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Sorption of Indium over Modified Montmorillonite in Dynamic Mode

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Abstract

A method for the selective removal of indium from solutions (sol.) of acid leaching of Waelz zinc oxide (0.02–0.1 g/dm^3 In) was proposed. It is an alternative technique for extraction. Adsorption over modified montmorillonite that is the Metosol reagent (reag.) in dynamic mode allows maximally implementing the reagent exchange capacity with the optimum cycle of sorption/desorption operations. Adsorption of iron (II) and zinc ions in static mode was detected. It is driven by the formation of intermolecular bonds with the developed surface of modified aluminosilicate. The formation of a stationary front of indium ion sorption from a polycomponent solution over the Metosol mineral sorbent due to predominant adsorption of In^{3+} compared to Fe^{2+} and Zn^{2+} was found in dynamic mode. The latter cations are replaced by In^{3+} ions that form chelates with ionogenic groups of di(2-ethylhexyl)phosphoric acid. Output curves of sorption of In ions at unit load V_{sol}/V_{reag} = 1–2.7 h^{-1} and temperatures of 298–328 K are mainly S-shaped. The inflection point is shifted to the low-value range of the specific volume of the past solution (V_{sol}/V_{reag}), which indicates slowing down the ion diffusion rate in sorbent. Indium ions passing into the filtrate comes much earlier ($V_{sol(1)}/V_{sol}$ = 3.33–0.66), the width of the chromatographic front (ΔV_{sol} /V_{reag} = 12.1–12.35) increases, the full dynamic exchange capacity (FDEC = 0.572–0.237 μmol-eq/g) and the utilization rate of the resin bed are decreased with increasing the linear rate ($\omega_{0.5}$) of the transmission of the eluent through a column in the range 4.78 to 12.74 cm/h. The width of the chromatographic front (ΔV_{sol} /V_{reag} = 12.1–10.24) decreases; the full dynamic exchange capacity (FDEC = 0.572–1.293 μmol-eq/g) and the utilization rate of the resin bed (η = 0.226–0.256) are increased, which testifies monitoring the process of sorption of indium by mixed diffusion. The Metosol reagent allows selectively extracting indium from production solutions in dynamic mode.

Key words: sorption, indium, diffusion, dynamic mode, montmorillonite

Introduction

Indium minerals (dzhalindite, yixunit) have no commercial reserves, therefore, zinc production wastes and intermediate products (to a lesser extent, lead and tin) containing 0.001–0.1 % of indium are the main source of the metal. Indium concentration in solutions during leaching, for example, of Waelz zinc oxide, is 0.02–0.1 g/dm^3. Organic compounds fall into zinc solutions during its further leaching from these solutions [1–3], which hinders subsequent zinc electrolysis. Sorption over modified Metosol montmorillonite appears to be an alternative method for selective extraction of indium (the name was proposed by the authors of the paper who carried out natural sorbent modification) using columns in a dynamic mode that allowed maximally implementing the reagent exchange capacity and sorption/desorption operation cycle.

The purpose of the carried out studies was to identify conditions and parameters of the process of selective indium extraction from multicomponent model solutions over modified aluminosilicate and assess opportunity of its use during the recycling of process solutions.

EXPERIMENTAL

Sorption of indium from a solution with a composition (g/dm_3) of H_2SO_4 19.6, Fe^{2+} 6.2, Zn^{2+} 67.0, In^{3+} 0.084 was carried out in columns (diameter is 2 cm, height is 40 cm) over the Metrosol reagent (reag.) obtained by modification of natural layered montmorillonite $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2(H_2O)_n)$ with alkyl phosphates from industrial reagent D_2EHPA (Technical specifications 2435-259-05763458–98) containing a mixture of di-(2-ethylhexyl)phosphoric and 2-ethylhexylphosphoric acids in the amount of 20 % relatively to the mass of aluminosilicate in accordance with patented methods [4, 5] and with the most likely structure given in the Scheme 1.

