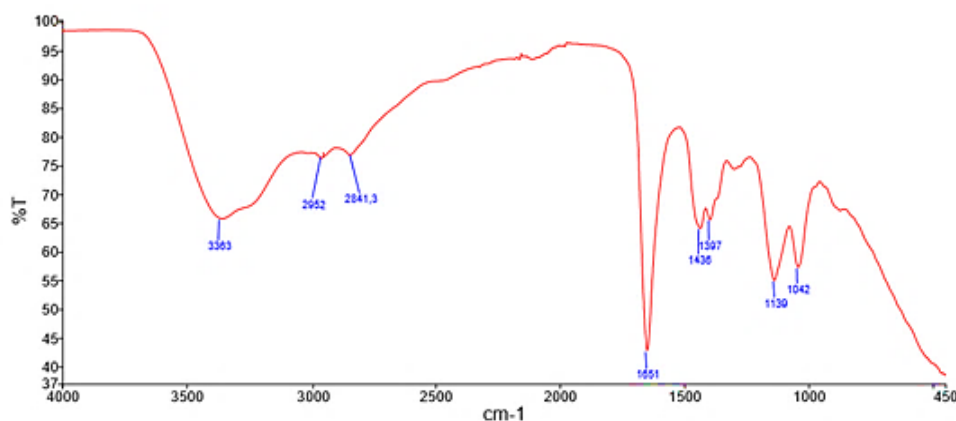
*Fig. 3: FTIR Spectra of phosphonated polyethylenimine resin (PEMPO).*

Experimental results for the elemental analysis (%) of the PEMPO resin was: N: 28.35; C: 52.17; ; P: 5.85 H: 10.58. On the basis of this analysis, the proposed monomer was $(C_{23}H_{58}N_{10}PO)_n$ and which presents the hypothetical elemental analysis N: 26.87; C: 52.97; P: 5.95; H: 11.13. The surface texture of the phosphonated polyethyleneimine resin was studied by the (SEM). Findings, presented in Fig. 4, revealed that the PEMPO material is composed of small irregular particles. The size of these particles was relatively few µm and the surface was irregularly rough. These results indicated that the PEMPO resin could potentially provide suitable sorption sites for metallic ions.

Table 1 represents the results of the BET surface analysis (Brunauer Emmett Teller) conducted using $N_2$ sorption-desorption isotherms, which were employed for analysis and represent the surface area, the volume and diameter pores

The mesopores were distributed over the range of 74-105 nm. BET area surface of PEMPO resin was 2.61 $m^2 . g^{-1}$, while the overall pore volume was established as 0.28 $cm^3 . g^{-1}$. To conclude, the pore structure of PEMPO composite can support the penetration, diffusion and adsorption of metal ions into the sorbent.
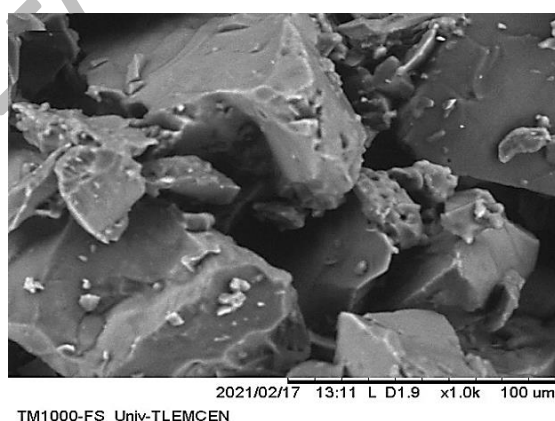


*Fig. 4: the PEMPO resin powder morphology.*

*Table 1: The main parameters obtained through  BET analysis of PEMPO resin.*

| Materials | Volume's Pore | Average  pore Size | BET  Surface Area |
|---|---|---|---|
| **PEMPO** | 0.28 $cm^3 . g^{-1}$ | 74 - 105 nm | 2.61 $m^2 . g^{-1}$ |

The analysis of thermogravimetric (TGA) and the derived thermogram (DTG) of the PEMPO composite are shown in Fig.5. The TGA curve shows the first step (below 160 °C) which denotes the reduction in water that is physically adsorbed (about 7% weight loss) can be attributed to the moisture contents of the sample and possibly impurities. Then, a set of undulations is reported between 160 and 500 °C Associated to valleys on the DTG curve (at 215.14, 318.62, 395.69, and 413.41 °C). These weight losses are linked to various modes of thermal degradation related to the decay of the amine groups of PEI (below 250 °C). In the range 250-500 °C, depolymerisation of PEI occurs, as well as char formation. The total weight reduction is nearly to 68.5%. On the whole, PEMPO composite as an adsorbent had good stability.
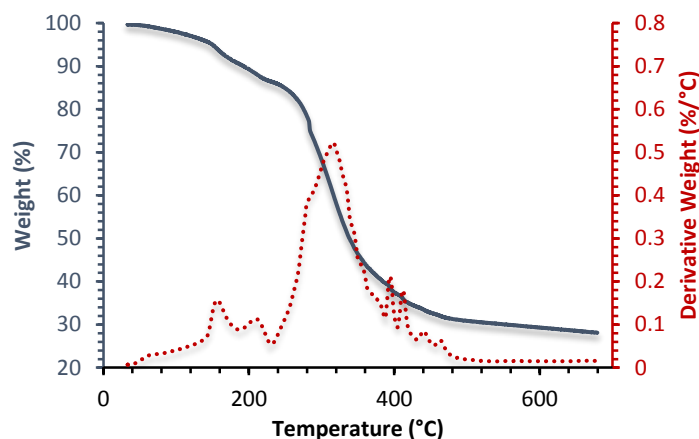


