



Study of the kinetics of sorption of praseodymium and neodymium ions using interpolymer systems based on KU-2-8 and AB-17-8 in salt forms

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<p>Received: April 10, 2025 Peer-reviewed: May 22, 2025 Accepted: June 5, 2025</p>	<p>ABSTRACT This paper presents a study of the kinetics of neodymium and praseodymium ions sorption using interpolymer systems based on KU-2-8 and AB-17-8 in salt forms. Sorption of target ions was carried out in a dynamic mode (with constant stirring) in interpolymer systems in molar ratios of 4:2 and 3:3 (cation exchanger to anion exchanger). Aliquots were collected during certain time intervals, then widely known kinetic models of sorption were used to construct linear graphs. According to the obtained results, the best model for describing sorption was pseudo-first order (the highest value for the 4:2 system = 0.97885 and 0.98112; for the 3:3 system = 0.9647 and 0.98779). Such results are important for understanding the mechanisms of the sorption process and establishing the limiting factor that can slow down this process. The kinetic model of pseudo-first order may indicate the need to improve the washing out of counterions from the polyelectrolyte matrix for their high ionization and accessibility of functional groups for metal ions. This assumption can be used in the future to optimize industrial schemes of ion-exchange sorption of REE.</p>
	<p>Keywords: interpolymer systems, kinetic models, sorption, neodymium and praseodymium ions, cation exchanger KU-2-8, anion exchanger AB-17-8.</p>
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Introduction

Rare earth metals are a strategic resource and are increasingly used in various fields. Rare earth elements are a group of 17 metallic elements that share similar chemical properties [1]. REEs consist of the 15 lanthanides, as well as scandium and yttrium lanthanides [[2], [3]]. REEs are typically categorized into light rare earth elements and heavy rare earth elements. The latter have grown crucial for numerous emerging technologies, especially in the green energy sector, including wind turbines, large-scale energy storage systems, and new energy vehicles [4]. They also provide a bridge from fossil fuels to low-carbon energy [5]. As for the metals themselves, which are studied in this article, they

also have a huge variety of applications, and therefore, the demand for them will only grow in the future. For example, Nd is applied in supermagnets for disk drives [6], Nd-Fe-B magnets [7], in Al-Mg alloys, and steel, also for magnetic resonance imaging (MRI) contrasting agents [8]. Praseodymium is widely used in magnets [9], optical Fibres, carbon-arc lamps [7], in alloys for aircraft engines, capacitors, sensors, and semiconductors, in flat display electronics [8]. Therefore, considering the great need for these rare earth metals, this study aims to study the sorption kinetics to better understand the absorption mechanism, which will improve the technologies of concentration and extraction of target ions. This goal was achieved through several steps: 1) selection of interpolymer

systems for sorption from a model solution; 2) sampling aliquots at certain time intervals; 3) selection of the most suitable kinetic model among the most common in the literature; 4) based on the selection of the most suitable kinetic model, suggest a possible sorption mechanism, a limiting factor, and how this factor can be compensated. The selection of sorption and the composition of interpolymer systems are also supported by the fact that "adsorption provides advantages such as simplicity, low capital investment, low energy usage, and good environmental sustainability, making it the ideal choice for separating and removing rare earth elements"[10]. The development of simple but effective sorbents that can be used repeatedly is an urgent need in modern realities [11].

By now, a huge number of works have accumulated on various methods of extracting REE from primary and secondary sources. Some of them also pay attention to kinetic factors, especially in articles where sorption is the main process. The authors [12] introduced a technique for extracting neodymium from permanent magnet waste (WPM) through a hydrometallurgical process that includes separation using a hollow fiber liquid membrane (HFSLM). Neodymium in WPM was recovered via solvent extraction with D2EHPA. The separation of Nd from Fe was achieved successfully using 0.6 M D2EHPA at an O/A phase ratio of 3, with a pH range of 1.26–2.0, resulting in a neodymium recovery rate of 97.48%.

