The Kinetics of Sorption Extraction of Lanthanum and Aluminum Cations from a Phosphoric Acid Solution by Sulfocathionite

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Abstract

The kinetics of sorption extraction of Al^{3+} and La^{3+} cations from a solution of phosphoric acid by synthetic macroporous cation exchange resin was studied. In order to obtain the limiting stage of the process, the kinetic data obtained at various temperatures were approximated by pseudo-first, pseudo-second-order models, as well as the Boyd model for various cases of diffusive drag. It was found that the kinetics of adsorption of lanthanum ions is determined primarily by the rate of surface chemical reaction, while the adsorption of aluminum ions is limited by diffusion processes. A probable reason for the selectivity of adsorption may be the formation of complex compounds of different shapes and strengths between metal cations and phosphate anions.

Keywords

Rare-earth elements; sulfocationite; adsorption; phosphoric acid; lanthanum; aluminum.

Notation

τ – time, min;

a_τ – adsorption at time τ, mg/g;

a_e – equilibrium adsorption, mg/g;

c_τ – cation concentration at time τ, mg/l;

c_0 – initial concentration of cation in solution, mg/l;

k_1 – rate constant in a pseudo-first order model, min^{-1};

k_2 – rate constant in a pseudo-second order model, g/(mg·min);

α – initial adsorption rate, mg/(g·min);

β – desorption constant, g/mg;

F – dimensionless parameter of the Boyd diffusion model, which has the meaning of the driving force of the diffusion process and is equal to the ratio a_τ/a_e;

η – dynamic viscosity, Pa·s;

E_a – activation energy, kJ/mol;

m – cation exchanger mass, g;

V – volume of solution, l.

Introduction

Phosphoric acid obtained by acid decomposition of phosphate ores contains up to 10 g/l of rare earth elements and other cationic impurities dissolved in it.

Therefore, the extraction of these impurities from extraction phosphoric acid would make it possible, on the one hand, to obtain higher quality H_3PO_4, and, on the other hand, rare-earth metals, which are a rare and valuable industrial raw material.

To date, the adsorption method of purification of phosphoric acid from impurities dissolved in it is one of the most promising ones from the point of view of capital costs and current costs of production [1]. A wide range of scientific studies can be found in the periodic literature on the adsorption extraction of cations, including rare-earth metals from phosphoric acid using various types of adsorbents: activated carbon [2], strongly acidic cation exchangers [3–5], phosphorus-containing ion-exchange resins [6–8] zeolites [9], etc.

The main difficulties in the industrial application of ion exchange adsorption for the H_3PO_4 purification are, firstly, the phenomenon of strong competing adsorption from protons, and secondly, the pronounced selectivity of the adsorption of cations of one metal over others, the reason for which remains unclear.

One of the main impurity elements contained in extraction phosphoric acid in sufficiently high concentrations is aluminum, which gets into it as a

result of acid destruction of the framework of natural aluminosilicates, which are usually present in the composition of phosphate raw materials.

This paper presents a study of the kinetics of adsorption of La^{3+} and Al^{3+} from a solution of phosphoric acid on macroporous synthetic sulfocationionite, which has proven itself in previous studies [10].

Experimental

The sorption of ions was carried out using a model solution of phosphoric acid with a concentration of 26 wt. % using P_2O_5, which is comparable with the concentration of unpaired extraction phosphoric acid obtained by the sulfuric acid decomposition of apatite according to the dihydrate method. The model solution of phosphoric acid contained La^{3+} ions with a concentration of 1 g/l and Al^{3+} –1.5 g/l, the concentration of metal ions also correlated with their content in extraction phosphoric acid. Studies of the kinetics of adsorption were carried out under static conditions. The volume ratio of solid and liquid phases was 1 : 10, the temperature varied from room temperature to 70 °C.

The adsorbent was macroporous sulfocationite MTC1600 manufactured by Purolite Corporation, synthesized by polystyrene crosslinked with divinylbenzene.

The concentration of impurity ions was determined by the atomic absorption method using a Kvant-AFA spectrometer (Kortek, Russia) at the D.I. Mendeleev resource sharing center at Russian University of Chemical Technology.

