

ADSORPTION OF ARSENIC, CHROMIUM, LEAD, CADMIUM BY ADSORBENTS ON THE BASIS OF Zr(IV), Ti(IV), Sn(IV), Al(III), Fe(III) OXIDES

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It was studied sorption of As (V), Cr (VI), Cu (II), Cd (II), Pb (II) ions by inorganic and organic-inorganic ionites based on hydrated oxides of Zr (IV), Ti (IV), Sn (IV), Al (III), Fe (III) from isotherms of sorption and values of the distribution coefficients are calculated. High selectivity of oxides was observed in the presence of singly charged competing ions. It was found that in the case of the use of Zr (IV), Ti (IV), Sn (IV) oxyhydrates as a hybrid ionite in the composition, regeneration of 0.1 M with NaOH results in a 70-80% reduction in the absorptivity. The use of Fe (III) oxide as adsorbent leads to formation of intraspheric complexes. In this case, regeneration of ion-exchange adsorbents is difficult and requires higher concentrations of regenerating reagents and/or energy inputs.

Key words: adsorption, distribution coefficient, organic-inorganic oxide, multivalent metal.

INTRODUCTION

The values of the distribution coefficients of the target component K_d and the selectivity coefficients K_s are criteria for choosing adsorbents for the solution of a particular problem. The distribution coefficient equals how many times the concentration of adsorbate on the sorbent surface exceeds the concentration of this substance in the solution volume. The selectivity coefficient is the ratio of the distribution coefficients of the target component and the inert salt. In some cases, selectivity is the most important criterion, for example, when it is necessary to extract and concentrate valuable, toxic, radioactive components from solutions of complex composition. The peculiarities of the spatial structure are the reason of the high selectivity of the inorganic compounds. The inorganic compounds with a tunnel or layered structure possessed the highest selectivity. The oxyhydrates of the Group IV are constructed from MO₆ octahedra forming spatial tunnels 0.5-1 nm in size and exhibit high selectivity with respect to oxygen-containing anions and multiply charged cations [1-3]. The individual and double hydrated metal oxides Zr (IV), Ti (IV), Sn (IV), Fe (III), Zr (IV)-Fe (III), Sn (IV)-Fe (III), Zr (IV)-Al (III), Sn (IV)-Al (III) were studied in this research as selective sorbents with respect to some toxic component of water. The adsorption of As (V), Cr (VI), Cu (II), Cd (II), Pb (II), K⁺ and boric acid ions are studied from dilute aqueous solutions of salts and model solutions of more complex composition containing I-I-charged electrolyte. A sol-gel method was chosen for the synthesis of oxides. The oxyhydrates were also precipitated in the bulk of strongly basic anion exchangers of Dowex SBR-P, Dowex Marathon-11 and strong acid cation exchange resin Dowex HCR-S to improve hydrodynamic properties. The objectives of the research included a quantitative assessment of the selectivity of adsorbate absorption, as well as the possibility of regenerating adsorbents.

EXPERIMENTAL PART

The oxyhydrates were synthesized by precipitation from solutions of salts followed by hydrolysis, gel formation and subsequent granulation during drying at 70 ° C. Hybrid organic-inorganic adsorbents were prepared by introducing into the polymer matrix of solution of salts followed by hydrolysis. The ion exchange resin was placed in 1 M (1 M, 1: 1) solution and held for 24 hours with periodic mixing. The granules were filtered, washed with a small amount of distilled water and treated with a solution of the gelling agent for 24 hours with intermittent stirring. The granules were dried in air to constant weight after washing with distilled water. The impregnation was carried out repeatedly. The quantity of oxyhydrates in the hybrid adsorbents was determined by the weight of the residue after combustion at 700°C [4]. The distribution of the pores along the radii and the specific surface area of the oxides was calculated from the isotherms of the thermal desorption of nitrogen [5].