The extraction of neodymium and other REE from recycled magnets was also studied in the work [13]. They were extracted as oxalates using various amounts of oxalic acid relative to its stoichiometric quantity. When oxalic acid was used in stoichiometric amounts, about 93% of the rare earth elements present in the solution precipitated [13].

Miguel Nogueira et al. [14] used activated carbon obtained from tire rubber after CO₂ activation for sorption, and the most effective adsorbent achieved a maximum absorption capacity of 24.7 mg g⁻¹ for Nd³⁺ and 34.4 mg g⁻¹ for Dy³⁺. The authors also noted that the synthesized adsorbents made from waste materials demonstrated better performance than commercially available activated carbon. This study also has environmental implications, as it demonstrated the potential use of waste to create effective adsorbents.

Organic acids, such as acetic and oxalic acids, have been used for Nd leaching, showing promising efficiencies. Under standard conditions (27°C, 3 M acid concentration, 20 g/L pulp density, 200 rpm stirring, 500 µm particle size, 300 min leaching), Nd

extraction reached 50% with acetic acid and 44% with oxalic acid [15]. However, optimized parameters (80°C, 0.4 M acetic acid, 10 g/L pulp density, 106–150 µm particle size) significantly increased Nd extraction to 99.99% [16].

Recent research introduces electrokinetic mining (EKM) as an innovative technique for extracting REEs from ion-adsorption deposits (IADs) while addressing environmental concerns associated with conventional ammonium-salt-based leaching methods. Traditional methods exhibit low recovery efficiencies (40–60%) and contribute to significant water contamination and soil degradation. EKM applies an electric field to facilitate the selective migration of ions, significantly reducing the need for chemical leaching agents (by up to 80%). Experimental results demonstrate that EKM achieves 90–96% recovery efficiency, outperforming conventional techniques. Furthermore, the method results in higher purity REEs, with up to 70% fewer metallic impurities [4].

Deep eutectic solvents (DESs) have gained attention as a viable substitute for aqueous solutions in the recovery of valuable metals from NdFeB magnets. A study [17] investigated a DES composed of choline chloride and lactic acid in a 1:2 molar ratio for the leaching of REEs and other metals. A separation process was devised using Aliquat 336 SCN diluted in toluene to effectively extract Fe, B, and Co from Nd and Dy. Purified Dy was recovered by water stripping, while Nd was precipitated using oxalic acid, yielding Nd₂O₃ (99.87% purity) and Dy₂O₃ (99.94% purity).

The use of chelate sorbents has also become a popular direction for research and development for the selective extraction of REE ions. For example, ion-exchange resins IRC-747 and TP-260 have shown high affinity for REEs from highly concentrated 4 M H₃PO₄ produced by OCP. These resins achieve REE extraction yields ranging from 20% to 60% [18].

The ion exchange process is highly selective and environmentally friendly, making it effective for treating low metal concentrations. However, at the same time, there are also some difficulties: high cost of selective chelating separation materials and limited capacity, slow desorption kinetics and the need for selection of desorbing reagents [[19], [20], [21]].

It is worth noting that many works have been devoted to the problem of extracting REE from model solutions, as well as from primary and secondary sources using various cross-linked polyelectrolytes. The general direction of all these works is the search for high extraction efficiency,

selectivity, and optimal conditions. For example, industrial sorbents Purolite S940 and Lewatit TP 260 were used in the work [[22], [23]] to extract neodymium and scandium from sulfate solutions. According to the results, neodymium strongly bound with functional groups to form coordination bonds, and scandium sorption was strongly dependent on the sulfate concentration. In two other experiments [22] were used cation exchangers with the same functional group as in our work (sulfo group) to extract neodymium and separate it from calcium, iron and strontium. An important discovery was that calcium and neodymium ions compete with each other during sorption on the polymer matrix.

