
PHYSICAL CHEMISTRY
OF WATER TREATMENT PROCESSES

Hybrid Adsorbents Based on Hydrated Oxides of Zr(IV), Ti(IV), Sn(IV), and Fe(III) for Arsenic Removal

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Received September 14, 2016

Abstract—Synthesized are hybrid organoinorganic adsorbents based on organic resins Dowex SBR-P, Dowex Marathon II and hydrated oxides Zn(IV), Ti(IV), Sn(IV) and Fe(III). Specific conductivity was measured of the specified resins and hybrid organoinorganic adsorbents in the initial form and after absorption of ions As(V) from 10^{-2} M aqueous solution of NaH_2AsO_4 . Introduction of hydrated tin oxide increases ionic conductivity of organic resin Dowex SBR-P by 2.5 times. During the conversion to the arsenate form the conductivity of hybrid adsorbents changes insufficiently at the adsorption from the solution with pH 7 and increased by 2–10 times at adsorption from the solution with pH 2.

DOI: 10.3103/S1063455X17040063

Keywords: arsenate-ions, hydrated oxides of multivalent metals, ionic conductivity, organoinorganic ion-exchange adsorbents.

INTRODUCTION

For increasing the efficiency of continuously gradient-controllable processes of target purification of dissolved aqueous solutions of valuable or toxic ions important is the synthesis of ion-exchange adsorbents ensuring high mobility of ions being removed at preserving selectivity of absorption [1–3]. Individual and complex hydrated compounds based on metal oxide of group IV of the periodic system of elements— MO_2 (M—Zr(IV), Ti(IV) and Sn(IV)) and hybrid adsorbents on their basis are characterized by selectivity with respect to multi-charged cations manifesting affinity to oxygen of surface hydroxyl groups of oxides and also with respect to multi-charge anions [4–6]. In this case, as was shown earlier [7], constitutional and adsorbed water on the surface of structural fragments of such fragments determines rather high mobility of adsorbed ions, good kinetics and reversibility of adsorption.

The objective of the present study is determination of the influence of surface modification of ion-exchange resins by hydrated oxides (hydr)oxides, oxihydrates) of multivalent metals on conductivity and mobility of adsorbed ions As(V).

As is known, arsenic is a natural element and its concentration in natural water is linked with geochemical conditions in this case out of two natural forms of this element (trivalent and pentavalent) more spread, hazardous and hardly removable is considered As(III). A rational technological solution of the issue is the removal from water of both forms of arsenic and the employment in water treatment of iron compounds in the form of salts, oxide granules or zerovalent iron [8]. However, in this case the possibility of regeneration of filtration material, concentration and a repeated use of both arsenic and other toxic or valuable components of aqueous solutions is ruled out. A principally new solution is the use of hybrid adsorbents based on hydrated metal oxides of group IV of the periodic system of elements— MO_2 (M—Zr(IV), Ti(IV) and Sn(IV)) manifesting selectivity to multicharged anions [5, 6, 9] determined by the surface charge of spatial tetrahedrons MO_6 [10] at preserving sufficient mobility of adsorbed ions.

Organic anion-exchangers Dowex SBR-P and Dowex Marathon were chosen as an organic matrix. The organic matrix is a carrier for an inorganic component and improves hydrodynamic characteristics of the absorption process and desorption; in addition in the case of using anion exchangers it possesses its own adsorption capacity with respect to arsenate-ions [5].

The choice of hydrated oxides (oxihydrates) of multivalent metals as a selective components of hybrid adsorbents is determined by their rather high selectivity with respect to arsenate-ions and good kinetic characteristics [4]. The formation of heterovalent complex oxides, as was shown earlier [9], substantially increases

mobility of adsorbed ions therefore hybrid adsorbents containing coprecipitated hydroxides Zr(IV) and Fe(III), Sn(IV) and Fe(III) were investigated too.

EXPERIMENTAL

The synthesis of hybrid composite materials was carried out according to the sol-gel method from solutions of corresponding salts or mixture of salts in the ratio 1 : 1 [5, 6].

