

**CHARACTERIZATION OF SORPTION MATERIALS CONTAINING OXIDES OF MULTIVALENT METALS FOR USE IN PROCESSES OF LITHIUM EXTRACTION FROM SALT SOLUTIONS**

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*Since lithium is one of the most popular materials for the electronics industry, it is of interest to consider alternative sources of its receipt. The article analyzes the main sources of lithium production, global stocks and the dynamics of its production. We have considered the possibility of obtaining lithium from sea water by sorption method. The comparative characteristic of sorption materials based on the multivalent metal oxides was conducted, their structure parameters were determined. By method of X-ray analysis structure of the sorbents was studied. It is shown that the titanium-manganese sorbent is composite material consisting of particles of TiO<sub>2</sub>, rutile coated with amorphous MnO<sub>2</sub>. By electron paramagnetic resonance method valence states of manganese component in the sorbent structure were set. Adsorption isotherms from lithium solutions simulating sea water were obtained. The effect of modification of sorption materials by ion application was studied. It is shown that the highest sorption capacity to Li<sup>+</sup> ions corresponds to titanium-manganese sorbent.*

*Keywords: lithium, composite materials, titanium dioxide, titanium-manganese sorbent, ion application*

Number of high-tech products and alternative energy products that are developed and used, is growing, particularly in the areas of information, communication technology, energy and mobility. This growth contributes to the demand for metals.

Most of these technological metals are geochemically rare, their average mass concentration in the earth's crust is less than 0.01%. Because they are very important in modern technology, scientists engaged in search of sources of metal extraction.

Due to its unique properties, lithium plays an important role in the industrial development of modern society. Among the consuming industries a variety of chemical power sources, construction, glass ceramics, refrigerants and air drying systems, energy, special oils and lubricants, polymers, metallurgy of light structural alloys, disinfectants for water treatment, etc. can be named. For each of them lithium materials of defined specification are required.

Current estimates of world reserves of lithium are in total approximately 30,000,000 tons of lithium or 150,000,000 tonnes of lithium carbonate [1].

New directions for use of lithium mineral resources, which are currently being developed around the world, especially for the production of batteries, particularly lithium carbonate production, demonstrate the change in economic conditions that promote the growth of lithium sales [2].

Basic Li-containing salts that are consumed commonly are carbonate, hydroxide and lithium chloride. Current capacity of the segment "lithium salt" is about 7800 tons of Li, of which 61% (4700 tons Li) accounted for lithium carbonate, 23% (1826 tonnes Li) - on lithium hydroxide, 6% (500 tons Li) - lithium chloride and 10% (774 tons Li) - to other products, including chemicals for the production of batteries [3].

World consumption of lithium only by existing electronics manufacturers is now about 110 thousand tons per year and could double by 2020.

Table 1. Production of lithium (2009) and the world reserves, in metric tons

Country	Production	Reserves
Argentina	2,200	800,000
Australia	4,400	580,000
Brazil	110	190,000
Canada	480	180,000
Chile	7,400	7,500,000
People's Republic of China	2,300	540,000
Portugal	490	Not available
United States	Withheld	38,000
Zimbabwe	350	23,000
World total	18,000	9,900,000

According to reports of the British information and research firm Roskill Information Services, the global demand for lithium for the past ten years is estimated at about 13 000-14 000 tonnes Li (in terms of lithium metal), and in equivalent of money - more than 1 billion USD. (data at the end of 2005). The average annual growth of this indicator - 2-5%, although at the 16th Congress of industrial minerals, held in early April 2003, analysts predicted a steady growth in demand for lithium products 4,7-10% annually. This percentage of increase can be called optimistic, if not to take into account the dependence of the demand for lithium on the general state of the global economy and business activity in the sectors of final consumption. It should be noted that the opinion of manufacturers differs from the views of analysts. One of the leading players on the lithium market - Chilean company SQM - suggests a 30% growth that occurred in the past three years, and its US competitor FMC, being less categorical, is talking about 10%.

Existing lithium extraction from natural brines is known in Chile, Argentina, USA, and China. All processes are based on solar evaporation to concentrate brine, sometimes in combination with precipitants or sorbents based on aluminum oxide for the selective recovery of lithium. The largest lithium producer SQM processes material brines from the Salar de Atacama in Chile, the initial concentration of lithium in which is 0.15%. Use of "free" solar energy for evaporation is a very important aspect in reducing the energy needs of the enterprise. Performance of production depends on the topographic conditions (average temperature, wind, humidity) and brine composition (initial content of lithium and other elements, including magnesium, which forms hygroscopic salt and keeps part of lithium-containing brine).

Active development of ore deposits are in Australia (Talison - the largest producer), Brazil, Canada, China, Portugal and Zimbabwe. Lithium is found in many minerals, but only petalite spodumene ores are commercially interesting. Concentrates of ores containing lithium oxide, are mainly used in glass and ceramic industry and are not converted into lithium carbonate as production of carbonate from brine is much cheaper.

Almost all chemical elements that are found in the earth's crust as solid minerals can also be found in the ocean waters.

Naturally, the ocean currents negate the content of these elements in seawater. However, it must be assumed that in some regions of the world that are not exposed to global movements of water masses (creeks, local seas, etc.) increased content of certain dissolved elements can be stored. Unfortunately, information about the content of local excesses of those components in the coastal waters is practically absent in the available sources.

Nevertheless, literature describes the results of a sufficiently large number of researchers attempting to develop technologies for extraction from seawater of various practically important elements [5-9]. It is believed that these researchers before the experimental work had more information about the content of these elements in some regions of the world ocean.

All commercially recoverable components of seawater are contained therein in relatively high concentrations, so their extraction technology is tried and true and is not a complicated problem. The situation is different with the microcomponents.

For preconcentration of seawater microcomponents a variety of techniques can be used: chemical or electrochemical deposition, solvent extraction, flotation, sorption, membrane and biological concentration, etc. However, in practice, when dealing with large volumes of water it is necessary to immediately renounce all methods that entail the use of solutions of any reagents due to huge amounts of them. Therefore, such processes as precipitation, extraction, flotation, requiring pre-treatment of water or the introduction of new, not contained in water substances should be immediately discarded.

