

T.K. Jumadilov, R.G. Kondaurov, A.M. Imangazy

*JSC "Institute of chemical sciences after A.B. Bekturov", Almaty, Kazakhstan
(E-mail: r-kondaurov@mail.ru)*

Features of sorption of rare-earth metals of cerium group by intergel systems based on polyacrylic acid, polymethacrylic acid and poly-4-vinylpyridine hydrogels

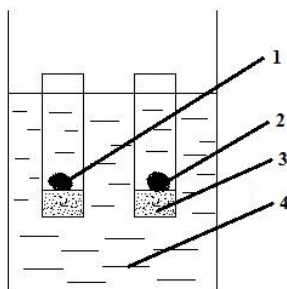
The work is devoted to study of sorption process of cerium and neodymium ions by individual hydrogels of polyacrylic acid (hPAA), polymethacrylic acid (hPMAA), poly-4-vinylpyridine (hP4VP) and intergel systems on their bases. Obtained results show that sorption properties (sorption degree, polymer chain binding degree, effective dynamic exchange capacity) of individual hydrogels of PAA, PMAA, P4VP are not sufficiently high: sorption degree is not high than 65 %; polymer chain binding degree is not high than 55 %; effective dynamic exchange capacity is not high than 4.5 mmol/g. Remote interaction of the polymer hydrogels in the intergel systems provides significant increase (over 30 %) of the sorption properties. Sorption degree increases up to 93.50 %; polymer chain binding degree increases up to 76.50 %; effective dynamic exchange capacity grows to 6.16 mmol/g. Such strong increase is a consequence of the mutual activation of the initial polymers in the intergel systems during their remote interaction. Macromolecules undergo ionization with further unfolding of the polymer globe with formation of optimal conformation for sorption of low-molecular ions.

Keywords: Intergel systems, remote interaction, polyacrylic acid, polymethacrylic acid, poly-4-vinylpyridine, cerium ions, neodymium ions, sorption

Introduction

At present technologies of rare earth metals concentration and extraction in hydrometallurgy are based on application of ion-exchangers [1–4]. However, ion-exchange resins do not have high extraction degree of metals and their regeneration is a rather complicated process. The major drawback of ion-exchangers is their regeneration, the process which is very complicated. It should be also noted that application of ion-exchangers is directed to selective extraction of one metal. As known, industrial solutions usually contain several valuable components. In this regard it is relevant to develop modern sorption technologies based on remote interaction of functional macromolecules, in other words creation of selective intergel systems seems to be concerned as the real alternative to the existing methods of sorption of rare-earth elements (mainly ion-exchangers) [5]. Remote interaction of functional polymers leads to significant changes of initial properties (conformational and electrochemical) of the macromolecules. Also, it should be noted that there is strong increase of sorption properties of the polymers in intergel systems due to transition into highly ionized state in result of mutual activation of the macromolecules during remote interaction [6]. There is a formation of optimal conformation during the process of remote interaction of rare-crosslinked polymer hydrogels in intergel systems. It was found earlier [7–10] that rare-crosslinked polymer hydrogels in intergel systems undergo additional ionization of the functional polymers during remote interaction. Such transfer provides significant changes in electrochemical, conformational and sorption properties of macromolecules [11–13].

Intergel system is a multicomponent system, which contains polybasis and polyacid. Intergel system is presented on figure. As seen from the figure, two polymers interact with each other on the distance. The glass filter has a pores, which are permeable for low-molecular ions and impermeable for hydrogels dispersion.



1 — polyacid; 2 — polybasis; 3 — glass filter; 4 — solution

Figure. Schematic illustration of typical intergel system

In this regard the aim of the paper is to study extraction properties (relatively to cerium and neodymium ions) of intergel systems based on polyacrylic acid, polymethacrylic acid and poly-4-vinylpyridine hydrogels.

Experimental

Equipment. Rare-earth metals (REM) ions concentration in solutions was determined on spectrophotometers KFK-3KM (Russia).

Materials. Polyacrylic acid hydrogel (hPAA) and polymethacrylic acid hydrogel (hPMAA) were synthesized in presence of crosslinker (methylenebisacrylamide) and initiator (potassium peroxydisulphate — sodium tiosulphate) in water medium. Synthesized hydrogels were crushed into small dispersions and washed with distilled water until constant conductivity value of aqueous solutions was reached. Linear polymer of poly-4-vinylpyridine of Sigma-Aldrich company was initial reactant for further synthesis of the hydrogel (hP4VP) in presence of divinylbenzene, which was subsequently used as polybasis. Based on the obtained polymers the following intergel pairs: hPAA-hP4VP and hPMAA-hP4VP were made. The general experiments were carried out in the corresponding salts solutions of cerium and neodymium (nitrates hexahydrates, concentration 0.005 mol/L).

Determination of the rare-earth metals. Measurement of the cerium and neodymium concentration in the solution is based on application of the complexant arsenazo III [14].

