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ИЗВЛЕЧЕНИЕ Li^+ ИЗ ВОДНЫХ РАСТВОРОВ МЕМБРАНАМИ НА ОСНОВЕ ПВДФ, СОДЕРЖАЩИМИ ЧАСТИЧНО ПРОТОНИРОВАННЫЙ ПОЛИТИТАНАТ КАЛИЯ

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Извлечение лития из природных водных растворов как альтернативного источника этого химического элемента становится актуальной и востребованной задачей. Среди множества известных методов ионообменная адсорбция считается целесообразной как с точки зрения чистоты конечного продукта, так и с точки зрения экономической эффективности технологических операций. Соединения со слоистой и туннельной структурой являются перспективными ионообменными материалами. В данной работе в качестве адсорбента ионов Li^+ исследуется частично протонированный полititанат калия. Это аморфное вещество химического состава $K_{1,3}H_{0,7}Ti_{4,1}O_9$ синтезировано путем обработки рентгеноаморфного слоистого полититаната калия $K_2O·nTiO_2$ ($n = 4,1$) в растворе неорганической кислоты. Мембраны на основе ПВДФ и порошка $K_{1,3}H_{0,7}Ti_{4,1}O_9$ изготовлены методом фазовой инверсии. С использованием кинетических моделей и изотерм адсорбции показано, что модель псевдопервого порядка ($q_e = 0,5$ мг/см^2; $k_1 = 0,014$ мин$^{-1}$) и изотерма адсорбции Фрейндлиха ($K_F = 0,028$ (л)$^{1/n}$ (мг)$^{1-1/n}$/см^2; $n = 1,595$) лучше всего подходят для описания взаимодействия полученных мембран с ионами лития. Рассчитанные параметры адсорбционной емкости, коэффициента распределения (K_d), коэффициента разделения (α) и коэффициента концентрации (CF) подтверждают высокую селективность исследуемого ионообменного композита по отношению к ионам лития в присутствии ионов натрия и калия. Полученные результаты показывают, что мембрана на основе ПВДФ с частично протонированным полититанатом калия является хорошим кандидатом для селективного извлечения лития из природных водных растворов.

Ключевые слова: полититанат калия, протонирование, поливинилиденфторид, мембрана, ионный обмен, литий

Li^+ EXTRACTION FROM AQUEOUS SOLUTIONS BY PVDF-BASED MEMBRANES CONTAINING PARTIALLY PROTONATED POTASSIUM POLYTITANATE

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Extraction of lithium from natural aqueous solutions as alternative source of this chemical element becomes the actual and demanded task. Among the variety of known methods, ion exchange adsorption is considered to be suitable both in terms of the final product purity and economic efficiency of the technological operations. Compounds with layered and tunnel structures are promising ion-exchange materials. In this study, the partially protonated potassium polytitanate

is investigated as the Li^+ ions adsorbent. This amorphous substance characterized with the $K_{1.3}H_{0.7}Ti_{4.1}O_9$ chemical composition is synthesized by acid treatment of X-ray amorphous layered potassium polytitanate $K_2O{\cdot}nTiO_2$ (n = 4.1). The PVDF-based membranes filled with the $K_{1.3}H_{0.7}Ti_{4.1}O_9$ powder are prepared by the phase inversion technique. Using the kinetic and isotherm technique, it is shown that a use of the pseudo-first order model ($q_e = 0.5$ mg/cm^2; $k_1 = 0.014$ min^{-1}) and the Freundlich adsorption model ($K_F = 0.028$ (L)$^{1/n}$(mg)$^{1-1/n}$/cm^2; n = 1.595) are the best models to describe the interaction of the obtained membranes with lithium ions. The calculated parameters of the adsorption capacity, distribution coefficient (K_d), separation factor (α) and concentration factor (CF) confirm a high lithium ions selectivity of the investigated ion-exchange composite in the presence of sodium and potassium ions. The obtained results show that the PVDF-based membrane with partially protonated potassium polytitanate is a good candidate for selective lithium extraction from natural aqueous solution.