It is believed that the main focus in the area of the concentration of trace elements in sea water may be the use of sorption processes. First of all, this is due to the simplicity of the technology - contact of easily separable phases of water and solid insoluble sorbent, presence of a wide range of mineral and organic sorbents, their adjustable selectivity with respect to various elements. It is also important that hydrometallurgy and water treatment have long experience with large-scale sorption processes.

There are several schemes for increasing the concentration of lithium salts in sea water, due to evaporation using solar energy and selective adsorption on specially designed surfaces. The degree of readiness of these schemes for industrial applications is significantly different. Evaporative technologies are known and used in the development of lithium brine deposits. Unfortunately, adsorption methods are still at the level of laboratory research. Recent prospective studies were associated with granulated adsorbents based on manganese oxide. It has been shown that such adsorbents can be used again and again. After elution of adsorbed lithium and other ions by acid solutions, sorbents can be reused for the extraction of lithium. It is believed that such multi-purpose use of sorption materials may give effective use of investment funds with capital investments.

However, the creation and study of chemically stable sorption materials, which are characterized by a large number of adsorption/desorption cycles without sacrificing capacity for lithium, is a major scientific and technical challenge at the moment [10].

Recent studies show that the greatest interest today is aroused not only by industrially produced sorption materials [11, 12], but by the composite [13, 14], and inorganic ion-exchange materials and adsorbents [15-16].

As the most promising sorbents for the extraction of our lithium inorganic materials based on double oxides of multivalent metals  $\text{Al}_2\text{O}_3 - \text{MnO}_2$ ,  $\text{TiO}_2 - \text{MnO}_2$ ,  $\text{ZrO}_2 - \text{MnO}_2$  и  $\text{SnO}_2 - \text{MnO}_2$  were determined.

To increase the selectivity of the developed sorption materials for lithium ions additional processing was used, resulting in the formation of directional characteristics, namely, ion application. For this, initial sorbent was saturated with lithium ions and subjected to heat treatment, which resulted in the incorporation of lithium into the structure of the sorption material. Subsequent removal of lithium ions from the matrix led to the formation of structural-organized selective sorption sites.

### **Chemical analysis**

For prepared experimental batches of inorganic sorption materials analysis of the chemical and fractional composition was made. Data are presented in Table 2.

As it can be seen from Table 1, the developed synthesis technology for inorganic oxide-based sorption materials allow the preparation of these materials at the stage of the synthesis in the form of granules with size of 0,5-1,5 mm, particularly suitable for the dynamic sorption processes.

### **X-ray analysis**

As it is known from the literature, when oxide sorption material is heat treated structural changes are possible. In this connection X-ray analysis of the manganese-titanium sorbent was conducted, including the original samples, those applied and not applied with lithium ions. Diffractograms of  $\text{TiO}_2 - \text{MnO}_2$  sorbent with heat treatment at temperatures of 18, 400, 600 °C are shown in Fig. 1-3.

Table 2. Characteristics of synthesized sorption materials based on double oxides of polyvalent metals

Material	Initial ratio of components Me : Mn	Chemical composition of obtained materials	Fractional composition, %		
			< 1.0 mm	1.0-2.0 mm	> 2.0 mm
Al <sub>2</sub> O <sub>3</sub> - MnO <sub>2</sub>	1 : 1	Al <sub>0.6</sub> Mn <sub>0.4</sub> O <sub>1.5</sub> ·nH <sub>2</sub> O	20	75	5
TiO <sub>2</sub> - MnO <sub>2</sub>	1 : 1	Ti <sub>0.6</sub> Mn <sub>0.4</sub> O <sub>2</sub> ·nH <sub>2</sub> O	15	80	5
ZrO <sub>2</sub> - MnO <sub>2</sub>	1 : 1	Zr <sub>0.6</sub> Mn <sub>0.4</sub> O <sub>2</sub> ·nH <sub>2</sub> O	13	82	5
SnO <sub>2</sub> - MnO <sub>2</sub>	1 : 1	Sn <sub>0.6</sub> Mn <sub>0.4</sub> O <sub>2</sub> ·nH <sub>2</sub> O	10	80	10

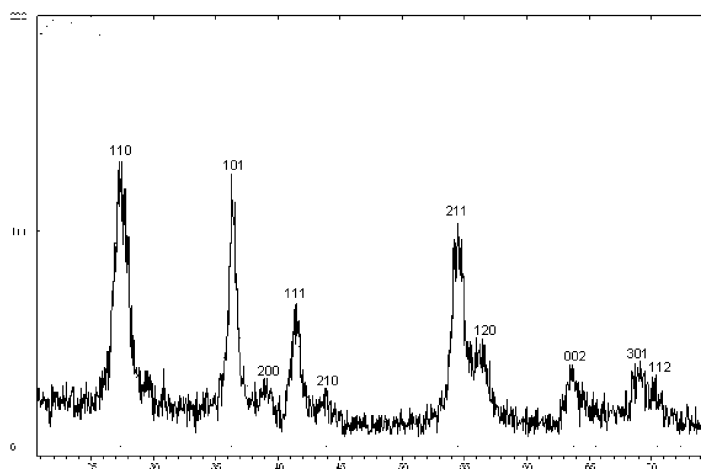


Fig. 1. Diffractograms of initial non-applied adsorbent TiO<sub>2</sub> - MnO<sub>2</sub> at 18°C.

It can be assumed that the investigated sorption material consists of crystalline TiO<sub>2</sub> with rutile lattice, covered with x-ray amorphous MnO<sub>2</sub>. Sorbent particle size is 11.7 nm. Parameters of the TiO<sub>2</sub> crystal lattice:  $a = 4,6075$ ;  $c = 2,9267$ .

