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«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ  
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»  
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

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## ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

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**COMPARISON OF ETHYL ALCOHOL AND NITRIC ACID  
AS DESORBENTS FOR LANTHANUM IONS FROM MATRIX  
OF RARE-CROSSLINKED POLYMER HYDROGELS  
OF ACID AND BASIC NATURE**

**Abstract.** Desorption process of lanthanum ions by 95 ethyl alcohol and 2M nitric acid from matrix of polymer hydrogels of polyacrylic acid (hPAA), polymethacrylic acid (hPMAA), poly-4-vinylpyridine (hP4VP), poly-2-methyl-5-vinylpyridine (hP2M5VP) was studied. For desorption hydrogels in the ratio: 33%hPAA:67%hP4VP, 17%hPMAA:83%hP4VP, 67%hPAA:33%hP2M5VP and 50%hPMAA:50%hP2M5VP were taken. Extraction degree of lanthanum ions at these ratios after 48 hours is 94.05; 90.34; 91.09; 89.65 respectively. Total desorption degree with ethyl alcohol is( %) 85.46; 82.26; 80/17; 77.27 respectively. Total desorption degree by nitric acid is( %) 96.27; 94.43; 92.55; 93.09 respectively. Such difference is due to the nature of the desorbents (as known, ethyl alcohol is a polar organic solvent, nitric acid – strong mineral acid).

**Key words:** intergel systems, desorption, La<sup>3+</sup> ions, hydrogels, polyacrylic acid, polymethacrylic acid, poly-4-vinylpyridine, poly-2-methyl-5-vinylpyridine.

**Introduction.** Previous studies were devoted to investigation of sorption properties of intergel systems based on rare-crosslinked hydrogels in relation to ions of rare-earth metals [1-9]. In result of these studies it was found that there is significant increase of sorption properties of initial macromolecules due to their mutual activation. Sorption properties increase on 25-30% comparatively to individual hydrogels.

For desorption of lanthanum ions after its sorption by ion-exchangers polar organic compounds and mineral acids can be used [10, 11].

The goal of this work is study desorption properties of ethyl alcohol and nitric acid in relation to lanthanum ions.

**EXPERIMENTAL PART**

*Equipment.* Measurements of optical density of solutions for further calculation of La<sup>3+</sup> ions concentration were carried out by spectrophotometer Jenway-6305 (UK).

*Materials.* Studies carried out in 95% solution of ethyl alcohol and 2M solution of nitric acid. Hydrogels of polyacrylic (PAA) and polymethacrylic (PMAA) acids were synthesized at the presence of crosslinking agent N,N-methylene-bis-acrylamide and redox system K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>–Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Hydrogel of poly-4-vinylpyridine (hP4VP) was synthesized by “Sigma Aldrich” company (2% of crosslinking agent). Hydrogel of poly-2-methyl-5-vinylpyridine was synthesized

in medium of dimethylformamide at the presence of crosslinking agent epichlorohydrine. From synthesized hydrogels intergel pairs were created. Swelling degrees of the hydrogels are:  $\alpha_{(hPAA)}=27.93$  g/g,  $\alpha_{(hPMAA)}=20.65$  g/g;  $\alpha_{(hP4VP)}=3.27$  g/g, and  $\alpha_{(hP2M5VP)}=3.20$  g/g.

*Experiment.* Experiments were carried out at a room temperature. Study of desorption of lanthanum ions was made as follows: calculated amount of each hydrogel in dry initial state were put in special glass filters, pores of which is permeable for low-molecular ions and molecules, but impermeable for hydrogels dispersion. After that intergel pairs in the relation 33%hPAA:67%hP4VP, 17%hPMAA:83%hP4VP, 67%hPAA:33%hP2M5VP, 50%hPMAA:50%hP2M5VP were put into 0.005M solution of lanthanum nitrate and were left for sorption during 48 hours. After that filters with hydrogels undergo desorption by ethyl alcohol and nitric acid for separating from each other.

*Methodology of determination lanthanum ions.* Determination of lanthanum ions in solution is based on formation of colored complex compound of organic analytical reagent arsenazo III with ions of rare-earth metals [12].

Lanthanum ions extraction degree was calculated in accordance following equation:

$$\eta = \frac{C_{\text{initial}} - C_{\text{residual}}}{C_{\text{initial}}} \cdot 100\%$$

where  $C_{\text{initial}}$  – initial concentration of lanthanum in solution, g/L;  $C_{\text{residual}}$  is residual concentration of lanthanum in solution, g/L.

