

## Study of thorium retention using different functionalized resins

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### ABSTRACT

Thorium ( $\text{Th}^{4+}$ ), a naturally occurring radioactive element often co-existing with rare earth elements (REEs), poses significant environmental, radiological, and regulatory concerns during REE extraction but also presents potential recovery opportunities as a valuable by-product. Effective thorium removal and retention are therefore essential for sustainable REE purification processes and for ensuring safe radioactive waste management. This study investigates the thorium adsorption behaviour and kinetic characteristics of three functionally distinct ion exchange resins which is WA21j (a weak base anion exchange resin), PE-F (a fluoride-based chelating resin), and PM401 (an iminodiacetate-functionalized chelating resin). Batch adsorption experiments were conducted using a 10 ppm  $\text{Th}^{4+}$  solution and 0.5 M ammonium sulphate under controlled agitation and temperature conditions by using the agitation shaker to evaluate performance consistency. Thorium concentrations were quantified by inductively coupled plasma–optical emission spectroscopy (ICP-OES), while adsorption data were analysed using non-linear pseudo-first-order and pseudo-second-order kinetic models to determine the rate-controlling mechanisms. Among the tested resins, PE-F exhibited the highest thorium uptake and the strongest correlation with the pseudo-second-order model ( $R^2 = 0.9921$ ), confirming chemisorption as the dominant mechanism. PM401 showed comparable performance ( $R^2 = 0.9896$ ), attributed to multidentate chelation via iminodiacetate groups, whereas WA21j demonstrated weaker retention due to limited amine interaction. The results emphasize the critical role of functional group chemistry in determining adsorption efficiency and selectivity. These findings highlight the potential of fluoride- and iminodiacetate-based resins for thorium recovery, radioactive waste remediation, and REE purification, providing valuable guidance for future development of efficient and sustainable ion exchange systems.

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## 1. INTRODUCTION

Thorium ( $\text{Th}^{4+}$ ), often associated with rare earth elements (REEs) in minerals such as monazite and xenotime, poses environmental and regulatory challenges due to its radiotoxicity (Xu et al., 2021). Effective thorium separation is therefore critical for both REE purification and radioactive waste management.

The presence of thorium in waste streams poses long-term environmental risks, necessitating efficient remediation strategies (Lan et al., 2025). Adsorption using ion exchange and chelating resins has emerged as a promising method because of its selectivity, tunable functional groups, and cost-effectiveness (Li et al., 2011). Recent studies highlight advances in functionalized resins for actinide removal, yet direct comparisons across different resin chemistries remain limited (Zahakifar & Khanramaki, 2024).

This study addresses that gap by comparing three resins with distinct functionalities: WA21j (tertiary amine), PE-

F (fluoride ligands), and PM401 (iminodiacetate). Their contrasting binding mechanisms electrostatic attraction, hard base coordination, and multidentate chelation provide insights into the role of functional groups in thorium uptake. Kinetic modelling is also essential, as adsorption rate and mechanism determine practical feasibility. Applying pseudo-first-order and pseudo-second-order models enables mechanistic interpretation and guides optimization for large-scale separation processes.

The objective of this study is to evaluate the retention efficiency of thorium ( $\text{Th}^{4+}$ ) using three different functionalized resins, namely WA21J, PE-F, and PM401. In addition, the study aims to analyze the adsorption kinetics by applying both pseudo-first-order and pseudo-second-order models. Another important aspect is to determine the influence of the functional group chemistry on thorium binding behavior. Finally, this work also seeks to assess the potential application of these resins in rare earth purification and radioactive waste treatment.

## 2. MATERIALS AND METHODS

### 2.1. Material

All reagents used in this research were of analytical grade and were sourced from reputable chemical suppliers. The stock solutions of thorium were prepared by diluting standard thorium nitrate solutions in deionized water. The background electrolyte employed for ionic strength control was 0.5 M ammonium sulphate. The extractants used in other purification steps, such as perchloric acid (HClO<sub>4</sub>), boric acid (H<sub>3</sub>BO<sub>3</sub>), hydrofluoric acid (HF), tartaric acid (C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>), nitric acid (HNO<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and hydrochloric acid (HCl), were purchased from Sigma-Aldrich (USA), R&M Chemicals (Malaysia), and Merck (Malaysia).