Calculation of degree of sorption (extraction):

$$\eta = \frac{C_{ini} - C_{res}}{C_{ini}} \cdot 100\% ,$$

C_{ini} — concentration before sorption of Ce or Nd, g/L; C_{res} — concentration after sorption of Ce or Nd, g/L.

Calculation of binding degree of the polymer chain:

$$\theta = \frac{v_{srb}}{v} \cdot 100\% ,$$

v_{srb} — amount of links of the polymers, which participate in the sorption process of cerium or neodymium, mol; v — total amount of links of the polymers, mol.

Calculation of effective dynamic exchange capacity:

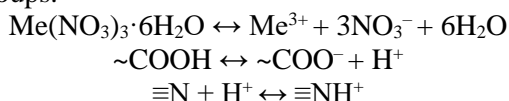
$$Q = \frac{v_{srb}}{m_{srbt}} ,$$

v_{srb} — quantity of sorbed cerium or neodymium, mol; m_{srbt} — mass of the sorbent (polyacid or polybasis or intergel pair), g.

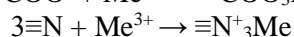
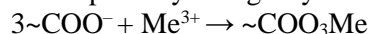
Results and Discussion

Nitrates of cerium and neodymium present in solution in dissociated state. In presence of individual hydrogels and intergel systems the following processes take place:

1) REM (cerium or neodymium) nitrate dissociation, ionization of heteroatom (nitrogen) by binding of cleaved proton from carboxyl groups:



2) REM (cerium or neodymium) ions sorption by intergel system:



where Me — rare-earth metal (cerium or neodymium).

Cerium ions sorption.

Sorption degree (Table 1) of cerium ions of the intergel system hPAA-hP4VP and individual hydrogels of PAA and P4VP have different values (extraction degree of hPAA and hP4VP is not very high — no more than 65 %). It can be said, that in presence of the only polyacid or polybasis the equilibrium is almost reached at 24 hours of interaction, at this time sorption degree is 58.33 % for hPAA and 52.67 % for hP4VP. For the next 24 hours the parameter in this case increases very slightly and the final values (63.33 % and 56.67 %) are reached. In intergel pairs it can be seen that the phenomenon of mutual activation provides additional ionization of the internode links of the initial hydrogels. Maximum sorption occurs at ratio hPAA:hP4VP=17 %:83 % hydrogels ratio, at 48 hours of interaction 92.33 % of cerium is extracted by the intergel system.

Table 1

Sorption degree of cerium ions of intergel system hPAA-hP4VP

τ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	$\eta(\text{Ce})$, %						
0	0	0	0	0	0	0	0
0.5	11.67	13.33	14.00	16.33	17.67	21.67	6.67
1	17.67	22.33	24.67	27.33	31.67	35.67	10.33
2	26.33	30.67	35.67	40.33	44.33	52.67	18.33
6	39.00	52.00	58.00	66.67	75.33	77.00	30.00
24	58.33	75.00	77.00	82.33	85.67	88.33	52.67
48	63.33	79.67	81.67	86.00	88.67	92.33	56.67

Polymer chain binding degree shows the amount of the active (which provides sorption of cerium) links of the individual polymer hydrogels and the intergel system. Polymer chain binding degree is presented in Table 2. Over the half of the links of the individual polymers of PAA and P4VP take part in sorption of cerium, binding degree at 48 hours is 52.53 and 47.00 % respectively. Formation of optimal conformation in intergel system for sorption of cerium occurs at ratio hPAA:hP4VP = 17 %:83 %. Binding degree is 76.59 % at 48 hours of remote interaction.

Table 2

Binding degree of polymer chain (relatively to Ce^{3+} ions) of the intergel system hPAA-hP4VP

τ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	$\theta(\text{Ce})$, %						
0	0	0	0	0	0	0	0
0.5	9.68	11.06	11.61	13.55	14.65	17.97	5.53
1	14.65	18.53	20.46	22.67	26.27	29.59	8.57
2	21.84	25.44	29.59	33.46	36.77	43.69	15.21
6	32.35	43.13	48.11	55.30	62.49	63.87	24.88
24	48.39	62.21	63.87	68.29	71.06	73.27	43.69
48	52.53	66.08	67.74	71.34	73.55	76.59	47.00

Effective dynamic exchange capacity (relatively to Ce^{3+} ions) of the intergel system hPAA-hP4VP is presented in Table 3. The overwhelming majority of cerium is sorbed by hPAA and hP4VP during 24 hours, at this time exchange capacity is 3.89 mmol/g and 3.51 mmol/g respectively. The further increase is very slight, the final values can be seen at 48 hours of interaction, exchange capacity is 4.22 mmol/g and 3.78 mmol/g. The parameter's highest values are observed at ratio hPAA:hP4VP = 17 %:83 % after 2 days, effective dynamic exchange capacity is 6.16 mmol/g.

