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Selective lithium extraction from aqueous solutions by layered amorphous protonated potassium polytitanate

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Abstract: In this work, using a technologically simple and low-cost method, as an alternative to the known layered inorganic ion exchangers of manganese and titanate type, protonated potassium polytitanate ($K_{0.8}H_{1.2}Ti_{4.3}O_{8.5}$) was obtained and studied to extract lithium from secondary natural resources. X-ray diffraction analysis confirmed the retention of the original X-ray amorphous structure of potassium polytitanate after the protonation process, which ensures good ion-exchange and adsorption capacity of the material. Functional groups of protonated potassium polytitanate, which are potential active sites for interaction with Li^+ ions, were analyzed by FTIR spectroscopy. When lithium was extracted from an aqueous solution with a concentration of 0.01 $mol{\cdot}L^{-1}$, protonated potassium polytitanate demonstrated an equilibrium adsorption capacity of 0.52 $mmol{\cdot}g^{-1}$. In this case, the experimental data are in good agreement with the pseudosecond order kinetic model ($R^2 = 0.999$). The adsorption process is described by the Freundlich isotherm and is characterized by the constant $K_F = 0.0013\ (L)^{1/n}(mmol)^{1-1/n}g^{-1}$. The good selectivity of protonated potassium polytitanate with respect to Li^+ ions in the presence of Na^+, K^+, Mg^{2+}, and Ca^{2+} ions is shown, while the adsorption capacity is maintained at the level of 0.50–0.52 $mmol{\cdot}g^{-1}$.The results obtained indicate that protonated potassium polytitanate is a promising and competitive material for the extraction of Li^+ ions from low concentration aqueous solutions.

Keywords: potassium polytitanate; protonation; ion exchange; lithium extraction; aqueous solutions; kinetics; adsorption isotherms; selectivity.

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Селективное извлечение лития из водных растворов слоистым аморфным протонированным полититанатом калия

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Аннотация: В данной работе по технологически простой и дешевой методике в качестве альтернативы известным слоистым неорганическим ионообменникам марганцевого и титанатного типа получен и исследован протонированный полититанат калия ($K_{0,8}H_{1,2}Ti_{4,3}O_{8,5}$) в целях извлечения лития из вторичных природных ресурсов. Методом рентгеновского фазового анализа (РФА) подтверждено сохранение исходной рентгеноаморфной структуры полититаната калия после процесса протонирования, обеспечивающей хорошую ионообменную и адсорбционную способность материала. Методом инфракрасной спектроскопии проанализированы функциональные группы протонированного полититаната калия, представляющие собой потенциальные активные центры для взаимодействия с ионами Li^+. При извлечении лития из водного раствора с концентрацией 0,01 моль/л протонированный полититанат калия продемонстрировал равновесную адсорбционную емкость 0,52 ммоль/г. При этом экспериментальные данные хорошо согласуются с кинетической моделью псевдовторого порядка ($R^2 = 0,999$). Адсорбционный процесс описываются изотермой Фрейндлиха и характеризуются константой $K_F = 0{,}0013$ (л)$^{1/n}$(ммоль)$^{1-1/n}$/г. Показана хорошая селективность протонированного полититаната калия по отношению к ионам Li^+ в присутствии ионов Na^+, K^+, Mg^{2+} и Ca^{2+} при сохранении адсорбционной емкости на уровне 0,50…0,52 ммоль/г. Полученные результаты свидетельствуют о том, что протонированный полититанат калия является перспективным и конкурентоспособным материалом для извлечения ионов Li^+ из водных растворов с низкой концентрацией.

Ключевые слова: полититанат калия; протонирование; ионный обмен; извлечение лития; водные растворы; кинетика; изотермы адсорбции; селективность.

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1. Introduction

With the current emphasis on maintaining a sustainable environment, the design, development and implementation of environmental technologies, in particular electric-powered vehicles, is a global priority. Lithium is an indispensable element in the production of electrode materials for batteries in hybrid cars and electric vehicles, as well as in portable electronics [1–8].