### 2.2. Potential resins

The resins evaluated in this study were WA21j, PE-F, and PM401. These resins were chosen based on their functional group diversity and availability in commercial markets. WA21j was weak base anion exchange resin containing tertiary amine groups known for their affinity toward anionic complexes. PE-F was a chelating resin with fluoride ligands capable of forming strong coordination bonds with hard metal ions like thorium. PM401 contained iminodiacetate groups, which were known for their bidentate complexation capabilities and high affinity for multivalent metal ions. Each resin was pre-treated prior to use. Each resin was pre-treated prior to use by soaking in deionized water, followed by washing with 1 M HCl and 1 M NaOH to remove impurities and convert the resins into their operational ionic forms. Anion exchange resins were converted to the sulphate form, and cation exchangers to the sodium form. The pre-treatment procedure was based on that of (Gupta et al., 2010). Table 1 shows that physicochemical properties of potential resins. This preconditioning process was essential to ensure that all resins were in their active ionic states and free from residual contaminants that could interfere with thorium adsorption.

**Table 1:** Physicochemical properties of potential resins

Resin	Type	Functional group
WA21J	Weak base anion exchange	Tertiary amine
PE-F	Chelating	Fluoride
PM 401	Chelating	Iminodiacetic acid

### 2.3. Batch Method

Batch adsorption studies were conducted using 250 mL Erlenmeyer flasks containing 200 mL of 10 ppm Th<sup>4+</sup> solution and 1 g of pre-treated resin. The flasks were placed on an orbital shaker and agitated at 150 rpm for predetermined time intervals ranging from 5 to 360 minutes. Experiments were conducted at room temperature (25 ± 2°C). At the end

of each contact time, the solutions were filtered using 0.45 µm membrane filters, and the supernatant was collected for thorium analysis.

The thorium concentration in the filtrate was analysed using inductively coupled plasma-optical emission spectrophotometer (ICP-OES; PerkinElmer Optima 8300). Calibration standards were prepared using thorium nitrate solutions to ensure accuracy. Each experiment was performed in triplicate, and mean values with standard deviations were reported.

### 2.4. Kinetic study

The study of adsorption kinetics is essential in understanding the mechanism and efficiency of the adsorption process, particularly in determining how fast an adsorbate is removed from solution by an adsorbent. Kinetic models describe the rate at which adsorption occurs, and they provide insights into the possible mechanisms controlling the process, such as mass transfer, surface adsorption, or chemical interaction. The equations 1 (Azizian, 2004) and 2 (Ho & McKay, 1999) below represent the non-linear forms of the pseudo- first order and pseudo-second-order kinetic models that were applied in this study, respectively.

#### 2.4.1 Pseudo First Kinetic Model (Non-linear)

This equation assumes that the rate of adsorption is directly proportional to the number of available, unoccupied active sites on the resin surface.

$$q_t = q_e (1 - e^{-k_1 t}) \quad \text{equation 1}$$

where,

- $q_t$  = Amount of adsorbate adsorbed at time  $t$  (mg/g)
- $q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g)
- $k_1$  = Pseudo-first-order rate constant
- $t$  = Contact time (min)
- $e$  = Euler's number (base of natural logarithm)

It typically describes adsorption processes where the dominant mechanism is physical in nature such as van der Waals interactions or weak electrostatic forces occurring on the external surfaces of the adsorbent. A good fit to this model suggests rapid surface adsorption, with diminishing adsorption rates as sites become occupied. In the context of this study, the pseudo-first-order model helps assess the initial interaction between thorium ions and resin surfaces.

By applying both kinetic models and comparing the degree of fit (e.g., through coefficient of determination,  $R^2$  values), this study aims to provide deeper insight into how different functionalized resins interact with thorium ions. This

approach not only allows the identification of the most efficient resin but also supports a mechanistic understanding that can be used to optimize future separation processes in radioactive waste management and rare earth purification.

#### 2.4.2 Pseudo Second Kinetic Model (Non-linear)

The equations 2 (Ho & McKay, 1999) represent the pseudo-second-order kinetic models. This model assumes that the adsorption process is governed primarily by chemisorption, involving electron sharing or exchange between the thorium ions and specific binding sites on the resin.

$$q_t = \frac{k^2 q_e^2 t}{1 + k_2 q_e t} \quad \text{equation 2}$$

where,

- $q_t$  = Amount of adsorbate adsorbed at time  $t$  (mg/g)
- $q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g)
- $K_2$  = Pseudo-second-order rate constant (g/mg)
- $t$  = Contact time (min)

Such chemical interactions often result in stronger, more stable complexes that take longer to form but contribute to a higher and more sustained adsorption capacity. When experimental data show a better fit to this model, as observed for PE-F and PM401 resins, it indicates that the rate-limiting step is likely a chemical bonding process rather than physical adsorption alone. These resins, functionalized with fluoride and iminodiacetate groups respectively, are capable of forming strong inner-sphere complexes with thorium ions, reinforcing the dominance of chemisorption mechanisms.