**Fig 5: TGA and DTG thermograms of PEMPO.**

*Impact of pH on the sorption process*

In general, the acidity of the adsorbed solution is a principal factor in sorption studies due to its importance in the characteristic existence of surface charges and the formation of ionic species present in the solution [2, 17, 31]. A study was performed to investigate this important effect on efficiency of metal ion extraction. Metal solutions with a concentration equal to $5.10^{-4}$M of Thorium and Uranium and ions were prepared at different values of pH from 1.0 to 8.0. As shown in Fig. 6, an improvement in extraction efficiency was revealed when the pH was increased.
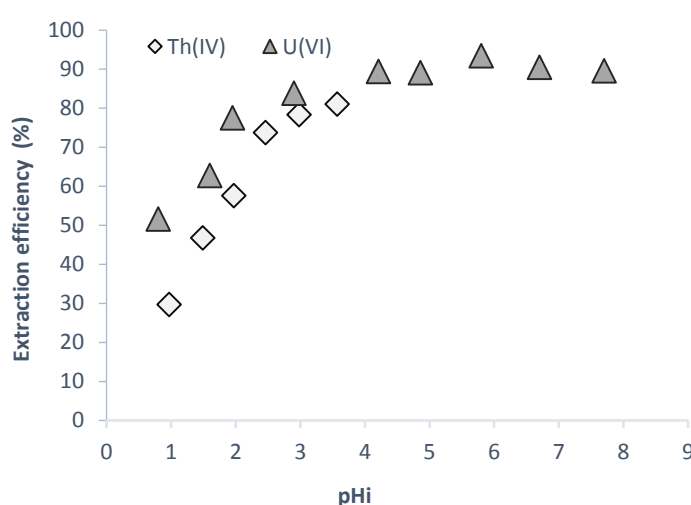


**Fig. 6: Extraction yield of Thorium and Uranium by PEMPO depending on pH.**
**(w = 0.030 g, V= 5 mL, Ø= 300 rpm, T=22 °C).**

The adsorbent surface shall be heavily involved with $H_3O^+$ at lower pH values, which prevents metal ions from reaching the functional surface. This could be due to the competition that exists in an acidic environment between $H^+$ ions and $UO_2^{+2}$ and $Th^{+4}$ ions. Furthermore, in an acid medium, the PEI chain structure is positively charged as a result of protonation of secondary amines along the backbone [17-19], which does not favor the adsorption of positively charged metal ions through electrostatic interaction. Thorium and Uranium ions sorption at pH higher than 8.0 [10, 32] and 4.0 [6, 33], respectively, was not considered because a precipitation occurred in the solution that indicated the metal's ion hydrolytic reaction, with the formation of the corresponding insoluble hydroxide. Furthermore, the adsorption mechanism between metal and PEMPO was dominated by chemical chelating rather than electrostatic attraction. Indeed, the mechanism of attachment of the metal ions to the PEMPO resin is based on the complexes formation with multi dentate N-donor ligands and hardsoft theory of Lewis's acidbase, in which the oxygen atom on the chelating group (-P=O) acts as a Lewis-base and donates electrons to metal ions, which are considered as Lewis's acids [27].

In order to understand the mechanisms of the adsorption process, FTIR spectra were registered to analyze the PEMPO composite before and after metal asorption. The characteristic peak at 1139 cm$^{-1}$ attributed to the vibration of the P=O group is shifted to 1147 and 1152 cm$^{-1}$ for the U-PEMPO and Th-PEMPO complex respectively, indicating the coordination reaction between the both metal and the P=O group [34, 35]. The characteristic peaks at 3312 and 1676 cm$^{-1}$ attributed to the vibration of the N-H group are also shifted but weakly, suggesting that the N-H group may be involved in the extraction mechanism [36]. Similarly, new weak bands were seen at 820 cm$^{-1}$ and 900 cm$^{-1}$ which can be attributed to Thorium (VI) and Uranium(VI) respectively. In addition, other fine bands between 500 and 850 cm$^{-1}$ can be assigned to the stretching vibration of nitrate and acetate ions in the extracted complex. All these data suggest that, in parallel with the displacement of certain characteristic groups, chelation occurs between the functional groups present on the PEMPO surface (-N, -NH, -NH$_2$ and P=O) and the positively charged U (VI) and Th (IV) ions. Based on these discussions, it can be deduced that electrostatic binding and chelation coexist throughout the sorption mechanism.