Desorption degree of lanthanum ions was calculated by formula:

$$R = \frac{m_{\text{desorbed}}}{m_{\text{sorbed}}} \cdot 100\%$$

where  $m_{\text{desorbed}}$  is mass of desorbed lanthanum, g;  $m_{\text{sorbed}}$  is mass of sorbed lanthanum, g.

## RESULTS AND DISCUSSION

For desorption of the rare-earth element, which was sorbed in a form of hydrophobic complex, strong mineral acids or polar organic solvents can be used. For the desorption the hydrogels from the following ratios 33%hPAA:67%hP4VP, 17%hPMAA:83%hP4VP, 67%hPAA:33%hP2M5VP, 50%hPMAA:50%hP2M5VP were taken. Extraction degree of lanthanum ions at these ratios after 48 hours is 94.05%; 90.34%; 91.09%; 89.65%.

*Features of lanthanum ions desorption by ethyl alcohol.* Dependence of lanthanum ions desorption degree by ethyl alcohol from matrix of hydrogels of polyacrylic acid and poly-4-vinylpyridine from time is presented on figure 1. Strong increase of the metal ions desorption is observed during 6 hours as for acid as for basic hydrogels. After this time desorption degree is 47.64% for hPAA and 15.52% for hP4VP.

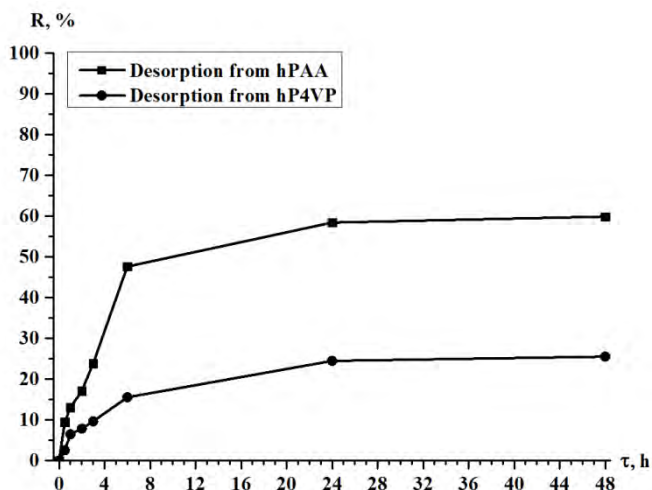


Figure 1 – Dependence of lanthanum ions desorption degree versus of duration of the time by ethyl alcohol from PAA and P4VP hydrogels from time

Further increase of lanthanum ions desorption degree is not so intensive, after 24 hours of interaction of the hydrogels with ethyl alcohol desorption degree from hPAA is 59.92%, from hP4VP – 24.46%. Consequent interaction of the hydrogels with the desorbent provides slight increase of lanthanum ions concentration in solution, what indicates that equilibrium is almost achieved. Total desorption degree from matrix of both hydrogels at 48 hours is 85.46%.

Figure 2 represents dependence on desorption degree of lanthanum ions versus duration by ethyl alcohol from matrix of hPMAA and hP4VP from time.

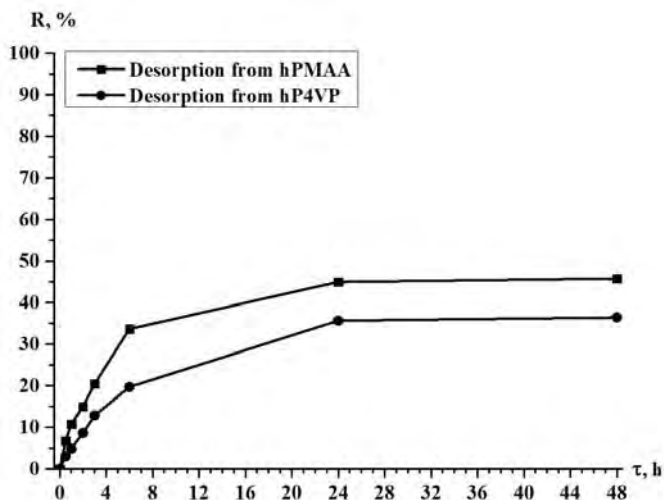


Figure 2 – Dependence of lanthanum ions desorption degree versus of duration of the time by ethyl alcohol from PMAA and P4VP hydrogels

Overwhelming majority of lanthanum is released during 6 hours. Obtained results show that better part of lanthanum during its sorption was sorbed by the polyacid. Further desorption occurs more slightly for both hydrogels. Total desorption degree at 48 hours is 82.26%.

