

Article



Kinetics Study of Solvent and Solid-Phase Extraction of Rare Earth Metals with Di-2-Ethylhexylphosphoric Acid

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Abstract: The kinetic features of solvent and solid-phase extraction of yttrium and iron (III) from simulated and industrial phosphoric acid solutions are revealed. Di-2-ethylhexylphosphoric acid (D2EHPA) was used as a liquid extractant, and D2EHPA-containing Levextrel resin—a co-polymerization product of styrene and divinylbenzene in the presence of D2EHPA—was used as a solid-phase extraction agent. Significant dependence of yttrium extraction rate constant on the stirring rate was revealed using the formal first-order kinetic equation. The data obtained characterizes a diffusion-limited process with an activation energy of 16.2 ± 1.3 kJ/mol. Temperature increase during the iron (III) extraction process leads to a changeover of a rate-limiting stage from kinetic to diffusion, accompanied by drop of activation energy from 40.0 ± 1.4 to 11.4 ± 1.2 kJ/mol. Effective separation of elements at the extraction stage is possible at temperatures of 283–300 K under non-equilibrium conditions of the ferric ions transport from aqueous to organic phase. This condition ensures a high yttrium–iron separation coefficient of 23.2 in 1.5-2 min. Extraction kinetics by Levextrel resin are described by Fick's second law equation, which establishes the laws of diffusion in the solid grain of the organic phase with an activation energy of 18.5 ± 2.0 kJ/mol.

Keywords: extraction; solid extractant; solvent-impregnated resin; di-2-ethylhexylphosphoric acid; phosphoric acid; ferric iron; yttrium; sorption kinetics

1. Introduction

Rare earths metals (REM) are widely used in various high-tech industries due to their unique optical, electrical, and magnetic properties. Mineral ores are still the main source of rare earth metals. These ores are characterized by a low yttrium (Y) and lanthanides content. REM are often presented as a collateral admixture in other minerals. For this reason, extraction remains the main method to recover them from complex water–salt solutions with low pH values caused by the specifics of rare metals ores reprocessing techniques [1,2].

A well-known factor complicating the implementation of solvent extraction is the use of flammable, volatile, and toxic organic solvents. The formation of interfacial emulsion can also be attributed to undesirable side effects of the solvent extraction process. The use of solid-phase extraction has a number of advantages compared to solvent extraction during the process of extracting the target component, such as compatibility with a continuous stream of acidic saline solutions, which can provide scalability of the process [3]. The disadvantage of this technology is the need for additional space and equipment to ensure the regeneration of materials used as solid carriers for reuse [4].

As materials for the solid-phase extraction process, extractant-impregnated porous inert supports based on a polystyrene matrix are used. There are two concepts to produce solid extractant. The first

one is the adsorption of extraction solvent on the surface of polymer support to obtain so-called solvent-impregnated resin (SIR). The second method to produce solid extractant—extraction resin—is direct polymerization of the monomer in the presence of the extractant [5]. Unlike SIR, extraction resins, or Levextrel resins, are characterized by a lower outwashing of the organic phase and a more uniform distribution in the granule volume [6,7]. A change in the extraction mechanism during solid–liquid extraction, compared with the liquid–liquid extraction, could be expected in the direction of similarity with an ion exchange sorption mechanism.

Zhang et al. [1] studied the kinetics of solid-phase extraction of zirconium (IV) and neodymium (III) ions using Levextrel resin containing trialkylphosphine oxide. The extraction kinetics were described by a second order formal kinetics equation, and the process rate constant was determined. Second order of Cd (2+) ions extraction process by acidic organophosphorous extractant immobilized in a styrene/ethylene glycol dimethacrylate polymer matrix was established by Valenzuela et al. [8]. The acquired activation energy value of 47.2 ± 2.2 kJ/mol points to a diffusion kinetic rate-limiting stage of the system.