*Sorption kinetics*

The kinetic sorption study of metal ions was carried out at room temperature (22 °C) and Fig. 7 shows the variation of the sorption capacity as a function of contact time. Contact time ranged from 1 to 120 minutes. A escalation in the quantity of adsorbed metal ions was observed as a function of time. An equilibrium time equal to 40 minutes was considered for thorium (IV) and uranium (VI), with maximum sorption capacities of 18.29 and 13.19 mg g$^{-1}$ respectively.
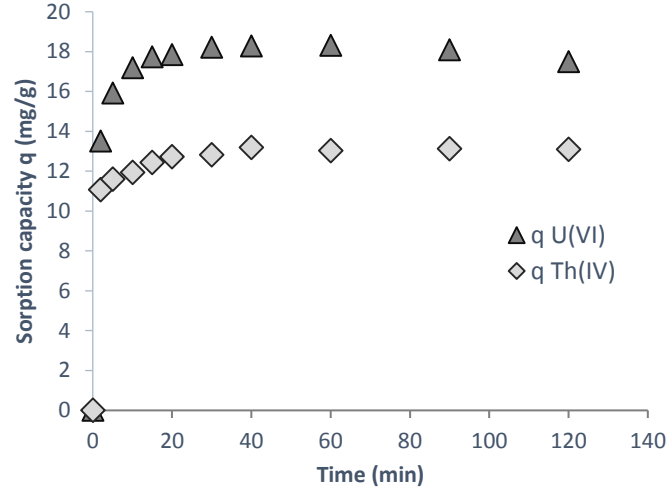
*Fig. 7: Sorption capacities of Th (IV) and U (VI) by PEMPO influenced by contact time*

Therefore, the curve can be devised into two steps. The first was from 0 to 15 min, which was considered as rapid adsorption because of the active sites [12-14]. The second step for both metals was considered as an equilibrium sorption-desorption stage, with the complete filling of the active sites [2]. The fast and efficient adsorption of metal by PEMPO was largely due to the porosity and number of active sites on the surface of the PEMPO resin that could effectively capture these ions. The optimum contact time is selected as 40 min for continued experiments.

In addition, the study of kinetic models allows a better interpretation of the mechanism and strength of metal ion sorption. Consequently, the pseudo 1st order and pseud 2nd order and diffusion models were studied in this research [2, 14]. The pseudo 1st order model proposed by Lagergren and used to explain the sorption kinetics of organic and inorganic solutes [37]. It is founded on the linear relationship between the quantities of solute bonding to the surface of the sorbent depending on time. The linear form is expressed in equations 3:

$$Ln(q_e - q_t) = Lnq_e - K_1 \qquad\qquad (3)$$

Ho and Coll presented the pseudo 2nd order model, and it is expressed in equation 4 [38]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad\qquad (4)$$

The model of intraparticle diffusion developed by Weber-Morris was used to examine the metal ions diffusion within pores [39]. The linear expression is presented in equation 5:

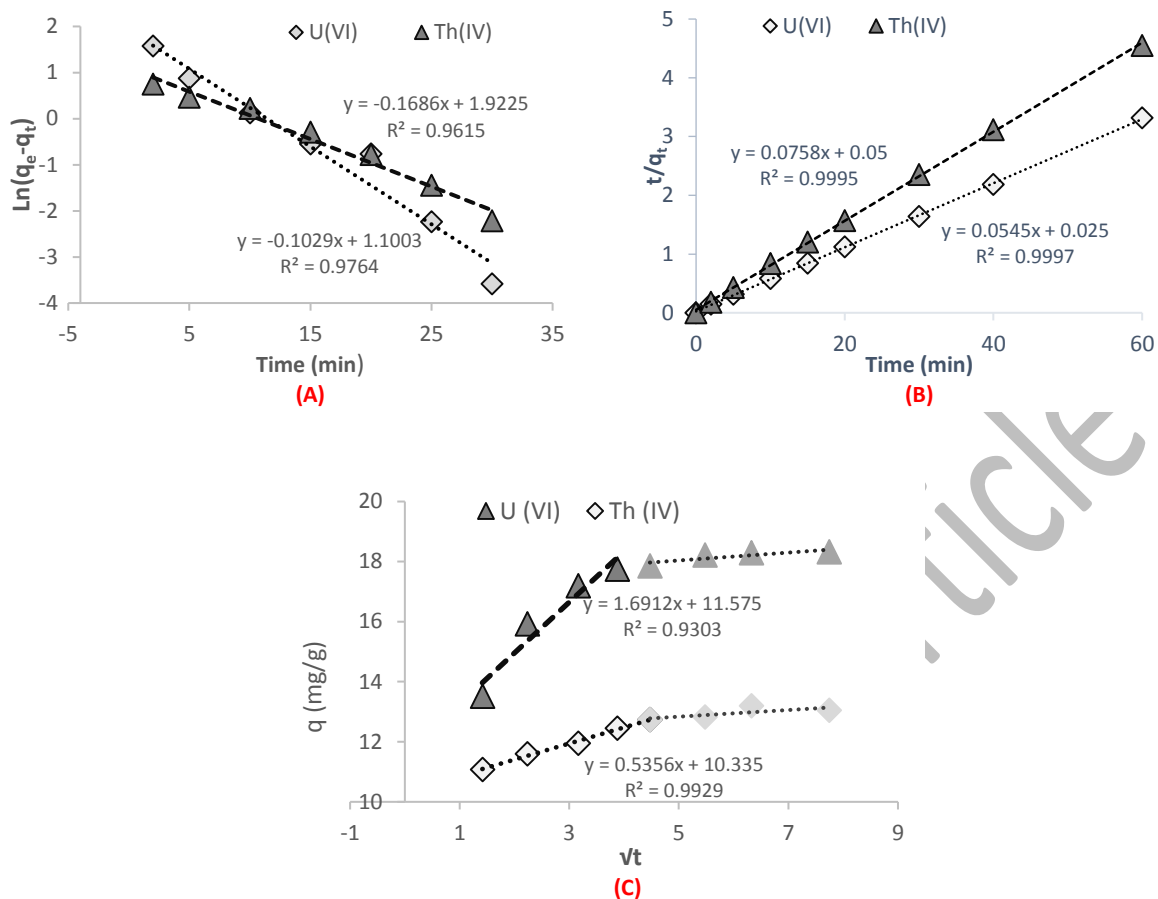$$q_t = K_3 \times \sqrt{t} \qquad\qquad (5)$$