Our research is aimed at using interpolymer systems, which are composed of cationite and anionite. When in one solution, they mutually activate each other, changing the most important characteristics (pH, electrical conductivity, and swelling degree increase) [[24], [25], [26]]. In our previous studies, we considered interpolymer systems based on various industrial sorbents for the extraction of REE from solutions [[27], [28]]. In these works, the sorption characteristics of a mixture of praseodymium and neodymium, as well as lute-tium individually, were demonstrated using mutually activated cross-linked polyelectrolytes. It was possible to find that the interpolymer system has increased sorption characteristics compared to its application. It was also possible to find that in the static mode, greater selectivity to one of the REEs is possible. However, at the moment, no experiments have been conducted to study the kinetics of sorption in such systems, so this work will pay more attention to this aspect.

Experimental part

Equipment. The required mass of the ion exchanger was measured using a Shimadzu TX-423 electronic analytical balance. The residual concentration was determined using an atomic emission analysis (Thermo Scientific™ iCAP™ PRO XP ICP-OES, USA).

Materials. In the experiment, aqueous solutions of neodymium and praseodymium hexahydrate nitrate with a concentration of 30 mg/l were used (Sigma-Aldrich, Darmstadt, Germany). Ion-exchange resins in salt forms: KU-2-8 (Na⁺) strongly acidic (Azot, Cherkassy, Ukraine) cation exchanger and strongly basic AB-17-8 (Cl⁻) (Azot, Cherkassy, Ukraine) gel-type anion, were used.

Experiment. An interpolymer system was created using KU-2-8 and AB-17-8 in a molar ratio of

4:2 and 3:3. These ratios were chosen for study based on previous work. In it, these interpolymer systems showed satisfactory sorption indices (extraction degree and sorption capacity). The masses of ionites in these systems were: 4:2 (0.079 g.: 0.041g.); 3:3 (0.059 g.: 0.062g.). Then, sorption was carried out in solutions containing neodymium and praseodymium nitrates. Aliquots were collected during the following time intervals: 5 min, 10 min, 15 min, 30 min, 1 h, 2 h, 3 h, 4.5 h, 6 h. The solutions were stirred using a magnetic stirrer, since in static mode, the sorption processes occur slowly. The main task of the algorithm of this experiment is to find which of the kinetic models best describes the process of sorption of these rare earth metals by interpolymer systems.

Results and Discussion

Kinetics in sorption processes characterizes the rates of sorbate adsorption and desorption from an aqueous solution onto a solid phase. The kinetic analysis can be linear or nonlinear, depending on the system's complexity and the underlying mechanisms. In our work, we used several popular models of sorption kinetics to establish the mechanism and limiting factors of REE extraction using activated interpolymer systems. These models are: pseudo-first order, pseudo-second order, Elovich model, and intraparticle diffusion.

Pseudo first-order kinetic model fit

Widely used models to describe adsorption kinetics are the pseudo-second order (PS2) and pseudo-first order models (PS1) [[29], [30]]. These models are adaptations for heterogeneous systems, in which it is assumed that the concentration of the sorbent does not change over time. Also, in these models, the value of adsorption capacity is important. The equation for the pseudo-first order model and its linear form are usually presented as follows [[29], [31]]:

$$q(t) = q_e(1 - e^{-k_1 t}) \quad (1)$$

$$\ln[q_e - q(t)] = -k_1 t + \ln q_e \quad (2)$$

The Pseudo-First-Order (PFO) kinetic model posits that the adsorption rate is directly proportional to the difference between the maximum adsorption capacity and the current amount of adsorbate already adsorbed at any given time. This means the adsorption process is primarily controlled by the concentration of the sorbate in the solution. It is typically used when the adsorption

process is diffusion-controlled, meaning mass transfer plays a significant role.

In this work, we used the linear form of the equation to plot the graph. Figures 1 and 2 show a linear approximation for the sorption kinetics of neodymium and praseodymium in different systems.