### 3. RESULT AND DISCUSSION

The removal of thorium ( $\text{Th}^{4+}$ ) from aqueous systems is a critical step in the purification of rare earth elements and the management of radioactive waste due to its inherent radiotoxicity and environmental persistence (Bie et al., 2022). In this study, the adsorption performance of three functionally distinct resins WA21j, PE-F, and PM401 was investigated through batch experiments to determine their thorium retention efficiency. The structural diversity of these resins, including weak base anion exchange and chelating functionalities, provides varying affinities and mechanisms for thorium uptake, thereby influencing the adsorption kinetics and capacity.

Adsorption kinetics play a vital role in elucidating the mechanism of interaction between adsorbent and adsorbate. To this end, the non-linear forms of the pseudo-first-order and pseudo-second-order kinetic models were applied to interpret

the experimental data (Lin & Wang, 2009). In the pseudo-first-order model, the rate of adsorption is assumed to be proportional to the number of available active sites, and it is typically associated with physical adsorption processes. (Rudzinski & Plazinski, 2006). In contrast, the pseudo-second-order model, as developed by Ho and McKay (1999), assumes that chemisorption involving valence forces is the rate-limiting step (Lowell et al., 2004). These models allow the quantification of adsorption parameters such as equilibrium capacity and rate constants, offering insight into the underlying adsorption mechanisms.

#### 3.1 Retention Rate of Thorium

Table 2 presents the thorium adsorption data for three different resins WA21j, PE-F, and PM401 over a contact time ranging from 0 to 360 minutes. The data reflect the retention rate of thorium at each time interval, showcasing the dynamic adsorption behaviour of the resins.

The results of the batch adsorption experiments demonstrated distinct differences in thorium ion uptake among the three resins, reflecting the influence of their respective functional group chemistries on adsorption performance. An initial rapid adsorption phase was observed during the first 30 minutes, indicating the presence of numerous readily available active sites on the resin surfaces that facilitated fast binding of  $\text{Th}^{4+}$  ions from solution. This was subsequently followed by a slower approach toward equilibrium as the active sites became progressively occupied and the adsorption process transitioned from surface interaction to diffusion-controlled stages. Such behaviour is characteristic of a two-step mechanism, involving an initial external surface adsorption dominated by electrostatic or ligand exchange interactions, followed by a slower intraparticle diffusion of thorium ions into internal pores or chelating sites within the resin matrix. This gradual transition reflects the combined effects of resin structure, pore accessibility, and the specific chemical affinity of each functional group toward thorium ions.

**Table 2:** Thorium adsorption by different resins over time

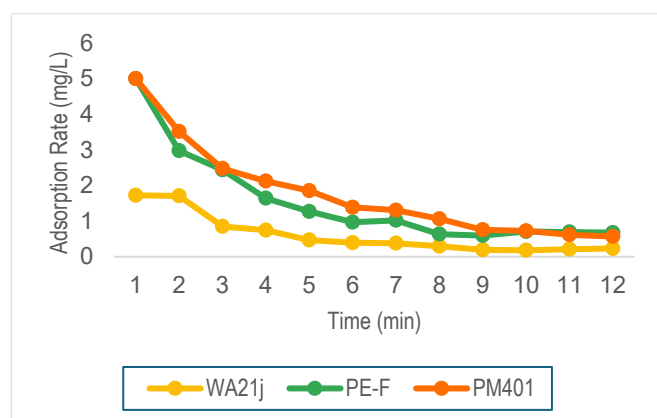
Time	WA21J	PE-F	PM 401
0	1.725	5.002	5.002
5	1.71	2.976	3.515
10	0.85	2.44	2.477
15	0.746	1.643	2.123
30	0.468	1.271	1.855
45	0.395	0.971	1.389
60	0.38	1.021	1.307
90	0.297	0.636	1.065
120	0.196	0.595	0.757
180	0.181	0.71	0.727
240	0.214	0.693	0.618
360	0.234	0.678	0.569

The results of the batch adsorption experiments demonstrated distinct differences in thorium ion uptake among

the three resins. Initial rapid adsorption was observed during the first 30 minutes, followed by a slower approach toward equilibrium. This behaviour indicated a two-step process involving external surface adsorption followed by diffusion into internal sites.