Table 3

Effective dynamic exchange capacity (relatively to Ce^{3+} ions) of the intergel system hPAA-hP4VP

τ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	Q(Ce), mmol/g						
0	0	0	0	0	0	0	0
0.5	0.78	0.89	0.93	1.09	1.18	1.44	0.44
1	1.18	1.49	1.64	1.82	2.11	2.38	0.69
2	1.76	2.04	2.38	2.69	2.96	3.51	1.22
6	2.60	3.47	3.87	4.44	5.02	5.13	2.00
24	3.89	5.00	5.13	5.49	5.71	5.89	3.51
48	4.22	5.31	5.44	5.73	5.91	6.16	3.78

Process of cerium ions sorption by the intergel system hPMAA-hP4VP occurs less intensive due to the fact that ionization of the initial polymers is complicated by the presence of bulky methyl substituent. Values of extraction degree of cerium ions are presented in Table 4. More than half of the sorbed metal is extracted during 6 hours after the beginning of the sorption process. The final values of the parameter in case with individual hPMAA and hP4VP are observed at 48 hours, the values are 60.33 % and 56.67 % respectively. The optimal conformation for cerium ions sorption is formed at ratio 50 % hPMAA-50 % hP4VP. At 48 hours of remote interaction at this ratio sorption degree is 89.33 %.

Table 4

Sorption degree of cerium ions of intergel system hPMAA-hP4VP

τ , h	hPMAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	η (Ce), %						
0	0	0	0	0	0	0	0
0.5	10.00	12.67	13.33	18.33	15.00	16.33	6.67
1	15.33	18.33	21.33	28.67	25.67	26.67	10.33
2	23.67	25.67	31.00	48.00	33.67	35.33	18.33
6	35.00	48.33	51.00	72.33	55.33	59.33	30.00
24	55.67	68.33	70.67	85.00	73.67	77.33	52.67
48	60.33	76.00	79.00	89.33	81.00	83.00	56.67

As can be seen from table 5, the part of active links of the individual hydrogels of PMAA and P4VP is over 50 %. Such low values are directly connected with the fact that equilibrium between the nitrates of the REM and the polymer hydrogels is reached rather fast. Additional activation of the internode links of the macromolecules leads to strong growth of binding degree. The area of maximum binding of cerium ions is ratio 50 % hPMAA – 50 % hP4VP, the share of active links is 74.10 %.

Table 5

Polymer chain binding degree (in relation to cerium ions) of intergel system hPMAA-hP4VP

τ , h	hPMAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	θ (Ce), %						
0	0	0	0	0	0	0	0
0.5	8.29	10.51	11.06	15.21	12.44	13.55	5.53
1	12.72	15.21	17.70	23.78	21.29	22.12	8.57
2	19.63	21.29	25.71	39.82	27.93	29.31	15.21
6	29.03	40.09	42.30	60.00	45.90	49.22	24.88
24	46.18	56.68	58.62	70.51	61.11	64.15	43.69
48	50.05	63.04	65.53	74.10	67.19	68.85	47.00

Table 6 represents the difference in values of effective dynamic exchange capacity in presence and absence of the phenomenon of mutual activation. As was mentioned above, the equilibrium is almost reached at

24 hours of interaction of individual hPMAA and hP4VP with the salt solution. This is evidenced by the fact that the further increase is very low. As seen from the table, the significant increase in the intergel pair 50 % hPMAA – 50 % hP4VP points to the high ionization degree of the initial polymer structures. Maximum values of the exchange capacity are observed at this ratio at 48 hours of the remote interaction, exchange capacity is 5.96 mmol/g.

Table 6

Effective dynamic exchange capacity (in relation to cerium ions) of intergel system hPMAA-hP4VP

τ , h	hPMAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	Q (Ce), mmol/g						
0	0	0	0	0	0	0	0
0.5	0.67	0.84	0.89	1.22	1.00	1.09	0.44
1	1.02	1.22	1.42	1.91	1.71	1.78	0.69
2	1.58	1.71	2.07	3.20	2.24	2.36	1.22
6	2.33	3.22	3.40	4.82	3.69	3.96	2.00
24	3.71	4.56	4.71	5.67	4.91	5.16	3.51
48	4.02	5.07	5.27	5.96	5.40	5.53	3.78

Neodymium ions sorption.

During the sorption process of neodymium ions there is an occurrence of the areas of minimum and maximum sorption (table 7). The lowest values of the sorption degree are observed in case when there is presence of only polyacid or polybasis in the salt solution, extraction degree is 61.60 % for hPAA and 54.67 for hP4VP. Significant increase of the parameter is seen at hPAA:hP4VP = 83 %:17 % and hPAA:hP4VP = 50 %:50 % ratios, sorption degree is 93.59 % and 91.74 % respectively.

Table 7

Sorption degree of neodymium ions of intergel system hPAA-hP4VP

τ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	η (Nd), %						
0	0	0	0	0	0	0	0
0.5	10.71	20.51	13.07	16.83	12.66	11.49	5.82
1	16.35	33.85	21.70	27.11	18.43	16.71	9.41
2	25.10	51.10	29.71	46.23	28.94	25.81	16.73
6	37.84	74.37	51.68	72.56	46.77	42.12	28.34
24	56.77	86.82	74.29	80.35	70.10	66.83	49.20
48	61.60	93.59	86.74	91.74	72.32	71.44	54.67

The part of active links (which take part in the sorption process of neodymium) of the individual macromolecules and the intergel pairs is presented in table 8. Obtained results show that the part of the active links of hydrogels (PAA and P4VP) is over 50 %, this is consequence of the absence of the high ionization process. The increase of the polymer chain binding degree in the intergel system occurs from 60 % to 73 %. It should be noted that maximum values of the parameter (73.24 %) are observed at ratio 83 % hPAA – 17 % hP4VP at 48 hours of remote interaction.

