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SORPTION AND ION-EXCHANGE PROCESSES

Sorption Recovery of Transplutonium Elements from Nitric Acid Solutions with Arsenazo Group Reagents

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Abstract—Sorption recovery of actinides and lanthanides from nitric acid solution with arsenazo group reagents, activated carbon modified with these reagents, and chelating sorbents containing arsenazo functional groups was studied.

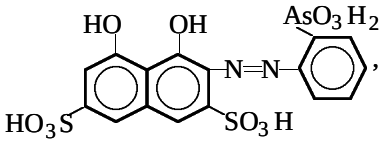
Recovery of transplutonium elements from acidic solutions is an important industrial problem, and search for reagents suitable for sorption and extraction recovery of these elements is urgent. It is known [1, 2] that arsenazo group reagents are widely used in analysis, because they form strong complexes with more then 30 elements including actinides and lanthanides. Reagents based on chromotropic acid, arsenazo I (monoazo derivative) and arsenazo III (bisazo derivative), are used for highly sensitive spectrophotometric determination of certain elements [1, 2] including americium and curium [3, 4]. The use of these reagents for metal extraction is limited because of their low solubility in organic solvents, which increases only in the presence of higher alcohols. Arsenazo III can be used for recovery and separation of actinides and lanthanides [5] including americium(III) and (V) [6] in two-phase, free of organic solvents aqueous systems based on water-soluble polymers. For sorption recovery, we synthesized a series of chelating sorbents containing arsenazo group reagents.[1] It is known [7] that chelating sorbents exhibit enhanced selectivity, which is due to the nature of functional groups reacting with metal ions. These groups are introduced into the polymeric matrix by appropriate chemical reactions or are formed during the synthesis of the polymeric sorbent. The chelating sorbent prepared by azo coupling of diazotized aminopolystyrene with arsenazo I was used for selective concentration of many elements [8–11] and determination of trace elements in uranium ores and concentrates, carbonate and silicate rocks, natural water, and wastewater [2, 7, 12, 13]. Cellulose fibrous sorbent with arsenazo groups is selective toward uranium and lanthanides and was used for selective recovery of these elements form solutions with high concentration of alkali and alkaline-earth metals [14]. A new fibrous chelating sorbent POLIORGS 33A containing amidoxime, hydrazine, oxy, and arsonoazo groups selectively recovers plutonium from acidic saline solutions and allows its separation from the other elements [15, 16].

In this work, we studied the recovery and concentration of transplutonium and rare-earth elements from nitric acid solutions with sorbents containing arsenazo fragments.

EXPERIMENTAL

Nitric acid solutions containing radiochemically pure radionuclides $^{242–244}$Cm, ^{243}Cm, ^{241}Am, ^{239}Pu, and $^{152–154}$Eu were used. Sorption was studied under static conditions by mixing nitric acid solution (V = 2–4 ml) containing a definite amount of radionuclide with the sorbents (m = 5–200 mg) for 0.1–20 h. Sorbents in form of powders were separated by centrifuging after the radionuclide sorption. The degree of radionuclide recovery (%) was estimated from the α- or γ-activity of the initial and resulting solutions (after sorption). The α-activity was determined on a proportional counter with 2π geometry, while the γ-activity was measured on an LP-4900 analyzer.

The following reagents were used: analytically pure grade arsenazo I [2-(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid]



[1] In the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences.

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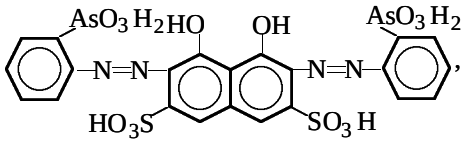
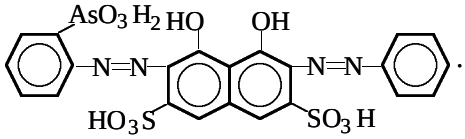
Table 1. Degree of curium and europium sorption from nitric acid solutions on carbons modified with arsenazo group reagents. V/m = 200, sorption time 2 h

C_{HNO_3}, M	Degree of sorption, %, on indicated carbon					
	Daukh					Alkaline-A
	unmodified		modified with arsenazo III		modified with arsenazobenzene	modified with arsenazo III
	Cm	Eu	Cm	Eu	Eu	Eu
2.5×10^{-4}	78	75	95	88	68	99
0.1	22	59	33	61	31	24

arsenazo III [2,7-bis-(2-arsonophenyazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid] prepared by the reaction between chromotropic and aminophenylarsonic acid