PE-F exhibited the highest thorium removal efficiency throughout the duration of the experiment. PM401 also performed well, while WA21j showed the least adsorption capacity. The stronger performance of PE-F and PM401 can be attributed to the nature of their functional groups. Fluoride ligands in PE-F strongly attract hard metal cations like  $\text{Th}^{4+}$  due to electrostatic interactions (Yuchi et al., 1996), while iminodiacetate groups in PM401 form stable chelate rings with thorium ions (Sharma et al., 2020). WA21j, which relies on weaker amine-based interactions, demonstrated lower affinity for  $\text{Th}^{4+}$  (Li et al., 2017).

The adsorption behaviour observed here aligns with the typical mechanism described in ion-exchange systems for multivalent cations, where the initial fast uptake corresponds to external film diffusion followed by intraparticle diffusion into the resin matrix (Cooney, 1990). During the first 30 minutes, the concentration gradient between the bulk solution and resin surface is high, accelerating mass transfer. As the process continues, diffusion resistance increases due to the occupation of active sites and the reduced mobility of  $\text{Th}^{4+}$  ions within the polymer network, thereby slowing the adsorption rate (Napolitano & Wübbenhorst, 2007). This table supports the kinetic evaluation of thorium uptake, which is further illustrated and validated in Figure 1.



**Figure 1:** Thorium adsorption rate (mg/L) as a function of contact time for WA21j, PE-F, and PM401 resins

Figure 1 illustrates the time-dependent adsorption profiles of thorium ( $\text{Th}^{4+}$ ) onto the three resins: WA21j, PE-F, and PM401, over a contact time of 360 minutes. All three resins exhibited a characteristic biphasic adsorption pattern: an initial rapid uptake phase within the first 30 to 60 minutes, followed by a gradual plateauing phase as equilibrium was approached. This two-step behavior has been demonstrated

by (Pahan et al., 2022), who showed that thorium adsorption proceeds through an initial surface interaction followed by intraparticle diffusion into the resin matrix.

The PE-F resin demonstrated the highest adsorption capacity across the entire contact period. The steep initial drop in thorium concentration during the first 30 minutes indicates a high density of active binding sites that are readily accessible. This rapid phase is likely dominated by electrostatic attraction and ligand exchange between the hard cationic  $\text{Th}^{4+}$  ions and the fluoride-functional groups, which act as hard bases. These strong interactions facilitate the formation of inner-sphere complexes, a phenomenon that has been demonstrated by (Moriyama et al., 2002) thereby supporting the pseudo-second-order kinetic behavior observed in later sections.

PM401 also showed effective thorium adsorption, with performance only slightly lower than that of PE-F. The functionalization with iminodiacetate groups enables bidentate coordination, forming chelate rings that stabilize thorium ion binding, as demonstrated by (Sharma et al., 2020). This stabilization effect explains why, in our experiments, PM401 although exhibiting marginally slower adsorption in the early phase compared to PE-F maintained high retention capacity throughout, indicating strong and stable complexation, particularly effective at moderate contact times (60–180 minutes).

WA21j, in contrast, exhibited significantly lower adsorption efficiency. The slower and more gradual decrease in thorium concentration suggests that the resin's tertiary amine functional groups provide weaker interaction with thorium ions, likely limited to weaker van der Waals forces or outer-sphere complexation. The less efficient binding may also be attributed to steric hindrance and the limited electrostatic attraction between amine groups and the highly charged  $\text{Th}^{4+}$  ions, a phenomenon reported by (Li et al., 2017).

As equilibrium approached (beyond 180 minutes), adsorption rates for all resins levelled off, indicating that most active sites were saturated. PE-F maintained the lowest residual thorium concentration, confirming its superior performance in both rate and capacity. The slow decline in adsorption after 240 minutes for WA21j and PM401 could be explained by desorption or redistribution of thorium ions between surface and internal sites, a behavior demonstrated by (Heshmati et al., 2014).

In practical terms, the comparative performance shown in Figure 1 suggests that PE-F would be the most efficient for rapid thorium capture, particularly in systems

requiring high removal rates within limited contact time. PM401, meanwhile, offers superior retention stability and regeneration potential, making it suitable for repeated operational cycles. The weaker response of WA21j, though less ideal for primary adsorption, indicates potential for use in secondary polishing stages where residual thorium removal is sufficient.

