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Specific features of praseodymium extraction by intergel system based on polyacrylic acid and poly-4-vinylpyridine hydrogels

Some technological solutions contain valuable components and can become an additional source of rare-earth elements to satisfy the current production demands. This research provides the study on using a combination of polyacrylic acid hydrogel (hPAA) and hydrogel of poly-4-vinylpyridine (hP4VP) in different molar ratios for praseodymium ions sorption from its nitrate solution. The mutual activation of the hydrogels in an aqueous medium provides their transformation into a highly ionized state by the conformational and electrochemical changes in properties during their remote interaction. The electrochemical properties of solutions were studied by the methods of electrical conductivity, and pH measurements of the solutions. The research showed that the maximum activation of hydrogels was revealed within the molar ratio of hPAA:hP4VP equal to 1:5. Moreover, the total praseodymium ions sorption degree after 24 hours of sorption by individual hPAA and hP4VP was 54 % and 47 %, respectively, whereas the praseodymium ions sorption degree by the hPAA–hP4VP intergel system in the molar ratio 1:5 became 62 %. A slight increase in the sorption degree of praseodymium ions by the intergel system in comparison with individual hydrogels can be explained by the achievement of a higher ionization degree of hydrogels being activated in the hPAA–hP4VP interpolymer system by the remote interaction effect.

Keywords: intergel systems, polyacrylic acid hydrogel, poly-4-vinylpyridinehydrogel, remote interaction, sorption, praseodymium ions.

Introduction

Rare-earth metals have various applications in chemical industry, in nuclear engineering, in metallurgy, etc. For example, praseodymium being a rare-earth metal is commonly used to make high-power magnets that are known for their strength and endurance when combined with another rare-earth element neodymium [1, 2]. The recovery of praseodymium from technological solutions might provide an additional source of this valuable element.

Sorption and extraction techniques for the recovery of certain metals have been successfully used in hydrometallurgy [3]. Moreover, sorption techniques are presently favored over extraction methods owing to a variety of advantages: they are more environmentally friendly and have fewer technical cycles [4]. For the recovery of rare-earth metals from the solutions, adsorption processes using various materials such as polymers have recently sparked increased interest [5]. For instance, polymer hydrogels are generally considered smart materials with evolving progressive functions for sorption technology. A common method for praseodymium ions sorption from solutions can be the use of polymer hydrogels: polyacrylic acid hydrogel (hPAA) and poly-4-vinylpyridinehydrogel (hP4VP).

Our previous research [6] showed that the remote interaction effect provided the changes in the electrochemical and conformational properties which influenced on the increase in the sorption activity of hydrogels in their intergel system. For present study we decided to choose “hPAA–hP4VP” intergel system to test it in praseodymium ions sorption. Furthermore, the combination of hydrogels in the “hPAA–hP4VP” intergel system with different molar ratios X:Y (6:0, 5:1, 4:2, 3:3, 2:4, 1:5, and 0:6) can also be applied to investigate the remote interaction effect for improving the process of praseodymium ions sorption.

The goal of this research was to study the influence of the preliminary mutual activation of polyacrylic acid hydrogel (hPAA) and poly-4-vinylpyridine hydrogel (hP4VP) (“hPAA–hP4VP” intergel system) in praseodymium ions sorption from its nitrate solution.

Experimental

The following measurement instruments and equipment were used: conductometer MARK-603 (Vzor, Nizhny Novgorod, Russia) for the measurements of the specific electric conductivity of solutions, which is important for characterizing the equilibrium of polyelectrolytes dissociation. The hydrogen ions concentration was determined by a Metrohm 827 pH-meter pH-Lab (Switzerland). Measurements of pH were provided to study the acid–base properties of the solution. The mass of the samples was measured using an analytical balance SHIMADZU AY220 (Shimadzu Corporation, Kyoto, Japan). The optical density measurements for the subsequent calculation of the praseodymium (III) concentration in solution was determined by aJenway-6305 (Cole-Parmer, Jenway, York, UK) spectrophotometer. For the residual praseodymium ions detection from liquid samples, the Varian Atomic Absorption SpectrometerAA240. Measurement errors did not exceed 1 %.