As the X-ray diffraction patterns of manganese-titanium sorbent applied with lithium and thermally treated at a temperature of 400 °C shows (Fig. 2), significant changes in the structure of the material do not occur. Sorbent particle size is 11.6 nm. Parameters of the TiO<sub>2</sub> crystal lattice:  $a = 4,5840$ ;  $c = 2,9274$ .

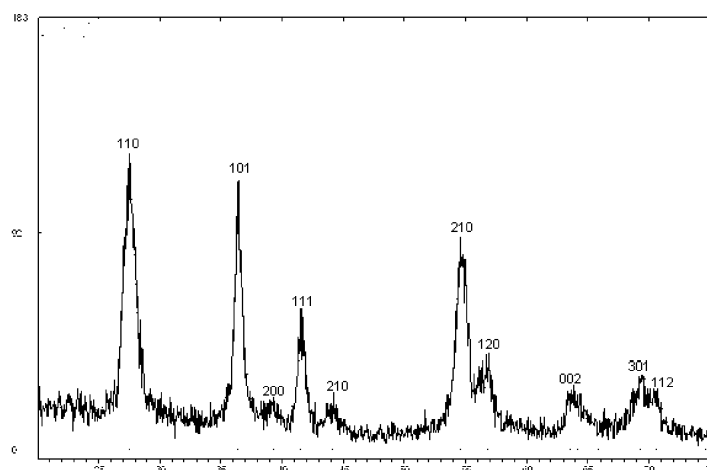


Fig. 2. Diffractograms of TiO<sub>2</sub> - MnO<sub>2</sub> adsorbent applied with lithium and thermally treated at 400 °C.

On the diffractogram (Fig. 3), it can be observed that further heat treatment of  $\text{TiO}_2\text{-MnO}_2$  adsorbent applicated with lithium at temperature of  $600\text{ }^\circ\text{C}$  causes composition of two crystal structures: rutile with lattice parameters  $a = 4,5905$ ,  $c = 2,9552$  and spinel with lattice parameters  $a = 4,5933$ ,  $c = 2,9522$ .

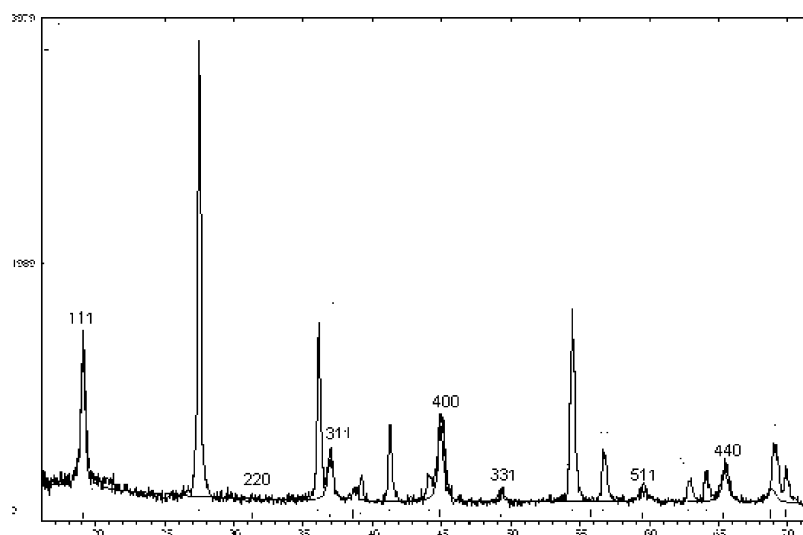


Fig. 3. Diffractograms of  $\text{TiO}_2 - \text{MnO}_2$  adsorbent applicated with lithium and thermally treated at  $600\text{ }^\circ\text{C}$ .

#### Electron paramagnetic resonance

Due to the fact that the X-ray analysis method can not identify the valence states of manganese ions in the manganese component of the sorbents, a study of applicated and non-applicated double adsorbents at various temperatures of heat treatment was conducted by electron paramagnetic resonance (EPR).

The EPR spectra of  $\text{TiO}_2 - \text{MnO}_2$  sorbent samples applicated with lithium are shown in Fig. 4, 5.

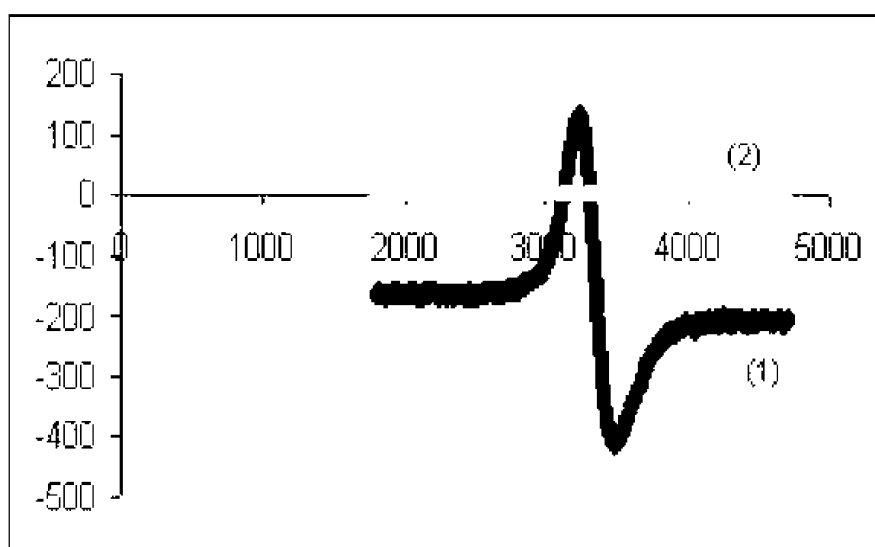


Fig. 4. EPR spectra of  $\text{TiO}_2 - \text{MnO}_2$  sorbent samples applicated with lithium at  $18\text{ }^\circ\text{C}$  (1) and after heat treatment at  $550\text{ }^\circ\text{C}$  (2).