Overall, Figure 1 visually reinforces the critical role of functional group chemistry in influencing adsorption efficiency and kinetics. PE-F's fluoride groups and PM401's iminodiacetate ligands provide stronger and more specific interactions with  $\text{Th}^{4+}$  compared to the weaker amine-based WA21j resin. These results are consistent with the kinetic model fitting presented later, where PE-F and PM401 exhibited high correlation with the pseudo-second-order model, indicating chemisorption dominance.

### 3.2. Kinetic study

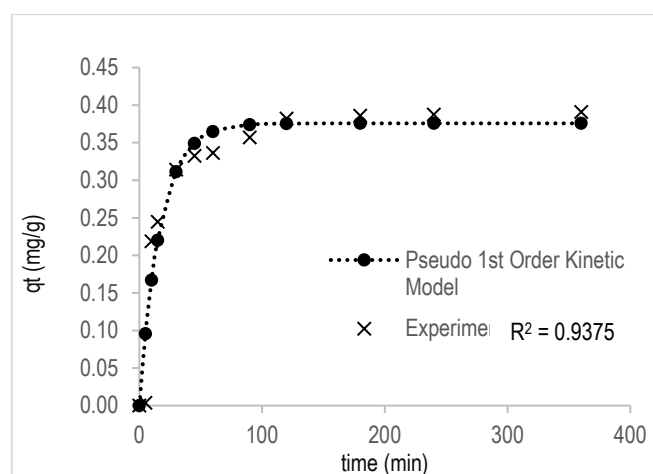
Kinetic modelling helps explain the rate and mechanism of adsorption whether it is more likely due to physical attraction or chemical bonding. The experimental data were fitted to the pseudo-first-order and pseudo-second-order models to better understand the adsorption mechanism of  $\text{Th}^{4+}$  ions onto the resins. These models offer insights into the nature of the interaction whether it is more physical or chemical and help quantify kinetic parameters such as rate constants and equilibrium capacities.

The application of kinetic modelling provides critical evidence regarding the controlling mechanisms of  $\text{Th}^{4+}$  uptake. The pseudo-first-order (PFO) and pseudo-second-order (PSO) models are widely used to describe ion exchange and chelation kinetics, representing physical and chemical adsorption respectively (Rudzinski & Plazinski, 2006). Comparing the fit of experimental data to these models allows for discrimination between surface-limited and chemically driven processes.

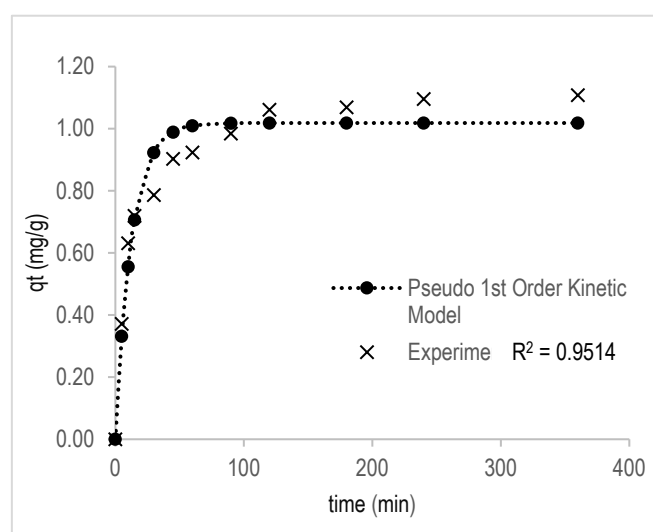
#### 3.2.1 Pseudo first order model (Non-Linear)

The pseudo-first order kinetic model is commonly used to describe adsorption systems where the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. This model helps to evaluate the adsorption behaviour over time and understand the interaction between adsorbent and adsorbate (Tran, 2022). In this study, the non-linear form of the pseudo-first order model was applied to fit the experimental thorium adsorption data for three different resins: WA21j, PE-F, and PM401. The fit of the model to the data is illustrated in Figures 2 to 4, along with the respective coefficient of determination ( $R^2$ ) values, which indicate how well the model describes the experimental behaviour.