Key words: potassium polytitanate, protonation, poly (vinylidene fluoride), membrane, ion exchange, lithium

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INTRODUCTION

Lithium is widely used in various applications [1-5] and especially in lithium-ion batteries for portable electronic devices as well as emerging electric and hybrid electric vehicles [1, 5]. Both lithium-containing minerals and salt-lake brines are the main natural sources of lithium, however, currently, new sources of Li such as seawater and other natural water resources are being actively investigated. A low concentration of lithium in the natural aqueous solutions (less than 300 mg (Li^+)/dm^3), as well as a complicated chemical composition (co-existing with Na^+, K^+, Mg^{2+}, Ca^{2+}) [6], are the key factors to select the effective techniques to extract lithium. Among the most common methods, the evaporative crystallization method is too time-consuming and costly due to a use of large amount of carbonates [7]; the co-precipitation method [8] is pH and temperature sensitive; the solvent extraction method causes undesirable environmental pollution and corrosion of equipment [9]. Based on the above, the ion exchange adsorption with a high lithium selectivity is the most cost-effective and environment-friendly approach. Nowadays, some ion-exchange materials such as protonated complexes of manganese oxides (HMn_2O_4, $H_{1.33}Mn_{1.67}O_4$ ($H_4Mn_5O_{12}$), and $H_{1.6}Mn_{1.6}O_4$ ($H_2Mn_2O_5$) as well as crystalline layered titanates ($H_4Ti_5O_{12}$ and H_2TiO_3) are recommended for these purposes [10-14]. Besides high efficiency (theoretical lithium-ion exchange capacity is up to 127 mg (Li^+)/g) and selectivity, the main advantages of titanate-type materials, in comparison with manganates, are: stable structure in lithiation-delithiation processes, good acid resistance, lower dissolution loss of Ti, relatively stable adsorption performance, and multiple recycling [15]. However, a use of powdered sorbents, especially in industry, is inconvenient in terms of separation of ion exchange material and lithium containing solution after their interaction. Various technologies and methods including foaming [16], granulation [17], use of membranes [18] and fiber non-woven and fabric materials [19] have been developed to solve this problem. For example, Zhang et al. prepared granular lithium-ion sieves based on composite materials of polyvinyl butyral (PVB)-H_2TiO_3 with Li^+ uptake of 25 mg/g from LiOH solution with 200 mg (Li^+)/L after 3 h [20]. Limjuco et al. incorporated H_2TiO_3 particles in poly(vinyl alcohol) (PVA) matrix, the obtained composite foam was characterized by Li^+ uptake of 13.54 mg/g from LiCl solution with 7 mg (Li^+)/L after 12 h [21]. Lawagon et al. used polyacrylonitrile (PAN) as polymer matrix for H_2TiO_3 nanofibers to create membranes and determined Li^+ uptake of 32 mg/g from LiCl + LiOH solution with 70 mg (Li^+)/L after 25 h [22]. Wei et al. prepared porous lithium ion sieves nanofibers based on $H_4Ti_5O_{12}$ and polyvinylpyrrolidone (PVP) with Li^+ uptake of 50 mg/g from LiCl + LiOH solution with 1000 mg (Li^+)/L after 12 h [23]. Lin et al. synthesized granular polyporous lithium-ion sieves consisting of H_2TiO_3, polyvinyl chloride as a binder and polyethylene glycol (PEG-6000) as a porogen [24]. The adsorption capacity of the developed material was 12.84 mg/g from the model geothermal water after 12 h of extraction.

In this work, the alternative titanate-type ion exchange material obtained by acid treatment of X-ray amorphous layered potassium polytitanate (PPT) with the general chemical formula $K_2O{\cdot}nTiO_2{\cdot}mH_2O$ (n = = 3.8-6.0, m = 0.5-3.0) is investigated. Unlike H_2TiO_3 and $H_4Ti_5O_{12}$ as well as manganite structure, no lithium-containing precursors are used for this synthesis, so the target product is low-cost. Potassium polytitanate layers are formed by chains of $TiO_{6/2}$ octahedrons stabilized by potassium cations, hydronium cations and water molecules replaced in the interlayer space. The atomic structure of the potassium polytitanates has no long-range order, hence the mutual arrangement of structural units varies, a value of the interlayer distance is much higher of this one typical for the crystalline H_2TiO_3 and $H_4Ti_5O_{12}$ and varies widely in the range from 0.2 to 1.1 nm. Quasi-amorphous potassium polytitanate particles represent nanoscale flakes forming larger agglomerates of various irregular morphologies [25]. Due to its well-developed outer and inner surface, potassium polytitanate is prone to adsorption and ion exchange processes. These characteristics of the PPT powders allow considering their protonated forms as promising to use in the field of lithium extraction from aqueous solutions. Adsorption is a widespread method for the extraction of ions from aqueous solutions [26, 27], that is why, in this research, a special attention is paid to the kinetics and the adsorption isotherms of the ion exchange processes, taking place in the PPT based systems. This data is necessary to estimate the rate constant and the adsorption capacity and important to develop the technological process of lithium extraction from different lithium containing natural waters.