As it can be seen from the analysis of EPR spectra at  $18\text{ }^\circ\text{C}$  ( $g_{\perp} = 2,08$ ,  $g_{\parallel} = 1,94$ ) EPR

spectra corresponding to paramagnetic ions of  $Mn^{4+}$  is observed . At a temperature of  $550\text{ }^{\circ}C$  paramagnetism in manganese component of the sorbent is not observed due to the short time of spin-lattice relaxation and large level splitting of  $Mn^{3+}$  in zero field, which is formed according to reaction

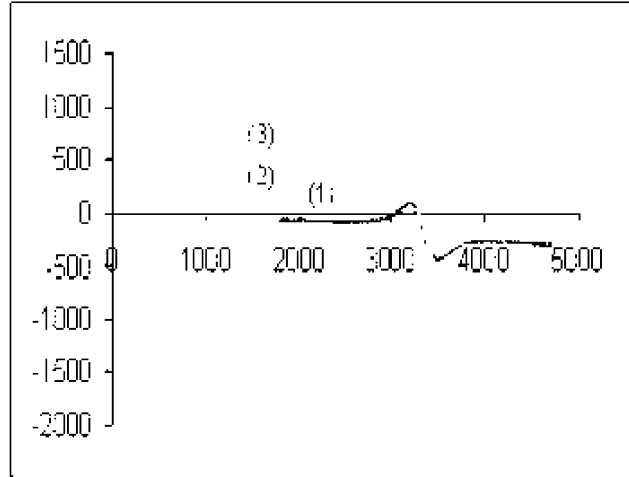


Fig. 5. EPR spectra of  $TiO_2 - MnO_2$  sorbent samples applied with lithium at  $18\text{ }^{\circ}C$  (1) and after heat treatment at  $700\text{ }^{\circ}C$  (2),  $800\text{ }^{\circ}C$  (3).

As it is seen from Figure 5, at heat treatment temperature of the applied sorbent around  $700-800\text{ }^{\circ}C$ , growth of paramagnetism is observed due to the formation of spinel structure with  $Mn^{2+}$ ,  $Mn^{4+}$  components.

#### Nuclear magnetic resonance

To clarify the qualitative composition, the nature of intermolecular interactions, chemical environment of nuclei, binary sorbents applied with lithium and thermally treated at various temperatures were studied by nuclear magnetic resonance (NMR).

NMR - spectra of samples of  $TiO_2 - MnO_2$  sorbent applied with lithium and thermally treated at temperature range of  $18- 600\text{ }^{\circ}C$  are shown in Fig. 6-7.

Fig. 6 shows NMR-spectrum of standard LiOH. As it is seen from Fig. 7, NMR-spectrum of applied at  $18\text{ }^{\circ}C$  is slightly broadened. This fact can be explained by diffusion of lithium ions to adsorbent matrix and by influence of paramagnetic  $Mn^{4+}$  ions.

Fig. 6. NMR-spectrum of LiOH (standard).

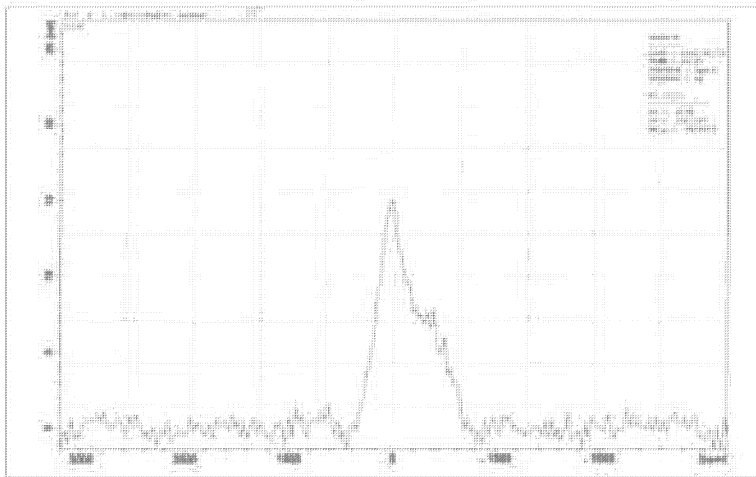


Fig. 7. NMR-spectrum of  $\text{TiO}_2 - \text{MnO}_2$  sorbent applied with lithium at  $18^\circ\text{C}$ .

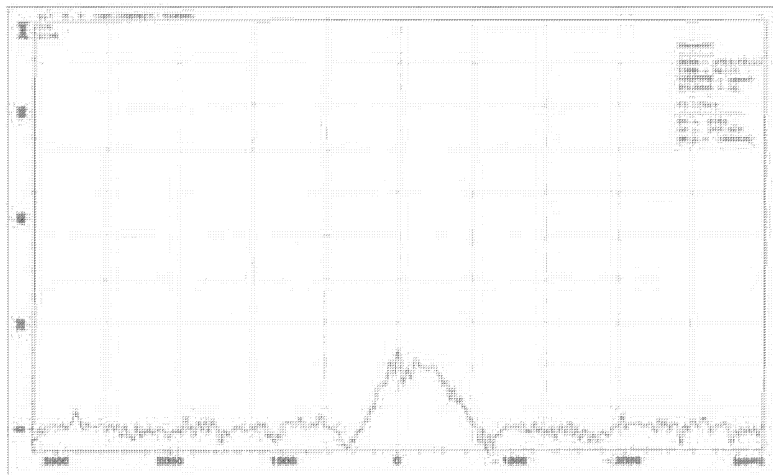


Fig. 8. NMR-spectrum of  $\text{TiO}_2 - \text{MnO}_2$  sorbent applied with lithium and treated at  $500^\circ\text{C}$ .

As it can be seen from Fig. 8, for heat treatment at a temperature of  $500^\circ\text{C}$  there is a slight broadening of the NMR - spectrum of applied sorbent, which indicates diffusion of lithium ions from the surface of pores into the sorbent volume.