Many studies show [9] that sorption equilibrium and metal ions stoichiometry in solvent extraction (SX) can be identical to solid extraction by Levextrel resin; however, sorption kinetics of metals on Levextrel resin may vary from SX. In concentrated solutions of H_3PO_4 , the use of acidic extractants (D2EHPA) increases the selective extraction of rare earth elements (REE). Furthermore, co-extraction of iron impurities in the presence of a neutral extractant (Cyanex 923) is significantly reduced [10].

A wide range of chelating ion-exchange resins for the rare earth metals extraction from phosphoric acid solutions was studied by Hérès et al. [11]. The authors point out the two most promising resins—Amberlite IRC 747 and Lewatit TP 260, both containing aminophosphonic groups. Considered resins are capable of providing a high extraction efficiency. However, they have a number of significant disadvantages, such as high impurity recovery degrees and low separation factors. Observed kinetics of the total REE uptake by IRC 747 and TP 260 are best explained by the moving boundary particle diffusion model.

The thorium sorption from acid medium by Aliquat 336-impregnated Chromosorb W material was investigated by Mahanty [12]. The results confirmed a pseudo-second order kinetics and Langmuir isotherm. The considered sorption method allows to effectively separate thorium from uranium.

Many studies are dedicated to the investigation of resins impregnated with a binary extractant system. The effect of a tributyl phosphate addition on the vanadium capability adsorption of D2EHPA-impregnated resins (DIR) was studied by Zheng et al. [13]. The results show that the impregnation ratio of the resins decreases gradually with the increasing proportion of tributylphosphate (TBP) in the extractant solution. Nevertheless, the addition of TBP leads to an increase in sorbent capacity by more than 20% with optimal D2EHPA to TBP ratio of 7:3, as well as significantly reducing the adsorption equilibrium time of vanadium. Moreover, TBP addition converts the pseudo-second order kinetic for the vanadium adsorption onto the D2EHPA-only impregnated resin to the pseudo-first order kinetic. The study of solvent-impregnated resins prepared from binary mixtures of 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (PC88A) and neodecanoic acid (Versatic 10) was carried out by Sharaf et al. [14]. Designed SIR was used for the separation and concentration of scandium (3+) from simulated nitrate solutions, with a maximum scandium loading capacity of 48 mg/g. Based on the obtained results, the SIR absorbs scandium according to second order kinetics.

Chemically modified resins, containing selective-to-REM ligands, can be used in continuous processes with adsorption columns with a fixed or fluidized bed. However, to develop and design a large-scale REE extraction and separation system, an understanding of the performance and selectivity trends, and, therefore, knowledge of the kinetic properties of solid-phase extraction, are necessary. In addition, when using solid-state extractants, a slower adsorption kinetics and a lower adsorption capacity of the target components can be expected.

The absence of physicochemical characteristics of solid-phase extraction of REE by D2EHPA-containing extraction resins from concentrated phosphoric acid solutions and the necessity

to confirm technological advantages of their use determined the subject of this study. The study of the kinetic features of solvent and solid-phase extraction of yttrium and iron (III) using Levextrel resin containing groups of di-2-ethylhexylphosphoric acid, which is a selective extractant with relation to REE, is the subject of this research.

2. Materials and Methods

As the objects of the study model, industrial solutions of phosphoric acid were used. Phosphoric acid solutions were obtained from PJSC PhosAgro (Balakovo Branch of Apatit, Saratov Region, Balakovo District, Russia) as a product of apatite processing. The composition of industrial phosphoric acid solutions obtained during the sulphuric acid leaching of phosphate ores is shown in Tables 1 and 2. Simulated solutions containing 4.5 mol/L H₃PO₄ (prepared by dilution from concentrated chemical pure grade phosphoric acid, obtained from OOO Komponent–Reaktiv, Moscow, Russia) and 0.19 mol/L H₂SO₄ were used as an analogue of the industrial phosphoric acid system.

Table 1. Industrial phosphoric acid solution composition (mass. %).