The solutions of salts (KNO_3 , CuCl_2 , CdCl_2 , $\text{Pb}(\text{NO}_3)_2$, $\text{K}_2\text{Cr}_2\text{O}_7$ and NaHAsO_4) were used for studies of sorption. Sorption of ions from one-component solutions was studied under static conditions at a ratio of solid and liquid phases ($\text{g}\cdot\text{cm}^3$) from 1:50 to 1: 200. The values of sorption, distribution coefficient and selectivity coefficient were calculated by decreasing the concentration in the solution after equilibrium was established. The concentration of ions in solutions was determined by the atomic-adsorption method on the Pye Unicam SP9 ("Philips") instrument.

Sorption of boric acid by individual oxyhydrates was also studied. To study the effect of the presence of a salt background on the adsorption properties of inorganic and inorganic organic adsorbents, the composition of a model solution of 0.02 M NaCl and 0.004 M H_3BO_3 was chosen. The titration method with mannitol was used to determine boric acid [6]. Sorption of arsenic from a two-component solution (0.1 M KCl and 0.001 M NaH_2AsO_4) was also investigated.

Regeneration of organic resins and hybrid sorbents was carried out with a 0.1 M solution of NaOH at a ratio of solid and liquid phases of 1:50.

RESULTS & DISCUSSIONS

In Fig. 1 shows pore distribution of radii for hydrated dioxides of zirconium (HDZ). It calculated from the thermal desorption of nitrogen using the Kelvin equation [5]. The sorbent is characterized by a considerable number of pores of radius less than 2 nm, mesopores predominate among the pore radius of 2, 3 and 4.3 nm. Based on the data obtained by thermal desorption of nitrogen, to determine the pore size radius is less than 1 nm is not possible. The presence of the selective pores on the surface of HDZ also confirmed by the adsorption of certain ions (Fig. 2).

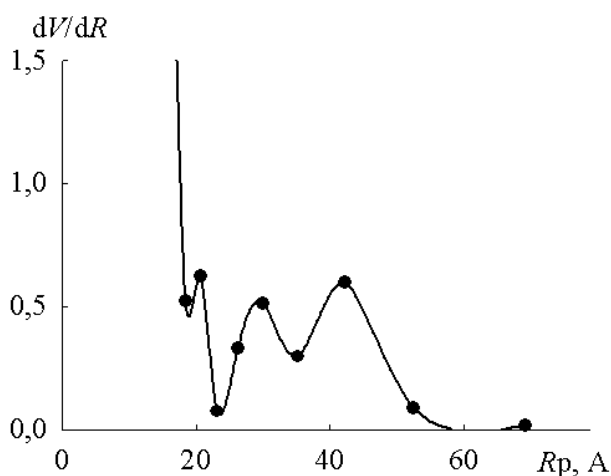


Fig. 1. Distribution of pores along radii for HDZ.

From the results shown in Fig. 2, it follows that strongly hydrated copper hexaaquacations [7] are not selectively adsorbed to the HDZ from the combined solution: the isotherms of adsorption of these ions are very close. Only in the case of lead cations, selective adsorption in three-dimensional cylindrical pores formed by ZrO_6 octahedra can be assumed. Less selective is HDZ for boric acid, however, in comparison with other individual oxyhydrates, the selectivity of this sorbent is most pronounced.