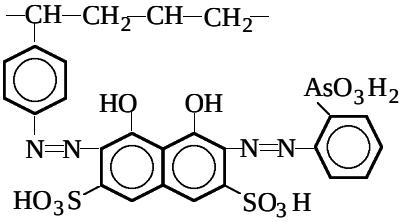


and arsenazobenzene [2-(2-arsonophenylazo)-7-(phenyl-azo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid]

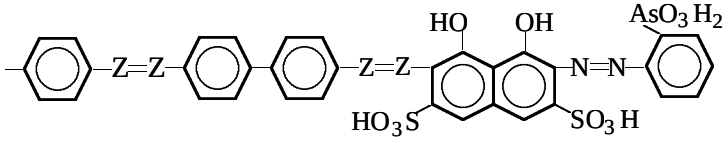


Daukh and Alkaline A activited carbons were used as sorbents. Iron-free carbon was prepared by washing with hydrochloric acid and water. Then it was saturated with reagent solution at agitation for 2 h, washed with water, and dried at 100°C.

The following chelating sorbents (all synthesized in Vernadsky Institute) were used. Polystyreneazoarsenazo was prepared by the reaction of diazotized aminopolystyrene with arsenazo I. It is a dark violet powder insoluble in water and acids. The exchange capacity of this sorbent for KOH is 1.6–2.8 mmol g^{-1}:



Arsenazo I polymers with benzidineazoarsenazo (BAAI and BPVAI):



(Z are various substutuents).

Polyarsenazo-n is filled fibrous chelating sorbent composed of polyacrylonitrile fiber and polystyreneazoarsenazo sorbent containing sulfo, *peri*-dihydroxy-, and *o*-hydroxy-*o*'-arsonoazo groups. The filling degree of the sorbent is 50%. It is a black fibrous material stable in strongly acidic, weakly alkaline, and neutral solutions. Its sorption exchange capacity for NaOH is 2.2 mmol g^{-1}.

We studied sorption of actinides and lanthanides from nitric acid solutions on activated carbons modified with arsenazo group reagents. It is known that a coomon procedure for concentrating and separating elements is sorption on matrices with active surface preliminarily saturated with complexing agents. Modified activated carbons are widely used to concentrate microelements. We modified carbons with arsenazobenzene and arsenazo III, which form the most stable complexes with transplutonium and rare-earth ions. The study of curium and europium recovery as influenced by the arsenazo III content showed that 1.2×10^{-4} M arsenazo III is required to saturate 1 g of carbon. Curium and europium sorption is strongly dependent on the solution acidity and is possible only from weakly acidic medium (<0.1 M HNO_3, Table 1). Car-

Table 2. Degree of metal sorption with chelating sorbents from nitric acid solutions. V/m = 200 (100 for polyarsenazo-n); sorption time 2 h

C_{HNO_3}, M	Sorption degree, %											
	BAAI		BPVAI		polystyreneazoarsenazo				polyarsenazo-n			
	Cm	Eu	Cm	Eu	Cm	Am	Pu	Eu	Cm	Am	Pu	Eu
0.1	98	99	97	96	>99	99	99	97	99	99	97	99
1.0	84	74	82	88	94	94	98	87	87	94	94	81
3.0	56	11	27	32	70	72	98	58	61	42	97	51

bons modified with arsenazo III recover metals better than the unmodified carbons. However, quantitative recovery of curium (98%) with unmodified carbons can also be reached at the ratio of the solution volume to sorbent mass equal to 200, when the time of contact of the solution with the sorbent increases to 18 h.

To recover elements from more acidic solutions, we studied their sorption with sorbents containing arsenazo functional groups in relation to the nitric acid concentration. As seen, quantitative recovery of actinides and lanthanides(III) is possible from solutions with nitric acid concentration no more than 1 M (Table 2). Plutonium can be recovered from 3 M HNO_3.