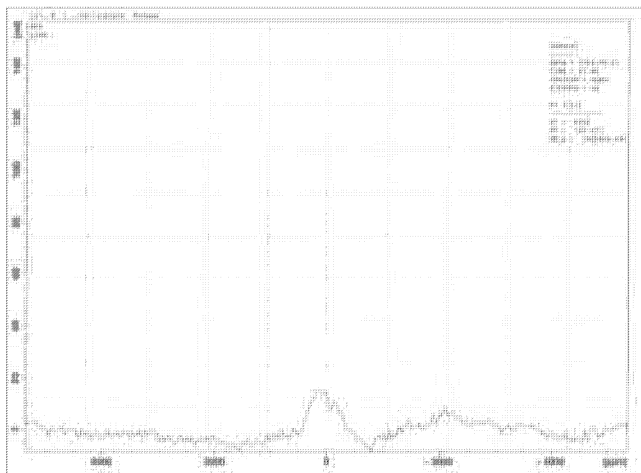


Fig. 9. NMR-spectrum of  $\text{TiO}_2 - \text{MnO}_2$  sorbent applied with lithium and treated at  $600^\circ\text{C}$ .

NMR - spectrum of applied  $\text{TiO}_2 - \text{MnO}_2$  at  $600^\circ\text{C}$ , shown in Fig. 9, is characterized by a

significant broadening. This is explained by the subsequent diffusion of lithium ions into the sorbent volume with a change in its structure.

Sorption of lithium ions from model solutions

The obtained sorption isotherms are shown in Figure 10.

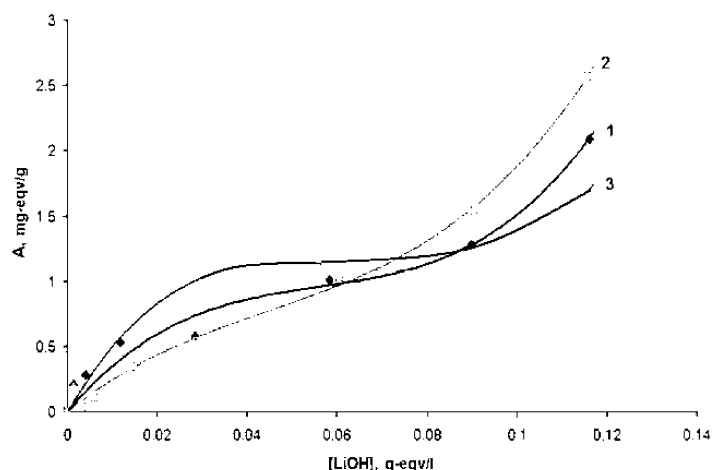


Fig. 10. Adsorption isotherms of lithium ions from LiOH solutions by binary oxides :  $\text{Al}_2\text{O}_3 - \text{MnO}_2$  (1),  $\text{TiO}_2 - \text{MnO}_2$  (2),  $\text{ZrO}_2 - \text{MnO}_2$  (3).

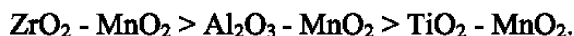
As seen from curves shown in the figure, the magnitude of lithium ions sorption isotherm in the substantial concentration range do not reach the limit values. Limitation in this case is low solubility of LiOH in water (12.9 g per 100 ml at room temperature).

From the obtained adsorption isotherms distribution coefficients ( $K_d$ ) were calculated, values of which are given in Table 3.

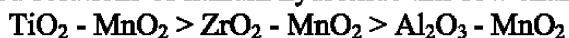
Table 3. Values of distribution coefficients for 0.01 and 0.1 M solutions of lithium hydroxide

Adsorbent	$K_d$ (0.01 M LiOH)	$K_d$ (0.1 M LiOH)
$\text{Al}_2\text{O}_3 - \text{MnO}_2$	50 (120)	14
$\text{TiO}_2 - \text{MnO}_2$	25 (80)	20
$\text{ZrO}_2 - \text{MnO}_2$	60 (150)	12

Analysis of curves in Fig. 10 and Table 3 shows that in the case of diluted solutions, absorptive capacity falls in a row:



As we approach saturated solutions of lithium hydroxide this row changes to:



And under these conditions lithium is the most absorbed by the sorption material based on  $\text{TiO}_2 - \text{MnO}_2$ .

Since modification of sorption materials by ion application requires maximum injection of applying ions (in this case, lithium ions), material based on  $\text{TiO}_2 - \text{MnO}_2$  was chosen to study the effects of these processes on selective properties. Number of samples with different ratios of Ti and Mn (1:1, 2:1, 1:2) were synthesized. Process flow of synthesis is shown in Figure 11.