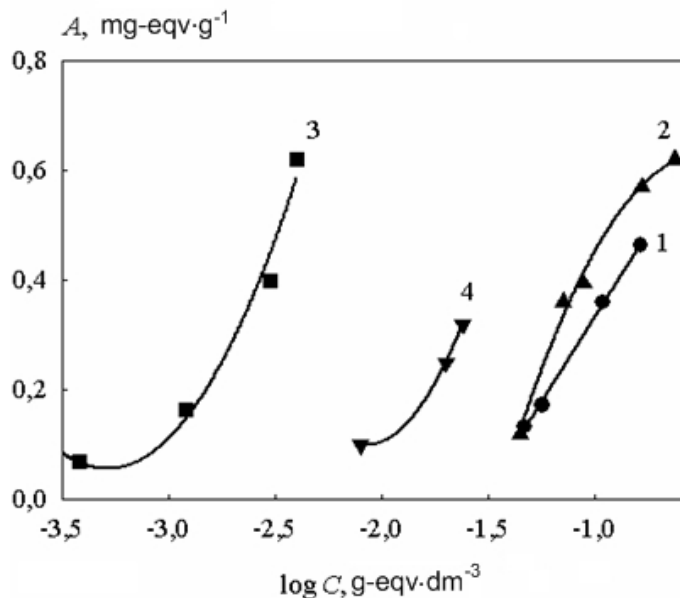
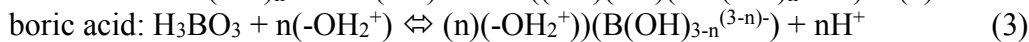
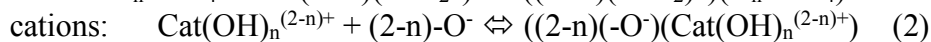
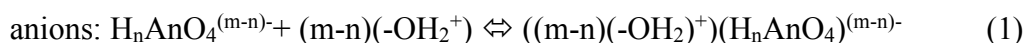


Fig. 2. Dependence of adsorption values ions K^+ (1), Cu^{2+} (2), Pb^{2+} (3), H_3BO_3 ($H_2BO_3^-$) (4) against the logarithm of the equilibrium concentration of solutions KNO_3 , $CuCl_2$, $Pb(NO_3)_2$, H_3BO_3

We have previously shown that double oxyhydrates of the composition $M_xAl_{1-x}O_y \cdot nH_2O$ ($M = Zr, Sn, Ti$) are characterized by increased microporosity ($(Zr_xAl_{1-x}O_y \cdot nH_2O - 70\%, Sn_xAl_{1-x}O_y \cdot nH_2O - 81\%, Ti_xAl_{1-x}O_y \cdot nH_2O - 50\%)$ [8]. In Fig. 3, isotherms of adsorption of anions and cations in the sorbent based on Sn (IV) and Al (III) oxyhydrates are shown in logarithmic coordinates. It can be concluded on the basis of the obtained data, that the charge of the surface also affects the value of the distribution coefficient of specific ions, in addition to the presence of micropores. In particular, for As (V) anions (see Fig. 2b), a change in the equilibrium pH value from 8-9 to 3-6 leads to an increase in K_d by two orders of magnitude. The mechanism of sorption on oxyhydrates can be the electrostatic interaction of the adsorbed ion and surface-OH groups [2], localized in both micro- and mesopores. At the same time, the sorption of ions depending on the pH of the solution and the near-surface layer can proceed with the formation of both intraspheric and outer-sphere (containing fragments of water) surface complexes ($H_nAsO_4^{(3-n)-}$, $H_nCrO_4^{(2-n)-}$, $Cu(OH)_n^{(2-n)+}$, $Cd(OH)_n^{(2-n)+}$, $Pb(OH)_n^{(2-n)+}$):



In the case of boric acid, at $pH < 9$, the interaction is carried out according to scheme (4) [9].

The difference in the degree of inclusion of selective micropores in the sorption process determines the selectivity of absorption of the ion with respect to the other.

The results obtained for individual, double oxyhydrates and organic-inorganic ionites in the pH range of 5-8 are summarized in Tables 1 and 2. The organic-inorganic HCR-S / TiO_2 ionite contains 22% of the inorganic component, and HCR-S / SnO_2 -12 %, anion exchange organic-inorganic ion exchangers contains from 2 to 51%.