The membrane technology as energy consumption, simple preparation and superior industrial application method is chosen to produce ion exchange composites in this research. Poly (vinylidene fluoride) (PVDF) was used as a polymer binder as a wide-range membrane material characterized with a good heat resistance, high mechanical strength and relatively low cost [28].

Thus, the aim of this study is to produce the porous composite membranes based on partially protonated potassium polytitanate and poly (vinylidene fluoride) and to investigate the kinetics and mechanism of the ion-exchange extraction of lithium from the model aqueous solution.

EXPERIMENTAL SECTION

Preparation of protonated potassium polytitanate and PVDF-based membranes

Partially protonated potassium polytitanate powder was obtained by acid treatment of initial potassium polytitanate $K_2O{\cdot}nTiO_2$ (n = 4.1) or $K_2Ti_{4.1}O_{9.2}$ according to the method in the literature [29]. Some quantity of the rest of potassium in the obtained partially protonated PPT support a large interlayer distance among the layers and supports ion-exchange processes in the product.

The PVDF-based membranes were obtained by the following procedure: 4 g PVDF power (Sigma Aldrich, Mw~530,000, St. Louis, MO, USA) was dissolved in 20 ml N, N-Dimethylformamide (DMF, C_3H_7NO, analytical grade, Ekos-1, Moscow, Russia) and then 2 g protonated potassium polytitanate was added into the polymer solution. This mixture was magnetically stirred at room temperature for 24 h until homogenization and then was spread on a glass plate using a doctor knife methodology followed by an immersion into distilled water. A use of higher contents of polymer in the composite reduces an availability of the ion exchange material for lithium ions, resulting in lower efficiency; lower PVDF amounts reduce a stability of the composite in the aqueous solution.

Water uptake and ion exchange capacity measurement

Before a measuring the water uptake parameter, the 1.5×1.5 cm samples of the obtained membrane were dried in an oven at 60 °C for 48 h and weighted (W_{dry}, g) was measured. The membranes were then washed with distilled water and introduced into the LiCl solution for 48 h. Further, a weight of the samples was measured again (W_{wet}, g). A water uptake was calculated by equation (1).

$$Water\ uptake\ (\%) = \frac{W_{wet}-W_{dry}}{W_{dry}} \cdot 100\% \qquad (1)$$

An ion-exchange capacity (IES) of the PVDF-based membrane was determined using the titration method. The sample was immersed in LiCl solution for 24 h for complete release of H^+ by exchange with Li^+. The released H^+ was titrated with NaOH solution (0.01M) using phenolphthalein as an indicator. The ion-exchange capacity was calculated with equation (2):

$$IEC, mmol/g = \frac{1000 \cdot C \cdot V_{NaOH}}{W_d}, \qquad (2)$$

where C is a concentration of the NaOH solution, mol/dm^3, V_{NaOH} is a volume of the NaOH solution consumed in titration, L, W_d is a weight of the dried membrane, g.

Lithium adsorption kinetics and isotherms study

Studies of the adsorption capacity for Li$^+$ were carried out by stirring of 2×2 cm PVDF-based membrane with partially protonated potassium polytitanate in various solutions containing 50, 80, 100, 150, and 175 mg/dm^3 LiCl for 20, 40, 60, 120, and 180 min at pH ~ 7.0. The concentration of Li$^+$ was recorded by the potentiometric method using a laboratory ion-meter I-160MP (Gomel Plant of Measuring Instruments, Belarus) with a lithium-selective electrode ELIS-142Li (Izmeritelnaya Tekhnika, Russia).

The adsorption capacity was determined by equation (3):

$$Q, mg/cm^2 = \frac{(C_0 - C_t)\cdot V}{S} \tag{3}$$

where C_0 and C_t are the initial Li$^+$ concentration and at time t in the solution, mg/L, respectively; V is the volume of the solution, L; S is the geometric area of the PVDF-based membrane containing partially protonated potassium polytitanate, cm^2.