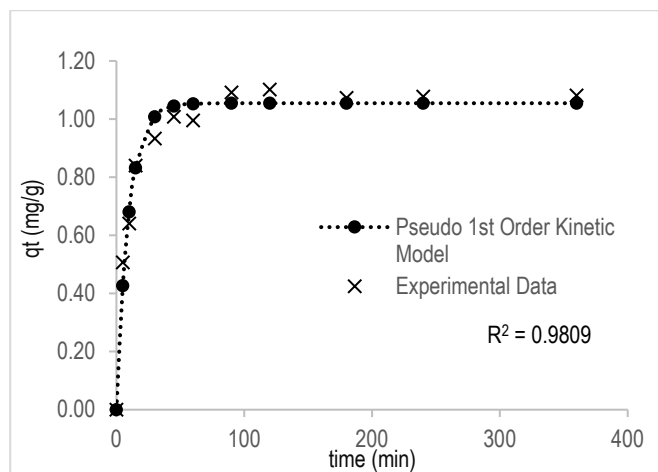
Figures 2 to 4 illustrate the fitted kinetic curves of each resin with corresponding  $R^2$  values. Among the three, the PE-F resin exhibited the highest  $R^2$  value of 0.9809, indicating excellent conformity between experimental and modelled values. This suggests that PE-F, despite being a chelating resin, may present significant surface-level interactions early in the adsorption process (Ye et al., 2020). The high correlation could be attributed to the initial availability of active sites and the rapid uptake of thorium ions due to the fluoride groups' affinity for hard metal cations. This has been demonstrated by (Zahakifar & Khanramaki, 2024), who reported that such affinity drives a fast initial binding mechanism consistent with pseudo-first-order kinetics, likely dominated by surface sorption before the slower intraparticle diffusion phase takes over. The enhanced adsorption performance of PE-F can also be associated with its high surface area and well-dispersed fluoride ligands, which provide multiple binding sites for  $\text{Th}^{4+}$  ions.



**Figure 2:** The pseudo first order kinetic model (non-linear) graph for WA21J resin.



**Figure 3:** The pseudo first order kinetic model (non-linear) graph for PM 401 resin



**Figure 4:** The pseudo first order kinetic model (non-linear) graph for PE-F resin

The PM401 resin followed with a high  $R^2$  value of 0.9514, signifying strong adherence to the pseudo-first-order model. Although iminodiacetate groups are typically associated with chemisorption processes, the slightly lower  $R^2$  compared to PE-F suggests that the initial thorium adsorption for PM401 may still be influenced by surface-level interactions that mimic first-order behavior. Such deviations from perfect fit are commonly observed in adsorption studies and may arise from the onset of concurrent chemical interactions not fully captured by the pseudo-first-order model (Revellame et al., 2020). Among the three resins, PE-F exhibited the highest  $R^2$ , indicating the best fit with the model and thus the least deviation, whereas WA21j showed the lowest  $R^2$ , reflecting a more complex adsorption mechanism.

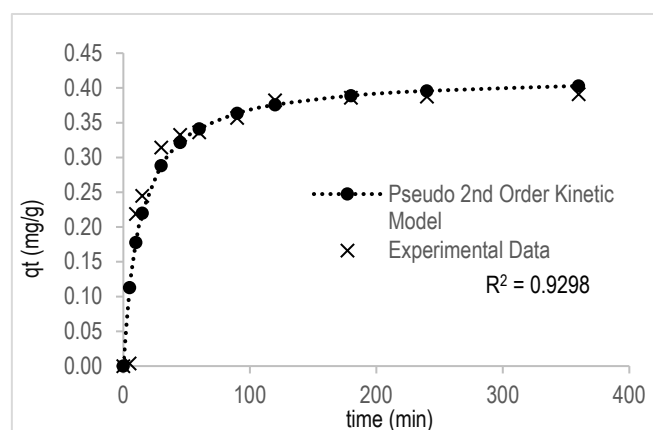
WA21j, a weak base anion exchange resin, showed the lowest  $R^2$  value of 0.9375 among the three. Although still a reasonable fit, this suggests a more complex mechanism of adsorption for this resin. The tertiary amine groups present in WA21j may not strongly attract  $\text{Th}^{4+}$  ions, leading to lower initial uptake rates and greater influence from intraparticle diffusion or steric hindrance. This behavior has been demonstrated by (Othman et al., 2020), who reported that the relatively lower affinity of such functional groups for thorium ions can result in partial desorption or delayed equilibrium, thereby reducing the predictive accuracy of the pseudo-first-order model.