Materials

The following reagents were used: praseodymium (III) nitrate hexahydrate (99.9 % trace metals basis, Sigma-Aldrich) as praseodymium ions source in solution, reagent arsenazo III (Sigma-Aldrich) in powder form as a color-forming reagent to determine cerium concentration, and perchloric acid ($HClO_4$) (Sigma-Aldrich, Darmstadt, Germany) for standard solution preparation. Poly-4-vinylpyridine hydrogel (hP4VP) (2 % cross-linked with divinylbenzene, Sigma-Aldrich) was used. Polyacrylic acid hydrogels were synthesized in the presence of the N,N-methylene-bis-acrylamide crosslinking agent and the $K_2S_2O_8$-$Na_2S_2O_3$ redox system in an aqueous medium in laboratory conditions.

Electrochemical research

The studies of the “hPAA–hP4VP” intergel system were carried out in the following order: each dry hydrogel was placed in separate polypropylene mesh, the pores of which were permeable to low molecular weight ions and molecules, but impermeable for dispersion of hydrogels. Then, the meshes with dry hydrogels were placed in a glass with distilled water for 48 hours for swelling. Upon reaching an equilibrium state in weight, the swollen hydrogels were taken, and according to molar ratios, the “hPAA–hP4VP” intergel system were composed for further mutual activation. The activation of the intergel system is required to transfer the hydrogels into a highly ionized state by changing their conformational and electrochemical properties by remote interaction [7]. For activation, the polypropylene meshes with swollen hydrogels inside (Fig. 1) were placed in a glass with distilled water at a distance of about 1–2 cm opposite each other, forming an interpolymer system “hPAA–hP4VP”. After the activation, the meshes with swollen hydrogels were placed in glasses with praseodymium nitrate solutions and the electrical conductivity with pH measurements of the overgel liquid were determined. The experiments were carried out at room temperature.

Figure 1. Polypropylene meshes (left) and the illustration of the activation process of the intergel system (right)

The polymer chain binding degree of internode links of the polymer chain was calculated according to Eq. (1):

$$\theta = \frac{\vartheta_{sorbed}}{\vartheta_1 + \vartheta_2} \times 100\ \%, \tag{1}$$

where ϑ_{sorbed} is the amount of sorbed praseodymium ions (in mol), ϑ_1 is the amount of hPAA (in mol), and ϑ_2 is the amount of hP4VP(in mol).

The sorption degree was calculated using the following Eq. (2):

$$\eta = \frac{C_{initial} - C_{residual}}{C_{initial}} \times 100\ \%, \tag{2}$$

where $C_{initial}$ and $C_{residual}$ are the initial and residual concentration (in g/L) of praseodymium ions in the solution, respectively.

For the experiments 1000 mL of the praseodymium (III) nitrate hexahydrate solution (C = 100 mg/L) was prepared and poured into 7 glasses with 100 mL each. The hydrogels were put separately into 2 polypropylene meshes (1 common glass with solution) in accordance with their molar ratios X:Y (6:0, 5:1, 4:2, 3:3, 2:4, 1:5, and 0:6) to form the intergel system hPAA:hP4VP (X:Y). For spectrophotometer analysis, one aliquot (1 mL) was taken from each solution at the set time. Finally, 63 aliquots of solution were obtained.

Results and Discussions

The presence of the intergel system in an aqueous solution of praseodymium (III) nitrate hexahydrate leads to various processes that affect the electrochemical equilibrium in the solution. Fig. 2 shows the dependence of the electrical conductivity of $Pr(NO_3)_3 \cdot 6H_2O$ solutions on the molar ratios hPAA:hP4VP in time. Mostly all ratios, an increase in electrical conductivity values was observed, which might be explained by an increase in the OH^- medium in solutions, released by the additional dissociation of the strongly basic P4VP hydrogel [8].