The adsorption value was calculated by the formula (1):

$$a = \frac{(c_0 - c_\tau)V}{m}. \tag{1}$$

Kinetic data were approximated by the following kinetic models [11–15]:

1. A pseudo-first-order model that takes into account the adsorption capacity of the adsorbent. The linear form of the equation of the pseudo-first order model (2):

$$\log(a_e - a_\tau) = \log a_e - \frac{k_1}{2.303}\tau. \tag{2}$$

2. A pseudo-second order model, which assumes that the adsorbate-adsorption center interaction of the adsorbent is chemisorption in nature and proceeds in a 1 : 1 ratio. The linear form of the equation of the pseudo-second order model (3):

$$\frac{\tau}{a_\tau} = \frac{1}{a_e^2 k_2} + \frac{1}{a_e}\tau. \tag{3}$$

3. The Elovich–Chen–Clayton model, taking into account the possibility of desorption of the adsorbate. The linear form of the equation of the Elovich model (4):

$$a_\tau = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(\tau). \tag{4}$$

4. The Boyd model, which allows one to estimate the contribution of external and internal diffusion inhibition to the adsorption kinetics. If the experimental kinetic curve is linear in the coordinates $-\lg(1 - F) = f(\tau)$, this indicates a limitation of the adsorption rate by external diffusion. If the experimental kinetic curve is linear in the coordinates $F = f(\tau^{1/2})$, this indicates a limitation of the rate of adsorption by internal diffusion.

The UV spectra of acid solutions were studied on an SF-2000 spectrophotometer in the wavelength range of 190–400 nm.

Results and Discussion

Kinetic adsorption curves indicate that in 60 minutes on the MTC1600 cation exchange resin, complete recovery of La^{3+} cations can be achieved. The degree of extraction of Al^{3+} cations is much lower and does not exceed 6 %, depending on temperature. Adsorption equilibrium for Al^{3+} occurs in about 30–40 minutes.

The rate and size of adsorption, both in the case of La^{3+} ions and in the case of Al^{3+} ions increased with temperature (Figs. 1a, b). The recovery in the first 5 minutes of the process for La^{3+} cations was 24.7 % at 20 °C, 60.8 % at 50 °C and 61.9 % at 70 °C; for Al^{3+} cations it reached 3.2, 5, and 5.2 %, respectively.

The results of the approximation of kinetic data by pseudo-first and pseudo-second-order models, as well as the Elovich–Chen–Clayton model, are presented in Tables 1 and 2.

In accordance with the values of the determination coefficient r^2, the most adequate model for describing the kinetics of ion-exchange adsorption of cations is the pseudo-second order model, which reflects the chemisorption mechanism of the process. From the presented data, it also follows that with increasing temperature, the initial adsorption rate rapidly increases, with a practically constant desorption constant, which is also characteristic of chemisorption.

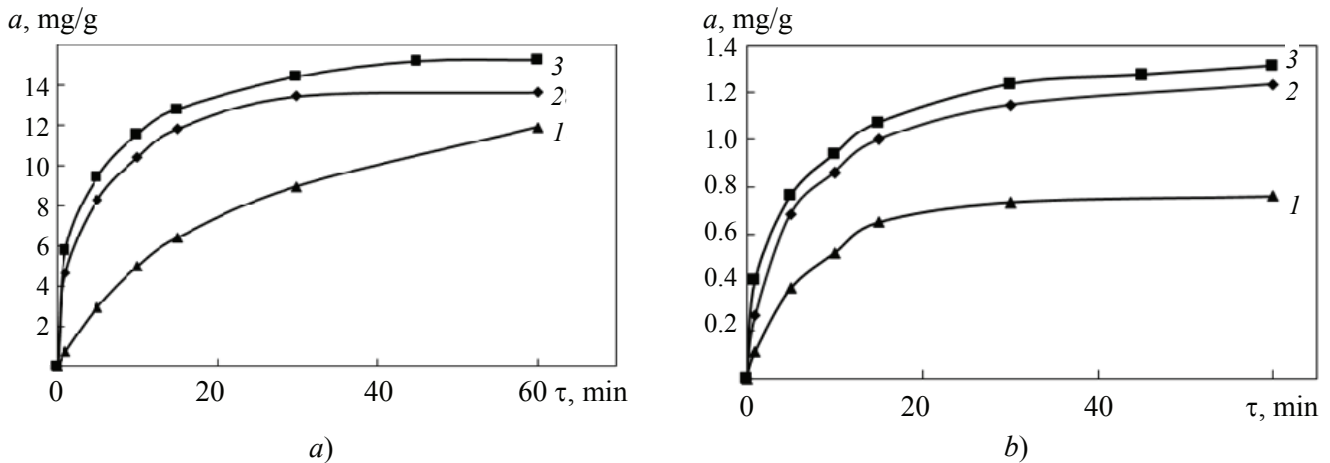The approximation of the experimental data by the Boyd model (Figs. 2, 3) allows us to conclude that