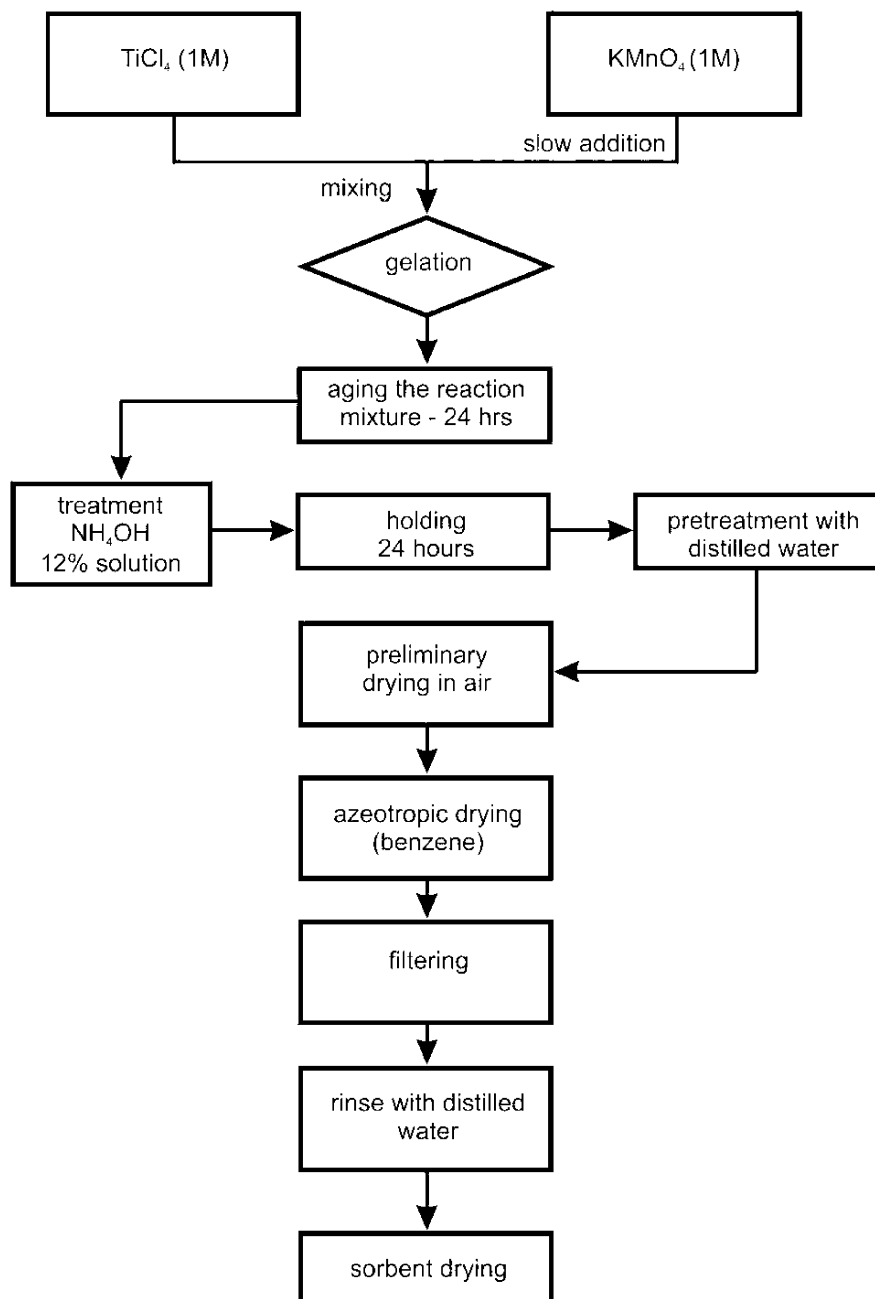


Fig. 11. Flow chart of  $\text{TiO}_2$  -  $\text{MnO}_2$  synthesis.

More detailed lithium-selective properties of the modified sorbents based on  $\text{TiO}_2$  -  $\text{MnO}_2$  were investigated in solutions simulating seawater.

Since for the processes of lithium ions extraction from seawater by sorption methods the major disturbing factor is the high concentration of sodium ions, as the model solution containing NaCl and LiCl was used. The concentration of sodium chloride was taken close to the average content of sodium ions in seawater. The content of lithium ions in sea water is very low, so to facilitate the analysis of lithium ions in the experiment, the concentration of lithium chloride in the model solution was increased in 10 times. Thus, test solution contained 0.5 mol/l NaCl and 0.0176 mol/l LiCl. That, in our opinion, was quite correct to study the sorption properties.

Study of lithium and sodium ions sorption by materials based on  $\text{TiO}_2$  -  $\text{MnO}_2$ , obtained by heat treatment at various temperatures was conducted with stirring under static conditions (0.1 g sorbent per 100 ml solution).

To determine the kinetic characteristics of sorption process sample of solutions were selected for the analysis. The resulting dependence of lithium and sodium ions sorption on the time of contact with adsorbents are shown in Figures 12 and 13.

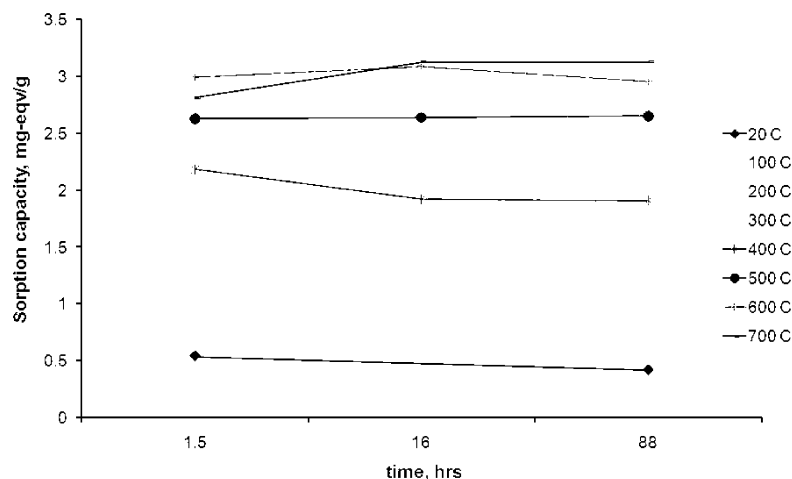


Fig. 12. Effect of application temperature of sorbent based on  $\text{TiO}_2 - \text{MnO}_2$  with lithium ions, on the kinetics of lithium ions sorption in the presence of sodium ions.

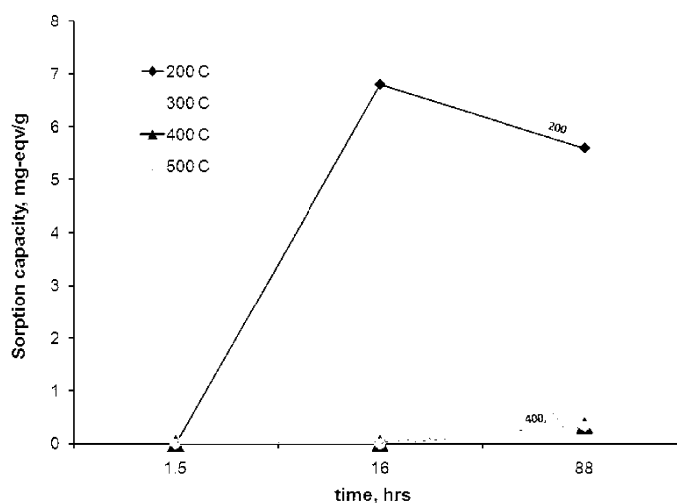


Fig. 13. Effect of application temperature of sorbent based on  $\text{TiO}_2 - \text{MnO}_2$  with lithium ions, on the kinetics of sodium ions sorption in the presence of lithium ions.