Ln ¹	P_2O_5	SO ₃	F	Al_2O_3	CaO	Fe ₂ O ₃	SiO ₂
0.07–0.1	26–28	1.2–1.8	1.4–1.5	0.1–0.4	0.3–0.8	0.3–0.4	0.8–1.1

¹ Ln—tota	l content of	rare eartl	h elements	(REE)
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REO	Content, %	REO	Content, %	REO	Content, %
La ₂ O ₃	15.1	Sm_2O_3	3.18	Dy ₂ O ₃	1.92
Ce_2O_3	37.6	Eu_2O_3	0.96	Yb_2O_3	0.51
Pr_2O_3	4.68	Gd_2O_3	3.52	Y_2O_3	12.85
Nd_2O_3	18.37	Tb_2O_3	0.43	Er_2O_3	0.88

Table 2. Content of rare earth oxides (REO) in phosphoric acid solutions².

² The element contents were determined by the inductively coupled plasma mass spectrometry method using a Shimadzu ICPE-9000 mass spectrometer (Shimadzu Europa GmbH, Duisburg, Germany).

Di-2-ethylhexylphosphoric acid produced by 'Acros Organics' (obtained from ZAO Acrus, Moscow, Russia), with a D2EHPA concentration of at least 95%, was used as a liquid extractant; 'pure' grade kerosene with a mass fraction of saturated hydrocarbons of at least 95% and sulphur mass fraction of less than 0.1% (supplied by OOO Komponent–Reaktiv, Moscow, Russia) was used as an inert diluent. Both reagents are recommended for use in the chromatographic separation of substances.

The solid extractant used was a styrene and divinylbenzene suspension copolymerization product in the porous matrix of which D2EHPA was introduced directly during synthesis. The solid extractant was obtained from the government enterprise 'Smoly', Ukraine. The qualitative indicators of a solid-phase extractant are white spherical opaque granules; mass fraction of the working fraction is not less than 97%; granule size of the working fraction of 0.63–2.5 mm; mechanical strength not less than 96%; and the mass fraction of phosphorus is not less than 5.3%. During operation of the solid extractant, mechanical damages, such as abrasion and grinding, were not observed.

The phase contact during the study of the extraction equilibria of the solvent extraction was ensured using the HEL Group Automate Parallel Chemistry reactor (HEL Ltd., Borehamwood, UK). The process parameters temperature, phase contact period, stirring rate, and acidity level of the system were set and maintained constant during the experiments using the SCADA automated reactor control system CitectSCADA (designed by Schneider Electric SE, Rueil-Malmaison, France, supplied by GK RTSoft, Moscow, Russia). The experiment was carried out in a continuous type reactor. The phase contact during the solid-phase extraction was carried out using a thermostatically controlled shaker GFL Shaking Incubator 3032 manufactured by LAUDA–GFL Gesellschaft für Labortechnik GmbH (Burgwedel, Germany), equipped with rate-controlled orbital shaker (shaking frequency range of 20–250 RPM, shaking amplitude of 25 mm).

During the solvent extraction process, the phase volume ratio $V_{aq}/V_{org} = 2$ was used, the organic phase volume was 250 mL, and the concentration of the extractant D2EHPA in kerosene was 0.54 M. The aqueous and organic phase was thermostated with a temperature measure error within 1 °C. The sampling of the aqueous phase for an analysis in an amount of 10 mL was carried out continuously during the extraction process.

During the solid-phase extraction process, a phase ratio of 2 g of solid sorbent to 20 mL of an aqueous phase of simulated or industrial solution was used. The aqueous phase and the sorbent were mixed in a 250 mL Erlenmeyer flask. After the process, the solid material was separated from the aqueous phase using a special sieve for sorption processes. The yttrium and iron (III) content in the simulated phosphoric acid solutions amounted to 1.2–3.3 mmol/L and, accordingly, 1.7–2.2 mmol/L. Quantitative analysis of the organic and aqueous phase samples was carried out using a Shimadzu ICPE-9000 (Shimadzu Europa GmbH, Duisburg, Germany) inductively coupled plasma mass spectrometer, PANalytical Epsilon 3 X-ray fluorescence energy-dispersive spectrometer (Malvern Panalytical Ltd, Malvern, United Kingdom) with a sensitivity threshold of 10–4 mol/L and a measurement error of less than 5%. To ensure the reliability of the obtained results, the samples were measured several times.

