ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

4 (64)

ОКТЯБРЬ – ДЕКАБРЬ 2018 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2018

UDC 541.132/.132.4:541.49

T. K. JUMADILOV, R. G. KONDAUROV

JSC « Institute of chemical sciences named after A. B. Bekturov», Almaty, Republic of Kazakhstan

COMPARATIVE CHARACTERISTICS OF SORPTION PARAMETERS OF INTERGEL SYSTEMS BASED ON POLYACRYLIC AND POLYMETHACRYLIC ACIDS AND POLY-4-VINYLPYRIDINE AT SIMULTANEOUS EXTRACTION OF LANTHANUM AND CERIUM IONS

Abstract. The work shows features of simultaneous extraction of lanthanum and cerium ions by intergel systems 33%hPAA-67%hP4VP and 17%hPMAA-83%hP4VP from common solution. It is found that formation of optimal ionization of the initial hydrogels for sorption lanthanum ions occurs at this composition. Results showed that during of the all time of sorption the intergel systems manifest selectivity to lanthanum. Extraction degree (at 48 hours) are: 82.87% and 42.65% for 33%hPAA-67%hP4VP and 72.55% and 32.22% for 17%hPMAA-83%hP4VP for lanthanum and cerium ions respectively. Polymer chain binding degree (in relation to lanthanum and cerium ions) are: 68.74% and 35.38% for 33%hPAA-67%hP4VP and 60.18% and 26.73% for 17%hPMAA-83%hP4VP respectively. Effective dynamic exchange capacity (in relation to lanthanum and cerium ions) are: 5.52 mmol/g and 2.84 mmol/g for 33%hPAA-67%hP4VP and 4.84 mmol/g and 2.15 mmol/g for 17%hPMAA-83%hP4VP.

Keywords: intergel systems, polyacrylic acid, polymethacrylic acid, poly-4-vinyl-pyridine, sorption, La^{3+} ions, Ce^{3+} ions.

Introduction. Previous studies of the intergel systems, which were devoted to sorption of various metals, showed that there is a formation of high density of ionized groups due to mutual activation at remote interaction of rare-crosslinked polymer hydrogels of acid and basic nature [1, 2]. Result of this phenomenon is significant increase of sorption parameters comparatively with individual hydrogels [3-6]. The goal of the work is study of sorption parameters of intergel systems 33%hPAA-67%hP4VP and 17%hPMAA-83%hP4VP at simultaneous extraction of lanthanum and cerium ions.

EXPERIMENTAL PART

Equipment. Measurements of optical density for further calculation of lanthanum and cerium ions concentration were carried out on spectrophotometer Jenway-6305 (UK).

Materials. Hydrogels of polyacrylic and polymethacrylic acids were synthesized in presence of cross-linking agent N,N-methylene-bis-acrylamide and redox system $K_2S_2O_8$–$Na_2S_2O_3$. Hydrogel of poly-4-vinylpyridine (hP4VP) (2% of cross-linking agent) was synthesized by «Sigma Aldrich» company. Synthesized hydrogels were put together to create intergel pairs 33%hPAA-67%hP4VP and 17%hPMAA-83%hP4VP. Swelling degrees of the hydrogels are: $\alpha_{(hPAA)}$=27.93 g/g; $\alpha_{(hPMAA)}$=20.65 г/г; $\alpha_{(hP4VP)}$=3.27 g/g.

Experiment. Experiments were carried out at a room temperature. The intergel systems were put into solution, which contains lanthanum and cerium ions (0.005 M solution of 6-water lanthanum and cerium nitrates). After After that, aliquots were taken for further calculation of rare-earth elements ions concentration during 48 hours.

Methodology of lanthanum and cerium ions determination. Methodology of lanthanum and cerium ions determination in solution is based on formation of colored complex compound of organic analytic reagent arsenazo III with rare-earth metals ions [7].

Lanthanum and cerium ions extraction degree (sorption degree) was calculated in accordance with equation:

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

where $C_{initial}$ is initial concentration of the metals in solution, g/L; $C_{residual}$ is residual concentration of the metals in solution, g/L.