The favourable electrochemical characteristics of lithium are responsible for the rapidly growing demand for it. It is therefore important to utilize primary (ores and brines) and alternative secondary (clays and seawater) lithium resources with high efficiency to ensure timely and adequate supplies of lithium raw materials.

Pyrometallurgical [9–12] and hydrometallurgical [13–15] processes can be used to extract lithium from primary and secondary resources. Although pyrometallurgical processes are economical from a technical point of view, they require an intensive financial investment and are accompanied by undesirable environmental pollution. Hydrometallurgical processes, including acid-alkali leaching followed by solvent extraction [16, 17], adsorption (ion exchange) [18, 19] and precipitation [20, 21], are considered promising methods for extracting lithium as pure carbonate (Li_2CO_3) and lithium hydroxide (LiOH) due to minimal energy costs and production waste. However, in solutions, lithium occurs as a cation together with other metal ions such as sodium, potassium, calcium, magnesium, etc. Therefore in the deposition method the existing impurities have to be removed before lithium is obtained. Otherwise, the product will have a lower purity due to co-deposition of other metals. Thus, for sources where the concentration of lithium ions is low and other ions are likely to be present, reactions based on adsorption and ion exchange are more effective. There are a number of inorganic ion-exchange materials with exceptionally high selectivity for lithium ions alone.

Manganese-type ion exchangers based on $LiMn_2O_4$, $Li_4Mn_5O_{12}$ and $Li_{1.6}Mn_{1.6}O_4$ show high efficiency in the extraction of lithium ions from concentrated and dilute solutions [22–24]. However, the destruction of the manganese structure during Li^+ deintercalation makes their reuse difficult [25, 26].

Many recent studies have focused on H_2TiO_3 metatitanic acid with layered structure due to its greater stability during lithium desorption and higher theoretical adsorption capacity [27]. It is traditionally produced by a two-step process. First, the Li_2TiO_3 precursor is synthesized by solid-phase [28], hydrothermal [29] or sol-gel method [30]. Li_2TiO_3 is then treated in acid to obtain the functional end product. The solid-phase method is preferred for industrial production due to its simplicity, cost-effectiveness and high throughput, but inadequate mixing of raw materials can lead to an inaccurate stoichiometric product, caking and large particles, which is bad for the adsorbent. Although sol-gel and hydrothermal synthesis methods provide uniform mixing of feedstocks, these techniques are relatively complex and expensive and therefore difficult to implement in industry.

In this connection, a novel technologically simple and cost-effective approach to obtaining an effective protonated form of ion exchange is proposed for the first time in this work. It uses a lithium-free precursor, potassium polytitanate, characterised by the formula $K_2Ti_{4.3}O_{9.6}$ and a semi-crystalline layered structure formed by K^+ cations and TiO_6^{n-} octahedra connected at different angles as a raw material. Synthesis in a hydroxide-salt melt provides the required uniformity in component mixing, and possible excess unreacted water-soluble compounds are removed by washing. The total and surface ion exchange capacities of potassium polytitanate are 134 mg·g^{-1} (3.43 mmol·g^{-1}) and 16 mg·g^{-1} (0.42 mmol·g^{-1}) respectively [31], which is competitive with known inorganic ion exchangers.

The aim of the work is to investigate the efficiency and selectivity of the protonated form of potassium polytitanate in the process of lithium extraction from aqueous solutions with low concentration.

2. Materials and Methods

2.1. Materials and reagents

The following reagents were used for the synthesis of potassium polytitanate: TiO_2 (99.5 %, TU 2321-001-17547702-2014, Vitahim Group, Russia), KOH (analytical grade purity, Russian Standard 24363–80, LLC “Reachem”, Russia) and KNO_3 (analytical grade purity, Russian Standard 4217–77, LLC “Reachem”, Russia). HCl (35 %, Russian Standard 3118–77, JSC “Vekton”, Russia) was used for protonation of potassium polytitanate. LiCl (99.2 %, TU 6-09-3751-838, RusChem Group, Russia) was used to study lithium ion-exchange extraction. NH_4OH (analytical grade purity, Russian Standard 3760–79, Sigma Tech Ltd., Russia) was used for pH correction during the ion-exchange process.