The Metosol reagent in each column was preliminarily immobilized in the intergrain air space of inert carrier, *i. e.* quartz sand (radius is 0.75–1.0 mm; layer height is 11.8 cm; layer porosity [6] $\varepsilon = (V - V_{sol})/V = (37-22)/37 \approx 0.4$) using Praestol-2500 nonionogenic flocculant (concentration is 1 %; volume is 0.25–0.3 cm^3). A portion of the sorbent defined by the ε indicator was 15 cm^3 (mass is 0.75 g; the radius of the cross section of a layer is ~25 nm; surface area is ~50 m^2). Immobilized montmorillonite in the intergranular space of the inert carrier does not form dense layers of aluminosilicate as flakes, without changing the radius of the cross section of the layer, which is then used during assessing sorption mass transfer model. The specific space velocity of the initial solution (eluent) during sorption was $V_{sol}/V_{reag} = 1-2.7\ h^{-1}$ or 4.8–12.7 $cm^3/(cm^2 \cdot h)$ at a temperature of 298–328 K. The constancy of solution feed was provided using a peristaltic pump. Solution portions after sorption with volumes of 10, 25 and 50 cm^3 were analysed for the residual concentrations of In^{3+}, Fe^{2+}, and Zn^{2+} ions by atomic absorption techniques using AAC-6650 plasma ionization spectrophotometer (Shimadzu).

The dynamics of absorption of $In^{3+,}$ Fe^{2+}, and Zn^{2+} ions with the Metosol reagent was studied by the frontal chromatography method [7] through plotting sorption curves at different specific eluent rates (specific load) and temperatures (Fig. 1). Output curves are presented in the coordinates $C/C_0 = f(V_{sol}/V_{reag})$, where V_{sol} and V_{reag} are eluent volumes passed through the column and the Metosol reagent, respectively; C/C_0 is the ratio of ion concentrations in filtrate portions and initial solution; α is the degree of extraction of metal ions from solutions (%):

$$\alpha = [(C_0 - C)/C_0] \cdot 100 \qquad (1)$$

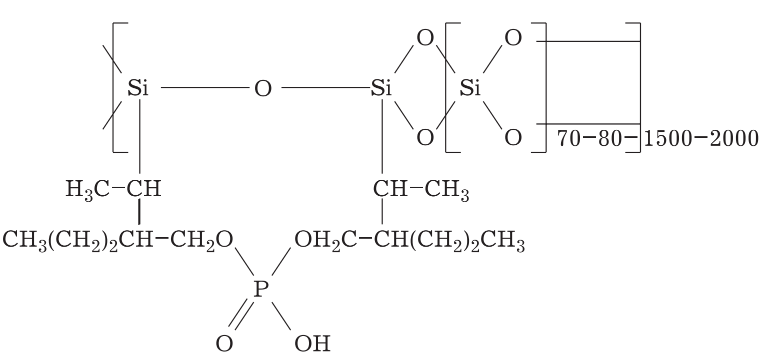
By the volume prior to passing and the saturation volume, the operating dynamic exchange capacity (DEC) and the full dynamic exchange capacity (FDEC) of sorbents were calculated:

$$\mathrm{DEC} = C_0 V_{sol\,(1)}/m \qquad (2)$$

$$\mathrm{FDEC} = (V_{sol\,(2)} C_0 - \Sigma V_{sol\,(3)} C)/m \qquad (3)$$

where $V_{sol\,(1)}$ is the volume of solution passed through an ion exchanger prior to the appearance of ions in the filtrate, *i. e.* before passing, cm^3; m is the mass of air-dried adsorbent, g; $V_{sol\,(2)}$ is the volume passed through an ion exchanger to equalize ion concentrations in the filtrate and the initial solution, cm^3; $\Sigma V_{sol\,(3)}$ is the total volume of filtrate portions after the appearance of ions (after passing), cm^3.

The relative volumetric width of the sorption front $\Delta V_{sol}/V_{reag\ (0.15-0.85)}$ was measured between points $C/C_0 = 0.15$ and $C/C_0 = 0.85$. The utilization degree of the resin bed (η) was defined as the ratio of DEC to FDEC.