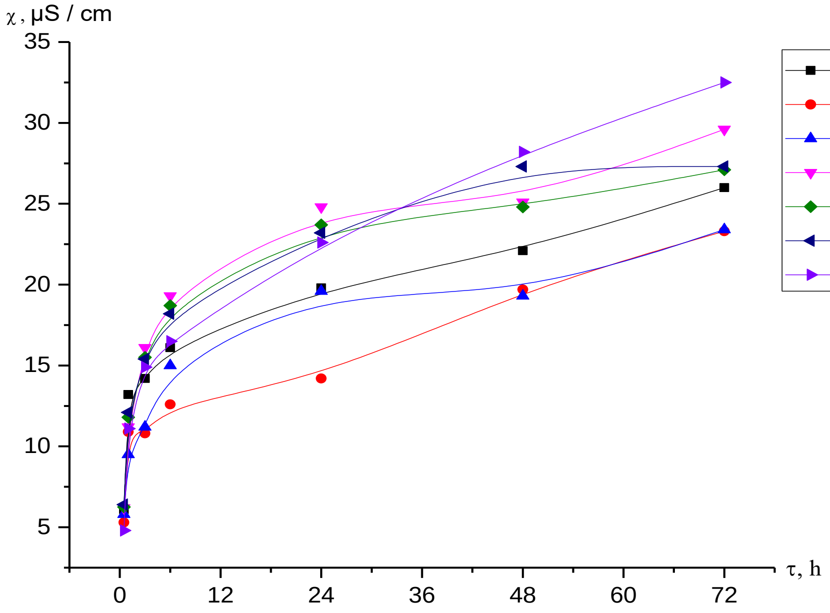

Figure 2. Dependence of specific electrical conductivity on the molar ratio of hydrogels on time

The conductivity of solutions increased with time for almost all ratios of hydrogels. However, the character of the parameter change was different for different ratios of hydrogels. As can be seen from Figure 2, there is an increase in electrical conductivity over time. This is due to the transition of the initial hydrogels of polyacrylic acid and poly-4-vinylpyridine to a highly ionized state due to mutual activation during their remote interaction.

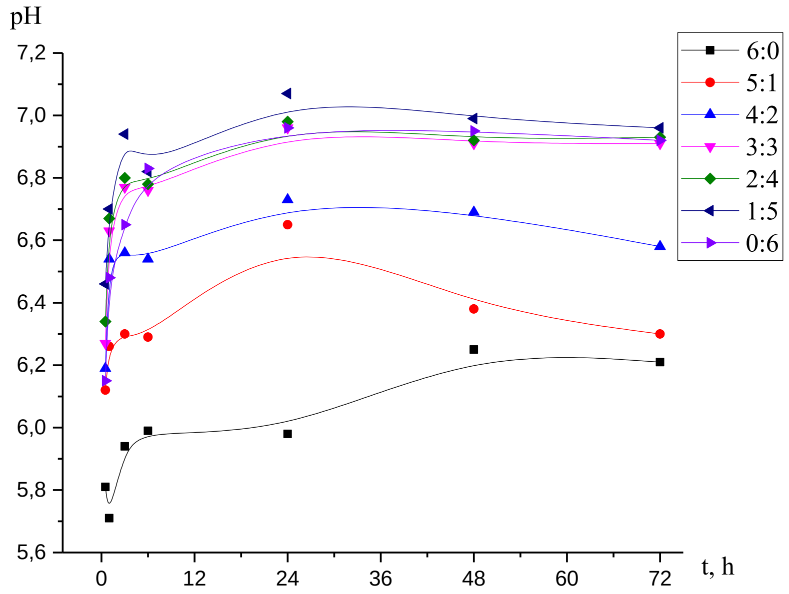

Figure 3. Dependence of pH on the molar ratio of hydrogels on time

The change in the pH of solutions is shown in Figure 3. As can be seen from the obtained results, an increase in pH values with the time of remote interaction was observed. The increase in pH may be explained due to the binding of the detached H^+ from the carboxyl group by poly-4-vinylpyridine, as a result, the process of protonation of the heteroatom in a ring occurred. This was evidenced by the maxima at the 1:5 ratio of hPAA–hP4VP, which correspond to the time of remote interaction after 24 and 48 hours. The minimum pH values were observed in the presence of only polyacid. This is due to the appearance of charged ions (H^+, OH^-) and groups (–COO^-). The maximum pH values indicated that the rate of dissociation of –COOH groups is lower than the rate of protonation of the poly-4-vinylpyridine heteroatom. This phenomenon indicates the process of ionization of the main polymer of the hydrogel. Consequently, both polymer hydrogels pass into a highly ionized state, undergoing mutual activation.

Figure 4 shows the change in the concentration of praseodymium ions during sorption by the intergel system hPAA–hP4VP.