The specific surface S and parameters of the porous structure of individual hydrated oxides were calculated from the data obtained by the method of thermal desorption of nitrogen (TDA) by means of a device Autp-sorb-6 (USA). Before measuring adsorption and desorption of nitrogen samples were activated in the nitrogen stream at 150–190°C for two hours. The concentration of structurally bound water was determined from derivatograms taken on a device Derivatograph Q-1500 D Paulik&Paulik (Hungary) in the mode heating stove 5°C/min.

The determination of the amount of the inorganic component was made according to the standard technique [12]. For calculating the efficient conductivity in the diluted solution ($C \approx 0$) and mobility of adsorbed ions the resistance of granules of organic resins and hybrid adsorbents (fractions 0.2–0.5 mm) were measured in the frequency range 10^{-3} – 10^5 Hz. For this purpose impedance spectra were taken on an electrochemical module PGSTAT302N Metrohm Autolab in a cell of a capacitor type with a titanium-platinized electrodes of 4.8 cm^2 each at a distance 0.8 cm in the presence of an equilibrium solution. Dependences of specific conductivity on the concentration of the equilibrium solution were extrapolated to the Y-axis for obtaining the value of the effective conductivity in distilled water modeling a heavily diluted solution.

The value of effective mobility of adsorbed ions \bar{u}_i was calculated from the value of conductivity in distilled water by conductivity the general equation of electrical conductivity allowing for the contribution of hydroxyl ions and hydroxonium ions similar to [7]:

$$\bar{u}_i = \kappa_i \cdot (z \cdot F \cdot X_i \cdot 0.6)^{-1},$$

where κ_i is specific conductivity of the adsorbent granules after adsorption of arsenate-ions from the 0.01 M solution, $\text{S} \cdot \text{m}^{-1}$; F —is Faraday's constant, $\text{C} \cdot \text{mol}^{-1}$; $z = 2$ —charge of the adsorbing ion; 0.6—the coefficient of filling the volume of the solid phase accepted for ball-shaped particles' X_i —volumetric concentration of centers occupied with ions of the given type i , $\text{mol} \cdot \text{m}^{-3}$ determined as

$$X_i = A \cdot p,$$

where A is a number of absorbed ions, $\text{mol} \cdot \text{g}^{-1}$; p is the bulk density of the adsorbent, $\text{g} \cdot \text{cm}^{-3}$.

RESULTS AND DISCUSSION

Table 1 gives values of the specific surface S , fractions of micropores $V_m \cdot V^{-1}$ and also of prevailing (r_1) and average (r_2) radii of some inorganic oxyhydrates.

Table 1. Properties of the surface of inorganic ion-exchange adsorbents

(Hydr)oxide, $\text{MO}_2 \cdot n\text{H}_2\text{O}$	$S, \text{m}^2 \cdot \text{g}^{-1}$	$V_m \cdot V^{-1}, \%$	r_1	r_2
			nm	
ZrO ₂	53	3	2.3	3.8
SnO ₂	94	28	—	—
TiO ₂	289	80	1.7	2,2

The specific surface and micropore fractions in the row increase. The charge of individual (hydr) oxides in neutral solutions determined by the method of pH-potentiometric titration is close to neutral (the point of the zero charge varies from 4 units of the pH in SnO₂ to 6–7 units of the pH in ZrO₂ and TiO₂). According to the data of thermogravimetry the content of formula water in individual (hydr)oxides constitutes two or three molecules in terms of one structural unit.

Figure 1 show the relationships between the concentration of the inorganic component as part of hybrid adsorbents and the number of precipitation cycles.