The study of the adsorption process kinetics with calculation of the adsorption rate constant and equilibrium adsorption capacity was carried out using pseudo-first-order (equation (4)) and pseudo-second-order (equation (5)) models [29-33].

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{5}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, mg/cm^2, respectively; k_1, min^{-1} and k_2, cm^2/mg·min are the rate constant of pseudo-first-order and pseudo-second-order models, respectively.

The study of the adsorption process equilibrium and the mechanism of the Li$^+$ ions interaction with the membrane active sites was carried out using the Langmuir (equation (6)) and Freundlich (equation (7)) isotherms [34].

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{6}$$

$$lnQ_e = lnK_F + \frac{1}{n} lnC_e \tag{7}$$

where Q_e and Q_m are the adsorption capacity at equilibrium and the maximum adsorption capacity, mg/cm^2, respectively; C_e is the equilibrium Li$^+$ concentration, mg/L; K_L is the Langmuir constant, L/mg; whereas, K_F, (L)$^{1/n}$(mg)$^{1-1/n}$/cm^2 and n are the Freundlich constants.

Adsorption selectivity study

The adsorption selectivity of the PVDF-based potassium polytitanate containing membranes for Li$^+$ was determined by stirring of 2 cm^2 membrane samples into two mixed solutions with 100 mg/L of LiCl and NaCl as well as LiCl and KCl. After reaching the equilibrium the metal ions concentrations were determined by a potentiometric method using a lithium-selective electrode ELIS-142Li (Izmeritelnaya Tekhnika, Russia), a sodium-selective electrode ELIS-112Na (Izmeritelnaya Tekhnika, Russia) and a potassium-selective electrode ELIS-121K (Izmeritelnaya Tekhnika, Russia). The distribution coefficient (K_d), separation factor (α) and concentration factor (CF) were calculated by the equations (8)-(10):

$$K_d = \frac{Q_e}{C_e} \tag{8}$$

$$\alpha = \frac{K_d(Li)}{K_d(Me)} \tag{9}$$

$$F = \frac{Q_e(Me)}{C_o(Me)} \tag{10}$$

where Me = Na and K.

RESULTS AND DISCUSSION

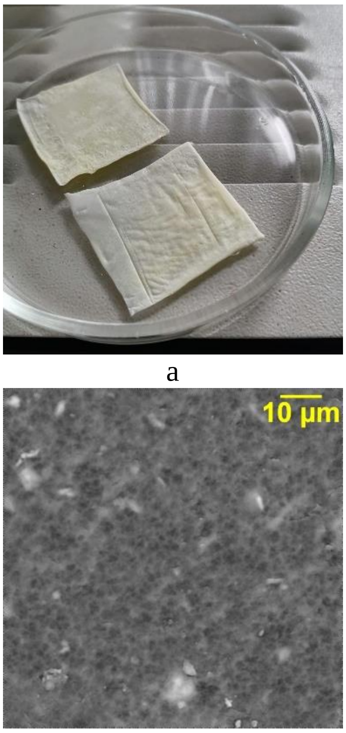
The potassium polytitanate powder obtained by acid treatment and used in the experiments is characterized by X-ray amorphous structure without pronounced reflexes in the XRD pattern. Its particles have a flake-like morphology have a trend of agglomeration and, according to the energy dispersive analysis (EDS) data, correspond to the $K_{1.3}H_{0.7}Ti_{4.1}O_9$ chemical composition [29].

The photograph of the dried PVDF-based polymer membrane filled with potassium polytitanate powder and micrograph of its surface are shown in Fig. 1. The PVDF-based membranes filled with partially protonated potassium polytitanate have porous structure. A water uptake (adsorption capacity) was applied as a parameter characterizing their porosity.

Water uptake values are typically used to indicate the diffusion process availability. The water (aqueous solution) uptake values, estimated with distilled water and 0.1% LiCl aqueous solution, correspond to 14.8% and 25.4%, respectively. IEC as the indication of the number of ion exchangeable sites is 0.922 mmol/g. Both parameters are in good agreement with the same parameters of analogs [35-37].

The ion-exchange capacity (IEC) of the PVDF-based composite membranes have been investigated to consider the prospects of the obtained functional materials application in the lithium ion extraction from aqueous solutions.