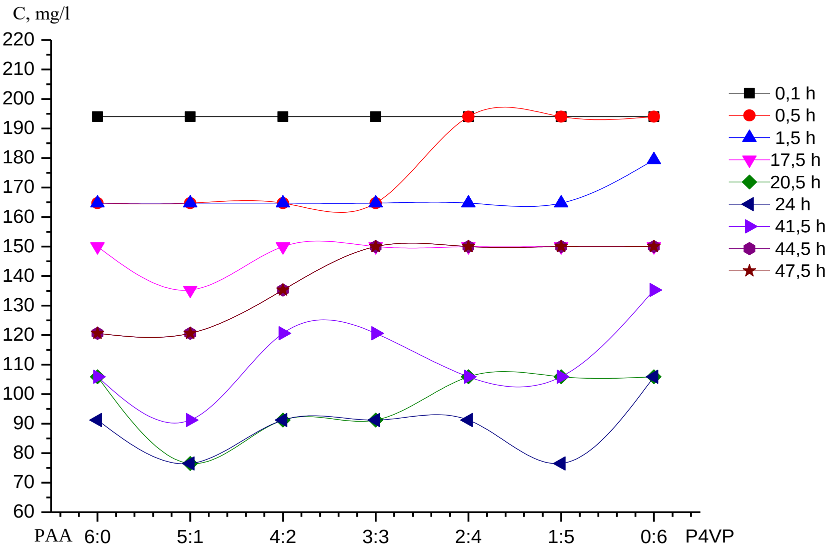

Figure 4. Dependence of the praseodymium ions concentration on the molar ratio of hydrogels in the intergel system hPAA:hP4VP in praseodymium (III) nitrate hexahydrate medium

The data shows (Fig. 4) that the concentration of Pr^{3+} ions in solution is much lower at molar ratios of hydrogels equal to 1:5 (that means the sorption is higher) after 24 hours of interaction. This may be explained that at a ratio 1:5, the hydrogels of polyacrylic acid and poly-4-vinylpyridine in intergel system reach the highly ionized state due to the mutual activation of hydrogels.

Table 1

Degree of praseodymium ionssorption, mol.%

Ratio	Time, h								
	0.1	0.5	1.5	17.5	20.5	24	41.5	44.5	47.5
6:0	3.1	17.6	17.6	25	47.0	54.4	47.0	39.7	39.7
5:1	3.1	17.6	17.6	32.3	61.7	61.7	54.4	39.7	39.7
4:2	3.0	17.6	17.6	25.2	54.4	54.4	39.7	32.3	32.3
3:3	3.1	17.6	17.6	25.5	54.4	54.4	39.7	25.3	25.3
2:4	3.1	3.2	17.6	25.3	47.0	54.4	47.0	25.1	25.1
1:5	3.2	3.2	17.6	25.3	47.0	61.7	47.5	25.1	25.1
0:6	3.0	3.1	10.3	25	47.0	47.0	32.3	25.2	25.2

Table 2

Polymer chains binding degree, mol.%

Ratio	Time, h								
	0.1	0.5	1.5	17.5	20.5	24	41.5	44.5	47.5
6:0	1.1	5.9	5.9	8.3	15.9	18.4	15.9	13.3	13.3
5:1	1.3	6.5	6.1	11.2	21	21	18.7	13.5	13.5
4:2	1.3	6.8	6.1	8.5	18.7	18.7	13.6	11.2	11.2
3:3	1.5	6.2	6.2	8.6	19.1	19.1	13.8	8.6	8.6
2:4	1.6	1.1	6.3	8.7	16.7	19.2	16.7	8.7	8.7
1:5	1.6	1.1	6.3	8.7	16.7	21.8	16.7	8.7	8.7
0:6	1.8	1.1	3.7	8.9	17	17	11.7	8.9	8.9

The polymer chain binding degree in relation to the praseodymium ions in the hPAA–hP4VP system is presented in Table 2. The obtained results indicated that the most intense polymer chain binding degree of praseodymium ions (21.8 %) by hPAA:hP4VP (1:5) intergel system occurred after 24 hours of sorption.

Conclusions

The obtained results demonstrate the potential of using intergel systems in rare-earth metal recovery. The activated hydrogels showed an increase in sorption activity in comparison with the individual hPAA (6:0) and hP4VP (0:6) hydrogels. This research showed that the maximum activation of hydrogels was revealed within the molar ratio of hPAA:hP4VP equal to 1:5. The total praseodymium ions sorption degree after 24 h. of sorption by individual hydrogels hPAA and hP4VP was 54 % and 47 %, respectively, whereas the praseodymium ions sorption degree by the intergel system of hPAA:hP4VP (1:5) was 62 %. An increase in the sorption degree of praseodymium ions by the intergel system of hPAA: hP4VP (1:5) in comparison with individual hydrogels can be explained by the achievement of a high ionization degree of the intergel system activated by the remote interaction effect, which opens up new opportunities for the development of innovative sorption technologies in Kazakhstan for the target rare-earth elements.