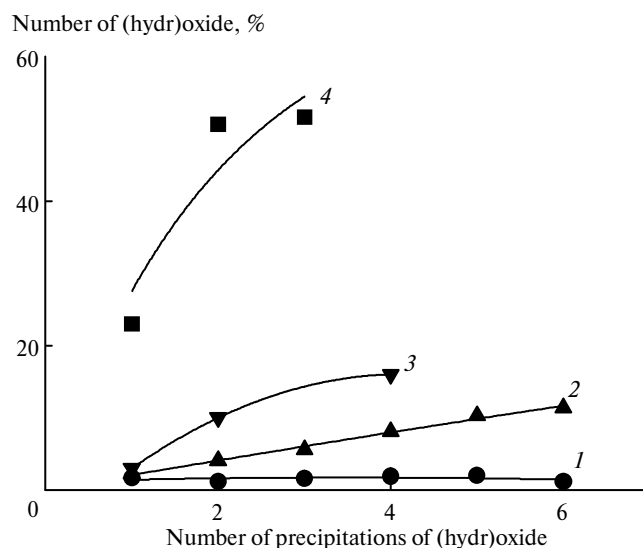
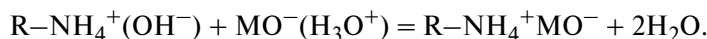


Fig. 1. Dependencies of the amount of (hydr)oxides, introduced to anion-exchanger Dowex Marathon 11 (titanium oxide) and Dowex SBR-P (all the rest) on the number of precipitation cycles: 1—ZrO₂; 2—Fe₂O₃; 3—TiO₂; 4—SnO₂.

Attention is drawn to the unequitable degree of interaction between organic and inorganic matrices, which is expressed in a decrease of the amount of the introduced inorganic component in the following series of oxides: SnO₂ > TiO₂ > Fe₂O₃ > ZrO₂. This may be related to the difference in the amount of the structural and physical adsorption water (the greater amount of it, the less is interaction) and also with the size of particle being precipitated.

Analyzing the obtained data one may presume that electrostatic interaction of the organic and inorganic matrices plays a substantial role in precipitation of hydroxides in organic resin. The charge of the surface of organic resins is positive while by the results of interaction between organic and inorganic matrices one may presume that under conditions of precipitation the surface charge of oxides of iron, zirconium and titanium is positive while that of tin oxide—most likely is negative according to the provision of the point of the zero charge of these oxides [12]. The interaction of the organic and inorganic matrices may be presented as follows:



Dependence of the effective specific conductivity of hybrid adsorbents on the number of inorganic component in the initial form is given in Fig. 2. Conductivity of resin Dowex SBR-P constitutes 0.038 S · m⁻¹.

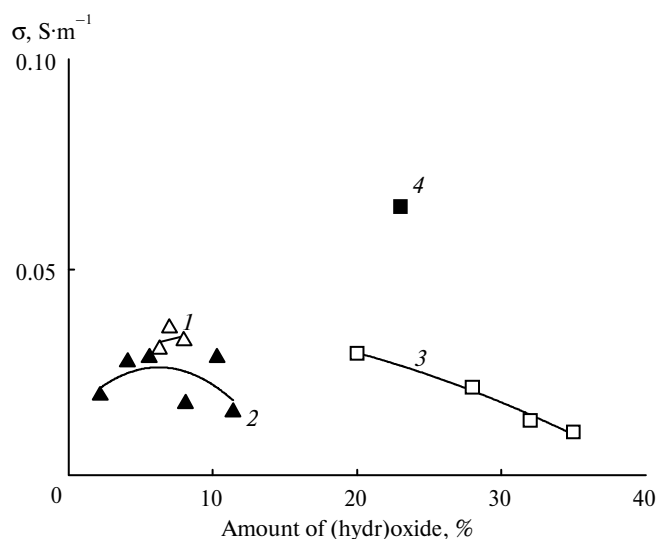


Fig. 2. Relationships between specific conductivity of hybrid adsorbents in initial form and the amount of introduced inorganic component: 1—ZrO₂/Fe₂O₃; 2—Fe₂O₃; 3—SnO₂/Fe₂O₃; 4—SnO₂.

As follows from the obtained data coprecipitation of oxides with different valence does not increase specific conductivity of hybrid adsorbents; measured values are comparable with such obtained in precipitation of individual oxyhydrates.