Scheme 1.

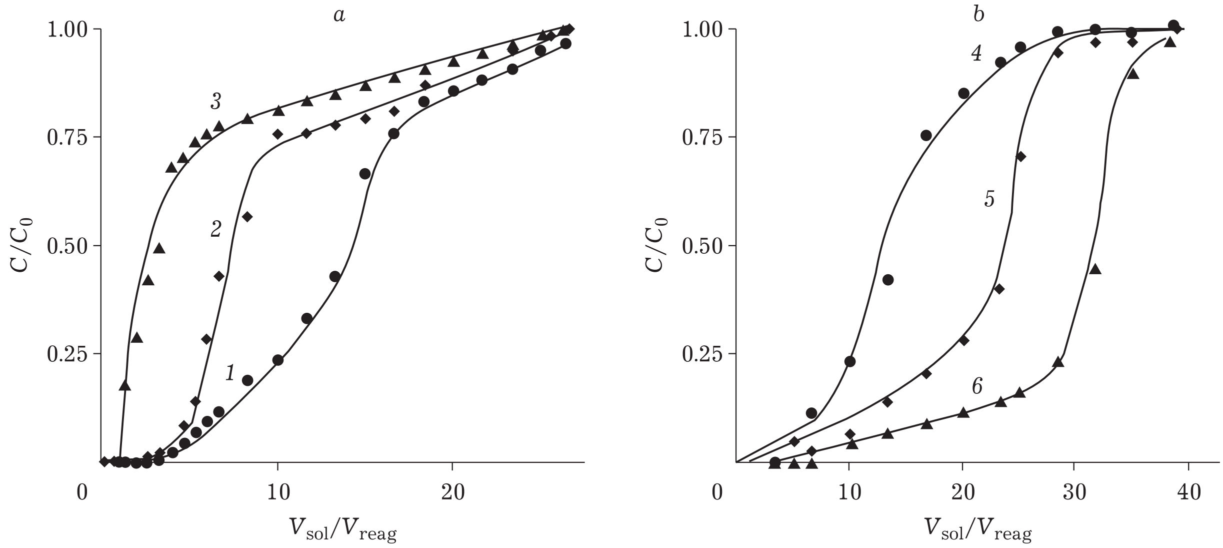


Fig. 1. C/C_0 ratio vs. the specific amount of the passed solution (V_{sol}/V_{reag}). The specific rate of the solution (h^{-1}): 1.0 (*1*, *4–6*), 2.0 (*2*), 2.7 (*3*); temperature (K): 298 (*1–4*), 313 (*5*), 328 (*6*).

RESULTS AND DISCUSSION

Fe^{2+} and Zn^{2+} ions are not sorbed over the Metosol reagent, as established. Perhaps, adsorption of the indicated macrocomponents [8, 9] detected in dynamic mode is driven by the formation of intramolecular bonds with the developed surface of modified aluminosilicate. The replacement of adsorbed Fe^{2+} and Zn^{2+} ions with In^{3+} ions that form chelates with ionogenic groups of di(2-ethylhexyl)phosphorous acid (DEHPA) proceeds under dynamic mode conditions [10, 11]. Output curves of In^{3+} ions in the studied ranges of unit loads and temperatures are mainly S-shaped; the inflection point is shifted to the low-value range of the specific volume of the passed solution of (V_{sol}/V_{reag}) or small process time, which indicates slowing of the diffusion rate of ions in the sorbent (see Fig. 1).

Assessing the width of the chromatographic front (ΔV_{sol}) and the movement rate of the midpoint of the front ($\omega_{0.5}$, cm/h) is given in Table 1.