2.2. Preparation of the ion-exchange material

The synthesis of the initial potassium polytitanate ($K_2Ti_nO_{2n+1}$ (n = 3.8–4.1)) was carried out using precursors TiO_2, KOH and KNO_3 at their mass ratio of 30:30:40 in the reaction mixture. This included distilled water in an amount 2:1 relative to the mass of TiO_2, as a result of temperature treatment at 500 °C for 3 hours followed by washing to pH = 10.0 ± 0.5.

Protonation of potassium polytitanate was carried out using 0.1 M HCl solution by stirring the dispersion with a concentration of 20 $g{\cdot}L^{-1}$ at pH = 2.0 ± 0.5 for 2 hours followed by decantation and drying at 60 °C.

2.3. Characterization of the ion-exchange material

Chemical composition of the protonated sample was determined on a BRA-135F spectrometer (Burevestnik, Russia). X-ray phase analysis was carried out on diffractometer ARL X'TRA (Thermo Scientific, Switzerland) using Cu K_α-radiation ($\lambda = 0.15412$ nm). Fourier-transform infrared spectrometer FT-801 (Simex, Russia) was used for the analysis of surface functional groups.

2.4. Investigation of the ion-exchange process

To investigate the kinetics and equilibrium state of the ion-exchange process 1 g of protonated potassium polytitanate was mixed with 100 ml of LiCl solution with Li^+ ions concentration 0.005; 0.01; 0.02; 0.025 and 0.05 $mol{\cdot}L^{-1}$. The resulting mixture was incubated under constant stirring, at room temperature $T = (25 \pm 2)$ °C and pH = 8.0 by adding an aqueous solution of NH_4OH. The choice of the indicated pH value during the ion-exchange process was due to the high efficiency of previously studied manganese and titanate-type ion-exchange materials under these conditions [30, 32], as well as the performance of seawater as a potential real source for lithium extraction using the obtained material [33]. The change in the concentration of Li^+ ions was recorded by potentiometric method on a laboratory ionometer I-160MP (Gomel Instrumentation Plant, Republic of Belarus) with a lithium selective electrode ELIS-142Li (IzmeritelnayaTehnika, Russia) every 5, 10, 20, 30, 60, 90, 120, 150, 180, 210 and 240 min.

To study selectivity of ion-exchange material 1 g of protonated potassium polytitanate was dispersed in 100 mL of solution, containing besides Li^+ ions (0.01 $mol{\cdot}L^{-1}$), the following ions: Na^+, K^+, Mg^{2+} and Ca^{2+} with concentration of 0.004 $mol{\cdot}L^{-1}$.

Based on the results of the study, the sorption capacity of protonated potassium polytitanate (q, $mmol{\cdot}g^{-1}$) was calculated by the formula (1):

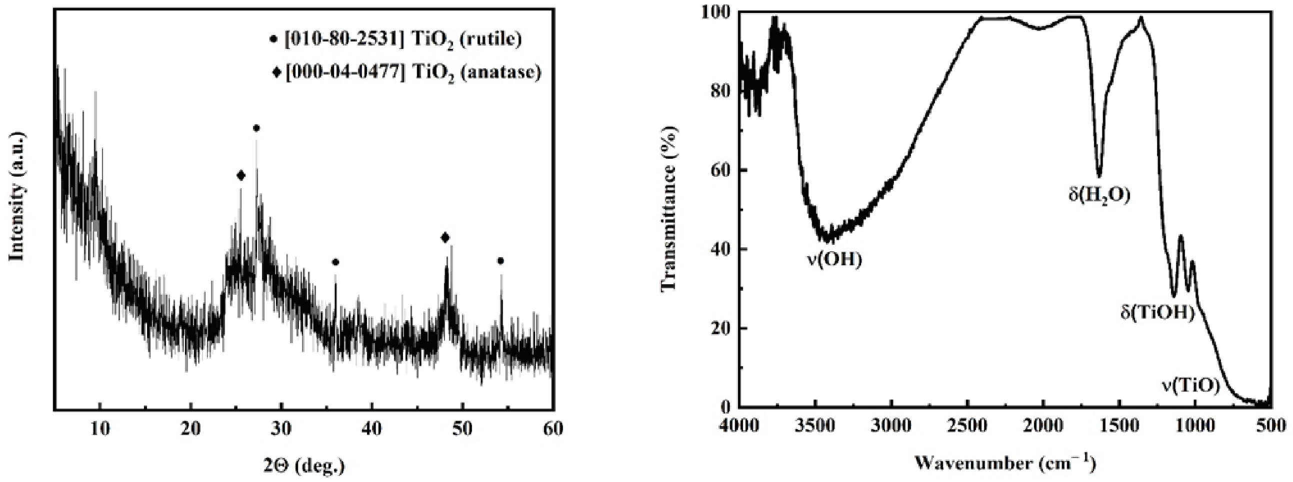
$$q = \frac{C_0 - C_t}{m} V, \qquad (1)$$