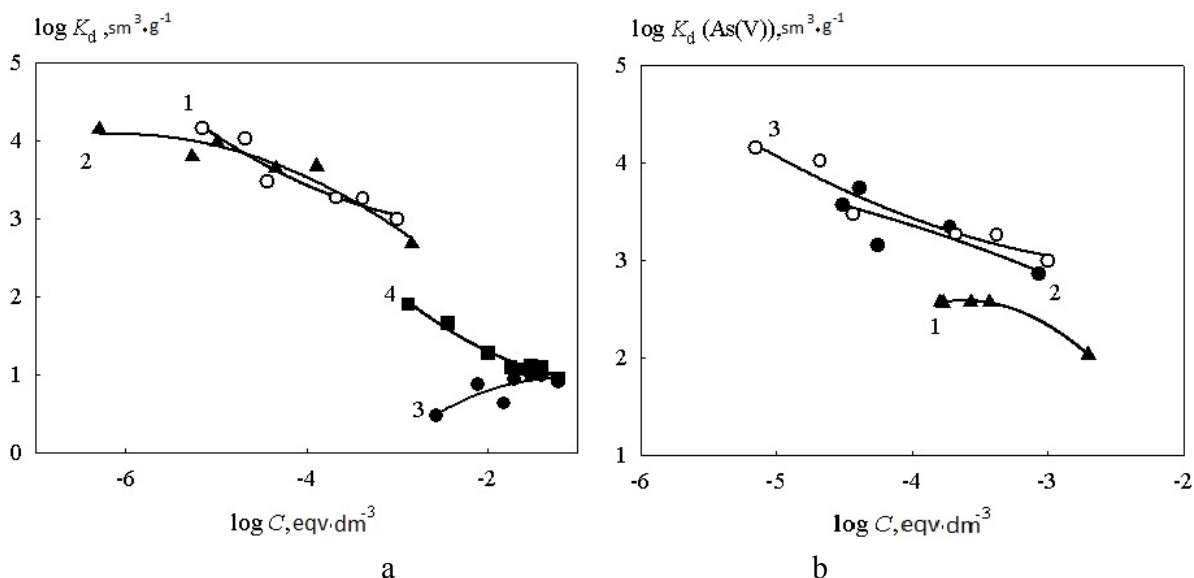


Fig. 3. Dependences of the logarithm of the distribution coefficient of the ионов $H_2AsO_4^-$ (1), $HCrO_4^-$ (2), Cd^{2+} (3), Pb^{2+} (4) ions on the logarithm of the equilibrium solution (Fig. 3, a) and $HAsO_4^{2-}$ ($H_2AsO_4^-$) ions at a pH value of 8-9 (1), 4-6 (2), 3-4 (3) (Fig. 3, b) for a double oxyhydrate of the composition $SnO_2-Al_2O_3$

As follows from the obtained results, the introduction of an inorganic component to the ion exchange resin decreases the adsorption capacity of ion-exchange resins with respect to Cu^{2+} ions and significantly increases the capacity with respect to Pb^{2+} and $HAsO_4^{2-}$ ($H_2AsO_4^-$) ions. When the initial solutions are acidified with nitric acid, the adsorption capacity of the polymeric anionite with respect to $HAsO_4^{2-}$ ($H_2AsO_4^-$) decreases significantly, but does not change with respect to $HCrO_4^-$. In Fig. 4 shows the logarithm of the distribution coefficient of the $HAsO_4^{2-}$ ($H_2AsO_4^-$) and $HCrO_4^-$ ions as a function of the logarithm of the equilibrium concentration for the anion exchange resin Dowex SBR-P and modified anion exchangers and hybrid anion exchangers containing tin oxyhydrate and tin-iron double oxyhydrate upon acidification of the solutions with nitric acid (pH of an equilibrium solution equal from 3 to 4).

Table 1. Adsorption characteristics of cation-exchange sorbents with respect to ions Cu^{2+} , Cd^{2+} , Pb^{2+} . A_{max} was determined from sorption of ion Pb^{2+}

Sorbent	Containing of the inorganic component, %	A_{max} , mg-equiv·g ⁻¹	K_d , sm ³ ·g ⁻¹		
			Cu(II)	Cd(II)	Pb(II)
TiO ₂	100	1,8	320	13200	18000
SnO ₂	100	1,1	14	-	2000
HCR-S	-	3,0	4900	5300	7000
HCR-S/TiO ₂	22	3,2	1000	-	12000
HCR-S/SnO ₂	12	3,1	-	-	10000