By the results of measuring maximum conductivity in wand of organic resins and hybrid adsorbents (see Fig. 2) one may come to a conclusion that introduction of (hydr)oxides of multivalent metals in most cases diminishes ionic conductivity of organic anion-exchangers in the initial form. Similar data were obtained also for the particles polymer anion-exchange membrane [13] and also for cation-exchange resin modified by aggregates of nanoparticles of zirconium phosphate [14]. Introduction of individual tin oxyhydrate in the amount of 23% dose not affect the value of specific conductivity of anion-exchangers Dowex SBR-P and precipitation of tin oxyhydrate in the amount of 50–53% results in its growth to up $0.1 \text{ S} \cdot \text{m}^{-1}$. Such an increase of conductivity can be explained by comparatively large amount of introduced amphoteric oxyhydrate sufficient for the formation of conductivity chains along hydroxyl ions between organic and inorganic ion-exchangers.

Figure 3 gives fragments of the Nyquist diagram and the equivalent pattern of the impedance of granules of hybrid adsorbents in distilled water for conditions: adsorption of adsorbate-ions from 10^{-2} M of the solution NaH_2AsO_4 (pH 7). In treating experimental data of the impedance by the equivalent pattern shown in Fig. 3 the relative error does not exceed 4%.

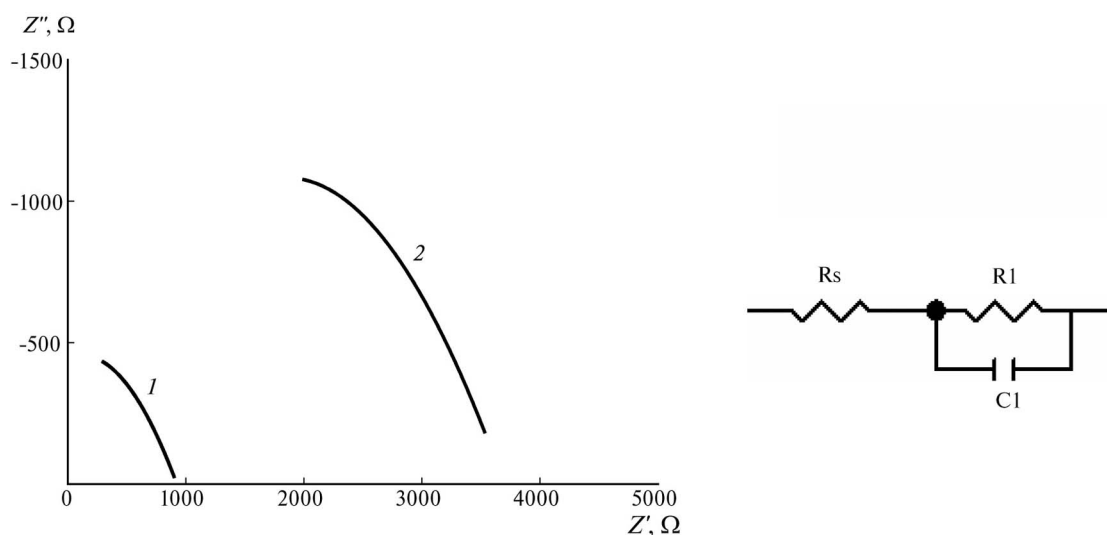


Fig. 3. Dependence of the imaginary part the complex resistance on the real part (Nyquist diagram) (a); the equivalent scheme of the impedance of granules of hybrid adsorbents in distilled water (b) for conditions: adsorption of arsenate-ions from the solution with the pH 7, potential difference on electrodes—3 V. (a) 1—Dowex SBR-P/SnO₂/Fe₂O₃ 20%), 2—Dowex SBR-P/SnO₂ (51%); (b) R_s —resistance of the solution, R_1 —resistance of the sorbent granules, C_1 —capacity of the double layer.

Indicated Nyquist diagrams show that active resistance of granules being determined by volumetric concentration and mobility of adsorbed ions is dissimilar for different adsorbents although at the final calculation of specific conductivity other factors, as, for instance, the degree of filling the measuring cell.