Indium ions passing into filtrate come much earlier ($V_{sol\ (1)}/V_{sol}$ = 3.33–0.66), the width of the chromatographic front increases (V_{sol}/V_{reag} = 12.1–12.35), the full dynamic exchange capacity (FDEC=0.572–0.237 μmol-eq/g) and the utilization rate of the resin bed (η = 0.226–0.123) are decreased with increasing the linear rate ($\omega_{0.5}$) of the transmission of the eluent through a column in the range 4.78 to 12.74 cm/h. The width of the chromatographic front ($\Delta V_{sol}/V_{reag}$ = 12.1–10.24) decreases; the full dynamic exchange capacity (FDEC = 0.572–1.293 μmol-eq/g) and the utilization rate of the resin bed (η = 0.226–0.256) are decreased with increasing temperature (298–328 K). This dependence of parameters of output curves on the rate of transmittance and eluent temperature indicates that the sorption process of indium ions is monitored by mixed diffusion.

The rate of absorption of ions is defined by their diffusion coefficients. Effective diffusion coefficients of indium ions (D, in cm^2/s) were calcu-

TABLE 1

Parameters of the output curves for sorption of indium (III) ions

	$\Delta V_{psol}/V_{reag}$	$V_{psol\ (1)}/V_{sol}$	$V_{psol\ (2)}/V_{sol}$	$\omega_{0.5}$,	DEC μmol-eq/g	FDEC μmol-eq/g	η
V_{sol}/V_{reag}, h^{-1}			**Temperature 298 K**				
1.0	12.1	3.33	28.3	4.78	0.146	0.572	0.226
2.0	12.2	1.99	26.6	9.55	0.087	0.397	0.221
2.7	12.4	0.66	24.9	12.7	0.029	0.237	0.123
T, K			**V_{sol}/V_{reag} = 1.0 h^{-1}**				
313	11.6	4.99	38.3	4.78	0.219	0.912	0.240
328	10.2	6.66	41.6	4.78	0.292	1.290	0.256

lated based on experimental results using the Tunitsky equation [12]:

$$b = 3600\tau = (r^2/D_r)(1/\pi^2)[\ln (C_0/C_{\min})] \\ -\ln (\pi^2/6)] \quad (4)$$

$$\Delta V_{sol} = a + bV_{sol} \quad (5)$$

$$\tau = (\Delta V_{sol}/V_{sol}) = (a/V_{sol}) + b \quad (6)$$

where r0 is the radius of the cross section of the layer, cm; C_0 is the initial concentration of solution, mol/dm^3; $C_{\min}$ is the minimum concentration absorbed by ions, mol/dm^3; b is coefficient (h) numerically equal to the tangent of the slope in the system "$\Delta V_{sol} - V_{sol}$"; a is a constant, cm^3; ΔV_{sol} is the absolute volume width of the sorption front, cm^3; V_{sol} is a filtration rate of solutions, cm^3/h; τ is the duration of smearing of the sorption front, h.

The applicability of equation (4) is justified by the presence of the stationary front and the convexity of the sorption isotherm. The width of the chromatographic front of indium ions, in accordance with the data of Table 1, is linearly increased with increasing the eluent flow rate (Fig. 2).

According to experimental conditions ($r_0 = 25 \cdot 10^{-7}$ cm; $C_0 = 73.16 \cdot 10^{-5}$ mol/dm^3; $C_{\min} = 0.03C_0$) and considering the found values of the coefficient b (Fig. 2), internal diffusion coefficients of indium ions in the Metosol reagent were calculated by equation (4) (Table 2). The internal diffusion coefficient in the temperature range of 298–328 K increases within $D_r = (36.6–51.4) \cdot 10^{-16}$ cm^2/s. The duration of smearing of the sorption front decreases in the range τ = 12.10–4.63 h with increasing eluent filtration rate (V_{sol}) from 15 to 40 см^3/h.

The ratio of the mass transfer coefficient and the rate of mass conductivity in the solid porous phase (the Biot similarity criterion) defines the speed of movement of a substance from the phase boundary of the liquid-solid system into the rinsing phase [13].