Table 8

Polymer chain binding degree (in relation to neodymium ions) of intergel system hPAA-hP4VP

τ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	θ (Nd), %						
1	2	3	4	5	6	7	8
0	0	0	0	0	0	0	0
0.5	9.18	15.22	12.64	13.31	10.34	10.07	4.84
1	13.25	24.39	18.75	20.86	17.45	16.53	7.45

Continuation of Table 8

1	2	3	4	5	6	7	8
2	17.98	39.98	30.24	34.59	25.68	23.61	14.31
6	30.37	60.57	51.91	58.79	44.33	40.12	22.62
24	46.73	70.45	68.34	68.24	60.11	59.48	41.83
48	50.15	73.24	68.35	70.91	64.37	62.85	45.66

Table 9 represents the impact of mutual activation phenomenon on effective dynamic exchange capacity. The most of the metal is extracted by initial polymers (PAA and P4VP respectively) during 24 hours of interaction, exchange capacity is 3.81 mmol/g and 3.46 mmol/g. Further increase is not so strong and the final values (4.13 mmol/g and 3.67 mmol/g respectively) are reached at 48 hours. The significant increase (over 30 %) of the exchange capacity is due to formation of optimal conformation in the intergel pair 83 % hPAA – 17 % hP4VP for neodymium ions sorption, at 48 hours of remote interaction the parameter is 6.03 mmol/g.

Table 9

Effective dynamic exchange capacity (in relation to neodymium ions) of intergel system hPAA-hP4VP

τ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	Q (Nd), mmol/g						
0	0	0	0	0	0	0	0
0.5	0.73	1.33	1.02	1.11	0.85	0.77	0.41
1	1.14	2.26	1.68	2.04	1.50	1.41	0.65
2	1.69	3.39	2.55	2.73	2.24	1.96	1.17
6	2.52	5.01	4.30	4.91	3.72	3.33	1.92
24	3.81	5.77	5.31	5.59	5.05	4.96	3.46
48	4.13	6.03	5.65	5.83	5.32	5.26	3.67

Sorption degree of neodymium ions of polymers (hPMAA, hP4VP) and intergel pairs (hPMAA:hP4VP) is presented in Table 10. Comparatively to intergel system hPAA-hP4VP (Table 7) the values of sorption degree are lower due to complication of the ionization process during unfolding of the macromolecular globe. The most intense sorption occurs during 6 hours of interaction with the salt solution as for the individual hydrogels of PMAA and P4VP as for the intergel system hPMAA-hP4VP. Sorption degree of neodymium ions of individual hPMAA and hP4VP is 57.91 % and 54.67 % respectively, while 92.41 % of the rare-earth metal is extracted at hPMAA:hP4VP = 67 %:33 % ratio.

Table 10

Sorption degree of neodymium ions of intergel system hPMAA-hP4VP

τ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	η (Nd), %						
0	0	0	0	0	0	0	0
0.5	8.33	15.72	19.89	11.71	9.60	9.13	5.82
1	12.18	25.61	31.46	19.83	15.12	14.32	9.41
2	18.56	42.40	47.71	27.34	23.61	23.05	16.73
6	31.25	70.86	73.05	46.76	38.85	38.41	28.34
24	51.71	78.10	83.90	70.29	60.11	58.23	49.20
48	57.91	90.63	92.41	84.33	70.72	69.45	54.67

The share of the active links of the following polymer structures: individual hPMAA and hP4VP and intergel pairs (hPMAA:hP4VP) is presented in Table 11. The part of active links in below 50 % for the individual hydrogels of PMAA and P4VP, polymer chain binding degree at 48 hours of interaction is 47.30 % and 45.66 % respectively. High ionization of the initial polyacid and polybasis at ratio 67 % hPMAA–33 % hP4VP provides strong increase of binding degree, it is 71.56 % after 48 hours.

Table 11

Polymer chain binding degree (in relation to neodymium ions) of intergel system hPMAA-hP4VP

τ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	θ (Ce), %						
0	0	0	0	0	0	0	0
0.5	6.71	12.13	14.11	11.31	10.01	8.97	4.84
1	10.97	18.87	21.69	15.49	14.42	12.33	7.45
2	16.65	27.64	36.54	24.38	22.18	19.89	14.31
6	26.84	47.44	57.58	43.56	40.86	37.98	22.62
24	43.83	61.79	68.54	58.57	55.78	52.43	41.83
48	47.30	66.33	71.56	64.81	62.35	59.99	45.66

Comparison of the effective dynamic exchange capacities (Table 12) of the individual hydrogels of PMAA and P4VP and the intergel system hPMAA-hP4VP shows that the remote interaction provides significant increase of the parameter in the intergel pairs. The overwhelming majority of the neodymium ions is extracted during 24 hours of interaction, exchange capacity is 3.86 mmol/g for hPMAA, 3.67 mmol/g for hP4VP, 5.55 mmol/g for ratio 67 % hPMAA – 33 % hP4VP. Further increase (up to 48 hours of interaction) is slight, the final values (3.86 mmol/g for hPMAA, 3.67 mmol/g for hP4VP, 5.84 mmol/g for 67 % hPMAA – 33 % hP4VP) are observed at 48 hours of interaction.