Total polymer chain binding degree was calculated as follows:

$$\theta = \frac{\nu_{sorbed}}{\nu} * 100\%$$

where ν_{sorbed} is quantity of polymer links with sorbed metal, mol; ν is total quantity of polymer mass (if there are 2 hydrogels in solution, it is calculated as sum of each polymer hydrogel mass), mol.

Effective dynamic exchange capacity was determined by calculations in accordance with equation:

$$Q = \frac{\nu_{sorbed}}{m_{sorbent}}$$

where ν_{sorbed} is amount of sorbed metal, mol; $m_{sorbent}$ is sorbent mass (if there are 2 hydrogels in solution, it is calculated as sum of their masses), g.

RESULTS AND DISCUSSION

These composition (33%hPAA-67%hP4VP and 17%hPMAA-83%hP4VP) of hydrogels in the intergel systems were taken for selective sorption of lanthanum ions from the solution, which contains ions of lanthanum and cerium. The mentioned ratios were selected due to the fact that in the intergel system hPAA-hP4VP and hPMAA-hP4VP there is an occurrence of maximum lanthanum sorption [8,9].

As seen from table 1, the extraction of lanthanum ions by the intergel system 33%hPAA-67%hP4VP is more intensive comparatively with cerium extraction. The main reason of it is formation of optimal ionization for lanthanum ions sorption. During of time of sorption of the mentioned above rare-earth elements amount of extracted lanthanum is almost 2 times higher in comparison with cerium. As a consequence, extraction degree of the intergel system at 48 hours has the following values: 82.87% for lanthanum and 42.65% for cerium.

Table 1 – Extraction degree of lanthanum and cerium ions
by intergel systems 33%hPAA-67%hP4VP and 17%hPMAA-83%hP4VP

τ, h	33%hPAA-67%hP4VP		17%hPMAA-83%hP4VP	
	η (La^{3+}), %	η (Ce^{3+}), %	η (La^{3+}), %	η (Ce^{3+}), %
0.5	21.84	9.88	12.35	3.35
1	32.36	15.32	23.29	8.85
2	38.94	23.02	30.23	11.65
6	51.45	24.49	41.52	17.63
24	70.73	34.27	63.13	24.46
48	82.87	42.65	72.55	32.22

As can be seen from table 1, sorption degree of lanthanum ions is almost 2 times higher comparatively with this parameter in sorption of cerium at simultaneous sorption of the rare-earth elements by intergel system 17%hPMAA-83%hP4VP. Sharp increase of extraction degree is observed during first 6 hours, the parameter has values: 41.52% for lanthanum ions and 17.63% for cerium ions. Further increase of sorption degree of the both metals occurs not so intense. As seen from the obtained data, at 24 hours of the hydrogels remote interaction 61.13% of lanthanum and 24.46% of cerium is extracted from the solution, at 48 hours – 72.55% of lanthanum and 32.22% of cerium is extracted from the solution. These data show that selectivity is manifested to lanthanum ions.

In table 2 represented dependence on polymer chain binding degree (in relation to lanthanum and cerium ions) of the intergel systems 33%hPAA-67%hP4VP and 17%hPMAA-83%hP4VP versus of duration. Obtained data shows, that sorption of the both metals by intergel system 33%hPAA-67%hP4VP provides selectivity to lanthanum ions. At 6 hours of remote interaction of hydrogels of PAA and P4VP 42.67% of lanthanum and 20.31% of cerium is extraction from the solution. Maximum values of binding degree of the both rare-earth elements are reached at 48 hours. At this time 68.74% of lanthanum and 35.38% of cerium is bind from the solution.

Intensive binding of lanthanum and cerium ions from the common solution is observed during 6 hours of remote interaction of polymer hydrogels of polymethacrylic acid and poly-4-vinylpyridine. At this time the intergel system 17%hPMAA-83%hP4VP binds 34.44% of lanthanum and 14.62% of cerium.