3. Results and Discussion

3.1. Kinetic Features of Solvent Extraction of Yttrium

The dependence of the yttrium extraction degree from simulated phosphoric acid solutions on the phase contact time at different stirring rates and various temperatures of the solvent extraction process was studied. The experimental results are presented in Figures 1 and 2.



Figure 1. The dependences of the yttrium extraction degree on the phase contact time at different stirring rate in revolutions per minute (RPM) under temperature of 300 K.



Figure 2. The dependences of the yttrium extraction degree on the phase contact time at different temperatures.

According to experimental data, the optimal stirring rate is 400 revolutions per minute (RPM); its further increase does not lead to a change in the equilibrium establishment time in the extraction system. With a decrease in temperature from 333 to 283 K, an increase in the extraction degree into the organic phase from 60% to 80% is observed.

When studying the kinetics of extraction, the course of the process in time is characterized by the dependence I = f(t), where *I* is the degree of approaching to equilibrium:

$$I = \frac{C_{org}}{C_{org}^*} = \frac{(C_0 - C_{aq})}{(C_0 - C_{aq}^*)}$$
(1)

 C_{org}^*, C_{aq}^* are the concentration of the extracted component in the organic and aqueous phases after equilibrium is established; C_0 is the initial concentration of the component in an aqueous solution.

The limiting stage of the process is determined by identifying the influence of extraction conditions on the value of the coefficient *k*, having the physical meaning of the rate constant of the extraction process with constant mass transfer coefficients and the distribution of the phase interface surface:

$$\ln(1-I) = -kt,\tag{2}$$

$$\frac{dI}{dt} = \frac{1}{\frac{1}{\beta_R} + \frac{1}{\alpha\beta_E} + \frac{1}{K}} \cdot \frac{1+\alpha}{\alpha} S(1-I),$$
(3)

where k

$$k = \frac{1}{\frac{1}{\beta_R} + \frac{1}{\alpha\beta_E} + \frac{1}{K}} \cdot \frac{1 + \alpha}{\alpha} S$$
(4)

S—interface contact area, $\frac{1}{\beta_R}$, $\frac{1}{\alpha\beta_E}$ —reciprocal values of the diffusion coefficients in the raffinate and organic phase, $\frac{1}{K}$ —reciprocal value of chemical reaction rate coefficient, and α —distribution coefficient.

The interface area value with a constant stirring mode is directly related to the stirring intensity under identical reactor geometry and size. If diffusion rate-limiting processes in the aqueous or organic phases are of primary importance, more intensive stirring in the corresponding phase will lead to a substantial increase in the rate constant k. The absence of the effect of stirring and dependence of k on temperature characterizes the kinetic limitation of the extraction process.

One of the main methods for studying the reaction's kinetics is to carry out extraction with intense stirring when the extraction rate of the substance ceases to depend on the interface. Based on the experimental results, the rate constant of yttrium extraction was determined at different phase stirring rates (Figure 3) and different temperatures (Figure 4).



Phase contact time, min

Figure 3. The logarithmic dependences of the degree of approaching to equilibrium on the stirring rate at a temperature of 300 K.



Figure 4. The logarithmic dependences of the degree of approaching to equilibrium on the temperature at a stirring rate of 400 RPM.

According to the obtained experimental data (the slope of the dependences on Figures 3 and 4), the rate constant of the yttrium extraction process depends more significantly on the stirring rate compared to the temperature dependence.

3.2. Kinetic Features of Solvent Extraction of Iron (III)

The dependence of the iron (III) extraction degree from simulated solutions on the phase contact time at different stirring rates and various temperatures of the solvent extraction process was studied. Iron (III) extraction rate dependence was investigated under intense stirring conditions (600 RPM) due to a minimization of the external diffusion effect. The experimental results are presented in Figures 5 and 6.



Figure 5. The dependences of the iron (III) extraction degree on the phase contact time at different stirring rates under a temperature of 300 K.