As it can be seen from the curves in Figure 12, consistent increase in the temperature of treatment from  $20^\circ\text{C}$  to  $700^\circ\text{C}$  leads to a significant increase in the sorption capacity to lithium ions from 0.5 to 3.0 meq/g. It is important to mention good kinetic characteristics of the obtained materials. For example, 1.5 hour contact is almost enough to reach maximum sorption values. Some drop of sorption capacity is observed for samples with low heat treatment temperature, possibly due to competing sodium sorption.

As it was shown above, the selectivity of the sorbent based on  $\text{TiO}_2 - \text{MnO}_2$  to lithium ions is increased with increasing of heat treatment temperature of applied sorbents. Adsorption capacity for lithium ions increases, and for sodium ions decreases. It should be noted that even sorbent that passed heat treatment at low temperatures ( $200\text{--}300^\circ\text{C}$ ), also in brief contact with a solution absorbs sodium ions in trace amounts. Only increase in duration of sorbent-solution contact leads to competitive adsorption of lithium and sodium ions. However, with increasing of heat treatment temperature, sorption capacity to sodium ions irreversibly decreases, and to lithium - increases.

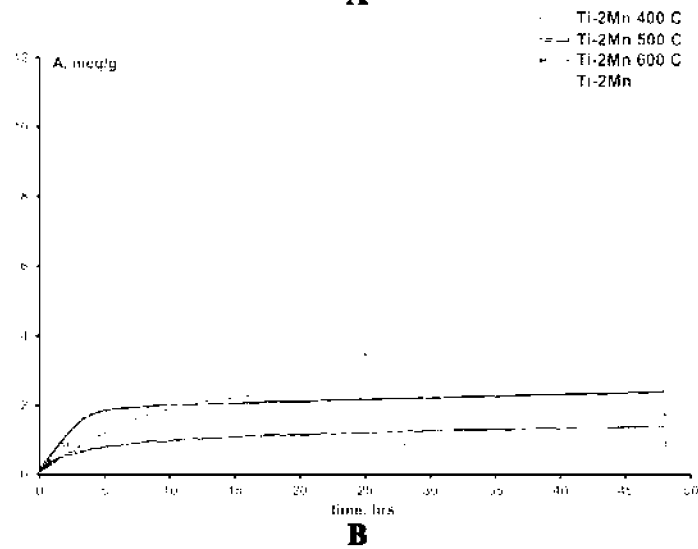
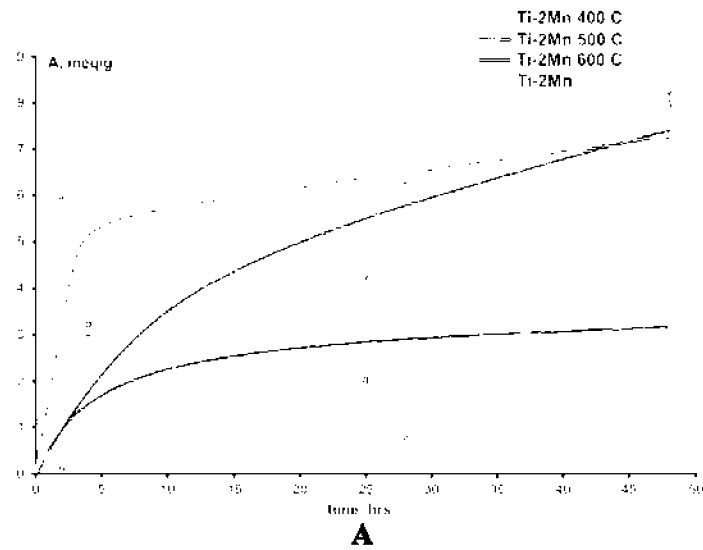


Fig. 14. Kinetics of adsorption of lithium (A) and sodium (B) ions by Ti-2Mn sample after heat treatment.

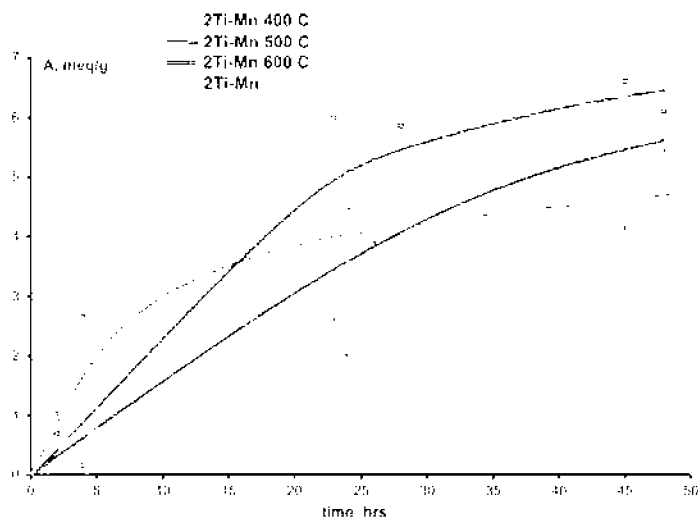


Fig. 15. Kinetics of lithium ions adsorption by 2Ti-Mn sample after heat treatment.