In this case, the K_d values of the organic-inorganic adsorbents are conserved, probably due to the buffer properties of the oxyhydrates. A similar result was obtained for the adsorption of the organic-inorganic ionite Marathon-11/TiO₂ (14%) without acidification. The K_d value was 1300 cm³·g⁻¹ for the adsorption of the organic-inorganic ionite Marathon-11 / TiO₂ (at pH = 3.5), (for unmodified anion exchange resin this value is 250 cm³·g⁻¹) [10]. Thus, the possibility of a positive effect of inorganic constituents on sorption of arsenate ions in the presence of competing ions (in this case NO₃⁻) is shown by the addition of polyvalent metal oxyhydrates selective to oxygen-containing multiply charged anions.

Table 2. Adsorption characteristics of anion-exchange adsorbents with respect to HCrO_4^- and HAsO_4^{2-} (H_2AsO_4^-) ions. A_{max} was determined from sorption of ion HAsO_4^{2-} (H_2AsO_4^-)

Adsorbent	Containing of the inorganic component, %	A_{max} , $\text{mg}\cdot\text{eqv}\cdot\text{g}^{-1}$	K_d , $\text{cm}^3\cdot\text{g}^{-1}$	
			Cr(IV)	As(IV)
$\text{ZrO}_2\text{-Al}_2\text{O}_3$	100	0,60	13000	2700
$\text{SnO}_2\text{-Al}_2\text{O}_3$	100	0,40	5000	4000
SBR-P	-	0,77	7300	1100
SBR-P/ ZrO_2	2	0,80	-	1900
SBR-P/ Fe_2O_3	6	0,80	-	2200
SBR-P/ SnO_2	51	0,83	20000	2000
SBR-P/ $\text{SnO}_2\text{-Fe}_2\text{O}_3$	34	0,85	55000	3200
SBR-P/ $\text{ZrO}_2\text{-Fe}_2\text{O}_3$	8	0,80	-	4000

In Fig. 5 shows the dependence of the absorption of the target component (H_3BO_3 , As (V)) from the solution of the complex composition on the equilibrium pH value for ion exchange resins, HDZ and organic-inorganic sorbents based on Dowex SBR-P ion exchanger and hydrated double zirconium and iron oxides [10].