Table 2 shows the values of adsorption A , the bulk density p , volumetric concentration of ions X , specific conductivity σ and the effective mobility of adsorbed arsenate-ions \bar{u}_i for $z = 2$ t absorbing from 10^{-2} M solution NaH_2AsO_4 (pH 7).

As follows from the obtained data the introduction of the inorganic component to organic anion-exchangers increases the volumetric concentration of arsenate-ions X at absorption from the solution with a relative high initial concentration (up to 1 g of arsenate-ions in 1 dm^3) and in some cases—even in great measure. For instance, the introduction of the inorganic component in the form of tin oxyhydrate makes it possible to increase the volumetric concentration of arsenate-ions in the phase of adsorbent by more than two fold. At absorbing arsenate-ions from the neutral solution one cannot notice any discernable changes in the value of ionic conductivity of adsorbents. It may be preconditioned by comparatively small contribution of arsenate-ions to the value of conductivity due to nonoptimal conditions of absorption for the inorganic component. To increase the contribution of arsenate-ions to the value of ionic conductivity it is necessary to carry out adsorp-

tion from the solution with a lower value of the pH. The effective mobility of adsorbed arsenate–ions increases maximally at the introduction of titanium–oxyhydrate, which may be explained by high concentration of intracrystalline water [8].

Table 2. Adsorption, bulk density, volumetric concentration, effective conductivity of hybrid adsorbents and mobility of adsorbed arsenate–ions for $z = 2$

Adsorbent	$A, \text{mg}\cdot\text{g}^{-1}$	$p, \text{g}\cdot\text{cm}^{-3}$	$X, \text{mol}\cdot\text{m}^{-3}$	$\sigma, \text{S}\cdot\text{m}^{-1}$	$\bar{u}_i \times 10^{-9}, \text{m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$
Dowex SBR-P	63	0.69	580	0.011	0.2
ZrO ₂ (1%)	64	0.71	606	0.038	0.5
ZrO ₂ (7%)	78	0.75	780	0.009	0.1
SnO ₂ (23%)	71	0.86	814	0.010	0.1
SnO ₂ (51%)	79	1.03	1085	0.006	0.1
SnO ₂ (52%)	82	1.27	1389	0.012	0.1
Fe ₂ O ₃ (12%)	67	0.74	661	0.017	0.2
TiO ₂ * (10%)	65	0.70	607	0.027	0.4
TiO ₂ * (14%)	72	0.71	682	0.033	0.4
ZrO ₂ /Fe ₂ O ₃ (6%)	64	0.70	597	0.017	0.2
ZrO ₂ /Fe ₂ O ₃ (8%)	58	0.71	549	0.015	0.2
SnO ₂ /Fe ₂ O ₃ (20%)	80	0.81	864	0.013	0.1

*Organic matrix: Dowex Marathon 11.

Figure 4 shows dependencies of the effective conductivity of the arsenate-form of hybrid anion–exchangers on the amount of the inorganic component at absorption of arsenate–ions from solutions with the initial value of pH 2.

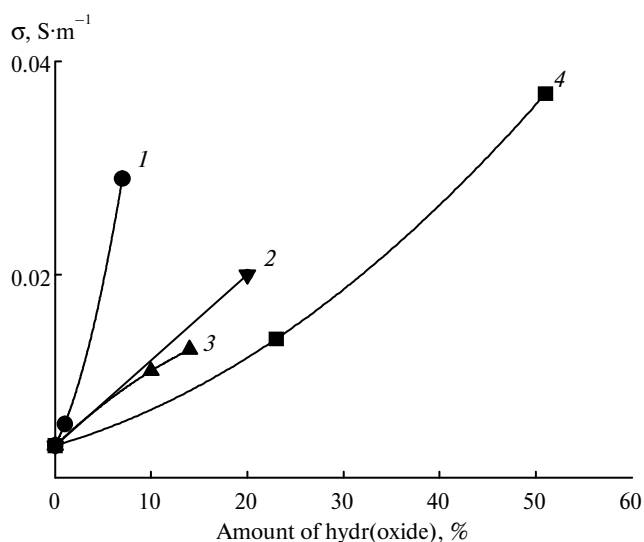


Fig. 4. Dependence of conductivity of arsenate form of hybrid anion–exchangers on the amount of inorganic component at absorption of arsenate–ions from solutions with the initial value of the pH 2: 1—ZrO₂; 2—SnO₂/Fe₂O₂; 3—TiO₂; 4—SnO₂.