Fig. 1. Kinetic curves of adsorption of La^{3+} (*a*) and Al^{3+} (*b*) cations on MTC1600 cation exchange resin:
1 – 25 °; 2 – 50 °C; 3 – 70 °C

Table 1

Parameters of kinetic models of adsorption of La^{3+} cations on MTC1600 cation exchange resin

Pseudo first-order model				
T adsorption, °C	k_1, min^{-1}	a_{max} (theor)	a_{max} (exp)	r^2
25	0.020	11.462	11.887	0,995
50	0.059	11.944	13.625	0,993
70	0.048	12.442	15.210	0,970
Pseudo second-order model				
T adsorption, °C	k_2, g/(mg·min)	a_{max} (theor)	a_{max} (exp)	r^2
25	0.003	12.216	11.887	0,998
50	0.013	14.374	13.625	0,999
70	0.019	16.023	15.210	0,999
Elovich–Chen–Clayton Model				
T adsorption, °C	α, mg/(g·min)	β, g/mg		r^2
25	2.315	0.366		0.941
50	17.954	0.423		0.973
70	26.616	0.492		0.991

Table 2

Parameters of kinetic models of adsorption of Al^{3+} cations on MTC1600 cation exchange resin

Pseudo first-order model				
T adsorption, °C	k_1, min^{-1}	a_{max} (theor)	a_{max} (exp)	r^2
25	0.049	0.713	0.763	0.995
50	0.037	0.992	1.238	0.972
70	0.033	0.916	1.313	0.969

Pseudo fsecond-order model			
T adsorption, °C	k_2, g/(mg·min)	a_{max} (theor)	a_{max} (exp)	r^2
25	0.107	0.846	0.763	0,998
50	0.158	1.333	1.238	0,999
70	0.188	1.389	1.313	0,999

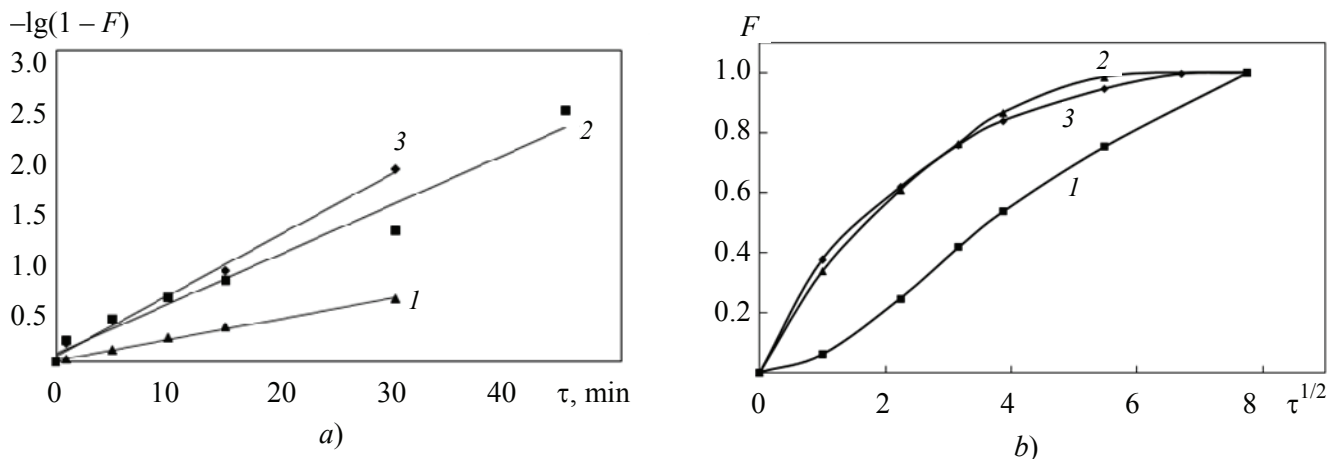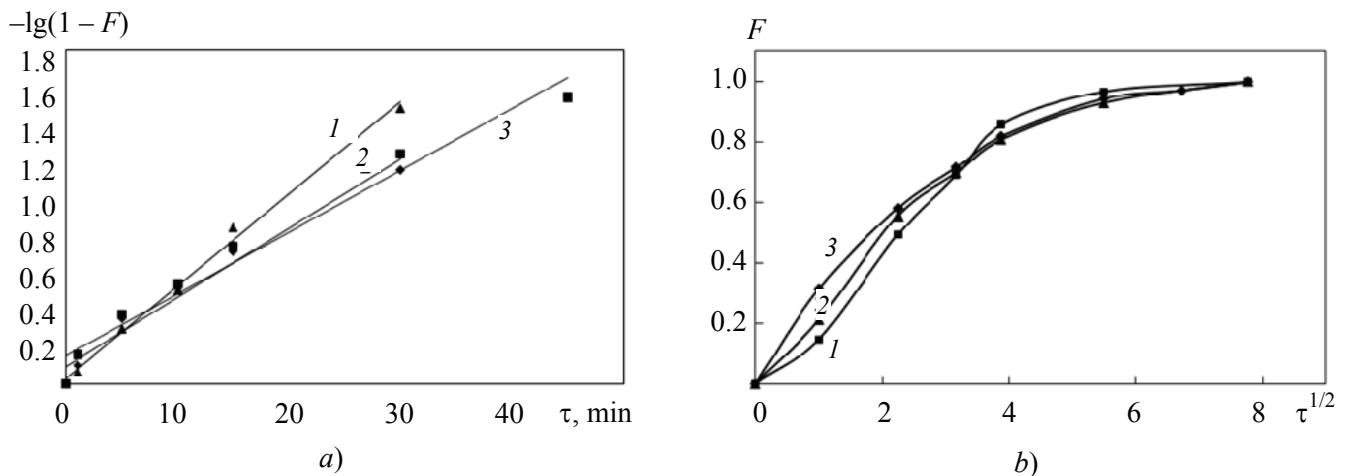| *Elovich–Chen–Clayton model*		
T adsorption, °C	α, mg/(g·min)	β, g/mg	r^2
25	0.358	3.866	0.968
50	0.794	4.066	0.989
70	1.415	4.376	0.991