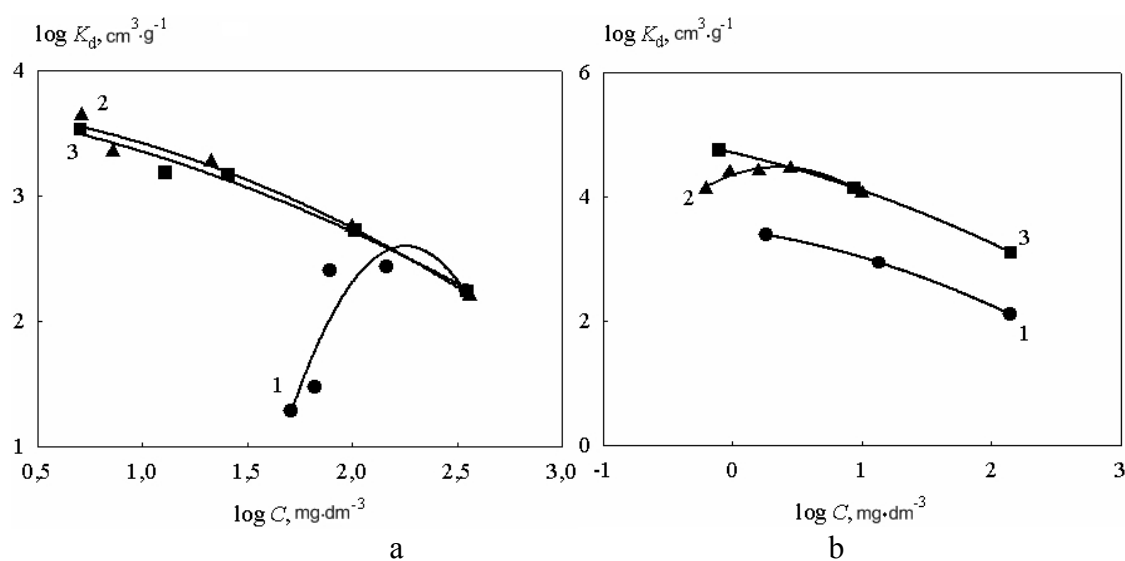


Fig. 4. Dependences of the logarithm of the distribution coefficient of the HAsO_4^{2-} (H_2AsO_4^-) (a), HCrO_4^- (b) ions on the logarithm of the equilibrium concentration for the anion exchange resin Dowex SBR-P (1) and anion exchangers containing tin oxyhydrate (2) and tin-iron double oxyhydrate (3)

At the same equilibrium concentration, the ratio of the distribution coefficients of the absorbed components (selectivity coefficient) approximately corresponds to the ratio of the sorption capacity. For ion-exchange resins, the value of selectivity coefficient of the extraction of the target component with respect to the chloride ions is in the first approximation the ratio of the initial salt concentration (NaCl , KCl) and the target component in the solution. These results (see Table 3) confirm the absence of selectivity for strongly basic resins and a sufficiently high selectivity of oxyhydrates and hybrid adsorbents on their basis.

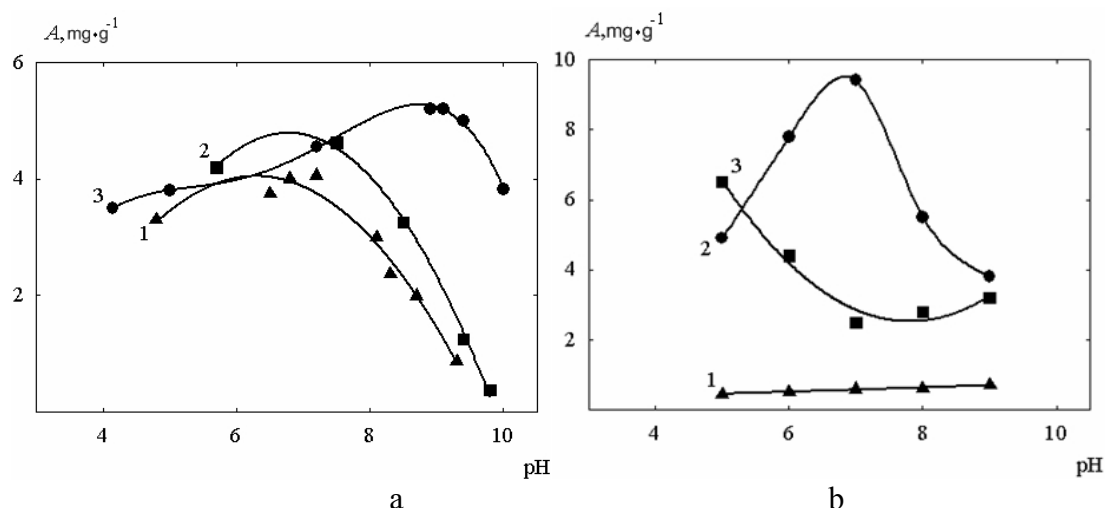


Fig. 5. Effect of pH of the solution on the sorption capacity of anion-exchange resins (a: 1 – AN-31, 2 – EDE-10P; b: 1 – Dowex SBR-P), HDZ (a: 3) and organic-inorganic anion exchangers (b: 2 – Dowex SBR-P/ZrO₂, 3 – Dowex SBR-P/Fe₂O₃) upon sorption from model solutions containing H₃BO₃ against sodium (a) and HAsO₄²⁻ against the background of potassium chloride (b)

Anion exchange resin Dowex SBR-P is regenerated by 54% after the establishment of sorption equilibrium sorbent solution Na₂HAsO₄. The results of the regeneration of organo-inorganic sorbents after sorption of arsenate ions are given in Table 4. For most organo-inorganic anion exchangers, a recovery of up to 70-80% of the capacity occurs, which makes it possible to predict the possibility of their reusable use.