In summary, while the pseudo-first-order kinetic model provided a good approximation for the adsorption behaviour of all three resins, its adequacy varied depending on the resin type and functional group chemistry. PE-F showed the best alignment with the model, followed by PM401 and WA21j. These trends suggest that surface adsorption plays a critical role in the early stages of thorium uptake, particularly for PE-F, a behavior demonstrated by (Yuan et al., 2025). However, their findings also indicate that surface

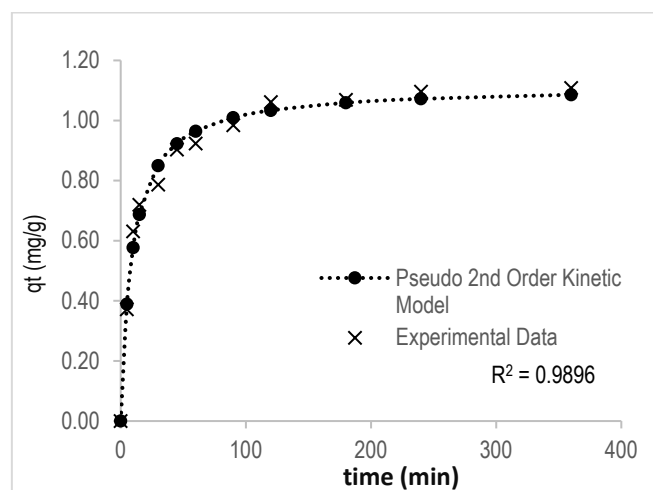
adsorption alone may not fully capture the complexity of the process, especially in resins with lower binding affinity or more chemically interactive functional groups.

### 3.2.2 Pseudo second order kinetic model (non-linear)

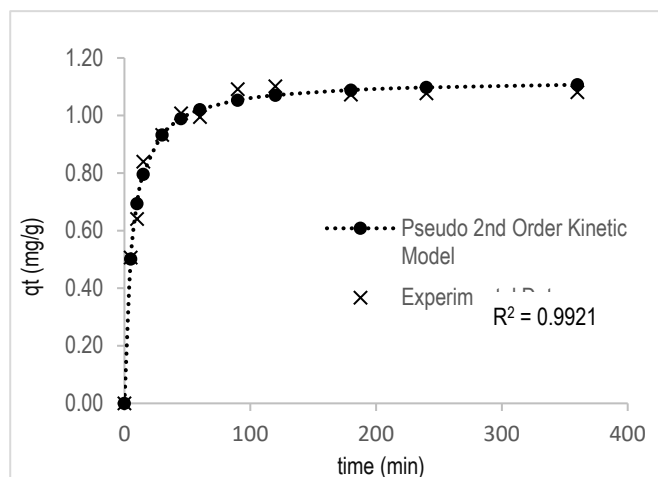
The pseudo-second order kinetic model is commonly employed to describe adsorption processes governed predominantly by chemisorption, where the rate-limiting step involves electron sharing or exchange between the adsorbent and the adsorbate (Ho & McKay, 1999). This model assumes that the adsorption capacity is proportional to the square of the number of unoccupied sites, indicating the involvement of chemical bonding rather than weak van der Waals interactions. In this study, the non-linear form of the pseudo-second order kinetic model was applied to the thorium adsorption data obtained for WA21j, PM401, and PE-F resins. This model was chosen because it effectively describes adsorption systems where chemical bonding plays a major role. The resulting model fit helps identify which resin exhibits the strongest chemisorption tendency and the most stable binding mechanism.



**Figure 5:** The pseudo second order kinetic model (non-linear) graph for WA21J resin



**Figure 6:** The pseudo second order kinetic model (non-linear) graph for PM 401 resin



**Figure 7:** The pseudo second order kinetic model (non-linear) graph for PE-F resin

Figures 5 to 7 show the curve fitting results for each resin. The  $R^2$  values indicate the level of model conformity with experimental data: PE-F ( $R^2 = 0.9921$ ), PM401 ( $R^2 = 0.9896$ ), and WA21j ( $R^2 = 0.9298$ ). The high correlation coefficients for PE-F and PM401 strongly support the dominance of chemisorption as the primary mechanism of thorium retention in these two materials.