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References

1 Gazulla, M.F. Praseodymium oxides. Complete characterization by determining oxygen content. /M.J. Ventura, C. Andreu, J. Gilabert, M. Orduña, & M. Rodrigo // Microchem. J. — 2019. — Vol. 148. — P. 291–298. https://doi.org/10.1016/j.microc.2019.05.013

2 Donia A.M. Selective Separation of Uranium (VI), Thorium (IV), and Lanthanum (III) from their aqueous solutions using a chelating resin containing amine functionality. /A.A. Atia, T.E. Amer, M.N. El-Hazek, M.H. Ismael // Journal of dispersion science and technology. — 2011. — Vol. 32. — P. 1673–1681.

3 Rombach E. Recycling of Rare Metals. / B. Friedrich // Handbook of Recycling. — 2014. — P. 125–150. https://doi.org/10.1016/b978-0-12-396459-5.00010-6

4 Miller D.D. Anion structural effects on interaction of rare earth element ions with Dowex 50W X8 cation exchange resin / R. Siriwardane, & D. Mcintyre // Journal of Rare Earths. — 2018. — No. 36(8). — P. 879–890. https://doi.org/10.1016/j.jre.2018.03.006

5 Noshin Mir. Self-separation of the adsorbent after recovery of rare-earth metals: Designing a novel non-wettable polymer / Carlos E. Castano, Jessika V. Rojas, NazgolNorouzi, Amir R. Esmaeili, Reza Mohammadi // Sep. Purif. Technol. — 2021. — P. 118-152. https://doi.org/10.1016/j.seppur.2020.118152

6 Jumadilov T.K. Phenomenon of remote interaction and sorption ability of rare cross–linked hydrogelsn of polymethacrylic acid and poly-4-vinylpyridine in relation to erbium ions / T.K. Jumadilov, R. Kondaurov, A. Imangazy, N. Myrzakhmetova, I. Saparbekova // Chem. Chem. Technol. — 2019. — Vol. 13, No. 4. — P. 451–458.

7 Jumadilov T. Effective Sorption of Europium Ions by Interpolymer System Based on Industrial Ion-Exchanger Resins Amberlite IR120 and AB-17-8 / K. Khimersen, Z. Malimbayeva, R. Kondaurov // Materials. — 2021. — Vol. 14, No. 14. — P. 3837. https://doi.org/10.3390/ma14143837

8 Petrukhin O.M. Workshop on Physical and Chemical Methods of Analysis / O.M. Petrukhin. — Moscow: Chemistry, 1987. — P. 77–80.

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Полиакрил қышқыл мен поли-4-винилпиридин интергельдік жүйесімен празеодимді бөлудің ерекшеліктері

Кейбір технологиялық ерітінділер құрамында құнды компоненттер бар және өндірістің әртүрлі қажеттіліктерін қанағаттандыру үшін сирек кездесетін элементтердің қосымша көзі бола алады. Мақала полиакрил қышқылы (гПАК) және поли-4-винилпиридин (гП4ВП) гидрогельдерінің қосындысын оның нитратты ерітіндісінен празеодим иондарының сорбциясы үшін әртүрлі мольдік қатынаста қолдануды зерттеуге бағытталған. Су ортасында гидрогельдердің өзара активтенуі олардың қашықтықтан өзара әрекеттесуі кезінде конформациялық және электрохимиялық қасиеттердің өзгеруіне байланысты гидрогельдердің жоғары иондалған күйге өтуін қамтамасыз етеді. Ерітінділердің электрохимиялық қасиеттері электр өткізгіштік және ерітінділердің PH өлшеу әдістерімен зерттелді. Зерттеу көрсеткендей, гидрогельдердің максималды активтенуі гПАК: гП4ВП-нің 1:5-ке тең моль қатынасында анықталды. Бұл ретте жеке гПАК және гП4ВП сорбциясынан кейін празеодим иондарының сорбция дәрежесі тиісінше 54 % және 47 %-ды құрады, ал празеодим иондарының гПАК-гП4ВП интергелдік жүйесімен сорбция дәрежесі 1:5 моль арақатынасында 62 %-ды құрады. Жеке гидрогельдермен салыстырғанда празеодим иондарының интергелдік жүйемен сорбция дәрежесінің біршама артуын қашықтықтан өзара әрекеттесу әсеріне байланысты гПАК–гП4ВП интергелдік жүйесінде белсендірілген гидрогельдердің иондалуының жоғары дәрежесіне қол жеткізумен түсіндіруге болады.