Table 12

Effective dynamic exchange capacity (in relation to neodymium ions) of intergel system hPMAA-hP4VP

τ , h	hPAA:hP4VP, mol.% : mol.%						
	100:0	83:17	67:33	50:50	33:67	17:83	0:100
	Q (Nd), mmol/g						
0	0	0	0	0	0	0	0
0.5	0.56	1.03	1.17	0.91	0.79	0.73	0.41
1	0.87	1.67	1.86	1.58	1.35	1.1	0.65
2	1.43	2.19	3.14	2.07	1.98	1.56	1.17
6	2.22	3.87	4.79	3.51	3.33	3.07	1.92
24	3.59	5.03	5.56	4.75	4.62	4.43	3.46
48	3.86	5.39	5.84	5.25	5.11	5.01	3.67

As seen from the tables 1–12, the individual hydrogels (PMAA and P4VP respectively) do not have sufficiently high sorption properties (in relation to cerium and neodymium ions) due to the rather fast equilibrium reaching between them and the corresponding salt solution. As can be seen from the tables, high ionization degree and change of conformation of initial polymer structures during remote interaction with consequent mutual activation provides significant increase (over 30 %) of sorption degree, polymer chain binding degree and effective dynamic exchange capacity comparatively with individual hydrogels.

Conclusions

Based on obtained data on sorption of cerium and neodymium ions, the following conclusions can be made:

1. Individual hydrogels do not have high sorption properties relatively to cerium and neodymium ions. Sorption degree of cerium ions is 63.33 % for hPAA, 60.33 % for hPMAA, 56.67 % for hP4VP. Sorption degree of neodymium ions is 61.60 % for hPAA, 57.91 % for hPMAA, 54.67 % for hP4VP. Polymer chain binding degree (relatively to Ce^{3+} ions) is 52.53 % for hPAA, 50.05 % for hPMAA, 47.00 % for hP4VP; binding degree (relatively to Nd^{3+} ions) is 50.15 % for hPAA, 47.30 % for hPMAA, 45.66 % for hP4VP. Effective dynamic exchange capacity (relatively to Ce^{3+} ions) is 4.22 mmol/g for hPAA, 4.02 mmol/g for hPMAA, 3.78 mmol/g for hP4VP; exchange capacity (relatively to Nd^{3+} ions) is 4.13 mmol/g for hPAA, 3.86 mmol/g for hPMAA, 3.67 mmol/g for hP4VP.

2. Mutual activation of the initial polymers provides their transition into highly ionized state in intergel pairs, this transition is accompanied with significant increase (up to 30 %) of the sorption properties

comparatively with individual hydrogels. The areas of maximum sorption are the following ratios: hPAA:hP4VP = 17 %:83 % ($\eta = 92.33$ %; $\theta = 76.59$ %; $Q = 6.16$ mmol/g) and hPMAA:hP4VP=50 %:50 % ($\eta = 89.33$ %; $\theta = 74.10$ %; $Q = 5.96$ mmol/g) for Ce^{3+} ions; hPAA:hP4VP=83 %:17 % ($\eta = 93.59$ %; $\theta = 73.24$ %; $Q = 6.03$ mmol/g) and hPMAA: hP4VP=67 %:33 % ($\eta = 92.41$ %; $\theta = 71.56$ %; $Q = 5.84$ mmol/g) for Nd^{3+} ions.

3. Presence of bulky methyl substituent complicates the process of ionization of hydrogel of PMAA in intergel system hPMAA-hP4VP, due to this fact the values of the sorption properties are lower comparatively with intergel system hPAA-hP4VP.

4. Differences of the values of the sorption parameters in dependence of the aimed ion (cerium or neodymium) are due to the differences of the main properties of these ions (atomic radius, polarizability, charge density).

5. Changing the polymer molar ratios in the developed intergel systems provides possibility to control «selectivity» in relation to each considered rare-earth metal. Developed intergel systems may be used at creation of innovative technologies for selective extraction of REM ions from industrial solutions.

Financial support of the study was made by Science Committee of Kazakhstan (projects of grant funding #AP05131302 and #AP05131451).