where C_0 is the initial concentration of Li^+ ions in solution, $mmol{\cdot}L^{-1}$; C_t is the concentration of Li^+ ions in the solution at time t, $mmol{\cdot}L^{-1}$; m is the mass of protonated potassium polytitanate, g; V is the volume of solution, L.

3. Results and Discussion

3.1. Characterization of the ion-exchange material

Protonation as a method of chemical modification of layered compounds is an ion-exchange replacement of interlayer cations of initial structure by hydroxonium or hydrogen cations as a result of appropriate treatment, mainly in aqueous solutions of strong inorganic acids [34, 35]. In the case of potassium polytitanates K^+ cations take part in the ionic exchange compensating the negative charge of titanium-oxygen octahedrons [36, 37].



(*a*) (*b*)

Fig. 1. X-ray diffractogram (*a*) and IR transmission spectrum (*b*) of protonated potassium polytitanate

By the recalculation of X-ray fluorescence analysis data on the mass content of potassium oxides (10.4 wt. %) and titanium (89.6 wt. %) and considering the conservation of titanium mole fraction and replacement of potassium ions by hydrogen ions the obtained protonated potassium polytitanate may be described by the chemical formula $K_{0.8}H_{1.2}Ti_{4.3}O_{8.5}$.

The protonated sample is characterized by an X-ray amorphous structure (degree of crystallinity is about 25 %). The low-intensity reflexes observed on the X-ray diffractogram relate to titanium dioxide phases of different modifications (anatase and rutile) (Fig. 1*a*). According to the results of the X-ray phase analysis, protonation under the specified conditions does not lead to the destruction of the X-ray amorphous structure of the original potassium polytitanate and the formation of high crystallinity phases as degradation products [38, 39].

Infrared transmission spectra of protonated potassium polytitanate reveal absorption bands, responsible for the stretching vibrations of hydroxyl groups (wide absorption band at 3750–3000 cm^{-1}) and titanium-oxygen bonds (less prominent absorption band at 550 cm^{-1}) as well as strain vibrations of physically adsorbed water (high intensity absorption band at 1630 cm^{-1}) and thianol groups (paired absorption bands at 1140 and 1050 cm^{-1}) (Fig. 1*b*). IR spectroscopy data feature the functional groups of protonated potassium polytitanate involved in the ion-exchange interaction with Li^+ ions [40–44].

3.2. Adsorption kinetics

Two distinct stages of the investigated process can be distinguished in Fig. 2 of the kinetic dependence. During the first 20–30 min the rate of Li^+ ions extraction is fast, sorption capacity of protonated potassium polytitanate reaches 0.47 $mmol \cdot g^{-1}$ during the first 30 min of interaction with lithium salt solution. Then the rate of increase of q value slows down and after 2 h sorption capacity reaches its maximum value of 0.52 $mmol \cdot g^{-1}$ (lithium recovery efficiency is 52 %). The decrease in the rate of ion-exchange adsorption is due to continuous saturation of the active sites of protonated potassium polytitanate in the process of interaction with Li^+ ions.