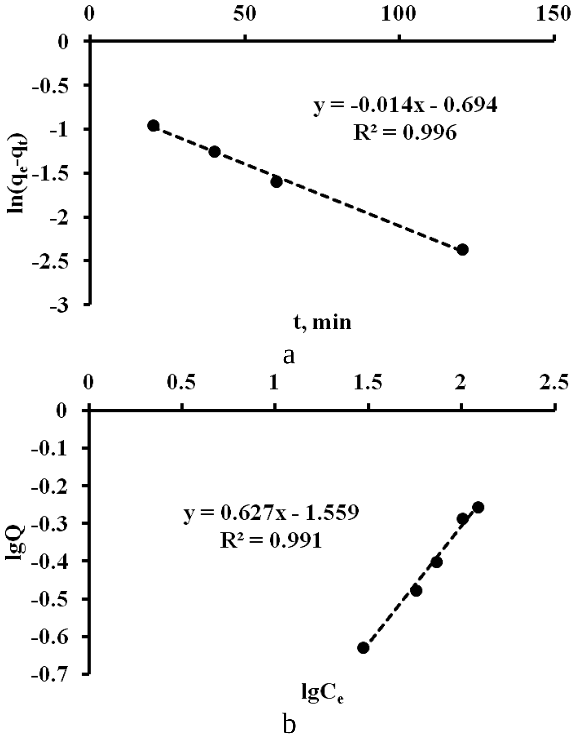
The adsorption kinetics has been analyzed to investigate the adsorption rate and rate-controlling mechanism of the adsorption processes. The pseudo-first-order (Fig. 2a) and pseudo-second-order models have been used to study the kinetics of Li$^+$ adsorption by the obtained PVDF-based composite membranes.



a

b

Fig. 1. The samples of PVDF-based membranes containing protonated potassium polytitanate (a) and SEM image of their surface (b)
Рис. 1. Образцы мембран на основе ПВДФ, содержащих протонированный полититанат калия (а), и СЭМ изображение их поверхности (b)



a

b

Fig. 2. Fitting curves of pseudo-first-order equation (a) ($C_0(Li^+)$ = 150 mg/L) and Freundlich model (b) (t = 180 min)
Рис. 2. Аппроксимационные кривые уравнения псевдопервого порядка (a) ($C_0(Li^+)$ = 150 мг/л) и модели Фрейндлиха (b) (t = 180 мин)

According to the determination coefficients (R^2) (Fig.2, Table 1) of these two kinetic models, the adsorption process is better followed by the pseudo-first-order equation with $R^2 = 0.996$, consequently lithium adsorption by the composite PVDF-based membrane is limited by ion diffusion: external in solution or internal in the membrane and in the structure of protonated potassium polytitanate. However, also the high fit of the experimental data to the pseudo-second-order model does not exclude chemisorption as a rate-limiting step of the investigated process [30]. The kinetic parameters of lithium adsorption by the PVDF-based membrane are shown in Table 1.

Table 1

Kinetic parameters of lithium adsorption by the PVDF-based membrane filled with partially protonated potassium polytitanate

Таблица 1. **Кинетические параметры адсорбции лития мембраной на основе ПВДФ с частично протонированным полититанатом калия**

Pseudo-first-order model			Pseudo-second-order model		
q_e, mg/cm^2	k_1, min^{-1}	R^2	q_e, mg/cm^2	k_2, cm^2/mg·min	R^2
0.500	0.014	0.996	0.750	0.015	0.989

The value of q_e calculated from the pseudo-first-order model is closed to the experimental data. This fact confirms that this kinetic model better describes the investigated ion-exchange process.

A plotting of the adsorption isotherms allows assuming the mechanism of interaction between the adsorbent and adsorbate, as well as estimating an adsorption capacity. The most common Langmuir and Freundlich models (Fig. 2b) are used for this purpose.

Experimental data with a higher determination coefficient (R^2) fit the Freundlich model (Table 2). Consequently, ion-exchange adsorption of lithium ions occurs on the heterogeneous surface of the investigated PVDF-based composite membranes characterized with the adsorption sites of different binding energy. The Langmuir isotherm, which implies adsorption on homogeneous sites and an absence of interaction between adsorbed particles, poorly describes the results obtained with $R^2 = 0.934$. The equilibrium parameters of lithium adsorption by the composite PVDF-based membranes are shown in Table 2.

A value of *n* in the Freundlich isotherm equation depends on heterogeneity of the surface and is about of 1.6, which indicates favorable adsorption. A value of the Freundlich constant K_F is related to the adsorption capacity. The maximum adsorption capacity is estimated from the equilibrium parameter of the Langmuir isotherm and reaches a value of 1.081 mg/cm^2.