References

- 1 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.M. Donia, 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.
- 2 Miller D.D. Anion structural effects on interaction of rare earth element ions with Dowex 50W X8 cation exchange resin / D.D. Miller, R. Siriwardane, D. McIntyre // Journal of rare earths. — 2018. — Vol. 36. — P. 879–890.
- 3 Abu Elgoud E.M. Sorption of Lanthanum (III) and Neodymium (III) from Concentrated Phosphoric Acid by Strongly Acidic Cation Exchange Resin (SQS-6) / E.M. Abu Elgoud, Z.H. Ismail, M.I. Ahmad, Y.A. El-Nadi, S.M. Abdelwahab, H.F. Aly // Russian journal of applied chemistry. — 2019. — Vol. 92. — P. 1581–1592.
- 4 Gedgagov E.I. Removal of Impurities from Saturated Ion-Exchange Resins by Frontal-Gradient Purification in Schemes for Recovery of Nonferrous, Rare, and Rare Earth Metals / E.I. Gedgagov, S.V. Zakhar'yan, O.M. Sinyanskaya, D.V. Zakhar'yan // Theoretical foundations of chemical engineering. — 2018. — Vol. 52. — P. 920–927.
- 5 Jumadilov T. Hydrogels remote interaction — basis of new phenomena and technologies / T. Jumadilov // Polyimides and high performance polymers (STEPI 10): Proceedings of 10th international conference (6–8 June 2016 year). — Montpellier: Institut Charles Gerhardt de Montpellier, 2016. — P. 7.
- 6 Jumadilov T. Mutual activation and high selectivity of polymeric structures in intergel systems / S. Kaldayeva, R. Kondarov, B. Erzhan, B. Erzhet / High performance polymers for engineering based composites; ed. O.V. Mukbaniani, M.J.M. Abadie, T. Tashvilli. — UK: CRC press, 2015. — P. 111–119.
- 7 Кондауров Р.Г. Электрохимическое и объемно-гравиметрическое поведение интергелевой системы на основе полиметакриловой кислоты и поли-2-метил-5-винилпиридина в водной среде / Р.Г. Кондауров // Фараби элэмі: материалы Междунар. конф. молодых ученых (9–10 апреля 2014 г.). — Алматы: КазНУ им. аль-Фараби, 2014. — С. 77.
- 8 Кондауров Р.Г. Влияние исходного состояния гидрогелей полиакриловой кислоты и поли-4-винилпиридина на их электрохимические и конформационные свойства в интергелевой системе / Р.Г. Кондауров // Фараби элэмі: материалы Междунар. конф. молодых ученых (14–15 апреля 2015 г.). — Алматы: КазНУ им. аль-Фараби, 2015. — С. 137.
- 9 Абилов Ж.А. Интергелевые системы — мощный инструмент для извлечения редкоземельных и драгоценных металлов из промышленных растворов / Ж.А. Абилов, Т.К. Джумадилов, Р.Г. Кондауров // Вестн. НИА РК. — 2015. — № 2. — С. 27–32.
- 10 Джумадилов Т.К. Исследование сорбционной способности интергелевой системы «гидрогель полиакриловой кислоты — гидрогель поли-4-винилпиридина» по отношению к ионам лантана / Т.К. Джумадилов // Специальные полимеры для защиты окружающей среды, нефтяной отрасли, био-, нанотехнологии и медицины: материалы VI Междунар. сем. (16–18 сентября 2015 г.). — Семей: СемГУ им. Шакарима, 2015. — С. 123.
- 11 Жунусбекова Н.М. Сорбционное извлечение лантана на взаимоактивных интергелевых сорбентах / Н.М. Жунусбекова, Р.Г. Кондауров, Г.К. Ескалиева, А.А. Акимов, М.Б. Умерзакова, Т.К. Джумадилов // Хим. журн. Казахстана. — 2016. — № 3. — С. 152–161.
- 12 Кондауров Р.Г. Особенности селективной сорбции ионов лантана интергелевой системой на основе гидрогелей полиакриловой кислоты и поли-4-винилпиридина и десорбции ионов лантана из матрицы гидрогелей / Р.Г. Кондауров // Фараби элэмі: материалы Междунар. конф. молодых ученых (11–12 апреля 2016 г.). — Алматы: КазНУ им. аль-Фараби, 2016. — С. 80.
- 13 Джумадилов Т.К. Влияние взаимной активации гидрогелей полиметакриловой кислоты и поли-2-метил-5-винилпиридина на сорбционную способность интергелевой системы по отношению к ионам лантана / Т.К. Джумадилов, Ж.А. Абилов, Р.Г. Кондауров // Хим. журн. Казахстана. — 2014. — № 4. — С. 128–136.
- 14 Петрухин О.М. Практикум по физико-химическим методам анализа / О.М. Петрухин. — М.: Химия, 1987. — С. 77–80.