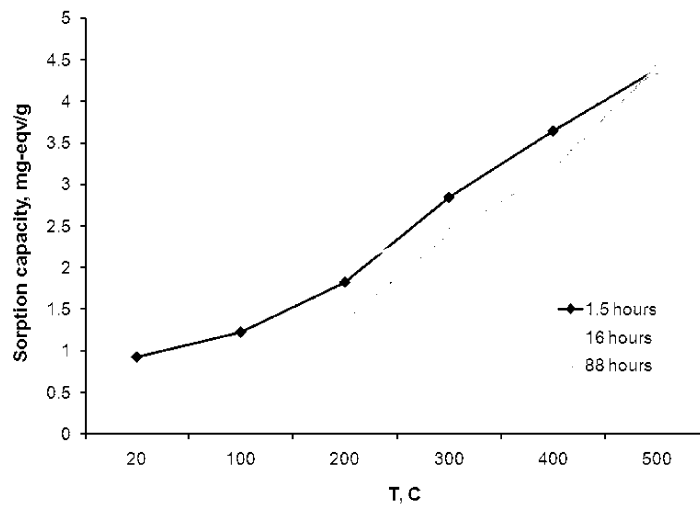


Fig. 16. Sorption capacity of sorbents based on  $\text{TiO}_2 - \text{MnO}_2$  for lithium ions on background of sodium ions, depending on the temperature of application of sorbent with lithium ions.

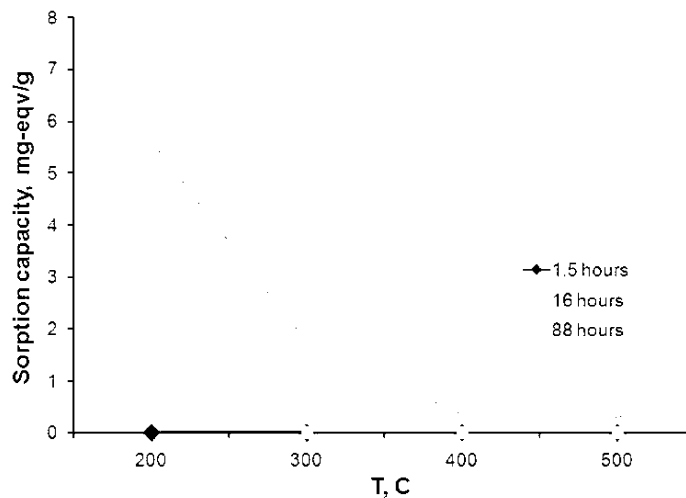


Fig. 17. Sorption capacity of sorbents based on  $\text{TiO}_2 - \text{MnO}_2$  for sodium ions on background of lithium ions, depending on the temperature of application of sorbent with lithium ions.

Sorption behavior of the composite titanium-manganese containing oxide materials is changing radically after passing the thermal stage of application with lithium ions, which is associated with introduction of lithium in the structure of the material and formation of transitional structures. From the showed data it can be concluded that thermal application greatly increases the sorption capacity of oxide material for lithium ions with a simultaneous drop in sorption of sodium ions. Moreover, absorption of lithium ions is accelerated. For some samples 90% of the maximum sorption capacity is achieved in 2-2.5 hours.

Although ion application significantly increases cost of produced materials, through the example of  $\text{TiO}_2 - \text{MnO}_2$  it is shown that the effectiveness of their use can be significantly greater. Material cost can be reduced by using waste as a raw material and obtain acceptable results in terms of price:performance.

## ХАРАКТЕРИЗАЦИЯ СОРБЦИОННЫХ МАТЕРИАЛОВ, СОДЕРЖАЩИХ ОКСИДЫ МНОГОВАЛЕНТНЫХ МЕТАЛЛОВ ДЛЯ ПРИМЕНЕНИЯ В ПРОЦЕССАХ ИЗВЛЕЧЕНИЯ ЛИТИЯ ИЗ СОЛЕВЫХ РАСТВОРОВ

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*Поскольку литий является одним из самых востребованных материалов для производителей электроники, представляет интерес рассмотреть альтернативные источники его получения. В статье проанализированы основные источники добычи лития, мировые запасы и динамика его добычи. Нами рассмотрена возможность получения лития из морской воды сорбционным методом. Проведена сравнительная характеристика сорбционных материалов на основе оксидов многовалентных металлов, определены параметры их структуры. Методом фазового рентгеноструктурного анализа установлено строение сорбентов. Показано, что титан-марганцевый сорбент является композитным материалом, состоящим из частиц  $TiO_2$ , рутила, покрытых аморфным  $MnO_2$ . Методом электронного парамагнитного резонанса установлено валентные состояния марганцевой компоненты в структуре сорбента. Получены изотермы адсорбции лития из растворов моделирующих морскую воду. Исследовано влияние модифицирования сорбционных материалов методом ионного апплицирования. Показано, что наибольшую сорбционную емкость по ионам  $Li^+$  имеет титан-марганцевый сорбент.*

*Ключевые слова: литий, композитный материал, оксид титана, титан-марганцевый сорбент, апплицирование*

## ХАРАКТЕРИЗАЦІЇ СОРБЦІЙНИХ МАТЕРІАЛІВ, ЩО МІСТЯТЬ ОКСИДИ БАГАТОВАЛЕНТНИХ МЕТАЛІВ ДЛЯ ЗАСТОСУВАННЯ В ПРОЦЕСАХ ВИЛУЧЕННЯ ЛІТІЮ З СОЛЬОВИХ РОЗЧИНІВ

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*Оскільки літій є одним з найбільш затребуваних матеріалів для виробників електроніки, представляє інтерес розглянути альтернативні джерела його отримання. У статті проаналізовано основні джерела видобутку літію, світові запаси і динаміка його видобутку. Нами розглянута можливість отримання літію з морської води сорбційним методом. Проведена порівняльна характеристика сорбційних матеріалів на основі оксидів багатовалентних металів, визначені параметри їх структури. Методом фазового рентгеноструктурного аналізу встановлено будову сорбентів. Показано, що титан-марганцевий сорбент є композитним матеріалом, що складається з частинок  $TiO_2$ , рутилу, покритих аморфним  $MnO_2$ . Методом електронного парамагнітного резонансу встановлено валентний стан марганцевої компоненти в структурі сорбенту. Отримано ізотерми адсорбції літію з розчинів, що моделюють морську воду. Досліджено вплив модифікування*

сорбційних матеріалів методом іонного апплікування. Показано, що найбільшу сорбційну ємність по іонам  $\text{Li}^+$  має титан-марганцевий сорбент.

Ключові слова: літій, композитний матеріал, оксид титану, титан-марганцевий сорбент, апплікування

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