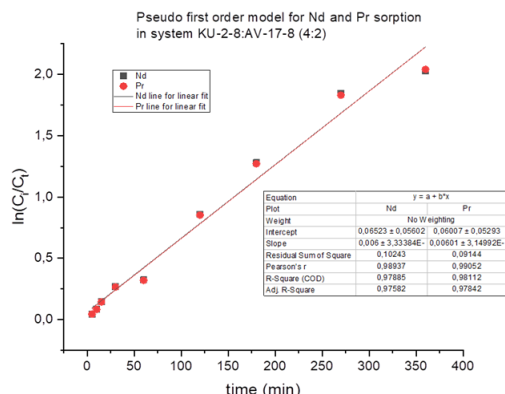


Figure 1 - Pseudo first order kinetics for neodymium and praseodymium sorption in a 4:2 system

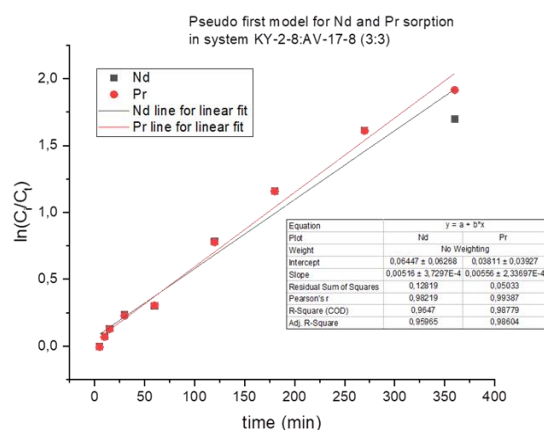


Figure 2 - Pseudo first order kinetics for neodymium and praseodymium sorption in a 3:3 system

According to the values of the quantity, the pseudo-first-order model describes well the sorption of both ions on the cation exchanger in interpolymer systems. However, this partly contradicts expectations because this model assumes physical adsorption and dependence on the concentration gradient. In turn, it is known that cross-linked polyelectrolytes contain functional groups with which metal ions directly interact (formation of ionic or coordination bonds). The model suggests that adsorption is driven by mass transfer, which occurs due to a concentration gradient between the solution and the adsorbent surface [32]. Therefore, the unexpected good pseudo-first-order correspondence can be explained

by the following assumptions. A field of counterions is formed around the charged polyelectrolyte, which is replaced by metal ions. At a certain moment, counterions begin to prevent the solution and other REE ions from penetrating the polymer matrix, so despite the chemical interaction between the functional groups and REE ions in the solution, the limiting factor becomes mass transfer.

Pseudo-second order kinetic model fit

The linear form of the equation for pseudo second order is represented by the following formula [31]:

$$\frac{t}{q_t} = \left(\frac{1}{q_e}\right)t + \frac{1}{k_2 q_e^2} \tag{3}$$

The Pseudo-Second-Order (PSO) model, also referred to as the Ho and McKay equation [33], is commonly employed to describe the adsorption of solutes from solution. The model is most applicable when adsorption is controlled by chemical interactions (chemisorption) rather than diffusion. The adsorption process depends on the availability of active sites rather than just mass transfer, meaning it is not solely controlled by diffusion [34].

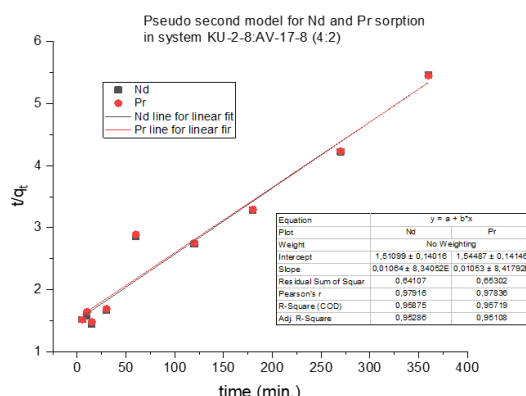


Figure 3 - Pseudo second order kinetics for neodymium and praseodymium sorption in a 4:2 system

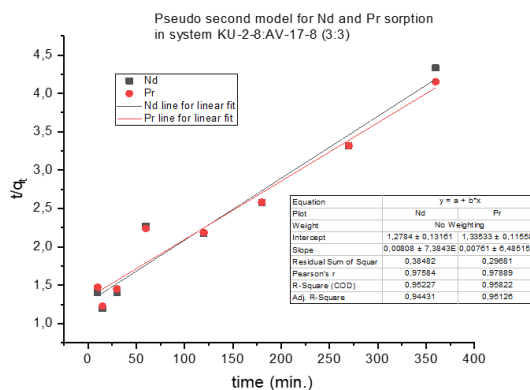


Figure 4 - Pseudo second order kinetics for neodymium and praseodymium sorption in a 3:3 system