Curves of dependence of lanthanum desorption by ethyl alcohol from time from matrix of hydrogels of polyacrylic acid and poly-2-methyl-5-vinylpyridine are presented on figure 3. As seen from the figure, the most of lanthanum was sorbed by the polyacid. Strong increase of desorption degree is observed during 6 hours, at this time 50.20% of lanthanum is desorbed from hPAA, 13.44% – from hP2M5VP. After 2 days (48 hours) total desorption degree of lanthanum is 80.17%.

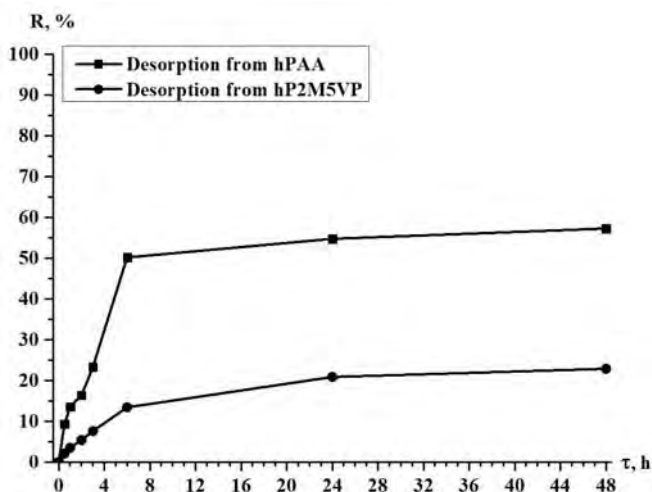


Figure 3 – Dependence on lanthanum ions desorption degree versus of duration of the time by ethyl alcohol from PAA and P2M5VP hydrogels from time

Figure 4 represents dependence of lanthanum desorption by ethyl alcohol from time. Similarly to previous cases (fig. 1-3), intensive desorption occurs during 6 hours, at this time 31.58% of the metal is desorbed from hPMAA, 17.83% – from hP2M5VP. Total desorption degree of lanthanum ions from hPMAA and hP2M5VP after 2 days is 77.27%.

Comparative analysis of total desorption degree of lanthanum ions by ethyl alcohol from hydrogels of PAA, PMAA, P4VP and P2M5VP at 48 hours is presented in table 1.

As seen from the obtained data, are represented in table 1 not high (~77-85%) desorption degree is in direct dependence from the nature of the desorbent (as known, ethyl alcohol is polar solvent). Due to this fact not full desorption of lanthanum ions from hydrogels matrix occurs.

*Features of lanthanum ions desorption by nitric acid.* Dependence on lanthanum ions desorption degree by nitric acid from matrix of polymer hydrogels of polyacrylic acid and poly-4-vinylpyridine is shown on figure 5.

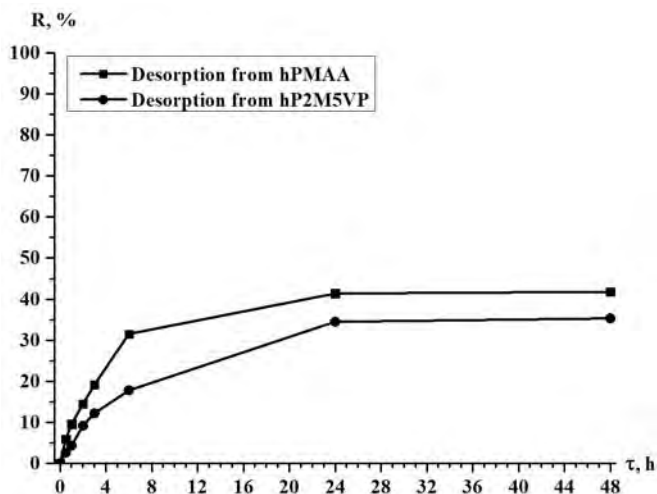


Figure 4 – Dependence on lanthanum ions desorption degree versus of duration of time by ethyl alcohol from PMAA and P2M5VP hydrogels