**Fig. 2. Kinetic curves of adsorption of La^{3+} cations in the coordinates of the Boyd model
for the case of external diffusion drag (*a*) and intra-diffusion drag (*b*):**
a: *1* – 25 °C (r^2 = 0.996); *2* – 50 °C (r^2 = 0.993); *3* – 70 °C (r^2 = 0.971)
b: *1* – 25 °C (r^2 = 0.991); *2* – 50 °C (r^2 = 0.817); *3* – 70 °C (r^2 = 0.836)

**Fig. 3. Kinetic curves of adsorption of Al^{3+} cations in the coordinates of the Boyd model
for the case of external diffusion drag (*a*) and intra-diffusion drag (*b*):**
a: *1* – 25 °C (r^2 = 0.995); *2* – 50 °C (r^2 = 0.972); *3* – 70 °C (r^2 = 0.969)
b: *1* – 25 °C (r^2 = 0.859); *2* – 50 °C (r^2 = 0.868); *3* – 70 °C (r^2 = 0.866)

external diffusion drag, which decreases with the viscosity of the solution with increasing temperature, has a significant effect on the speed of the process ($\eta_{20°C} = 2.2$ Pa·s; $\eta_{50°C} = 1.4$ Pa·s, $\eta_{70°C} = 0.7$ Pa·s). Internal diffusion also has a marked effect on the speed of the process, especially at normal temperature.

The similarity of the parameters of the kinetic models for La^{3+} and Al^{3+} ions and the tendencies of their changes with temperature suggest that the difference in their adsorbability may be due to the form of cations in the solution of phosphoric acid, which, in turn, may determine the efficiency of the interaction of the cation with the ionogenic group cation exchange adsorbent. It is known that lanthanide cations can form labile complex compounds in which phosphate anions act as ligands [16, 17]. The larger the number of phosphate anions coordinated around the metal complexing agent, the greater should be the screening of its positive charge, and the lower the likelihood of its interaction with the ionic group of cation exchange resin.

The structure of the phosphate complexes of La^{3+} and Al^{3+} cations in a solution of phosphoric acid can be judged on the basis of the results of UV spectroscopy (Fig. 4).