The PE-F resin, functionalized with fluoride groups, demonstrates the best fit to the pseudo-second order model. This suggests that thorium adsorption on PE-F is not merely dependent on surface accessibility, but also on the formation of stable inner-sphere complexes through strong electrostatic interactions and ligand exchange. This behaviour has been demonstrated by (Nezami et al., 2024), who showed that fluoride groups, as hard bases, coordinate effectively with hard acid cations like  $\text{Th}^{4+}$ , thereby facilitating electron-sharing and chemical bonding. The  $R^2$  value of 0.9921 confirms this mechanism and reflects a predictable, chemically driven adsorption process throughout the duration of contact.

PM401, which contains iminodiacetate functional groups, also exhibits strong alignment with the pseudo-second order kinetic model ( $R^2 = 0.9896$ ). Iminodiacetate is a bidentate ligand capable of forming stable chelate rings with multivalent metal ions, including thorium (Thuéry, 2011). The high degree of fit suggests a two-phase adsorption mechanism: an initial rapid uptake due to abundant active sites, followed by a slower phase where inner-pore diffusion and stronger chemical complexation become rate-limiting. This mechanism has been demonstrated by (Yuan et al., 2025), whose findings reinforce the applicability of PM401 in systems requiring selective and strong thorium retention, particularly under moderately acidic conditions typical of REE

leachates.

WA21j, in contrast, shows a noticeably lower  $R^2$  value of 0.9298. While still acceptable, this deviation implies that the adsorption of thorium onto WA21j may not be solely driven by chemisorption. The tertiary amine groups in WA21j are generally less effective in forming strong coordination bonds with  $\text{Th}^{4+}$  ions (Golub et al., 1996) compared to the chelating ligands in PE-F and PM401. Consequently, WA21j may rely more on weak electrostatic interactions or physical entrapment within the resin matrix. Additionally, the adsorption process for WA21j could be significantly influenced by intraparticle diffusion or surface heterogeneity, factors demonstrated by Pompeu et al., (2010) to reduce conformity with the ideal assumptions of the pseudo-second-order model.

From an application standpoint, PFO behavior is often desirable in systems requiring fast initial removal of contaminants, such as pre-treatment or rapid column processes. The ability of PE-F to exhibit both strong early sorption (PFO) and stable chemisorption (PSO) performance makes it a versatile candidate for hybrid adsorption systems that balance speed and capacity. Meanwhile, understanding the PFO response of PM401 and WA21j helps in predicting operational efficiency at short contact times and optimizing reactor design for batch or continuous adsorption setups.

Overall, the pseudo-second order kinetic analysis provides strong evidence for the dominance of chemisorption in PE-F and PM401 resins, reflecting their high affinity and functional specificity for thorium ions. The less consistent behaviour of WA21j underlines the importance of functional group chemistry in influencing adsorption pathways and kinetics. These insights are crucial for selecting suitable resins in practical applications such as nuclear waste remediation and REE purification, where strong, irreversible binding of thorium is often desired.

### 3.3 Practical Application Implication

Among the tested resins, PE-F shows the highest potential for industrial thorium removal due to its strong binding and fast kinetics. However, its higher cost and limited regeneration may restrict large-scale use. PM401 provides a more balanced option: it offers high uptake capacity and can often be regenerated with mild acids, making it more suitable for repeated applications. WA21j, though less efficient, remains cost-effective and could serve in pre-treatment or secondary polishing stages. Overall, PE-F is best for maximum efficiency, while PM401 offers the most practical compromise between performance and cost. These insights are valuable for selecting resins in rare earth purification and radioactive waste treatment, where both efficiency and sustainability are critical.



#### 4. CONCLUSION

This study assessed the retention efficiency of thorium ( $\text{Th}^{4+}$ ) on three functionalized resins (WA21j, PE-F, and PM401) through batch adsorption and kinetic modelling. The results showed that PE-F achieved the highest thorium uptake and strongest fit to the pseudo-second-order model, confirming chemisorption as the dominant mechanism. PM401 also performed well due to iminodiacetate chelation, while WA21j demonstrated comparatively weaker adsorption linked to its amine groups.

The study confirms that functional group chemistry is a key factor in thorium adsorption performance. While PE-F offers the highest efficiency, PM401 provides a more practical balance between adsorption strength, regeneration potential, and cost-effectiveness. Importantly, these findings provide a foundation for applying functionalized resins in column-based REE purification, where continuous separation processes require both efficiency and stability. Overall, this work contributes to the development of sustainable strategies for rare earth purification and radioactive waste management, where reliable and selective thorium removal is crucial.

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