**Fig. 8: Kinetic sorption data of Uranium and Thorium on PEMPO resin; (A) The linear 1st order kinetic (B) The linear 2nd order kinetic, and (C) Intra-particular adsorption kinetics.**

**Table 2: comparing kinetic models for the sorption of Uranium and Thorium on PEMPO resin.**

| Metal | $q_e$ (mg g$^{-1}$) | Pseudo-first order | Pseudo-second order | Intra-particle diffusion |
|-------|------|--------------------|---------------------|--------------------------|
| U(VI) | 18.31 | $R^2$ =0.9764<br>$K_1$ = 0.168<br>$q_e$ = 6.82 mg g$^{-1}$ | $R^2$ =0.9997<br>$K_2$=0.087<br>$q_e$=18.86 mg g$^{-1}$ | $R^2$ = 0.9303<br>$K_3$ =1.6912<br>S =11.575 |
| Th(IV) | 13.19 | $R^2$ =0.9615<br>$K_1$ = 0.083<br>$q_e$ = 2.54 mg/g | $R^2$ =0.9995<br>$K_2$ = 0.093<br>$q_e$ = 13,33 mg/g | $R^2$ = 0.9929<br>$K_3$ =0.5356<br>S =10.335 |

According to the findings acquired in Figure 8 and Table 2 and after comparing the correlation coefficients and the theoretical and experimental sorption quantities, it was revealed that the pseudo 2nd order provided a superior fit to the experimental data compared to the 1st order model, implying that the adsorption occurs via a chemisorption process. Following curve of Fig. 8c, the curve did not intersect the origin, this implies that the intra-particle diffusion was not the rate limiting step of the sorption process of Uranium and Thorium ions [14, 40]. Also, it was apparent that there were two stages. The first stage represented the intra-particle diffusion through the macropores, the second one concerned the diffusion of metals ions into the micropores [4, 12-14]. These findings indicate that the adsorption of Thorium and Uranium on PEMPO requires complicated mechanisms, including intraparticle diffusion and chemisorption processes.

***Adsorption isotherms***

The effect of the change of the quantity of adsorbed ions Thorium and Uranium according to their initial concentrations, was investigated, upon which several experiments have been achieved at different concentrations.

In Figure 9 the adsorption capacity of the tow ions increases proportionally with the metal concentration, which confirms a good efficiency of this organophosphorus material for the extraction of these ions. The mechanism of adsorbent-adsorbate interactions was revealed by a study of adsorption isotherms.
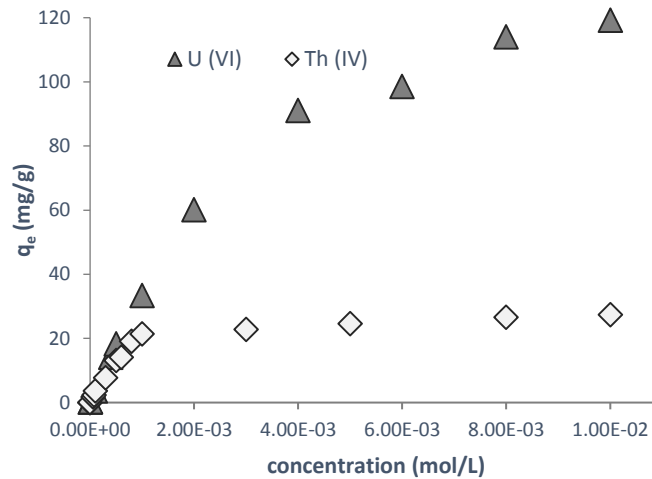


***Fig. 9: Uranium and Thorium uptake by PEMPO resin varied by concentration***
***(w = 0.03 g, V= 5 mL, pH(U) = 5.8, pH(Th) = 3.6, Ø = 300 rpm, T = 22 °C).***

The models: Freundlich, Langmuir, Timken and Dubinin-Radushkevich were adopted to illustrate equilibrium between thorium and uranium ions and the hyperbranched PEMPO resin. The Langmuir model is a model used in liquid-solid systems [41], which relies on the assumption that phases and interfaces of homogeneous materials demonstrate ideal characteristics with adsorption sites identical and energy levels [2, 9]. It has been largely used to describe the monolayer and it is defined by equation 6:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (6)$$