Table 1 – Total desorption degree of lanthanum ions by ethyl alcohol from intergel systems

Intergel system	hPAA-hP4VP	hPMAA-hP4VP	hPAA-hP2M5VP	hPMAA-hP2M5VP
Hydrogels ratio	33%hPAA: 67%hP4VP	17%hPMAA: 83%hP4VP	67%hPAA: 33%hP2M5VP	50%hPMAA: 50%hP2M5VP
Total desorption degree, %	85.46	82.26	80.17	77.27

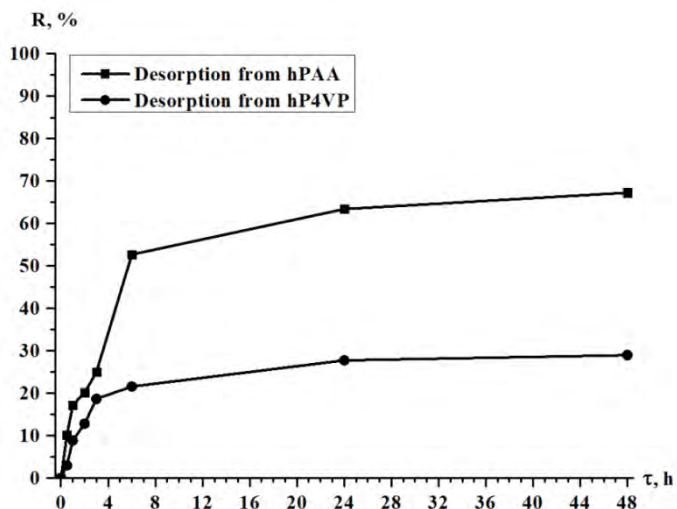


Figure 5 – Dependence on lanthanum ions desorption degree versus of duration of time by nitric acid from PAA and P4VP hydrogels

The most intensive desorption occurs at first 6 hours: at this time 52.70% of lanthanum is desorbed from hPAA, 21.56% – from hP4VP. Subsequent desorption provide increase of the parameter, at 24 hours 63.41% of the metal is released from hPAA and 27.75% – from hP4VP. Further increase is very slight, what indicates that system is almost reaches equilibrium state. Total desorption degree from the polymers at 48 hours is 96.27%.

Desorption process of lanthanum ions from polymer hydrogels of polymethacrylic acid and poly-4-vinylpyridine in time is presented on figure 6. Similarly to the previous system (figure 5), first six hours – area of high desorption of lanthanum ions from the macromolecules during their contact with desorbing agent. From all amount of sorbed lanthanum 36.55% is released from hydrogel of PMAA and 20.96% is released from hydrogel of P4VP. After end of the experiment (48 hours) total desorption degree from the macromolecules is 94.43%.

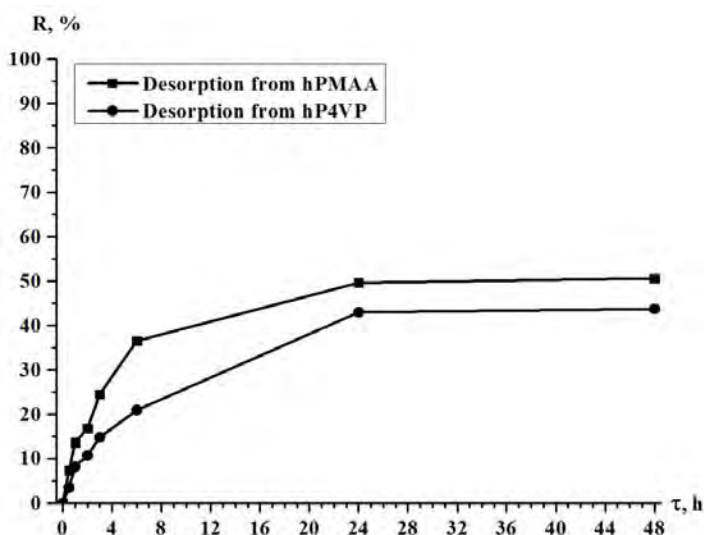


Figure 6 – Dependence on lanthanum ions desorption degree versus of duration of time by nitric acid from PMAA and P4VP hydrogels

Figure 7 represents dependence of desorption degree of lanthanum ions by nitric acid from matrix of the hydrogels of PAA and P2M5VP from time. After 6 hours after beginning of interaction of the desorbent with the hydrogels there is a release of main amount of lanthanum. As seen from the figure, polyacid sorbes 2 times more lanthanum than polybasis. Total desorption degree of lanthanum from hydrogels of PMAA and P4VP is 92.55% at 48 hours.