Figure 6. The dependences of the iron (III) extraction degree on the phase contact time at a different temperature and a stirring rate of 600 RPM.

According to the linear logarithmic dependences of the degree of approaching to equilibrium (Figures 7 and 8) on the stirring rate and temperature, the values of the angular coefficients of iron (III) extraction are lower than the yttrium extraction coefficients (Figures 3 and 4; Table 3), which can be explained by the difference in the radii of the aquated ions $Y(H_2PO_4)^{2+}$ and Fe^{3+} in the phosphoric acid solutions [15,16]. Iron ions (3+), which have a significantly smaller crystallographic radius and a high effective charge on the atom, have higher hydration energies, and as a result, a larger number of water dipoles are included into the hydration shell of the ion.



Figure 7. The logarithmic dependences of the degree of approaching to iron (III) extraction equilibrium on the stirring rate at a temperature of 300 K.



Figure 8. The logarithmic dependences of the degree of approaching to iron (III) extraction equilibrium on the temperature.

Angular Coefficients	Stirring Rate, RPM			Temperature, K							
	300	400	600	283	291	296	300	305	309	317	333
$k_{(Y)}$, min ⁻¹	0.94	3.01	4.57	0.79	0.90	-	0.97	-	1.26	1.66	2.1
$k_{(\text{Fe})}$ min ⁻¹	0.20	0.30	0.90	0.11	0.18	0.21	0.32	0.33	-	0.40	0.60

Table 3. The values of the angular coefficients—rate constants of the yttrium and iron (III) extraction process.

With a temperature increase by 10 K, the angular coefficients of yttrium extraction are increased by 1.0–1.14 times, whereas the iron extraction coefficients are increased by almost 2 times.

3.3. Yttrium and Iron (III) Separation during Solvent Extraction

To determine the activation energy of iron and yttrium extraction, the dependence of ln(k) on the reciprocal temperature was plotted (Figure 9).



Figure 9. The dependence of ln(k) on the reciprocal temperature for (a) yttrium and (b) iron.

The dependence of ln(k) of the iron extraction process on 1/T shows two straight lines with different slopes, which characterizes a change in the rate-limiting step within temperature ranges of 283–300 K and 305–333 K. At low temperatures (283–300 K), the chemical reaction is the limiting stage, which is confirmed by the high value of the activation energy of 40.0 ± 1.4 kJ/mol. With temperature increasing (above 305 K), the activation energy value amounts to 11.4 ± 1.2 kJ/mol, which characterizes the diffusion limiting stage. Within a small temperature range of 300–305 K, the extraction rate is limited by a combined diffusion and chemical rate-limiting stage. The activation energy of yttrium extraction is 16.2 ± 1.3 kJ/mol, which characterizes the diffusion limiting stage of the process.

Based on the experimental results, the separation of elements during the extraction process is effectively carried out in the low-temperature region under the conditions of the existence of differences in the extraction process limiting stages. The dependences of the yttrium and ferric cations extraction degree on the phase contact time under a temperature of 300 Kand a stirring rate of 400 RPM is presented in Figure 10.



Figure 10. The dependences of the yttrium and iron (3+) cations extraction degree on the phase contact time.

According to experimental data, equilibrium in the process of yttrium extraction is much faster achieved compared to the iron (III) extraction process. Therefore, the extraction of yttrium under nonequilibrium conditions of the iron ions phase transition from aqueous to organic medium (up to 2 min) is a condition for the effective separation of components at the extraction stage (separation coefficient between yttrium and iron (III) = 23.2).

The number of extraction steps at an initial content of iron (III) of 1.5 g/L and yttrium of 0.13 g/L in a phosphoric acid medium, which provides an iron and yttrium concentration ratio in raffinate of 99, corresponding to 1% yttrium with respect to iron, will be no more than 3 at a contact time of 2 min.

3.4. Parameters of Yttrium and Iron (III) Solid-Phase Extraction

The equilibrium time in a simulated yttrium solid–liquid extraction system under a temperature of 298 K and a shaking frequency of 60, 70, and 95 RPM is determined (Figure 11).