Table 3. The evaluation of the selectivity of ion exchangers for the target component (H₃BO₃, HAsO₄²⁻) with respect to chloride ion

Ionite	Composition of solution number 1	Composition of solution number 2	Capacitance 1 /Capacitance 2 (of the target component)	The ratio of partial ion concentrations in ion and in solution number 2
AN-31	0,004 M H ₃ BO ₃	0,02 M NaCl 0,004 M H ₃ BO ₃	24/4,0	1,0
EDE-10P	0,004 M H ₃ BO ₃	0,02 M NaCl 0,004 M H ₃ BO ₃	26/4,3	1,0
HDZ	0,004 M H ₃ BO ₃	0,02 M NaCl 0,004 M H ₃ BO ₃	7,5/4,3	3,4
Dowex SBR-P	0,001 M NaH ₂ AsO ₄	0,1 M KCl 0,001 M Na ₂ HAsO ₄	50/0,6	1,2
Dowex SBR-P /ZrO ₂	0,001 M NaH ₂ AsO ₄	0,1 M KCl 0,001 M Na ₂ HAsO ₄	55/9,3	17,1
Dowex SBR-P /Fe ₂ O ₃	0,001 M NaH ₂ AsO ₄	0,1 M KCl 0,001 M Na ₂ HAsO ₄	54/2,5	4,7

The obtained results can be explained by the fact that in the case of adsorbents based on Zr (IV), Ti (IV), Sn (IV) oxides, the adsorbate forms outer-surface complexes containing fragments of water with the surface [11]. Iron oxide impairs regeneration. In this case, the regeneration of ion-exchange adsorbents is difficult and requires higher concentrations of regenerating reagents (during chemical regeneration) and/or energy consumption (with thermal or electrochemical regeneration).

Table 4. Regenerability of organic resins and organo-inorganic ion exchangers with 0.1 M by NaOH after sorption of HAsO_4^{2-}

Ion exchanger	Containing of the inorganic component, %	Regeneration, %
Dowex SBR-P	0	69
Dowex SBR-P/ ZrO_2	1,5	92
Dowex SBR-P/ ZrO_2	2,0	75
Dowex SBR-P/ $\text{ZrO}_2/\text{Fe}_2\text{O}_3$	6,0	76
Dowex SBR-P/ $\text{ZrO}_2/\text{Fe}_2\text{O}_3$	8,0	70
Dowex SBR-P/ Fe_2O_3	10,0	3
Dowex SBR-P/ SnO_2	51,6	42
Dowex SBR-P/ $\text{SnO}_2/\text{Fe}_2\text{O}_3$	34,8	51

CONCLUSIONS

It was found that the introduction of individual and double oxyhydrates Zr (IV), Ti (IV), Sn (IV), Fe (III) into organic ionites leads to an increase in sorption capacity with respect to Pb^{2+} , CrO_4^- , HAsO_4^{2-} ions and a decrease with respect to Cu^{2+} ions. The possibility of a positive effect on the value of the sorption capacity of organic anion exchangers with respect to HAsO_4^{2-} under conditions of the presence of competing nitrate ions is shown by the addition of polyvalent metal oxyhydrate selective oxygen-containing multiply charged anions. The results of studies in model solutions of complex composition confirm the absence of selectivity in organic ion exchangers and a sufficiently high selectivity of inorganic sorbents and organo-inorganic ion exchangers. The regenerability of organo-inorganic sorbents is comparable and even higher than that of organic resins. With a relatively small amount of the introduced inorganic component, a recovery of up to 70-80% of the capacity occurs, which makes it possible to predict their effective use in multi-cycle operation modes. The regenerability of organo-inorganic sorbents containing only iron oxide under similar conditions is close to zero. In this case, the regeneration of ion-exchange adsorbents is difficult and requires higher concentrations of regenerating reagents (during chemical regeneration) and / or energy consumption (with thermal or electrochemical regeneration).