The kinetics of europium sorption from 1 and 3 M HNO_3 with polystyreneazoarsenazo and benzidineazoarsenazo is shown in Fig. 1. At the ratio of the solution volume to the sorbent mass of 200, the equilibrium recovery of europium with polystyreneazoarsenazo at stirring is reached within 1 h, and with benzidineazoarsenazo, within 4–6 h. The study of the degree of europium recovery from 1 M HNO_3 in 2 h as a function of the ratio of the solution volume (V) to the sorbent mass (m) showed that europium is quantitatively sorbed with polystyreneazoarsenazo and benzidineazoarsenazo at V/m 200 and 40, respectively. To recover metals from more concentrated HNO_3 solutions, the polystyreneazoarsenazo mass should be increased (Fig. 2, Table 3): e.g., at V/m 100, 60% europium is recovered even from 5 M HNO_3.

Since polystyreneazoarsenazo and benzidineazoarsenazo are fine powders, they should be separated from the solution by centrifuging, which is inconvenient with radioactive elements.

Fibrous chelating sorbents with high kinetic and selective characteristics are the most promising for recovery of actinides and lanthanides. To increase the efficiency of metal concentration (especially from large volumes), filled fibrous sorbents with higher kinetic characteristics and higher selectivity were used [17]. The study of metal sorption from nitric acid solutions with the filled fibrous chelating sorbent poyarsenazo-n containing polyacrylic fiber as a polymeric matrix and polystyreneazoarsenazo as a filler showed that this material well compares with the above-studied sorbents in sorption properties but has better kinetic characteristics (Fig. 1), since it exhibits

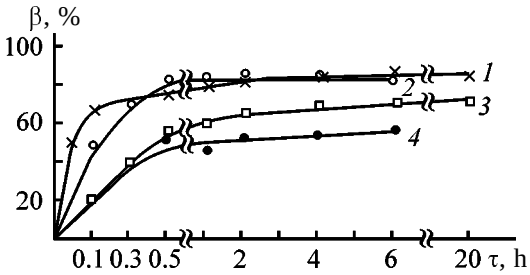


Fig. 1. Degree of europium sorption β with (*1*) polyarsenazo-n, (*2*, *4*) polystyreneazoarsenazo, and (*3*) BAAI as a function of sorption time t. HNO_3 concentration (M): (*1*–*3*) 1 and (*4*) 3. V/m: (*1*) 100 and (*2*–*4*) 200.

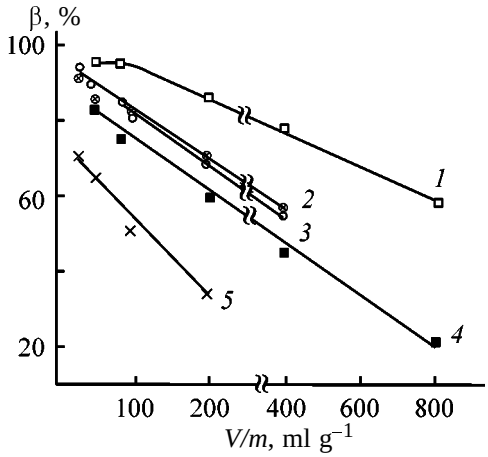


Fig. 2. Degree of europium sorption β with (*1*, *4*) polystyreneazoarsenazo, (*2*, *5*) polyarsenazo-n, and (*3*) BAAI as a function of V/m ratio. Sorption time 2 h. HNO_3 concentration (M): (*1*–*3*) 1 and (*4*, *5*) 3.

Table 3. Degree of europium sorption from nitric acid solutions. Sorption time 2 h

C_{HNO_3}, M	Degree of sorption, %, at indicated V/m			
	polystyreneazoarsenazo		polyarsenazo-n	
	200	100	100	50
3	58	72	48	56
4	54	69	42	53
5	46	60	30	53

rapid swelling and larger surface area. Triple-charged metals can be quantitatively recorded with polyarsenazo-n from nitric acid solution with concentration lower than 1 M, and plutonium, from solutions with higher acid concentration. As for polystyreneazoarsenaso, the increase of the polyarsenazo-n mass (Fig. 2, Table 3) increases the degree of metal recovery.

CONCLUSION

Chelating sorbents with arsenazo functional groups can be successfully used for sorption recovery and concentration of actinides and lanthanides from nitric acid solutions. Sorption can be accompanied by both chelation and ion exchange, because, along with chelating groups, these sorbents contain sulfo groups, which can be sites of usual ion exchange. It was shown that chelating sorbents with azo groups (especially those based on fibrous polymers) recover radionuclides from nitric acid solutions better than modified carbons.

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