Table 2 – Polymer chain binding degree (in relation to lanthanum and cerium ions)
of intergel systems 33%hPAA-67%hP4VP and 17%hPMAA-83%hP4VP

τ, h	33%hPAA-67%hP4VP		17%hPMAA-83%hP4VP	
	θ (La^{3+}), %	θ (Ce^{3+}), %	θ (La^{3+}), %	θ (Ce^{3+}), %
0.5	18.11	8.19	10.24	2.78
1	26.84	12.70	19.32	7.34
2	32.30	19.09	25.08	9.66
6	42.67	20.31	34.44	14.62
24	58.67	28.43	52.37	20.29
48	68.74	35.38	60.18	26.73

High values of polymer chain binding degree point to highly ionized state of initial hydrogels in the intergel pair. At 48 hours 60.18% of lanthanum and 26.73% of cerium is bind by the intergel system hPMAA-hP4VP. Obtained results show that selectivity is mainly manifested to lanthanum ions.

Table 3 represents dependence of effective dynamic exchange capacity (in relation to lanthanum and cerium ions) of the intergel systems hPAA-hP4VP and hPMAA-hP4VP from time. In case with intergel system 33%hPAA-67%hP4VP values of exchange capacity in case of lanthanum sorption are much higher comparatively to cerium sorption. Strong increase of effective dynamic exchange capacity (in relation to the both metals) is observed during 6 hours of the hydrogels interaction, what, in turn, indicates to high level of polymer structures ionization in result of their mutual activation. Obtained data show that final values of effective dynamic exchange capacity (at 48 hours) at lanthanum ions extraction are almost 2 times higher in comparison with cerium sorption.

Table 3 – Effective dynamic exchange capacity (in relation to lanthanum and cerium ions) of intergel systems 33%hPAA-67%hP4VP and 17%hPMAA-83%hP4VP

τ, h	33%hPAA-67%hP4VP		17%hPMAA-83%hP4VP	
	Q (La^{3+}), mmol/g	Q (Ce^{3+}), mmol/g	Q (La^{3+}), mmol/g	Q (Ce^{3+}), mmol/g
0.5	1.46	0.66	0.82	0.22
1	2.16	1.02	1.55	0.59
2	2.60	1.53	2.02	0.78
6	3.43	1.63	2.77	1.18
24	4.72	2.28	4.21	1.63
48	5.52	2.84	4.84	2.15

Table 3 also shows dependence of effective dynamic exchange capacity of the intergel system 17%hPMAA-83%hP4VP from time. High ionization level of the initial polymer structures of PMAA and P4VP in the intergel system provides significant increase of the parameter. Sharp increase during the remote interaction of the hydrogels occurs during 6 hours. At 48 hours of interaction the maximum values of exchange capacity are reached, values of capacity at lanthanum sorption are over 2 times higher comparatively with cerium sorption.

Conclusion. Basing on obtained results of the conducted studies it is possible to conclude that the intergel systems 33%hPAA-67%hP4VP and 17%hPMAA-83%hP4VP extract ions of lanthanum and cerium from the common solution, wherein selectivity is manifested to lanthanum ions. Extraction degree of lanthanum and cerium ions (at 48 hours) is: 82.87% and 42.65% for 33%hPAA-67%hP4VP and 72.55% and 32.22% for 17%hPMAA-83%hP4VP. Polymer chain biding degree (in relation to lanthanum and cerium ions) is: 68.74% and 35.38% for 33%hPAA-67%hP4VP and 60.18% and 26.73% for 17%hPMAA-83%hP4VP. Effective dynamic exchange capacity (in relation to lanthanum and cerium ions) is: 5.52 mmol/g and 2.84 mmol/g for 33%hPAA-67%hP4VP and 4.84 mmol/g and 2.15 mmol/g for for 17%hPMAA-83%hP4VP.

Acknowledgment. The work was financially supported (the work was made due to the grant funding of 2 Projects: AP05131302 and AP05131451) by the Committee of Science of Ministry of education and science of the Republic of Kazakhstan.

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 4th 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] Petruhin O.M. Practice book on physico-chemical methods of analysis. M.: Chemistry, 1987. P. 77-80.

[8] 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.

[9] 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.