According to the coefficient of determination in both systems (figures 3 and 4), both praseodymium and neodymium also correspond well to the pseudo-second order, but slightly less than the pseudo-first order. This is also contrary to expectations, since sorption on polyelectrolytes is usually a chemical process. But based on previous discussions of mass transfer, we conclude that although both models yielded high coefficients of determination, the actual mechanism and limiting factors are complex processes.

Elovich model

The Elovich model is commonly employed to characterize adsorption kinetics, particularly in systems where the sorbent surface is energetically heterogeneous and chemisorption is the rate-controlling step [[35], [36]]. This model posits that the adsorption rate diminishes over time as the surface coverage increases, resulting in a progressive reduction of available active sites. The linear equation for this model can be expressed by the following formula [36]:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{4}$$

where α is the initial rate of adsorption ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) and β is the desorption constant ($\text{g}\cdot\text{mg}^{-1}$) Figures 5 and 6 show graphs for the Elovich model.

According to the determination coefficient, this model describes the kinetics of neodymium and praseodymium sorption worse than the pseudo-first and pseudo-second order. This indirectly confirms that chemisorption is not a determining factor.

Intra-particle diffusion

The intraparticle diffusion model explains how adsorbate molecules, like dyes, move from the bulk solution into the solid adsorbent phase. This transport process often acts as the rate-limiting step in adsorption, especially in rapidly stirred batch reactors [37]. The formula that describes this model can be represented as follows:

$$q_t = K_{dif}t^{0.5} + C \tag{5}$$

where C ($\text{mg}\cdot\text{g}^{-1}$) is the intercept and K_{dif} is the intraparticle diffusion rate constant (in $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$).

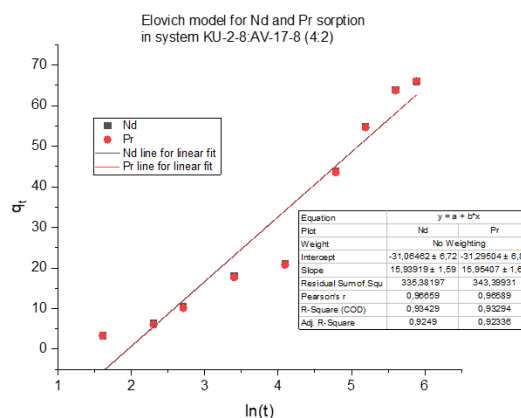


Figure 5 - Elovich model for neodymium and praseodymium sorption in a 4:2 system

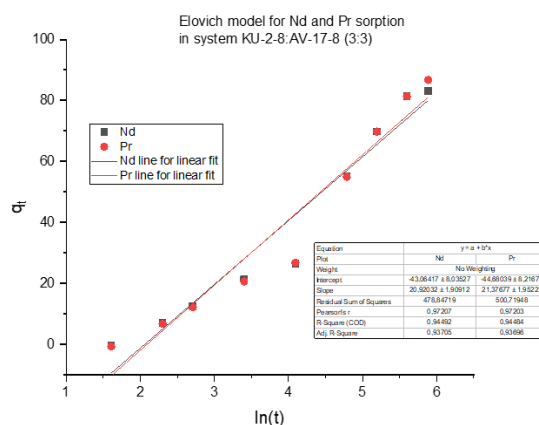


Figure 6 - Elovich model for neodymium and praseodymium sorption in a 3:3 system

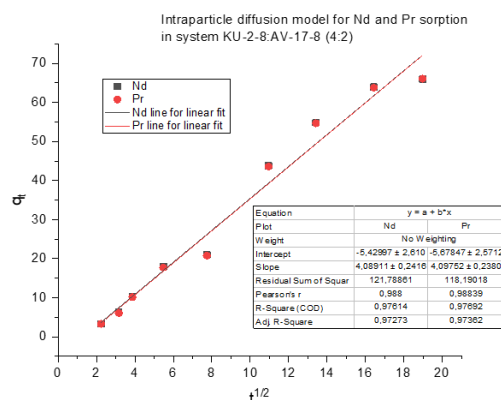


Figure 7 - Intraparticle diffusion model for neodymium and praseodymium sorption in a 4:2 system