Figure 11. The dependences of the yttrium extraction degree on the phase contact time at different shaking frequencies during the solid–liquid extraction process.

Regardless of the shaking frequency, the equilibrium in the system is established in 2 h. However, a further increase in the shaking frequency does not lead to a process intensification. Consequently, the convection rate does not significantly affect the extraction rate.

The dependence of a metal extraction degree on the quantitative ratio of solid and liquid phases at a temperature of 298 K and a shaking frequency of 90 RPM is shown in Figure 12. The phase ratio m_{solid}/V ($g_{\text{solid}}/m_{\text{solution}}$) is plotted along the abscissa.



Figure 12. The dependence of yttrium extraction degree on a solid and liquid phase ratio (g/mL).

Further tests were carried out with a phase ratio of 0.1, which is sufficient to ensure an equilibrium extraction degree of at least 80%. The temperature dependences of the yttrium extraction degree on the phase contact time at a shaking frequency of 90 RPM is shown in Figure 13.



Figure 13. The dependences of the yttrium extraction degree on the phase contact time at a different temperature.

The yttrium extraction degree is even less dependent on the temperature factor than with the solvent extraction. With an increase in temperature from 298 to 330 K it decreases by 8–9%, whereas the time required to reach equilibrium decreases to one hour.

Since D2EHPA extracts cations by the cation exchange mechanism, the solid-phase extractant can be considered similar to ion-exchange resins. Consequently, the possible limiting processes can be both the ions diffusion through a film of organic liquid (film diffusion), which is described by the equation of Fick's first law, and diffusion in the grain or organic phase of a solid material, which is described by the equation of Fick's second law. Along with diffusion processes, a chemical process is also possible.

A non-linear dependence (Equation (2)) under a different shaking frequency characterizes the absence of an external diffusion rate-limiting stage. Therefore, kinetic equations that describe the process of particle diffusion in grain were used:

$$I = 1 - \left(\frac{6}{\pi^2}\right) \exp(-kt),\tag{5}$$

$$\ln(1-l^2) = -kt,\tag{6}$$

where $k = \frac{D \cdot \pi^2}{r_0^2}$, *D*—diffusion coefficient and r_0 —mean radius of diffusing particle.

Temperature dependence $\ln(1 - I^2)$ on the phase contact time is presented in Figure 14. Values of the approximation coefficients and coefficients of the extraction process are given in Table 4.



Figure 14. The dependences $\ln(1 - l^2)$ of yttrium extraction on the phase contact time under temperatures of 295, 313, and 333 K.

Model	k	R^2
	$k_{295} = 0.041$	0.94
$\ln(1-I) = \ln\left(\frac{6}{\pi^2}\right) - kt$	$k_{313} = 0.053$	0.96
(//)	$k_{233} = 0.090$	0.98
	$k_{295} = 0.035$	0.98
$\ln(1-I^2) = -kt$	$k_{313} = 0.048$	0.98
()	$k_{233} = 0.083$	0.99

Table 4. Extraction and approximation coefficients.

According to the results obtained, the extraction rate coefficients, which were calculated using different models, adequately converge among themselves. The calculated value of the solid-phase extraction activation energy amounts to 18.5 ± 2.0 kJ/mol, characterizing the regularity of gel kinetics. The results of yttrium and iron cooperative sorption from industrial phosphoric acid solution by a

solid extractant at a temperature of 298 K, a solid to liquid ratio at 1:10, and a shaking frequency of 75 RPM are presented in Figure 15.



Figure 15. The dependences of the iron (III) and yttrium extraction degree from industrial phosphoric acid solution on the phase contact time.