The absorption spectrum of phosphate anions in a solution of phosphoric acid without cations is due to the forbidden $n \to \pi^*$ transition, which gives a weak band with a maximum at 190 nm. The addition of La^{3+} or Al^{3+} cations to the phosphoric acid solution leads to a significant bathochromic and hyperchromic shift of the absorption band ($\lambda_{max} = 220 - 230$ nm), as well as to the appearance of a new band of lower intensity with a maximum at $290 - 295$ nm. This may indicate the
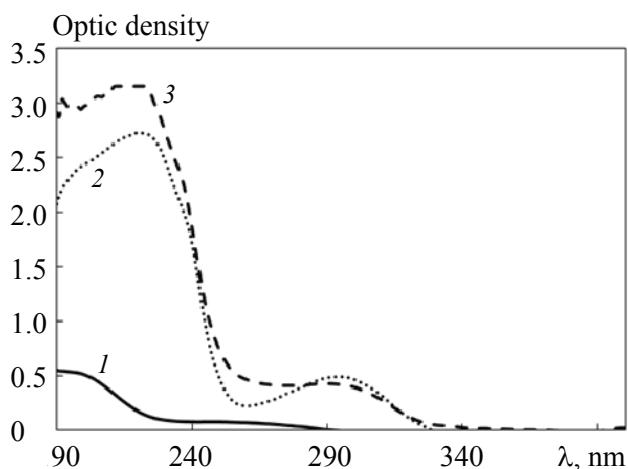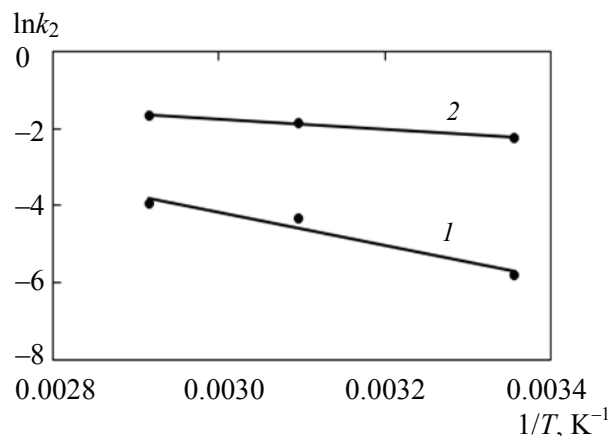

Fig. 5. Data in the coordinates of the linear form of the Arrhenius equation for calculating the activation energy of the adsorption process:
1 – La^{3+}; *2* – Al^{3+} on MTC 1600 cation exchange resin

formation of compounds with a system of conjugated chemical bonds in solution [18–20]. The strongly acidic environment of the H_3PO_4 solution prevents the cation from hydrolyzing. Therefore, the only possible compounds responsible for changing the spectrum may be complex compounds of lanthanum and aluminum with phosphate anions. A comparison of the absorption spectra of the proposed complexes of the two studied cations (with the same molar content in the acid solution) shows a certain hypochromic and hypochromic shift of the $\lambda_{max} = 290-295$ nm band in the case of the La^{3+} cation compared to the same band of the Al^{3+} cation, which may indicate different the magnitude and strength of these complexes. At the same charge, the radius of the aluminum cation (0.057 nm) is less than the radius of the lanthanum cation (0.122 nm). According to Pearson's classification, Al^{3+} cation is a more stringent acid than La^{3+} cation, and, therefore, it should interact more efficiently with the PO_4^{3-} anion, which is a rigid base. It can be assumed that the lower degree of extraction of Al^{3+} cations compared to La^{3+} cations is due to the greater degree of screening of its positive charge by phosphate anions.

The calculation of the activation energy (Fig. 5) showed that for La^{3+} cations ($E_a = 35.69$ kJ/mol) the process is closer to chemisorption, while for Al^{3+} cations ($E_a = 10.77$ kJ/mol), the ion-exchange reaction is more controlled by diffusion, which may also indicate a different form of cations in a solution of phosphoric acid.

Fig. 4. UV-spectra of phosphoric acid solution before and after the addition of La^{3+} or Al^{3+} cations:
1 – H_3PO_4; *2* – $H_3PO_4 + La^{3+}$; *3* – $H_3PO_4 + Al^{3+}$

Conclusion

As a result of the study, it was found that macroporous sulfocationite selectively adsorbs La^{3+} cations from a solution of phosphoric acid in comparison with Al^{3+} cations. Mathematical processing of experimental data showed that the kinetics of ion-exchange adsorption of Al^{3+} and La^{3+} cations is complex and is determined by both diffusion processes and the rate of surface chemical reaction. The similarity in the change in kinetic parameters depending on temperature for Al^{3+} and La^{3+} suggests that the adsorption selectivity is associated with the features of the interaction of the cation with the ionic group of cation exchange resin and is due to the type and strength of the complex compounds formed between the cation and phosphate anions, which is indirectly confirmed by a comparison of UV spectra solutions of Al^{3+} and La^{3+} cations in phosphoric acid.

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