To simulate the adsorption process and to identify the limiting stage of the process, linear equations of pseudo-first order (2) and pseudo-second order (3) models have been applied [45–47]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \; ; \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \, , \qquad (3)$$

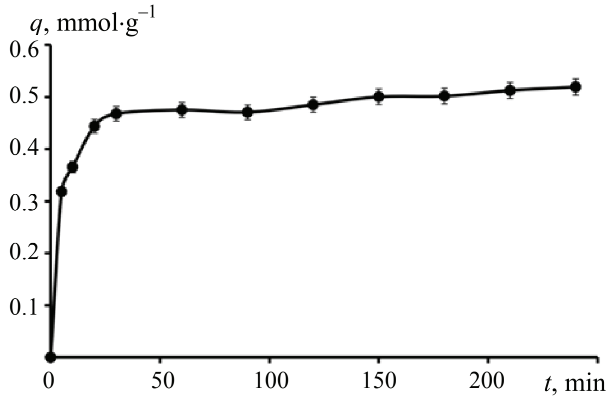


Fig. 2. Kinetics of protonated potassium polytitanate ion-exchange interaction with Li^+ ions

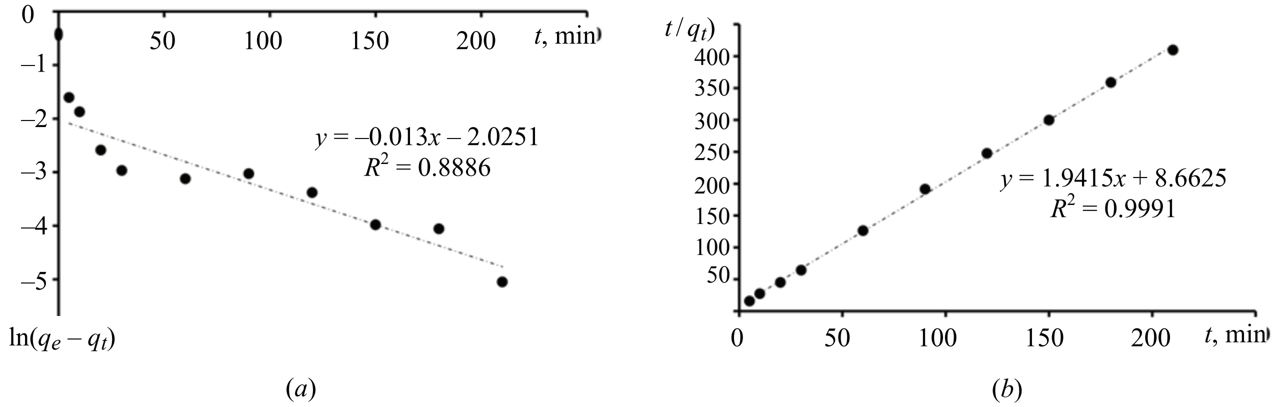


Fig. 3. Kinetics of protonated potassium polytitanate ion-exchange interaction with Li^+ ions in coordinates of pseudo-first (*a*) and pseudo-second (*b*) order models

Table 1. Kinetic parameters of protonated potassium polytitanate ion-exchange interaction with Li^+ ions

Pseudo-first order model			Pseudo-second order model		
R^2	q_e, mmol·g^{-1}	k_1, min^{-1}	R^2	q_e, mmol·g^{-1}	k_2, g(mmol·min)$^{-1}$
0.89	0.13	0.013	0.99	0.52	0.43

where q_e (mmol·g^{-1}) and q_t (mmol·g^{-1}) are the number of Li^+ ions subjected to ion exchange at equilibrium and at time *t*, respectively, k_1 (min^{-1}) and k_2 (g(mmol min)$^{-1}$) are kinetic constants of pseudo-first and pseudo-second order, respectively.

Modeling of experimental data using kinetic models shows that the pseudo-second order model ($R^2 = 0.9991$) describes the process of ion-exchange interaction of protonated potassium polytitanate with Li^+ ions better than the pseudo-first order kinetic model ($R^2 = 0.8886$).

The simulation results and calculated kinetic parameters are shown in Fig. 3 and Table 1.