As seen from figure 8, intensive desorption is observed during 24 hours. During 6 first hours 31.94% of lanthanum is desorbed from hPMAA and 20.04% from hP2M5VP. Total desorption degree is 93.09% for 48 hours.

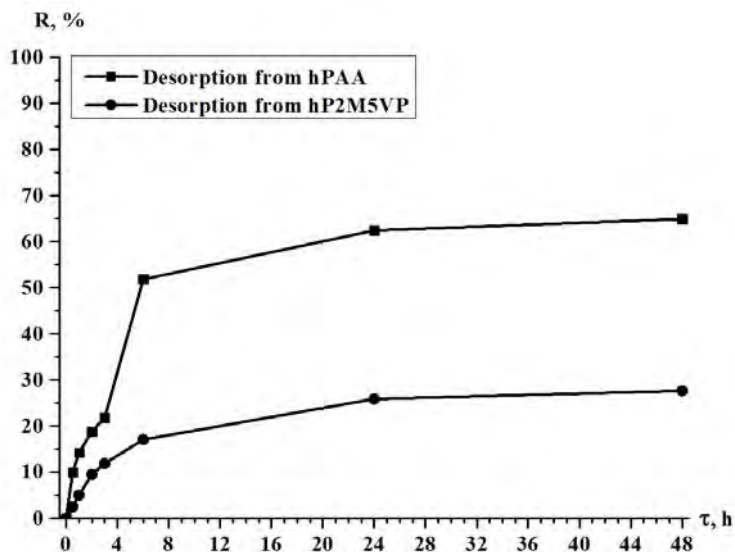


Figure 7 – Dependence on lanthanum ions desorption degree versus duration of time by nitric acid from PAA and P2M5VP hydrogels

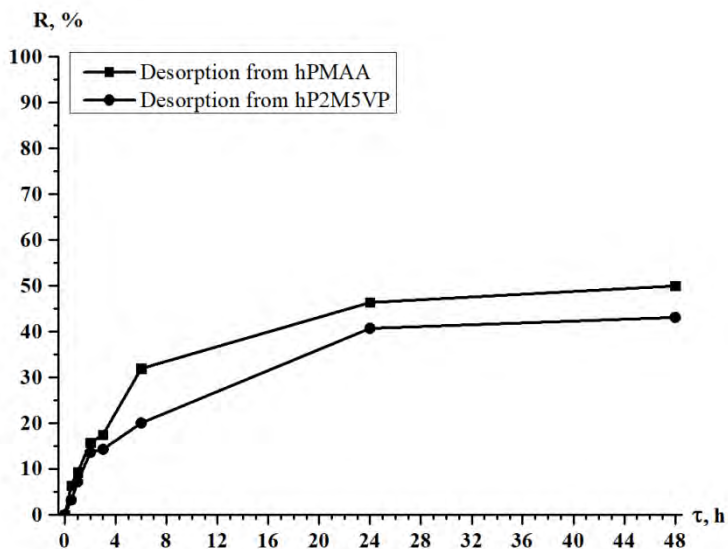


Figure 8 – Dependence of lanthanum ions desorption degree by nitric acid from PMAA and P2M5VP hydrogels from time

Table 2 shows comparison of total desorption degree of lanthanum ions by nitric acid from hydrogels of PAA, PMAA, P4VP and P2M5VP at 48 hours.



Table 2 – Total desorption degree of lanthanum by nitric acid from intergel systems

Intergel system	hPAA-hP4VP	hPMAA-hP4VP	hPAA-hP2M5VP	hPMAA-hP2M5VP
Hydrogels ratio	33%hPAA: 67%hP4VP	17%hPMAA: 83%hP4VP	67%hPAA: 33%hP2M5VP	50%hPMAA: 50%hP2M5VP
Total desorption degree, %	96.27	94.43	92.55	93.09

The obtained results indicate that nitric acid, being a strong mineral acid, interacts sufficiently with polymer hydrogels, what is evidenced by higher (~92-96%) desorption degree comparatively with ethyl alcohol.