Резюме

Т. Қ. Жұмаділов, Р. Г. Кондауров

ПОЛИАКРИЛ ЖӘНЕ ПОЛИМЕТАКРИЛ ҚЫШҚЫЛДАРЫ МЕН ПОЛИ-4-ВИНИЛПИРИДИН НЕГІЗІНДЕГІ ИНТЕРГЕЛЬДІ ЖҮЙЕЛЕРДІҢ ЛАНТАН ЖӘНЕ ЦЕРИЙ ИОНДАРЫН БІР МЕЗГІЛДЕ АЛУ КЕЗІНДЕГІ СОРБЦИЯЛЫҚ ПАРАМЕТРЛЕРІНІҢ САЛЫСТЫРМАЛЫ СИПАТТАМАСЫ

Жұмыста 33%гПАК-67%гП4ВП және 17% гПМАК-83% гП4ВП интергельді жүйелермен лантан және церий иондарын жалпы ерітіндіден бір мезгілде алу ерекшеліктері қарастырылған. Осы қатынас кезінде лантан иондарын сорбциялау үшін қышқылдық және негізгдік бастапқы полимерлік гидрогельдерінің оңтайлы иондануы пайда болатыны анықталды. Алынған мәліметтерден, қашықтықтан өзара

әрекеттесудің барлық уақыты ішінде интергельді жүйелердің лантан иондарына селективтілік танытатынын көруге болады. Лантан және церий иондарын алу дәрежесі мынадай мәндерге ие (48 сағат өткеннен кейін): 33% гПАК-67% гП4ВП үшін - 82,87 және 42,65% және 17% гПМАК-83% гП4ВПүшін - 72,55 және 32,22%. Полимерлік тізбектің байланысу дәрежесі (лантан және церий иондарына қатысты) мынадай мәндерге ие: 33% гПАК-67% гП4ВП үшін - 68,74 және 17% гПМАК-83% гП4ВП үшін 35,38% - 60,18 және 26,73%. Тиімді динамикалық алмасу сыйымдылығы (лантан және церий иондарына қатысты): 33% гПАК-67% гП4ВП үшін - 5,52 және 2,84 ммоль/г және 17% гПМАК-83% гП4ВПүшін - 4,84 және 2,15 ммоль/г құрайды.

Түйін сөздер: гидрогельдер, полиакрил қышқылы, полиметакрил қышқылы, поли-4-винилпиридин, сорбция, La^{3+} иондары, Ce^{3+} иондары.

Резюме

Т. К. Джумадилов, Р. Г. Кондауров

СРАВНИТЕЛЬНАЯ ХАРАКТЕРИСТИКА СОРБЦИОННЫХ ПАРАМЕТРОВ ИНТЕРГЕЛЕВЫХ СИСТЕМ НА ОСНОВЕ ПОЛИАКРИЛОВОЙ И ПОЛИМЕТАКРИЛОВОЙ КИСЛОТ И ПОЛИ-4-ВИНИЛПИРИДИНА ПРИ ОДНОВРЕМЕННОМ ИЗВЛЕЧЕНИИ ИОНОВ ЛАНТАНА И ЦЕРИЯ

В работе рассмотрены особенности одновременного извлечения ионов лантана и церия интергелевыми системами 33%гПАК-67%гП4ВП и 17%гПМАК-83%гП4ВП из общего раствора. Установлено, что при данных соотношениях образуется оптимальная ионизация исходных полимерных гидрогелей кислотной и основной природы преимущественно для сорбции ионов лантана. Из полученных данных видно, что на протяжении всего времени дистанционного взаимодействия интергелевые системы проявляют селективность к ионам лантана. Степень извлечения ионов лантана и церия имеет следующие значения (по истечении 48 ч): 82,87 и 42,65% для 33%гПАК-67%гП4ВП и 72,55 и 32,22% для 17%гПМАК-83%гП4ВП. Степень связывания полимерной цепи (по отношению к ионам лантана и церия) имеет следующие значения: 68,74 и 35,38% для 33%гПАК-67%гП4ВП и 60,18 и 26,73% для 17%гПМАК-83%гП4ВП. Эффективная динамическая обменная емкость (по отношению к ионам лантана и церия) составляет: 5,52 и 2,84 ммоль/г для 33%гПАК-67%гП4ВП и 4,84 и 2,15 ммоль/г для 17%гПМАК-83%гП4ВП.

Ключевые слова: гидрогели, полиакриловая кислота, полиметакриловая кислота, поли-4-винилпиридин, сорбция, ионы La^{3+}, ионы Ce^{3+}.