Table 2

Equilibrium parameters of lithium adsorption by the PVDF-based membrane filled with partially protonated potassium polytitanate

Таблица 2. **Равновесные параметры адсорбции лития мембраной на основе ПВДФ с частично протонированным полититанатом калия**

Langmuir model			Freundlich model		
Q_m, mg/cm^2	K_L, L/mg	R^2	K_F, $(L)^{1/n}(mg)^{1-1/n}/cm^2$	n	R^2
1.081	0.009	0.934	0.028	1.595	0.991

A correspondence of the pseudo-first order model to the investigated process can be explained by the membrane structure of the ion-exchanger, for which diffusion processes are of paramount importance. The Freundlich isotherm describes well the adsorption occurring in the system protonated potassium polytitanate powder – lithium salt solution, and is suitable to describe similar processes for a PVDF-based membrane using the same active component [38].

Considering a presence of other cations besides lithium ions in natural waters, there is a need to investigate a selectivity of the prepared PVDF-based composite membranes. To estimate selectivity of Li^+ adsorption, the adsorption capacity, distribution coefficient (K_d), separation factor (α) and concentration factor (CF) were determined using the mixed aqueous solutions containing either Li^+ and Na^+ or Li^+ and K^+ ions (Table 3).

Table 3

Adsorption selectivity of Li^+ by the investigated PVDF-based composite membranes in the mixed solution containing either Li^+ and Na^+ or Li^+ and K^+

Таблица 3. **Селективность адсорбции Li^+ исследованными композитными мембранами на основе ПВДФ в смешанном растворе, содержащем Li^+ и Na^+ или Li^+ и K^+**

Metal ions	C_e, mg/L	Q_e, mg/g	K_d, L/g	α	CF, L/g
Li^+	41.9	500.9	11.95	1.0	5.01
Na^+	92.2	67.2	0.73	16.4	0.67
Li^+	52.3	411.2	7.86	1.0	4.11
K^+	92.7	62.9	0.68	11.6	0.63

According to the Table 3, the adsorption capacity of Li^+ for the investigated PVDF-based composite membranes is higher compared to the two impurity cations at the same initial concentrations. A value of the distribution coefficients for these metal ions also reduces in the order of Li+ > Na^+ ~ K^+. The separation factor values for Li^+ to Na^+ and K^+ are much greater than 1 and equal to 16.4 and 11.6, respectively. The concentration factor for lithium also significantly exceeds that for the other two ions. The values of the calculated parameters confirm high selectivity of the adsorption of Li^+ by the PVDF-based membranes, filled with partially protonated potassium polytitanate, in a presence of sodium and potassium ions. This result may be explained with some structural features of partially protonated potassium polytitanate used as the active component of the investigated composite material, such as varied interlayer distance. A variable interlayer distance in the potassium polytitanate particles makes the internal sections of their interlayer space more accessible to Li^+ ions, which have a lower ionic radius in comparison with the ions of other alkali metals [38].

CONCLUSIONS

The composite ion exchange membranes were prepared using poly (vinylidene fluoride) (PVDF) as a binder for the partially protonated potassium polytitanate ($K_{1.3}H_{0.7}Ti_{4.1}O_9$) powder used as an active filler. Pseudo-first and pseudo-second order kinetic models were used to investigate the kinetics of Li^+ extraction from the LiCl model aqueous solution by the PVDF-based composite membranes obtained. It was found that the adsorption kinetics was fitted pseudo-first-order with the calculated equilibrium sorption capacity $q_e = 0.5$ mg/cm^2 and rate constant $k_1 = 0.014$ min^{-1}. The equilibrium of the ion exchange process was studied using the Langmuir and Freindlich isotherms. The adsorption isotherm was fitted Freundlich model with calculated equilibrium parameters of $K_F = 0.028\ (L)^{1/n}(mg)^{1-1/n}/cm^2$ and n = 1.595. It was shown, that the investigated PVDF-based composite membranes had high selectivity for Li^+ ions in the aqueous solutions containing other alkali ions (Na^+ and K^+). These characteristics allow considering the composite ion-exchange material, produced and investigated in this work, as a promising adsorbent to extract lithium from natural Li^+ containing waters, taking into account also it's relatively low-cost.

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CONFLICTS OF INTEREST

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

The authors declare no conflict of interest warranting disclosure in this article.

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