Freundlich model is a contradictory model to the Langmuir model because it is adopted to a multi-layer sorption [42]. Its mathematical equation is expressed by expression 7:

$$Lnq_e = Lnk_F + nLnC_e \qquad (7)$$

Temkin model indicates that the heat intensity of sorption changes depending on the degree of coverage $\theta$; the linear decay can be translated, on a consistent surface, into the following interactions between species sorbed on a non-uniform surface [43]. Equation for this model is expressed in equation 8:

$$\theta = \frac{RT}{A_t} Ln\, K_t\, C_e \qquad (8)$$

Dubinin-Radushkevish founded on the principle that the sorption potential changes, and that the free enthalpy has a relationship with the degree of pore filling [44]. Its equation is expressed as equation 9:

$$Lnq_e = Lnq_{mDR} - \left(\frac{R.T}{E}\right)^2 . \left(\ln\left(\frac{C_s}{C_e}\right)^2\right) \qquad (9)$$

According to the results presented in Table 3, and from the comparison of experimental and theoretical values, it appeared that the model of Langmuir proved to be more appropriate for the sorption data than the others, revealing a monolayer adsorption process of thorium and uranium on PEMPO resin. The maximal monolayer sorption capacities obtained were 200.08 and 28.57 mg g⁻¹ of uranium and thorium respectively.

*Table 3: Parameters of isothermal models of Thorium and Uranium adsorption on PEMPO.*

| Metal | Langmuir | Freundlich | D-R | Timken |
|-------|----------|------------|-----|--------|
| U(VI) | $R^2 = 0.9977$ | $R^2 = 0.9819$ | $R^2 = 0.9813$ | $R^2 = 0.9888$ |
|  | $K_L = 0.862$ | $K_F = 25.660$ | $\beta$ (mol·J⁻¹)² = 0.0091 | Kt (L mg⁻¹) = 4.879 |
|  | $Q_m$ =200.08 mg g⁻¹ | 1/n = 0.907 | E (KJ/moL) = 10.21 | At (KJ mol⁻¹) = 12.25 |
| Th(IV) | $R^2 = 0.9911$ | $R^2 = 0.8875$ | $R^2 = 0,9234$ | $R^2 = 0.9444$ |
|  | $K_L = 6.944$ | $K_F = 19.110$ | $\beta$ (mol·J⁻¹)² = 0.0066 | Kt (L mg⁻¹) = 3.6038 |
|  | $Q_m$ = 28.57 mg g⁻¹ | 1/n = 0.625 | E (KJ/moL) = 13.61 | At (KJ mol⁻¹) = 12.35 |

The favourability of PEMPO resin grains as a metal ion adsorption material can be obtained by determining the separation factor RL defined as follows [2, 12, 14]:

$$R_L = \frac{1}{1 + b\,C_0} \qquad (10)$$

For all tested concentrations of Thorium and Uranium, $0.02 < R_L < 0.09$ which proved that PEMPO resin was a favourable adsorbent. The model of Dubinin-Radushkevich is related to the sorption energy EDR (kJ /mol), was determinate founded on the equation [7, 11]:

$$E_{DR} = \frac{1}{\sqrt{\beta}} \qquad (11)$$

The sorption mechanism was suggested using the EDR values resulting using the isotherms. In light of this estimate, interaction between the adsorbent and the metal could be chemical, through ion exchange or complexation, or physical means Van der Waals forces [7-9]. When the EDR value is below 8 k J /mol, adsorption becomes physical, and is chemical if the EDR is above 8 kJ/mol [7-9]. Furthermore, the EDR values, which were calculated on the basis of the D-R model, equal to 10.21 and 13.61 kJ/mol for Uranium and Thorium respectively (> 8 kJ/mol), revealed that the sorption was relied on a chemisorption mechanism.

### *The impact of ionic strength and the nature of water*

Monitoring the effect of ionic strength is important for practical applications of the adsorption process, since most effluents, including wastewater, frequently contain considerable quantities of ionic substances, which could therefore have an impact on the sorption process [4, 20]. Consequently, it is very important to explore the influence of ions addition on sorption of thorium and uranium by PEMPO. A variety of sodium, potassium and organic salts, at 1 mol/L, were added to the water component.

From Fig. 10, it appeared that the extraction yields reached maximum values of 95% when KCl, KSCN and NaNO₂ were added to the Uranium's solution (synergistic effect), same thing with thorium's solution except the addition of NaNO₂, which have a negative effect on the sorption process. However, the addition of the organic salts CH₃COONa and NaCl show less important effect on sorption, and the lowest yields when Na₂S₂O₄ and Na₂SO₄ was added (antagonistic effect).

A change in ionic force through the introduction of an electrolyte affects the sorption at least two ways [29]: (i) the potential difference at the interface and consequently the activity of ions in the electrolyte and