It is known that both kinetic models assume that a chemical exchange reaction limits the sorption process. However, if the pseudo-first order model is feasible, it should be taken into account that adsorption is preceded by diffusion. If the experimental data of the pseudo-second order model are fulfilled, the studied interaction belongs to the reaction of the second order and reacting substances interact with each other in the ratio 1:1 [48].

Consequently, the ion-exchange chemical reaction occurring between Li^+ ions and functional groups of protonated potassium polytitanate —TiOH is very likely to be the limiting stage of interaction and the adsorption rate is mainly controlled by stoichiometric exchange between H^+ and Li^+ ions. The rate of lithium extraction is determined by both the concentration of the alkali metal ion in solution and the number of active sites of the ion-exchange material. Most of the manganese and titanate analogues show a similar pattern in their interaction with Li^+ [49–52].

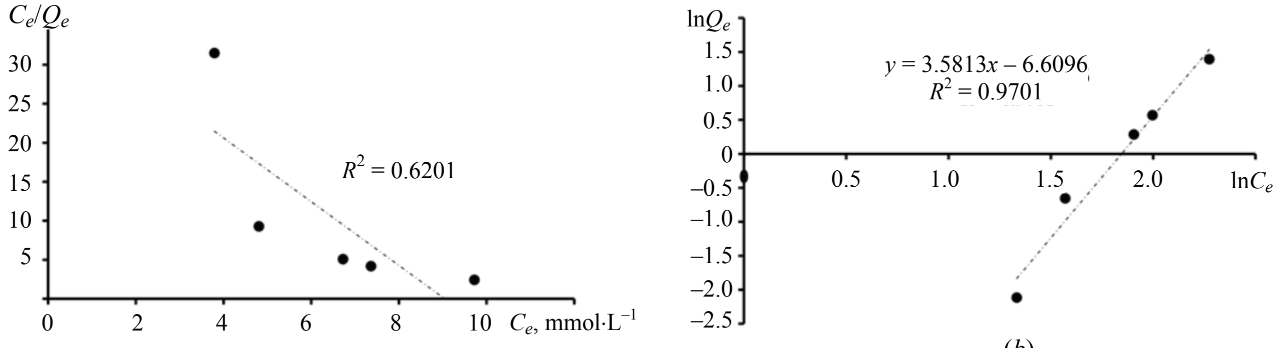
The calculated equilibrium sorption capacity is 0.52 mmol·g^{-1}, which is below the total ion exchange capacity (3.43 mmol·g^{-1}) and slightly higher than the surface ion exchange capacity (0.42 mmol·g^{-1}), as determined by the adapted Ming and Dixon method [53, 54]. This is mainly due to the fact that in the investigated time range the active sites of the outer surface and only a part of the inner surface of protonated potassium polytitanate participate in the ion-exchange process.

3.3. Adsorption isotherms

In addition, the Langmuir (4) and Freundlich (5) models of adsorption isotherms were used to analyze the experimental data obtained [55]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_\infty K_L} + \frac{C_e}{Q_\infty}; \quad (4)$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (5)$$



(*a*) (*b*)

Fig. 4. Isotherms of Li^+ ions adsorption by protonated potassium polytitanate in coordinates of the Langmuir (*a*) and Freundlich (*b*) models

where Q_e is the adsorption capacity at the time of adsorption equilibrium, mmol·g^{-1}; Q_∞ is the limiting adsorption capacity (monolayer capacity), mmol·g^{-1}; C_e is the equilibrium concentration of the solution, mmol·L^{-1}; K_L is the adsorption equilibrium constant, L·mmol^{-1}; n is Freundlich isotherm constant, showing the adsorption intensity; and K_F is Freundlich isotherm constant, corresponding to adsorption capacity (L)$^{1/n}$(mmol)$^{1-1/n}$g^{-1}.

The results show that the Freundlich model ($R^2 = 0.9701$) is better suited to describe the ion-exchange interaction of Li^+ ions with protonated potassium polytitanate compared to the Langmuir model ($R^2 = 0.6201$) (see Fig. 4).