The criterion characterizes externally the duration of stages, as applied to sorption processes.

$$T_1 = K_d/\beta t \quad (7)$$

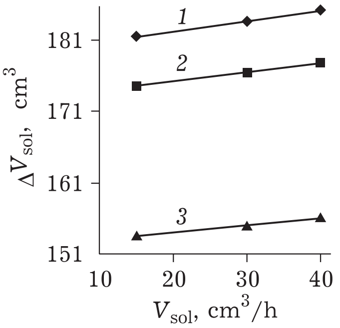


Fig. 2. Width of the chromatographic front of indium ions versus the volumetric rate of solution filtration at temperature, K: 298 (*1*); 313 (*2*); 328 (*3*).

It also describes the pore-diffusion mass transfer in adsorption of indium ions by reagent Metosol [14, 15]:

$$T_2 = r^2/D_r t \quad (8)$$

where $K_d = C_{In(reag)}/C_{In(sol)}$ is the distribution coefficient; β is the mass-transfer coefficient of the sorbate in an inter-diffusion model, s^{-1}; D_r is the diffusion coefficient of the sorbate within the sorbent granules, cm^2/s; r_0 is the average radius of the cross section of the layer, cm; t is the duration, s.

The mass transfer coefficient ($H = T_2 / T_1$) may be calculated based on equations (7) and (8):

$$H = \beta r^2/(D_r K_d) \quad (9)$$

According to (9), coefficient H is related to equilibrium and kinetic sorption parameters and defines the mechanism of the kinetics of the process: rates of external and internal diffusion in the mixed-diffusion mechanism of mass transfer are comparable ($H \approx 1$); at $H >> 1$, the kinetics is limited by internal diffusion; at $H << 1$, the rate of ion exchange is monitored by external diffusion [14, 15].

The value of the interdiffusion kinetic coefficient β reflects the combined effect of factors that define the interdiffusion mechanism of sorp-

TABLE 2

Parameters of sorption process of indium ions

T, K	a, cm^3	b, h	V_{sol}, cm^3/h	τ, h	R^2	$D_r \cdot 10^{16}$, cm^2/s
298	179	0.148	15	12.00		
			30	6.12	0.996	35.6
			40	4.63		
313	172	0.127	15	11.6		
			30	5.88	0.998	41.6
			40	4.45		
328	152	0.103	15	10.2		
			30	5.17	0.995	51.4
			40	3.91		

tion (concentration, viscosity, nature of ions, *etc.*) and hydrodynamic characteristics of the system (the rate of transmission of solutions, the size and shape of grains, layer porosity ε, etc.) related to solution properties.

Particularly, the value of β in diluted solutions for indium ions (λ_{In} = 63.8 cm^2/(Om · g-equiv) and reagent Metosol ($\varepsilon = (V-V_s)/V \cdot 0.3$; d_0 ~ 50 nm);

L_s = 30 cm; λ_{H+} = 349.8 cm^2/(Om · g-equiv) can be calculated by the equation:

$$\beta = 4.86 \cdot 10^{-4}[(1 - \varepsilon)/\varepsilon]^{1.53}\{1/[(Z_1/\lambda_1) +(Z_2/\lambda_2)]^{2/3}(\nu)^{0.47}/d_0^{1.53}\} \quad (10)$$

where Z_1 and Z_2 are the charges of exchanging ions; λ_1 and λ_2 are equivalent conductivities of the studied ions; ν is the linear rate of solution filtration, cm/s; V is layer volume ; V_s is layer volume of the solid phase [16].

Table 3 presents the values obtained of the kinetic coefficient β and the Biot criterion (H) for indium ions and reagent Metosol.

To assess the Biot criterion by equation (9) ion distribution coefficients K_d of ions found by the results of dynamic experiments in the in the region of the linear dependence C/C_0 on volume of the passed solution ($C_0 = 73.16 \cdot 10^{-5}$ mol/dm^3). K_d values were defined as the ratio of ion concentration in the sorbent and filtrate. The concentration of absorbed ions in the sorbent was calculated by the difference of the concentration in the eluent and filtrate (considering the volume of the filtrate) referred to the sorbent mass in the column (in terms of dry mass).