adsorption; (ii) the competition of electrolyte ions and adsorbing anions for sorption sites. The cations can be adsorbed onto the active sites of the sorbent, minimising and preventing the access of positively charged uranium and thorium ions due to repulsive forces. This can be attributed to the affinity of these cations and anions for the polymer's adsorption surface compared to uranium and thorium ions (competitions). In addition, the anions accumulate near the surface, resulting a localised overall negatively charged potential that attracts the positive charge of the metal to the area near the surface, thus boosting the adsorption effect. Conversely, the anion can also strengthen the adsorption capacity by associating with the metal's species, thus diminishing the repelling effect between nearby metal molecules sorbed on the surface. This feature enables the PEMPO composite to adsorb more positive uranium and thorium ions, as it reduces the repulsive forces between the surface and these ions, as well as the repulsive forces between the ions themselves.
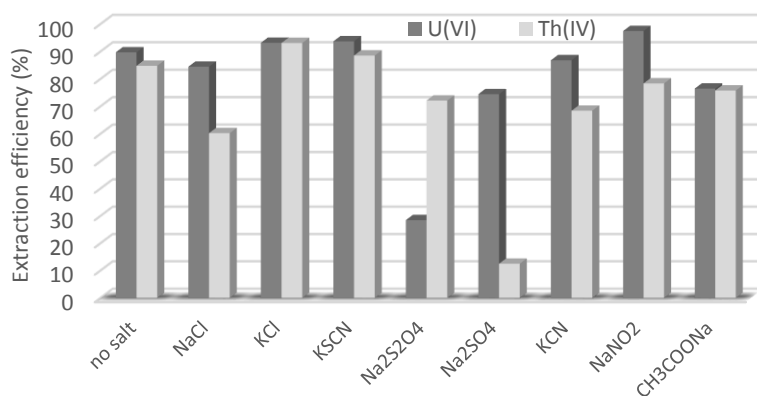


**Fig. 10: Salts addition effect on uranium and thorium sorption by PEMPO resin**
**([Salt] = 1.0  mol /L, w = 0.03  g,  Ø = 300 rpm, T = 22 • C)**

In addition, the batch sorption technique was also evaluated by analysing four different water matrices: the distilled, mineral, tap, the well, and finally, sea water (SW). The results of the analyses for three replicates (n =3) are presented in Fig. 11.
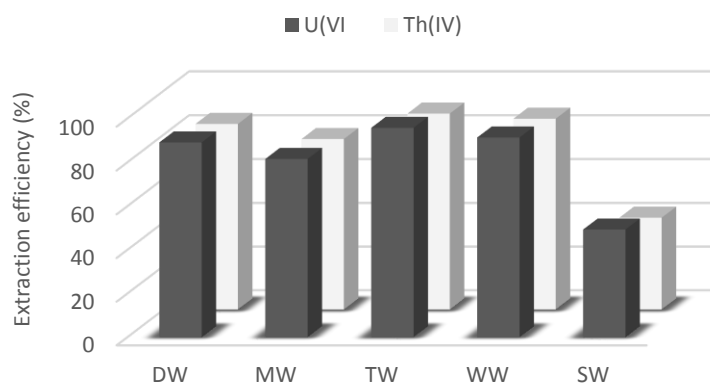


**Fig 11: The water type's effect  on the extraction of Uranium  and Thorium.**
**(Ø = 300 rpm, w = 0.03 g,  T = 22 • C).**

For these water matrices, the describe methodology was applied to samples containing known amounts ($5.10^{-4}$ M) of Thorium and Uranium. However, the solution's pH was adapted to the ideal pH value for the sorption of metal ions. This analytical procedure is necessary to evaluate the potential of PEMPO extraction of metals ions from different kind of water matrices. The results showed a fairly good recovery, above 80% in the cases of DW, MD, TW and WW; no significant interference has been found (deviations in the analytical signal of ±10). However, in the case of seawater, very low values were found (between 40 and 50%).

### *Adsorption Thermodynamics*

In addition, in order to confirm the impact of temperature on recovery efficacy, multiple experiments were conducted over a temperature range from 285 K to 320 K. various thermodynamic properties, were determined by studying the effect of temperature. These parameters were obtained based on the given formulas [6-9]:

$$\Delta G° = -RTLn(K°eq) \tag{12}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{13}$$

$$Ln(K°eq) = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{14}$$

Where:

The constant at equilibrium $K°_{eq}$ obtained from the best-fit isotherm model is not directly applicable as a dimensionless parameter for thermodynamic calculations; it is necessary to be convert ito a dimensionless parameter, as defined by Lima et al. [45-48].

As previously mentioned, the previous study of adsorption properties showed that the data at equilibrium corresponded good agreement with Langmuir isotherms, the correlation coefficient being greater than 0.99. Adsorption constant $K_L$ obtained through curve fitting using the adsorption isotherm model represent an empirical parameter, that represents a measurable property quantity and can be quantified in units (L mg$^{-1}$). In this regard, it is advisable to employ equation 15 as described below:

$$K°e = \frac{(1000 . KL . Mw). [M]°}{\gamma} \tag{15}$$

. A plot of $ln(K°_{eq})$ versus $(1/T)$ yields a linear relationship, as described by equations (13) and (14), by fixing temperature, the values $\Delta H°$ and $\Delta S°$ can be determined by the gradient (-$\Delta H°$/ R) and intersection ($\Delta S°$/ R) of the graph (Fig.12).
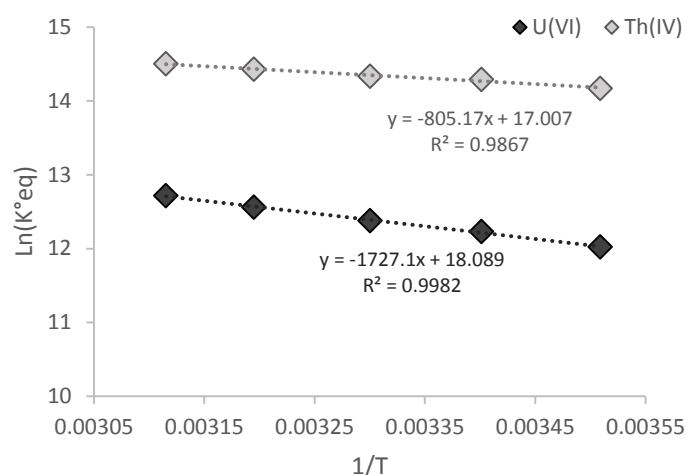
***Fig. 12: Variation of the ln K depending on the reciprocal of temperature 1/T***
***(w = 0.03 g, pH(U) =5.8, pH(Th) =3.6, V = 5 mL, Ø = 300 rpm.).***