### Conclusions.

1. Obtained results point to the fact, that 95% ethyl alcohol and 2M nitric acid can be used for desorption of lanthanum ions from PAA, PMAA, P4VP, P2M5VP polymer hydrogels matrix.

2. Desorption degree of lanthanum ions from polymer hydrogels matrix by ethyl alcohol do not have high values (not more than 85%) what is due to nature of polar solvent.

3. High values of desorption degree are achieved at desorption of the metal by nitric acid. Due to the fact that mineral acid is strong by its nature, and desorption degree have high (over 95%) values.

### REFERENCES

- [1] Kondaurov R.G., Abilov Zh.A., Jumadilov T.K. Application of intergel systems for selective sorption of rare-earth elements // Industry of Kazakhstan. 2014. N 4. P. 38-41.
- [2] Jumadilov T.K., Abilov Zh.A., Kondaurov R.G. Influence of mutual activation of hydrogels of polymethacrylic acid and poly-2-methyl-5-vinylpyridine of sorption ability of the intergel system in relation to lanthanum ions // Chemical journal of Kazakhstan. 2014. N 4. P. 128-136.
- [3] Jumadilov T.K., Abilov Zh.A., Kondaurov R.G. Intergel systems in recovery of precious and rare earth metals // International journal of applied and fundamental research: site. 2015. N 1. URL: <http://www.science-sd.com/460-24777>
- [4] Jumadilov T.K., Abilov Zh.A., Kondaurov R.G. Intergel systems – highly effective instrument for rare earth elements extraction from industrial solutions // Proceedings of 4<sup>th</sup> International Caucasian Symposium on Polymers and Advanced Materials, Batumi, Georgia, 2015. P. 64.
- [5] Jumadilov T.K., Abilov Zh.A., Grazulevicius J.V., Kondaurov R.G., Akimov A.A. Investigation of sorption ability of intergel system hydrogel of polyacrylic acid – hydrogel of poly-4-vinylpyridine in relation to lanthanum ions // Materials of VI international seminar special polymers for protection of environment, oil industry, bio-, nanotechnology and medicine, Semey, Kazakhstan, September 2015. P. 123.
- [6] Zhunusbekova N.M., Kondaurov R.G., Eskalieva G.K., Akimov A.A., Umerzakova M.B., Jumadilov T.K. Sorption extraction of lanthanum on mutual active intergel sorbents // Chemical journal of Kazakhstan. 2016. N 3. P. 152-161.
- [7] Jumadilov T., Abilov Zh., Grazulevicius J., Zhunusbekova N., Kondaurov R., Agibayeva L., Akimov A. Features of lanthanum ions sorption by intergel system based on polymethacrylic acid

and poly-4-vinylpyridine hydrogels // Proceedings of International scientific-technical conference “The modern technologies of polymer materials obtaining and processing”, Lviv, Ukraine, September 2016. P. 95.

[8] Jumadilov T.K., Abilov Zh.A., Grazulevicius J.V., Kondaurov R.G. Selective extraction of lanthanum ions by intergel system hydrogel of polyacrylic acid – hydrogel of poly-4-vinylpyridine from solution, which contains ions of lanthanum and cerium // Materials of international scientific-practice conference “Tendencies of development of science and education in area of natural science disciplines”, Almaty, Kazakhstan, October 2016. P. 182-185.

[9] Jumadilov T.K., Kondaurov R.G., Abilov Zh.A., Grazulevicius J.V., Akimov A.A. Influence of polyacrylic acid and poly-4-vinylpyridine hydrogels mutual activation in intergel system on their sorption properties in relation to lanthanum (III) ions // Polymer Bulletin. 2017. Vol. 74. P. 4701-4713. doi:10.1007/s00289-017-1985-3.

[10] Tereschenkova A.A., Statkus M.A., Tihomirova T.I., Tsizin G.I. Sorption concentration of lanthanum on modified low-polar sorbents // Bulletin of Moscow University. Series 2, chemistry. 2013. Vol. 54, N 4. P. 203-209.

[11] Xiong C., Zhu J., Shenq C., Chen J. Adsorption and Desorption of Praseodymium (III) from Aqueous Solution Using D72 Resin Author links open overlay panel // Chinese Journal of Chemical Engineering. 2012. Vol. 20. P. 823-830.