Values of the interdiffusion kinetic coefficient increase (β = 153.4–244.7 s^{-1}), and those of distribution coefficients decrease (K_d = 544–138 cm^3/g) with increasing the linear rate of solution transmission, as demonstrated. K_d values increase (544–2540 cm^3/g) with increasing temperature in the 298-328 K range. The values calculated for indium ions are $H \geq 100$, which corresponds to the criterion of the intramolecular mechanism of sorption kinetics. According to the equation $H = T_2/T_1$, the Biot criterion is equal to the ratio of the ratio of the time scales for intra- and interdiffusion stages of mass transfer. The times T_2 and T_1 can be represented as the inverse values of the rate of internal ($T_2 = 1/\nu_2$) and external diffusion ($T_1 = 1/\nu_1$), respectively, and $H = \nu_1/\ \nu_2$. In this case, it can be seen that the rate of internal diffusion of In^{3+} ions increases with increasing temperature at comparable rates of external diffusion of In^{3+}.

TABLE 3

Values of the kinetic coefficient and the Biot criterion

T, K	ν, см/s	β, s^{-1}	$D_r \cdot 10^{16}$, cm^2/s	K_d	H
298	4.78	153		544	495
	9.55	212	35.6	284	948
	12.7	244		138	1950
313	4.78	153		909	254
	9.55	212	41.6	475	485
	12.7	244		231	998
328	4.78	153		2540	73
	9.55	212	51.6	1320	141
	12.7	244		644	290

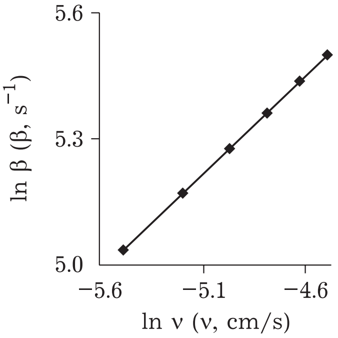


Fig. 3. Logarithmic dependence of the mass transfer coefficient of sorbate in the intradiffusion model on the linear rate of solution filtration.

Considering a high specific surface of reagent Metosol (~70 m^2/g), quantitative indicators of sorption of indium ions in dynamic mode are mainly defined by external diffusion processes via the boundary layer of a viscous fluid to the grain surface and subsequent chemical interaction with the ionogenic groups of the sorbent surface layer, and this confirms the presence of the linear dependence in the coordinates ln β − ln ν (Fig. 3): ln β = ln ν 0.4749 + 7.635; R^2 = 0.99.

In desorption of indium by hydrochloric acid solution (1 : 1) with the specific transmission rate V_{sol}/V_{reag} = 1.0 h^{-1}, two fractions were obtained: 1) the volume is 7.0 cm^3; the composition, g/dm^3: 0.63 In; 0 Zn; Fe^{2+} 0; 2) the volume is 8.3 cm^3; the composition, g/dm^3: 0.29 In; 0 Zn; Fe^{2+} 0.

The regeneration degree of sorbent Metrosol exceeded 95 %.

CONCLUSION

1. Iron (III) and zinc ions are not adsorbed over the Metosol reagent in dynamic mode due to their displacement by ions of indium forming chelates with ionogenic groups of intercalate, *i.e.* di-(2-ethylhexyl)phosphoric acid, as evidenced by the absence of Fe^{2+} and Zn^{2+} in the composition of eluates.

2. Output curves of sorption of indium ions in the studied ranges of specific load (V_{sol}/V_{reag} =

1–2.7 h^{-1}) and temperature (T = 298–328 K) are mainly S-shaped: the inflection point is shifted to the low-value range of the specific volume of the passed solution or short-term duration of the process which attests to slowing down the rate of diffusion of ions in the sorbent. As a whole, the sorption process of indium ions is monitored by a mixed diffusion.

3. The Metosol reagent may be recommended to carry out trials on selective sorption of indium in dynamic mode from industrial solutions of zinc production.

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