The yttrium extraction degree during extraction from the industrial solution decreased by 10–15% compared to the extraction from a simulated solution, which is explained by the loading effect of other metals, such as Ca(2+) and Mg(2+) [15]. During the solid-phase extraction, in contrast to solvent extraction, it is impossible to decrease the iron (III) extraction degree during the process under non-equilibrium conditions. The differences between solvent and solid-phase extraction of iron by a D2EHPA solution is explained by the extractant configuration in the styrene/divinylbenzene matrix. 'Entangled' long and branched alkyl radicals of D2EHPA, imbedded in the mesh structure of the matrix, inhibit the formation of a first coordination sphere around iron (III) ion, as in the case of the solvent extraction [15,16]:

$$Fe^{3+} + 3(HR_2PO_4)_2 = Fe(R_2PO_4)_3 \cdot 3HR_2PO_4 + 3H^+,$$
(7)
(CH₂)₃ - CH - CH₂
|
CH₂ - CH₃

where R:

CH3 -

At the same time, REE ions, which exist in concentrated phosphoric acid solutions in the form of dihydrogen phosphate ions, require a smaller number of D2EHPA molecules to form the first coordination sphere:

$$Y(H_2PO_4)^{2+} + 2(HR_2PO_4)_2 = Y(H_2PO_4)(R_2PO_4)_2 \cdot 2HR_2PO_4 + 2H^+.$$
(8)

However, the iron extraction degree into the solid phase is significantly less compared to the solvent extraction and does not exceed 9%. Obviously, the solvation effect of the extractant reduces in the resin matrix compared to the effect in the liquid phase. Therefore, the Levextrel extraction mechanism is intermediate between ion-exchange sorption and liquid extraction, where the similarity to a particular process with the same matrix (styrene/divinylbenzene) will apparently be determined by the properties of the extractant.

4. Conclusions

Experimental data obtained indicate differences of iron and yttrium solvent extraction kinetics from a phosphoric acid medium. With increasing temperature during iron (III) extraction process, there is a change in the limiting mode. At a temperature range of 283–300 K, the process is limited

by a chemical reaction with an activation energy of 40.0 ± 1.4 kJ/mol. At a temperature above 305 K, diffusion becomes the limiting stage, characterized by a decrease in activation energy to 11.4 ± 1.2 kJ/mol. The diffusion process determines the rate of yttrium extraction over a wide temperature range with an activation energy of 16.2 ± 1.3 kJ/mol. Moreover, the rate constant of the process depends more significantly on the stirring rate rather than on temperature. With a temperature increase by 10 K, the rate constant of yttrium extraction is increased by 1.0-1.14 times, whereas the iron extraction rate constant is increased by almost 2 times.

Based on the revealed differences in the element extraction kinetics, it is possible to carry out their effective separation at the extraction stage. A high yttrium and iron separation coefficient of 23.2 is ensured by the short phase contact time (up to 2 min).

Solid extractants have an undoubted technological advantage. Compared with solvent extraction, the use of solid extractants can reduce the dependence of the yttrium extraction degree on the temperature factor. However, the equilibrium in the system is established within 1–2 h. The convection presence in the heterogeneous system does not significantly affect the extraction rate. The extraction rate coefficients were calculated using different diffusion models and showed adequate converge. The calculated value of solid-phase extraction activation energy amounts to $18.5 \pm 2.0 \text{ kJ/mol}$, characterizing the regularity of gel kinetics.

The iron (III) extraction degree into the solid phase is significantly less compared to solvent extraction and does not exceed 9%. The differences between solvent and solid-phase extraction of iron by a D2EHPA solution is explained by the extractant configuration in the styrene/divinylbenzene matrix. Extraction resins have undoubted operational advantages. Such resins are characterized by high mechanical strength, high chemical stability in aqueous solutions of acids and alkalis, and can be used in coarse systems and bulk filters. The absence of significant amounts of flammable solvents, which accompany liquid extraction, complies with the principles of green chemistry.