Т.К. Джумадилов, Р.Г. Кондауров, А.М. Имангазы

Церий тобына жататын сирекжер металдарын полиакрил қышқылының, полиметакрил қышқылының және 4-винилпиридиннің гидрогельдеріне негізделген интергелдік жүйелермен сорбциялау ерекшеліктері

Мақала жекелеген гидрогелдер полиакрил қышқылы (ПАҚг), полиметакрил қышқылы (ПМАҚг), поли-4-винилпиридин (П4ВПг) және осы гелдердің негізінде құрылған интергелді жүйелер церий және неодим иондарын сорбциялау процесін зерттеуге бағытталған. Бұған дейін ПАҚ, ПМАҚ, П4ВП жекелеген гидрогелдерінің сорбциялық қасиеті (сорбция дәрежесі, полимерлік тізбектердің байланысу дәрежесі, әсерлі динамикалық көлемдік сиымдылық) аса жоғары емес екені анықталды: сорбциялық дәрежесі 65 % төмен; полимерлік тізбектердің байланысу дәрежесі 55 %-дан жоғары емес; әсерлі динамикалық көлемдік сиымдылығы 4,5 ммоль/г төмен). Интергелді жүйедегі полимерлік гидрогелдердің қашықтан әрекеттесуі гидрогелдердің сорбциялық қасиетінің анағұрлым жоғарылауына (30 %-ға жуық) ықпал етеді. Сорбциялық дәрежесі 93,5 %-ға дейін; полимерлік тізбектердің байланысу дәрежесі 76,5 %-ға дейін; әсерлі динамикалық көлемдік сиымдылығы 6,16 ммоль/г-ға дейін өседі. Интергелді жүйедегі полимерлік гидрогелдердің қашықтан әрекеттесу кезінде олардың өзара активтенуі салдарынан гидрогелдердің сорбциялық қасиеті жоғарылайды. Макромолекулалар ионизацияға ұшырайды, ары қарай полимерлік түйіндер айналып, төменмолекулалы иондарды сорбциялау үшін тиімді құрылымдар түзеді.

Кілт сөздер: интергелді жүйелер, өзара әрекеттесу, полиакрил қышқылы, полиметакрил қышқылы, поли-4-винилпиридин, церий иондары, неодим иондары, сорбция.

Т.К. Джумадилов, Р.Г. Кондауров, А.М. Имангазы

Особенности сорбции редкоземельных металлов цериевой группы интергелевыми системами на основе гидрогелей полиакриловой кислоты, полиметакриловой кислоты и поли-4-винилпиридина

Статья посвящена изучению процесса сорбции ионов церия и неодима индивидуальными гидрогелями полиакриловой кислоты (гПАК), полиметакриловой кислоты (гПМАК), поли-4-винилпиридина (гП4ВП) и интергелевыми системами на их основе. Полученные результаты показали, что сорбционные свойства (степень сорбции, степень связывания полимерной цепи, эффективная динамическая обменная емкость) индивидуальных гидрогелей ПАК, ПМАК, П4ВП недостаточно высоки: степень сорбции не выше 65 %; степень связывания полимерной цепи не выше 55 %; эффективная динамическая обменная емкость не выше 4,5 ммоль/г. Дистанционное взаимодействие полимерных гидрогелей в интергелевых системах приводит к существенному увеличению (около 30 %) сорбционных свойств. Степень сорбции возрастает до 93,5 %; степень связывания полимерной цепи — до 76,5 %; эффективная динамическая обменная емкость — до 6,16 ммоль/г. Такой существенный рост является следствием взаимной активации исходных полимеров в интергелевых системах во время их дистанционного взаимодействия. Макромолекулы подвергаются ионизации с последующим разворачиванием полимерного клубка с образованием оптимальной конформации для сорбции низкомолекулярных ионов.

Ключевые слова: интергелевые системы, дистанционное взаимодействие, полиакриловая кислота, полиметакриловая кислота, поли-4-винилпиридин, ионы церия, ионы неодима, сорбция.

References

- 1 Donia, A.M., Atia, A.A., Amer, T.E., El-Hazek, M.N., & Ismael, M.H. (2011). Selective Separation of Uranium (VI), Thorium (IV), and Lanthanum (III) from their aqueous solutions using a chelating resin containing amine functionality. *Journal of Dispersion Science and Technology*, 32, 1673–1681.
- 2 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, 879–890.
- 3 Abu Elgoud, E.M., Ismail, Z.H., Ahmad, M.I., El-Nadi, Y.A., Abdelwahab, S.M., & Aly, H.F. (2019). Sorption of Lanthanum (III) and Neodymium (III) from Concentrated Phosphoric Acid by Strongly Acidic Cation Exchange Resin (SQS-6). *Russian Journal of Applied Chemistry*, 92, 1581–1592.
- 4 Gedgagov, E.I., Zakhar'yan, S.V., Sinyanskaya, O.M., & Zakhar'yan, D.V. (2018). Removal of Impurities from Saturated Ion-Exchange Resins by Frontal-Gradient Purification in Schemes for Recovery of Nonferrous, Rare, and Rare Earth Metals. *Theoretical Foundations of Chemical Engineering*, 52, 920–927.
- 5 Jumadilov, T. (2016). Hydrogels remote interaction — basis of new phenomena and technologies. Proceedings from the Polyimides and high performance polymers (STEPI 10): 10th International conference (6–8 June 2016 year). (pp. 7). Montpellier: Institut Charles Gerhardt de Montpellier.