АДСОРБЦІЯ АРСЕНУ, ХРОМУ, СВИНЦЮ, КАДМІЮ АДСОРБЕТАМИ НА ОСНОВІ ОКСИДІВ Zr (IV), Ti (IV), Sn (IV), Al (III), Fe (III)

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Вивчено адсорбцію іонів As (V), Cr (VI), Cu (II), Cd (II), Pb (II) неорганічними та органо-неорганічними адсорбентами на основі гідратованих оксидів Zr (IV), Ti (IV), Sn (IV), Al (III), Fe (III) і розраховані величини коефіцієнтів розподілу. Введення індивідуальних та подвійних оксигідратів Zr (IV), Ti (IV), Sn (IV), Fe (III) у органічні іоніти призводить до збільшення сорбційної здатності відносно Pb^{2+} , CrO_4^- , HAsO_4^{2-} іони та зменшення відносно іонів Cu^{2+} . Виявлена висока селективність оксидів і органо-неорганічних адсорбентів у присутності однозарядних конкуруючих іонів. Показана можливість позитивного впливу на величину сорбційної ємності органічних аніонообмінників щодо HAsO_4^{2-} в умовах присутності конкуруючих нітрат-іонів шляхом додавання селективного полівалентного оксигідрату металу. Результати досліджень в двокомпонентних модельних розчинах підтверджують відсутність селективності в органічних іонітах та досить високу селективність неорганічних сорбентів та органо-неорганічних іонообмінників. Здатність до регенерації

органо-неорганічних сорбентів порівняннi i навіть вища, ніж у органічних смол. При відносно невеликій кількості введеного неорганічного компонента відбувається відновлення до 70-80% ємності, що дозволяє прогнозувати їх ефективне використання в режимах багатоступеневої експлуатації. Регенеруємість органo-неорганічних сорбентів, що містять лише оксид заліза в аналогічних умовах, близька до нуля. У цьому випадку регенерація іонообмінних адсорбентів є складною i вимагає більшої концентрації регенеруючих реагентів (під час хімічної регенерації) та / або споживання енергії (з термічною або електрохімічною регенерацією). Знайдено, що в разі застосування в складі органo-неорганічних адсорбентів гідратованих оксидів Zr (IV), Ti (IV), Sn (IV) адсорбат утворює з поверхнею зовнішньосферні комплекси. Застосування в якості неорганічного компоненту адсорбенту оксиду Fe (III) призводить до утворення внутрішньосферних комплексів. У цьому випадку регенерація іонообмінних адсорбентів ускладнена та для неї потрібні більш високі концентрації регенеруючих реагентів i/або енерговитрати.

Ключові слова: адсорбція, коефіцієнт розподілу, арсен, свинець, органo-неорганічний адсорбент, оксид, багатовалентний метал.

АДСОРБЦІЯ МЫШЬЯКА, ХРОМА, СВИНЦА, КАДМИЯ АДСОРБЕНТАМИ НА ОСНОВЕ ОКСИДОВ Zr(IV), Ti(IV), Sn(IV), Al(III), Fe(III),

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Изучена адсорбция ионов As(V), Cr(VI), Cu(II), Cd(II), Pb(II) неорганическими и органo-неорганическими адсорбентами на основе гидратированных оксидов Zr(IV), Ti(IV), Sn(IV), Al(III), Fe(III) и рассчитаны величины коэффициента распределения. Обнаружена высокая избирательность оксидов и органo-неорганических адсорбентов в присутствии однозарядных конкурирующих ионов. Найдено, что в случае применения в составе органo-неорганических адсорбентов оксидов Zr(IV), Ti(IV), Sn(IV) адсорбат образует с поверхностью внешнесферные комплексы. Применение в качестве неорганической компоненты адсорбента оксида Fe(III) приводит к образованию внутрисферных комплексов. В этом случае регенерация ионообменных адсорбентов затруднена и для нее требуются более высокие концентрации регенерирующих реагентов и/или энергозатраты.

Ключевые слова: адсорбция, коэффициент распределения, мышьяк, свинец, неорганo-органический адсорбент, оксид, многовалентный металл.

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