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References

- 1. Li, D. Development course of separating rare earths with acid phosphorus extractants: A critical review. *J. Rare Earths* **2019**, *37*, 468–486. [CrossRef]
- Cheremisina, O.V.; Schenk, J.; Cheremisina, E.A.; Ponomareva, M.A. Thermodynamic Model of Ion-Exchange Process as Exemplified by Cerium Sorption from Multisalt Solutions. *J. Min. Inst.* 2019, 237, 307–316. [CrossRef]
- Artiushenko, O.; Ávila, E.P.; Nazarkovsky, M.; Zaitsev, V. Reusable hydroxamate immobilized silica adsorbent for dispersive solid phase extraction and separation of rare earth metal ions. *Sep. Purif. Technol.* 2020, 231, 115934. [CrossRef]
- 4. Akkaya, R. Terbium adsorption onto polyhydroxyethylmethacrylate–hydroxyapatite composite and its modified composition by phytic acid. *Desalin. Water Treat.* **2014**, *52*, 1440–1447. [CrossRef]
- 5. Zhang, W.; Ye, G.; Chen, J. TRPO Impregnated Levextrel Resin: Synthesis and Extraction Behavior of Zr (IV) and Nd (III) Ions. *Sep. Sci. Technol.* **2012**, *48*, 263–271. [CrossRef]

- Callura, J.C.; Perkins, K.M.; Baltrus, J.P.; Washburn, N.R.; Dzombak, D.A.; Karamalidis, A.K. Adsorption kinetics, thermodynamics, and isotherm studies for functionalized lanthanide-chelating resins. *J. Colloid Interface Sci.* 2019, 557, 465–477. [CrossRef] [PubMed]
- 7. Kabay, N.; Cortina, J.L.; Trochimczuk, A.; Streat, M. Solvent-impregnated resins (SIRs)–Methods of preparation and their applications. *React. Funct. Polym.* **2010**, *70*, 484–496. [CrossRef]
- 8. Valenzuela, F.; Valdés, A.; Ide, V.; Basualto, C.; Sapag, J.; Araneda, C. Equilibrium, Kinetic, and Thermodynamic Analysis of Cd(II) Sorption from Aqueous Solutions using Polymeric Microcapsules containing an Acidic Organophosphonic Extractant. *Solvent Extr. Ion Exch.* **2012**, *30*, 422–430. [CrossRef]
- 9. Bao, S.; Tang, Y.; Zhang, Y.; Liang, L. Recovery and Separation of Metal Ions from Aqueous Solutions by Solvent-Impregnated Resins. *Chem. Eng. Technol.* **2016**, *39*, 1377–1392. [CrossRef]
- 10. Tunsu, C.; Petranikova, M. Perspectives for the recovery of critical elements from future energy-efficient refrigeration materials. *J. Clean. Prod.* **2018**, *197*, 232–241. [CrossRef]
- 11. Hérès, X.; Blet, V.; Di Natale, P.; Ouaattou, A.; Mazouz, H.; Dhiba, D.; Cuer, F. Selective extraction of rare earth elements from phosphoric acid by ion exchange resins. *Metals (Basel).* **2018**, *8*, 682. [CrossRef]
- 12. Mahanty, B.; Mohapatra, P.K. Highly efficient separation of thorium from uranium in nitric acid feeds by solid phase extraction using Aliquat 336. *Sep. Purif. Technol.* **2020**, 237, 116318. [CrossRef]
- Zheng, R.; Bao, S.; Zhang, Y.; Chen, B. Synthesis of Di-(2-ethylhexyl) Phosphoric Acid (D2EHPA)-Tributyl Phosphate (TBP) Impregnated Resin and Application in Adsorption of Vanadium(IV). *Minerals* 2018, *8*, 206. [CrossRef]
- 14. Sharaf, M.; Yoshida, W.; Kubota, F.; Goto, M. A Novel Binary-Extractant-Impregnated Resin for Selective Recovery of Scandium. *J. Chem. Eng. JAPAN* **2019**, *52*, 49–55. [CrossRef]
- 15. Cheremisina, O.; Sergeev, V.; Fedorov, A.; Iliyna, A. Specific features of solvent extraction of REM from phosphoric acid solutions with DEHPA. *Miner. Process. Extr. Metall.* **2019**, 1–7. [CrossRef]
- 16. Wang, L.; Long, Z.; Huang, X.; Yu, Y.; Cui, D.; Zhang, G. Recovery of rare earths from wet-process phosphoric acid. *Hydrometallurgy* **2010**, *101*, 41–47. [CrossRef]



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