- 6 Jumadilov, T., Kaldayeva, S., Kondaurov, R., Erzhan, B., & Erzhet, B. (2015). Mutual activation and high selectivity of polymeric structures in intergel systems. *High performance polymers for engineering based composites*. O.V. Mukbaniani, M.J.M. Abadie, T. Tatrishvilli (Ed.); UK, CRC press.
- 7 Kondaurov, R.G. (2014). Elektrokhimicheskoe i obemno-hravimetriceskoe povedenie interhelevoi sistemy na osnove polimetakrilovoi kisloty i poli-2-metil-5-vinilpiridina v vodnoi srede [Electrochemical and volume-gravimetric behavior of intergel system based on polymethacrylic acid and poly-2-methyl-5-vinylpyridine in an aqueous medium]. Proceedings from Farabi alemi: *Mezhdunarodnaia konferentsiia molodykh uchenykh (9–10 apreliia 2014 hoda)* — *International conference of young scientists*. (p. 77). Almaty: KazNU imeni Al-Farabi [in Russian].
- 8 Kondaurov, R.G. (2015). Vliianie iskhodnogo sostoiianiia hidrohelei poliakrilovoi kisloty i poli-4-vinilpiridina na ikh elektrokhimicheskie i konformatsionnye svoistva v interhelevoi sisteme [Impact of initial state of hydrogels of polyacrylic acid and poly-4-vinylpyridine on it's electrochemical and conformation properties in intergel system]. Proceedings from Farabi alemi: *Mezhdunarodnaia konferentsiia molodykh uchenykh (14–15 apreliia 2015 hoda)* — *International conference of young scientists*. (pp. 137). Almaty: KazNU imeni Al-Farabi [in Russian].
- 9 Abilov, Zh.A., Dzhumadilov, T.K., & Kondaurov, R.G. (2015). Interhelevye sistemy — moshchnyi instrument dlia izvlecheniia redkozemelnykh i drachotsennykh metallov iz promyshlennykh rastvorov [Intergel systems — strong instrument for extraction of rare-earth and precious metals from industrial solutions]. *Vestnik Natsionalnoi inzhenernoi akademii Respubliki Kazakhstan — Bulletin of National Engineering Academy of the Republic of Kazakhstan*, 2, 27–32 [in Russian].
- 10 Dzhumadilov, T.K. (2015). Issledovanie sorbtionnoi sposobnosti interhelevoi sistemy “hidrohel poliakrilovoi kisloty — hidrohel poli-4-vinilpiridina” po otnosheniiu k ionam lantana [Study of sorption ability of intergel system hydrogel of polyacrylic acid — hydrogel of poly-4-vinylpyridine in relation to lanthanum ions]. Proceedings from Special polymers for protection of environment, oil-, bioindustry, nanotechnology and medicine: *VI Mezhdunarodnyi seminar (16–18 sentiabria 2015 hoda)* — *VI international seminar*. (pp. 123). Semey: SemHU imeni Shakarima [in Russian].
- 11 Zhunusbekova, N.M., Kondaurov, R.G., Eskalieva, G.K., Akimov, A.A., Umerzakova, M.B., & Dzhumadilov, T.K. (2016). Sorbtionnoe izvlechenie lantana na vzaimoaktivnykh interhelevykh sorbentakh [Sorption extraction of lanthanum on mutually activated intergel sorbents]. *Khimicheskii zhurnal Kazakhstana — Chemical Journal of Kazakhstan*, 3, 152–161 [in Russian].
- 12 Kondaurov, R.G. (2016). Osobennosti selektivnoi sorbtсии ionov lantana interhelevoi sistemoi na osnove hidrohelei poliakrilovoi kisloty i poli-4-vinilpiridina i desorbtсии ionov lantana iz matritsy hidrohelei [Features of selective sorption of lanthanum ions by intergel system based on hydrogels of polyacrylic acid and poly-4-vinylpyridine and features desorption of lanthanum ions from hydrogels matrix]. Proceedings from Farabi alemi: *Mezhdunarodnaia konferentsiia molodykh uchenykh (11–12 apreliia 2015 hoda)* — *International conference of young scientists*. (p. 80). Almaty: KazNU imeni Al-Farabi [in Russian].
- 13 Dzhumadilov, T.K., Abilov, Zh.A., & Kondaurov, R.G. (2014). Vliianie vzaimnoi aktivatsii hidrohelei polimetakrilovoi kisloty i poli-2-metil-5-vinilpiridina na sorbtionnuiu sposobnost interhelevoi sistemy po otnosheniiu k ionam lantana [Influence of mutual activation of hydrogels of polymethacrylic acid and poly-2-methyl-5-vinylpyridine on sorption activity of intergel system relatively to lanthanum ions]. *Khimicheskii zhurnal Kazakhstana — Chemical Journal of Kazakhstan*, 4, 128–136 [in Russian].
- 14 Petrukhin, O.M. (1987). Praktikum po fiziko-khimicheskim metodam analiza [Workbook on physicochemical methods of analysis]. Moscow: Khimiia [in Russian].