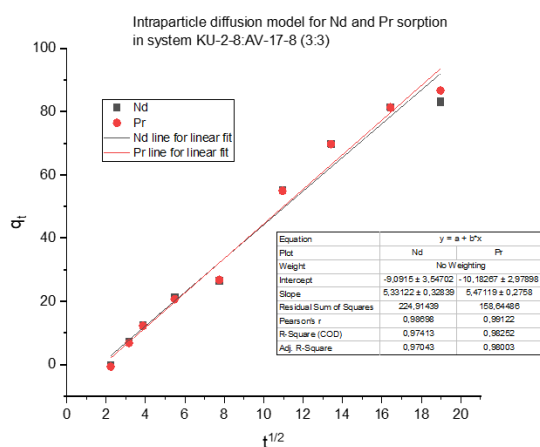


Figure 8 - Intraparticle diffusion model for neodymium and praseodymium sorption in a 3:3 system

Based on the determination coefficient, it can be concluded that this model also satisfactorily describes the sorption kinetics for neodymium and praseodymium in two systems (Figures 7 and 8). Thus, the pseudo-first-order and Elovich models turned out to be the most suitable for describing the processes occurring in interpolymer systems. The good fit of the intraparticle diffusion model suggests that mass transfer resistance within the resin plays a significant role.

Tables 1, 2 summarise the results of the linear correlation of all four sorption models (in the 4:2 system and 3:3 system) relative to the determination coefficient presented in the work.

Table 1 - Determination coefficient for Nd and Pr in 4:2 system

Kinetic model	Nd (R ²)	Pr (R ²)
Pseudo first	0.97885	0.98112
Pseudo second	0.95875	0.95719
Elovich	0.93429	0.93294
Intraparticle diffusion	0.97614	0.97692

Table 2 - Determination coefficient for the Nd and Pr 3:3 system

Kinetic model	Nd (R ²)	Pr (R ²)
Pseudo first	0.9647	0.98779
Pseudo second	0.95227	0.95822
Elovich	0.94492	0.94484
Intraparticle diffusion	0.97043	0.98003

Conclusions

This study investigated the sorption kinetics of neodymium (Nd³⁺) and praseodymium (Pr³⁺) ions using interpolymer systems KU-2-8:AB-17-8. Experimental data were fitted to pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models to determine the best kinetic description.

The pseudo-first-order model (PFO) provided the best fit, with R² values of 0.97885–0.98779, suggesting that mass transfer limitations and external diffusion play a key role in sorption kinetics. The pseudo-second-order model (PSO) also showed good agreement but performed slightly worse, indicating that chemisorption is not the sole controlling mechanism. The Elovich model, which typically describes heterogeneous chemisorption, exhibited the poorest fit, confirming that physical interactions and counterion exchange dominate the process. The intraparticle diffusion model demonstrated that internal diffusion resistance contributes to the sorption rate but is not the only limiting step.

The findings indicate that sorption kinetics in interpolymer systems are influenced by the counterion exchange effect, external mass transfer, and intraparticle diffusion. These insights can be applied to improve industrial ion-exchange sorption technologies for rare earth element recovery. Future studies should focus on the thermodynamics of the process, the effect of pH control, and the long-term regeneration efficiency of the interpolymer system. Another important conclusion is that under active stirring both metals are sorbed almost equally, which confirms our previous results regarding static and dynamic regimes.

Conflicts of interest. The authors declare no conflict of interest.

CRedit author statement: T. Jumadilov: Conceptualization, Methodology, Validation and Data curation; K. Kabzhalelov: Formal analysis, Investigation, Data curation and Writing - Original draft preparation; Kh. Khimersen: Writing - review and editing, Data curation, Visualization; B. Totkhuskyzy: Validation and Supervision; Zh. Mukatayeva: Software and Validation. All authors have read and agreed to the published version of the manuscript.