Кілт сөздер: интергелдік жүйелер, полиакрил қышқылының гидрогелі, поли-4-винилпиридин гидрогелі, қашықтықтан әрекеттесу, сорбция, празеодим иондары.

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Особенности извлечения празеодима интергелевой системой на основе гидрогелей полиакриловой кислоты и поли-4-винилпиридина

Некоторые технологические растворы содержат в своем составе ценные компоненты и могут стать дополнительным источником редкоземельных элементов для удовлетворения различных потребностей производства. Данная работа направлена на исследование применения комбинации гидрогелей полиакриловой кислоты (гПАК) и поли-4-винилпиридина (гП4ВП) в различных мольных соотношениях для сорбции ионов празеодима из его нитратного раствора. Взаимная активация гидрогелей в водной среде обеспечивает переход гидрогелей в высокоионизированное состояние за счет конформационных и электрохимических изменений свойств при их дистанционном взаимодействии. Электрохимические свойства растворов изучались методами электропроводности и измерения pH растворов. Исследование показало, что максимальная активация гидрогелей была выявлена при мольном соотношении гПАК:гП4ВП, равном 1:5. При этом степень сорбции ионов празеодима после 24 ч сорбции индивидуальными гПАК и гП4ВП составила 54 и 47 % соответственно, тогда как степень сорбции ионов празеодима интергелевой системой гПАК–гП4ВП в мольном соотношении 1:5 составила 62 %. Некоторое увеличение степени сорбции ионов празеодима интергелевой системой по сравнению с индивидуальными гидрогелями можно объяснить достижением более высокой степени ионизации гидрогелей, активированных в интергелевой системе гПАК–гП4ВП за счет эффекта дистанционного взаимодействия.

Ключевые слова: интергелевые системы, гидрогель полиакриловой кислоты, гидрогель поли-4-винилпиридина, дистанционное взаимодействие, сорбция, ионы празеодима.

References

1 Gazulla, M.F., Ventura, M.J., Andreu, C., Gilabert, J., Orduña, M., & Rodrigo, M. (2019). Praseodymium oxides. Complete characterization by determining oxygen content. *Microchem. J*, *148*, 291–298. https://doi.org/10.1016/j.microc.2019.05.013

2 Donia, A.M. (2011). Selective Separation of Uranium (VI), Thorium (IV), and Lanthanum (III) from their aqueous solutions using a chelating resin containing amine. *Journal of dispersion science and technolog*, 1673–1681.

3 Rombach, E., & Friedrich, B. (2014). Recycling of Rare Metals. Handbook of Recycling, 125–150. https://doi.org/10.1016/b978-0-12-396459-5.00010-6

4 Miller, D.D., Siriwardane, R., & Mcintyre, D. (2018). Anion structural effects on interaction of rare earth element ions with Dowex 50W X8 cation exchange resin. *Journal of Rare Earths, 36(8)*, 879–890. https://doi.org/10.1016/j.jre.2018.03.006

5 Noshin Mir, Carlos E. Castano, Jessika V. Rojas, NazgolNorouzi, Amir R. Esmaeili, & Reza Mohammadi (2021). Self-separation of the adsorbent after recovery of rare-earth metals: Designing a novel non-wettable polymer, *Sep. Purif. Technol.*, 118-152. https://doi.org/10.1016/j.seppur.2020.118152.

6 Jumadilov, T.K., Kondaurov, R., Imangazy, A., Myrzakhmetova, N., & Saparbekova, I. (2019). Phenomenon of remote interaction and sorption ability of rare cross–linked hydrogelsn of polymethacrylic acid and poly-4-vinylpyridine in relation to erbium ions, *Chem. Chem. Technol., 13(4)*, 451–458.

7 Jumadilov, T, Khimersen, K, Malimbayeva, Z, & Kondaurov, R. (2021). Effective Sorption of Europium Ions by Interpolymer System Based on Industrial Ion-Exchanger Resins Amberlite IR120 and AB-17-8. *Materials, 14(14),* 3837. https://doi.org/10.3390/ma14143837

8 Petrukhin, O.M. (1987). Workshop on Physical and Chemical Methods of Analysis. Moscow: Chemistry.

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