[12] Petruhin O.M. Practice book on physico-chemical methods of analysis. M.: Chemistry, 1987. P. 77-80.

## Резюме

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### ТАБИҒИ НЕГІЗДІК ЖӘНЕ ҚЫШҚЫЛДЫҚ СИРЕК ТОРЛАНҒАН ГИДРОГЕЛЬ МАТРИЦАСЫНАН ЛАНТАН ИОНДАРЫН ДЕСОРБЦИЯЛАУДА ЭТИЛ СПИРТІ МЕН АЗОТ ҚЫШҚЫЛЫН ДЕСОРБЕНТ РЕТІНДЕ САЛЫСТЫРУ

Полиакрил қышқылы (ПАҚГ), полиметакрил қышқылы (ПМАҚГ), поли-4-винилпиридин (П4ВПГ) және поли-2-метил-5-винилпиридин (П2М5ВПГ) гидрогельдерінің полимерлік матрицасынан лантан ионын 95% этанолда және 2М азот қышқылында десорбциялау процесі жүргізілді. Десорбциялау үшін интергелді жүйелеріндегі гидрогельдер мынадай қатынастарда алынды: 33%ПАҚГ:67%П4ВПГ, 17%ПМАҚГ:83%П4ВПГ, 67%ПАҚГ:33%П2М5ВПГ, 50%ПМАҚГ:50%П2М5ВПГ. Осы қатынастарда 48 сағаттық десорбциядан кейінгі лантан иондарын бөліп алу дәрежесі келесідей: 94,05; 90,34; 91,09; 89,65%: Этил спиртіндегі десорбцияның жалпы бөліп алу дәрежесі 85,46; 82,26; 80,17; 77,27% құрайды. Азот қышқылындағы десорбцияның жалпы бөліп алу дәрежесі 96,27; 94,43; 92,55; 93,09% құрайды. Бұндай айырмашылық десорбенттердің табиғатының ерекшеліктеріне байланысты (белгілі, этил спирті – полярлық органикалық еріткіш, ал азот қышқылы - күшті минералды қышқылы) болып табылады.

**Түйін сөздер:** интергелді жүйе, десорбция,  $\text{La}^{3+}$  иондары, гидрогель, полиакрил қышқылы, полиметакрил қышқылы, поли-4-винилпиридин, поли-2-метил-5-винилпиридин.

## Резюме

*Т. К. Джумадилов, Р. Г. Кондауров*

### СРАВНЕНИЕ ЭТИЛОВОГО СПИРТА И АЗОТНОЙ КИСЛОТЫ В КАЧЕСТВЕ ДЕСОРБЕНТОВ ДЛЯ ИОНОВ ЛАНТАНА ИЗ МАТРИЦЫ РЕДКОСШИТЫХ ПОЛИМЕРНЫХ ГИДРОГЕЛЕЙ КИСЛОТНОЙ И ОСНОВНОЙ ПРИРОДЫ

Исследован процесс десорбции ионов лантана 95% этиловым спиртом и 2М азотной кислотой из матрицы полимерных гидрогелей полиакриловой кислоты (гПАК), полиметакриловой кислоты (гПМАК), поли-4-винилпиридина (гП4ВП) и поли-2-метил-5-винилпиридина (гП2М5ВП). Для десорбции были взяты следующие соотношения гидрогелей в интергелевых системах 33%гПАК:67%гП4ВП, 17%гПМАК:83%гП4ВП, 67%гПАК:33%гП2М5ВП, 50%гПМАК:50%гП2М5ВП. Степень извлечения ионов лантана при этих соотношениях по истечении 48 ч составляет 94,05; 90,34; 91,09; 89,65%. Суммарная степень десорбции этиловым спиртом составляет 85,46; 82,26; 80,17; 77,27%. Суммарная степень десорбции азотной кислотой составляет 96,27; 94,43; 92,55; 93,09%. Подобная разница обусловлена природой десорбентов (как известно, этиловый спирт – полярный органический растворитель, азотная кислота – сильная минеральная кислота).

**Ключевые слова:** интергелевые системы, десорбция, ионы  $\text{La}^{3+}$ , гидрогели, полиакриловая кислота, полиметакриловая кислота, поли-4-винилпиридин, поли-2-метил-5-винилпиридин.