Obtained results confirm the assumption about the dependence of ionic conductivity of hybrid adsorbents in the arsenate form on the conditions of ion absorption mainly on the pH value. The maximum of absorption of ions by oxyhydrates of metals of group IV is determined by the position of the point of the zero charge and the ionic potential of oxideforming metal, but, in any case, it is located in the area of pH values lower than neutral ones.

In conclusion it should be added that dissolution and transfer to the water medium of elements of oxides is not observed.

CONCLUSIONS

Introduction of oxides of multivalent metals into organic resins diminishes ionic conduction of hybrid conduction of organic anion-exchangers in the initial form. An exception is hydrated tin oxide whose introduction increases the ionic conductivity of organic resin 2–3 times. Conductivity of arsenate form of hybrid adsorbents depends on the pH of the solution, from which the adsorption was conducted: at a decrease of the equilibrium value of the pH from 7 to 2 the conductivity of arsenate form of hybrid anions increases 2–10 times. Obtained results allow us predicting the lowering of power costs on gradient-controllable processes of removing arsenate-ions for these conditions. Possessing the property of conduction and high values of mobility of adsorbed ions, hybrid adsorbents based on oxyhydrates of metals Zn, Sn and Ti at superposition of the electric field may be effective in electrodeionization schemes of water purification of arsenic anions.

REFERENCES

1. Alvarado, L., Ramirez, A., and Rogrigez-Torres, I., *Desalination*, 2009, vol. 249, no. 1, pp. 423–428.
2. Perez J., Toledo, L., Campos, C., et al., *Chem. Eng. J.*, 2016, vol. 287, pp. 744–754.
3. Dzyazko, Yu.S., Ponomaryova, L.N., Volfkovich, Yu.M., et al., *Separ. Sci. Technol.*, 2013, vol. 48, no.14, pp. 81–84..
4. Pechenyuk, S.I., *Successes of Chemistry*, 1992, vol. 61, issue 4, pp. 711–733.
5. Kolomiets, E., Belyakov, V.N., Pal'chik, A.V., et al., *Ukr. Khim. Zhurn.*, 2014, vol. 80, no. 10, pp. 81–84.
6. Kolomiets, E., Belyakov, V.N., Pal'chik, A.V., et al., *Ibid.*, 2015, vol. 81, no. 9, pp. 25–29.
7. Mal'tseva, T.V., Pal'chik, A.V., Kudelko, E.O., et al., *J. Water Chem. and Technol.*, 2015, vol. 37, no. 1, pp. 8–24.
8. Shtripling L.O., and Turenko, F.P., *Fundamentals of wastewater purification and reprocessing of solid wastes, Manual*, Omsk: Izd-vo GTU, 2005.
9. Kudelko, E.O., *Author's abstract of dissertation of the candidate of chemical Sci., Institute of general and inorganic chemistry, NAN of Ukraine, Kiev*: 2013.
10. Moller, T., *Selective crystalline inorganic materials ion exchanger in a treatment of nuclear waste solutions*, Thesis Academic Dissertation, Helsinki, 2002.
11. *GOST 2642.2-86. Metody izmeneniya massy pri prokalivanii* (Methods of Determining the Change of Weight in Calcination), introduced on June 39, 1987.
12. Parks, G.A., *Chem. Rev.*, 1965, no. 65, pp. 177–198.
13. Dzyazko, Yu.S., Ponomaryova, L.N., Volfkovich, Yu. M., et al., *Micropor. and Mesopor. Mat.*, 2014, vol. 198, pp. 55–62.
14. Dzyazko, Yu., Rozhdestvenskaya, L., Zmievsii, Yu., et. al., *Materials Today: Proceedings*, 2015, vol. 2, no. 6, pp. 3864–3873.

Translated by A. Kozij