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Тұз түріндегі КУ-2-8 және АВ-17-8 негізіндегі интерполимерлі жүйелерді қолдану арқылы празеодим және неодим иондарының сорбциялану кинетикасын зерттеу

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<p>Мақала келді: 10 сәуір 2025 Сараптамадан өтті: 22 мамыр 2025 Қабылданды: 5 маусым 2025</p>	<p>ТҮЙІНДЕМЕ Бұл жұмыста тұз түріндегі КУ-2-8 және АВ-17-8 негізіндегі интерполимерлі жүйелерді қолдану арқылы неодим және празеодим иондарының сорбциялану кинетикасын зерттеу ұсынылған. Мақсатты иондарды сорбциялау динамикалық режимде (тұрақты араластырумен) 4:2 және 3:3 молярлық қатынастағы интерполимерлі жүйелерде (катион алмастырғыштан анион алмастырғышқа) жүргізілді. Белгіленген уақыт аралықтарында аликвоттар алынып, сызықтық графиктерді құру үшін сорбцияның белгілі кинетикалық үлгілері пайдаланылды. Алынған нәтижелер бойынша сорбцияны сипаттаудың ең жақсы үлгісі псевдо-бірінші ретті модель болды (4:2 жүйесі үшін ең жоғары мән = 0,97885 және 0,98112; 3:3 жүйесі үшін = 0,9647 және 0,98779). Мұндай нәтижелер сорбция процесінің механизмдерін түсіну және осы процесті баяулататын шектеуші факторды анықтау үшін маңызды. Псевдо-бірінші ретті кинетикалық моделі полимерлердің жоғары иондануы және металл иондары үшін функционалдық топтардың қолжетімділігі үшін полиэлектрлиттік матрицадан қарсы иондарды жууды жақсарту қажеттілігін көрсетуі мүмкін. Бұл болжамды болашақта СЖЭ ионалмасу сорбциясының өнеркәсіптік схемаларын оңтайландыру үшін пайдалануға болады.</p>
	<p>Түйін сөздер: интерполимерлі жүйелер, кинетикалық модельдер, сорбция, неодим және празеодим иондары, катионалмастырғыш КУ-2-8, анионалмастырғыш АВ-17-8.</p>
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Изучение кинетики сорбции ионов празеодима и неодима интерполимерными системами на основе КУ-2-8 и АВ-17-8 в солевых формах

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<p>Поступила: 10 апреля 2025 Рецензирование: 22 мая 2025 Принята в печать: 5 июня 2025</p>	<p>АННОТАЦИЯ</p> <p>В данной работе представлено исследование кинетики сорбции ионов неодима и празеодима интерполимерными системами на основе КУ-2-8 и АВ-17-8 в солевых формах. Сорбцию целевых ионов проводили в динамическом режиме (при постоянном перемешивании) в интерполимерных системах в мольных соотношениях 4:2 и 3:3 (катионит к аниониту). Аликвоты отбирались через определенные промежутки времени, затем для построения линейных графиков использовались широко известные кинетические модели сорбции. Согласно полученным результатам, наилучшей моделью для описания сорбции оказалась модель псевдопервого порядка (наибольшее значение для системы 4:2 = 0,97885 и 0,98112; для системы 3:3 = 0,9647 и 0,98779). Подобные результаты важны для понимания механизмов процесса сорбции и установления лимитирующего фактора, способного замедлить этот процесс. Кинетическая модель псевдопервого порядка может указывать на необходимость улучшения вымывания противоионов из полиэлектrolитной матрицы для их высокой ионизации и доступности функциональных групп для ионов металлов. Данное предположение может быть использовано в дальнейшем для оптимизации промышленных схем ионообменной сорбции РЗЭ.</p> <p>Ключевые слова: интерполимерные системы, кинетические модели, сорбция, ионы неодима и празеодима, катионит КУ-2-8, анионит АВ-17-8.</p>
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