The Freundlich isotherm constant showing the adsorption intensity is 0.28, which falls within the range of 0.1–0.5 for adsorption from solutions. The K_F constant is 0.0013 (L)$^{1/n}$(mmol)$^{1-1/n}$g^{-1}. Experimental data on Li^+ adsorption involving manganese and titanate ion-exchange materials of different composition and structure show higher correlation with Langmuir isotherm than with Freundlich isotherm [50, 51, 56]. This indicates the presence of homogeneous adsorption sites, in contrast to protonated potassium polytitanate, which is characterized by a heterogeneous (external and internal) adsorption surface.

3.4. Selectivity of the ion-exchange material

The study of selectivity of protonated potassium polytitanate was carried out in solutions containing 0.01 mol·L^{-1} of Li^+ ions and 0.004 mol·L^{-1}of impurity ion (Na^+, K^+, Mg^{2+} or Ca^{2+}). Extraction of lithium in the presence of the mentioned ions reaches 0.51 mmol·g^{-1}, which is somewhat lower in comparison with the pure LiCl solution. However, the decrease of the sorption capacity does not exceed 4 %, which may indicate good selectivity of protonated potassium polytitanate in relation to lithium in complex chemical systems (Table 2).

Table 2. Selectivity of protonated potassium polytitanate with respect to lithium in the presence of impurity ions

Impurity ion	C_e(Li^+), mmol·L^{-1}	q, mmol·g^{-1}
–	4.81 ± 0.2	0.52 ± 0.05
Na^+	4.94 ± 0.3	0.51 ± 0.03
K^+	4.91 ± 0.2	0.51 ± 0.03
Mg^{2+}	4.89 ± 0.2	0.51 ± 0.03
Ca^{2+}	4.96 ± 0.3	0.50 ± 0.02

The obtained value of the sorption capacity is slightly inferior to that of manganese and titanate spinels. Yet, because of the use of lithium-containing precursors and technologically complicated operations during synthesis, their cost is high and that allows considerably cheaper materials such as protonated potassium polytitanate to compete with them [31].

4. Conclusion

Protonated potassium polytitanate was obtained by treatment in hydrochloric acid solution of X-ray amorphous layered potassium polytitanate characterized by the general chemical formula $K_2Ti_nO_{2n+1}$ (n = 3.8–4.1). The level of substitution of potassium ions in the interlayer space of the initial potassium polytanate by hydrogen ions as a result of the protonation process is estimated by using X-ray fluorescence method. The empirical formula of the obtained compound is $K_{0.8}H_{1.2}Ti_{4.3}O_{8.5}$. According to the X-ray phase analysis data, protonation does not lead to the destruction and crystallization of the X-ray amorphous structure of potassium polytitanate. In the infrared transmission spectrum a broad absorption band responsible for vibrations of hydroxyl groups (—OH) and an intense absorption band associated with vibrations of thianol groups (—TiOH) are identified. These functional groups are involved in the ion-exchange interaction with Li^+ ions in aqueous solution. The kinetics study showed that the equilibrium adsorption capacity of protonated potassium polytitanate was 0.52 $mmol·g^{-1}$. The experimental data fit the kinetic model of pseudo-second order with rate constant $k_2 = 0.43$ $g(mmol·min)^{-1}$ which confirms the chemical reaction as the limiting stage of the process under investigation. The ion-exchange interaction is described by the Freundlich adsorption isotherm and characterized by the constant $K_F = 0.0013$ $(L)^{1/n}(mmol)^{1-1/n}g^{-1}$. It was found that protonated potassium polytitanate is selective towards Li^+ ions in the presence of both univalent (Na^+, K^+) and divalent cations (Mg^{2+}, Ca^{2+}), keeping q at 0.50–0.51 $mmol·g^{-1}$.

The simplicity of synthesis and high selectivity of protonated potassium polytitanate with respect to Li^+ ions in the presence of other cations typical for natural aqueous solutions make the investigated material a promising ion-exchanger for lithium extraction from solutions.

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6. Conflict of interests

The authors declare no conflict of interest.

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