While the equation of Van't Hoff that was employed to study the spontaneity and energy required in the interactions of adsorbent adsorbate, the ($\Delta$H) energy, ($\Delta$S) energy and free enthalpy values ($\Delta$G) were evaluated. The results are illustrated in Table 4. The positive enthalpy result suggest that the reaction is endothermic as it is driven by the enhanced mobility of metal ions and their affinity to adsorb onto the sorbent surface, additionally, the binding sites exhibit elevated activity as the temperature rises, further contributing to the overall process. However, the negatives values of the free enthalpy allow us to conclude that the sorption of ions by the PEMPO resin is spontaneous under these experimental conditions. These positive $\Delta$S° values could be explained by an augmentation in the stochastic nature of the solid solution interface [2, 6]. This phenomenon can be ascribed to the dehydration of metal ions during the sorption phenomenon [49].

***Table 4: The thermodynamic properties associated with the sorption of thorium and uranium on PEMPO resin.***

| Metal | $\Delta$H° (kJ/ mol) | | $\Delta$S° (J mol/˚K) | $\Delta$G° (kJ/mol) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | T (K) | 285 | 293 | 303 | 313 | 320 |
| U (VI) | 14.36 | | 150.39 | | -28.49 | -29.90 | -31.19 | -32.69 | -33.94 |
| Th (IV) | 6.69 | | 141.40 | | -33.58 | -34.94 | -36.12 | -37.55 | -38.71 |

***Comparison of adsorption capacity Q_max of various sorbents***

For the evaluation of the potential of the synthesized PEMPO sorbent, the adsorption capacity was compared to other types of sorbents that were studied for the retention of uranium and Thorium in a water- based solution, as shown in Table 5.

*Table 5: Comparing the sorption of uranium and thorium ions using different sorbents.*

| Sorbents | Uranium (VI) | | | Thorium (IV) | | | REF |
|---|---|---|---|---|---|---|---|
| | $q_{max}$ (mg g$^{-1}$) | Time (min) | pH | $q_{max}$ (mg g$^{-1}$) | time | pH | |
| Carminic acid -XAD- 16 resin | 188.8 | 120 | 5.0 | 192.1 | 120 | 5.0 | [2] |
| Olive cake | 17.0 | 40 | 4.0 | 15.0 | 40 | 5.0 | [4] |
| Hydrated manganese dioxide HMO | 55.1 | 360 | 3.5 | 218.3 | 360 | 5.0 | [5] |
| Hydroxyquinoline Immobilized Bentonite | 63.9 | 15 | 4.0 | 65.4 | 8 | 3.0 | [6] |
| Activated carbon from olive stones | 57.8 | 5 | 6.0 | 21.3 | 30 | 4.0 | [7] |
| Insolubilized humic acid from Azraq soil Jordan | 18.1 | 900 | 3.0 | 25.3 | 900 | 3.0 | [9] |
| Crystalline nano tin oxide nanoparticles | 66.6 | 200 | 6.0 | 62.5 | 200 | 6.0 | [10] |
| Insolubilized humic acid from Ajloun soil Jordan | 16.9 | 360 | 3.0 | 20.0 | 360 | 3.0 | [11] |
| Mannich type resin | 5.4 | 90 | 3.5 | 2.3 | 90 | 3.5 | [12] |
| Glycidyl methacrylate chelating resin (GMA) | 56.0 | 180 | 3.5 | 83.6 | 90 | 4.5 | [13] |
| Biochar derived from Salvadora persica branches | 85.7 | 120 | 3.0 | 84.9 | 120 | 3.0 | [14] |
| humic acid-silica gel composite (HASi) | 33.2 | 180 | 3.0 | 32.3 | 180 | 2.5 | [50] |
| Diatomite-hexadecyltrimethylammonium | 26.1 | 1440 | 4.0 | 30.3 | 1440 | 3 | [51] |
| Acid activated Na-bentonite | 11.8 | 120 | 4.2 | 26.2 | 900 | 2.5 | [52, 53] |
| Alizarin red S-impregnated | 20.2 | 10 | 3.5 | 18.2 | 10 | 4.5 | [54] |
| Chelating resin (GMA/DVB/PEHA) | 114.0 | 90 | 3.5 | 78.0 | 15 | 4.5 | [55] |
| Humic Acid Silica Gel | 28.0 | 180 | 3.0 | 31.3 | 180 | 3.0 | [56] |
| Salvadora Persica branches biomass | 24.8 | 120 | 4.0 | 24.8 | 120 | 4.0 | [57] |
| Hyperbranched PEMPO resin | **200.1** | 40 | 5.8 | **28.6** | 40 | 3.6 | *This work* |

The most crucial parameters influencing the effectiveness of an adsorbent are adsorption capacity (qmax), pH and equilibrium time. A comparison of these characteristics with respect to the Thorium and Uranium ions presented by different adsorbents reveals that the PEMPO resin was significantly more effective than most adsorbents (Table 5). This indicated that the material had exceptional adsorption capacity and application potential for metal ions.

*Desorption process*

The regeneration process of the sorbent is essential to improve feasibility and cost-efficiency, as it decreases expenses associated with waste disposal costs and environmental impacts [18, 58, 59]. The regeneration of the PEMPO material was carried out using three different acids HCl, $H_2SO_4$ and $HNO_3$ at a specific concentration equal to 1 mol/L to study the desorption phenomenon. The mixtures underwent stirring for a duration of 1 hour, followed by filtration and the material underwent a washing process using distilled water and subsequently dehydrated before reuse. According to the results obtained (Fig. 13), the maximum elution percentages were obtained with $H_2SO_4$ at 94.77% for Uranium (VI) and HCl at 98.80 % for Thorium (IV), respectively.
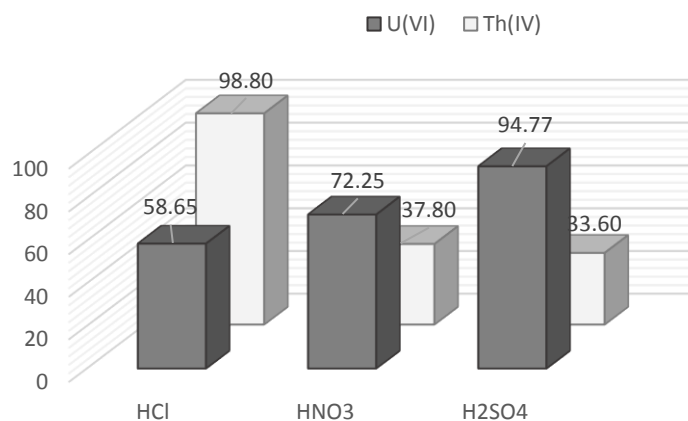
**Fig. 13: Recovery rates of different solvents for desorption of Uranium and Thorium.**
**V = 5 mL, w = 0.030 g, Ø = 300 rpm, T= 22 ° C.**

In order to ascertain the number of uses of this resin, extraction and de-extraction cycles were carried out. The adsorption-desorption experiment with HCl (1 M) for Thorium (IV) and $H_2SO_4$ ( 1 M) for Uranium (VI) was repeated for five cycles. Generally, the results confirmed that PEMPO resin could be regenerated for re-use and after third cycles, and that desorption efficiency could still be above 85%. The experimental result revealed that the synthesized hyper-branched material could be used as an cost-effective and potential sorbent in the process of treating metal contaminated aqueous media.

**CONCLUSION**

According to this study, the newly synthesized organophosphorus extractant PEMPO appeared to be a powerful sorbent for elimination of thorium and uranium ions from water. This material presented high sorption capacity, fast kinetics and high regeneration properties. The study exploring the impact of variation in $pH_{int}$ revealed a significant influence on the extraction yield by reaching 93.5% at pH 5.8 and 86.0% at pH 3.6 for Uranium and Thorium, respectively. The time needed to reach equilibrium for the sorption of Thorium and Uranium ions was determinate after 40 min. The obtained results from the isotherms and kinetic models showed that this sorption process took place in a monolayer for each of metal ions. The highest sorption capacities were 200.1 mg/g for Uranium and 26.46 mg/g for Thorium. The results of the thermodynamic computations demonstrated the endothermic and spontaneity properties that followed positive entropy and enthalpy values and negative free energy values. The addition of (KCl, KSCN) increased the extraction capacity, which showed the existence of an ionic force. The desorption study indicated that the best eluents for the eradication of uranium and thorium were sulfuric acid and hydrochloride acid, respectively. The mechanism of attachment of the metal to the polymer is founded on electrostatic interactions and hard-soft Lewis acid-base theory with a pronounced interaction among the oxygen in the P=O functional group and metal which caused a better adsorption efficiency. The sorption capacity was compared with the literature concluding that hyper-branched polyethylene methylene phosphine oxide (PEMPO) could be an interesting material for sorbing thorium and uranium from solutions in an aqueous medium.

**Highlights**

- The novel synthesized adsorbent was characterized by FTIR, SEM and elemental analysis.

- The PEMPO sorption kinetics and sorption isotherms were used to explain the sorption process.

- The PEMPO sorption affinity of metal ions was U(VI) >> Th(IV).

- Bifunctional sorbents (i.e. N and P=O) contribute to the retention of metal ions.

- Phosphonated polyethyleneimine (PEMPO) proved to have great potential for the efficient removal of U(VI) and Th(IV) ions.

## DECLARATIONS

**Ethical Approval**

Not applicable

**Competing interests**

The authors have no competing interests to declare that are relevant to the content of this article.

**Funding**

Not applicable

**Availability of data and materials**

The authors confirm that the data supporting the findings of this study are available within the article

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