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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Influence of the Composition of Double Oxyhydrates $M_xMn_{1-x}O_2 \cdot nH_2O$ (M^{z+} = Zr, Al, Sn, Ti) on the Sorption Activity and Cation Mobility

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Abstract—Adsorption of Cr(VI) on Fe_2O_3 from model solutions with various Cr(VI) concentrations was studied. The adsorption capacity was determined, the constants of chromium(VI) adsorption on iron(III) oxide for the pseudo-second-order model were calculated, and the diffusion coefficients for the process were evaluated.

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Commonly used ion-exchange processes for water treatment have numerous drawbacks. The weight of substances formed in the course of regeneration of ion-exchange installations and discharged into sewage is by an order of magnitude higher than the weight of substances recovered from solutions being treated. Membrane processes for treatment of dilute aqueous solutions are an environmentally safe alternative to the classical ion exchange. An advanced electrodialysis process is electrodeionization (EDI), in which, in treatment of solutions containing less than 1 g l^{-1} salts, granulated sorption-active intermembrane fillers are used to reduce power consumption and improve mass transfer [1].

It was demonstrated recently that EDI can be efficiently used for recovering certain metal ions: cesium(I) from process solutions [2, 3]; copper(II) and nickel(II) from electroplating wash waters [4–6]. Comparison of a series of organic and inorganic phosphate-containing ion-exchange fillers showed that, in some cases, specifically the sorption selectivity characteristic of inorganic ion exchangers gives rise to the selectivity in electrolytic transport of the sorbed ions [3]. The use of this effect allows not only selective recovery but also separation of ions, e.g., of sodium and cesium. There are virtually no data on the use of another class of inorganic ion exchanges, oxide and oxyhydrate adsorbents, in a selective EDI process for recovery of ions and ionized substances.

In this study we examined the sorption properties of inorganic ion exchangers based on amorphous oxyhydrates Al_2O_3, ZrO_2, SnO_2, and TiO_2 and containing a proton-donor component, hydrated manganese dioxide (MnO_2), and the mobility of sorbed ions in these materials. The sorbents were synthesized via gelation. When determining the composition of the synthesized sorption materials, we assumed that introduction of a proton-donor component into oxyhydrate adsorbents would cause redistribution of acid–base properties and change the sorption behavior toward prevalence of the cation-exchange function. Our goal was to compare the properties of the double oxyhydrates and assess their applicability in an EDI process.

EXPERIMENTAL

Oxyhydrate amorphous materials were prepared by joint precipitation of hydroxides from solutions of the corresponding chlorides. The synthesis procedure involved gelation, washing to remove excess salts, and drying at 70°C. The initial ratios of the introduced components in the synthesis were 1 : 1 and 1 : 3 (with the content of hydrated manganese dioxide indicated first). According to the results of thermal gravimetric analysis, the content of constitutional water in the double oxyhydrates obtained was 15–30%. The zero-charge point (ZCP) was determined by potentiometric titration in 0.12 M KNO_3 [7]. To examine the sorption properties of oxyhydrates, we used as adsorbates solutions of KNO_3, $CuCl_2$, $CdCl_2$, and $Pb(NO_3)_2$. The content of K^+, Cd^{2+}, and Pb^{2+} ions in solution was determined by atomic

Table 1. Cation-exchange properties of double oxyhydrates

Oxyhydrate composition	pH°	K_d, cm^3 g^{-1}			K_{u+}, mol mol^{-1}	A_{max}, mmol g^{-1}
		Pb(II)	Cd(II)	Cu(II)		
$ZrO_2 \cdot MnO_2 \cdot nH_2O$ (3:1)	4.7	31	_	20	0.0	1.3
$ZrO_2 \cdot MnO_2 \cdot nH_2O$ (1:1)	5.2	24	24	24	0.0; 0.4	0.7
$Al_2O_3 \cdot MnO_2 \cdot nH_2O$ (3:1)	5.7	91	_	43	0.0	1.0
$Al_2O_3 \cdot MnO_2 \cdot nH_2O$ (1:1)	5.1	78	35	29	0.0; 0.4	2.1
$SnO_2 \cdot MnO_2 \cdot nH_2O$ (3:1)	3.8	23	_	19	0.6	1.1
$SnO_2 \cdot MnO_2 \cdot nH_2O$ (1:1)	3.7	45	41	24	1.2	0.7
$TiO_2 \cdot nMnO_2 \cdot nH_2O$ (3:1)	3.9	35	_	18	0.0; 0.2	1.3
$TiO_2 \cdot nMnO_2 \cdot nH_2O$ (1:1)	4.2	46	35	35	1.4	0.9

adsorption spectroscopy, and the content of Cu^{2+} ions, spectrophotometrically at a wavelength of 812 nm. The concentration of the adsorbed ions was calculated from the difference between their concentrations in the initial and final solutions.

The sorption rate was estimated by comparison of the half-exchange times $t_{0.5}$ (s) of Cu(II) ions in sorption from 0.05 M $CuCl_2$ solutions. The choice of the solution concentration was governed by the fact that the limiting step of the sorption under these conditions is internal diffusion. The diffusion concentrations D were calculated by the equation [8]

$$D = 0.03 \frac{d^2}{4t_{0.5}}, \quad (1)$$

where d is the effective radius of oxyhydrate particles.

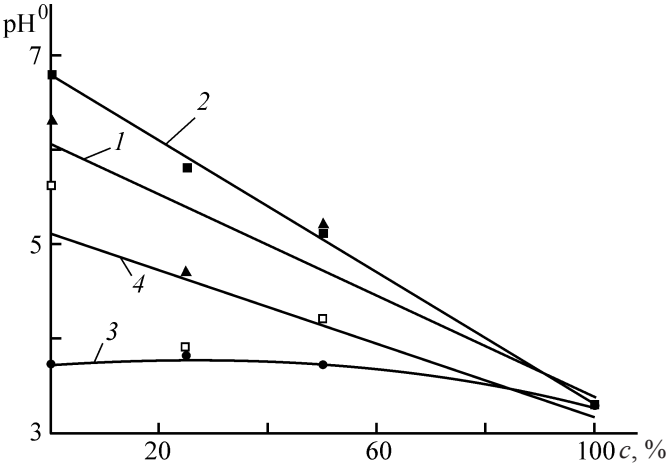

Fig. 1. Plot of ZCP of the surface vs. content of MnO_2 c in oxyhydrates $M_xMn_{1-x}O_y \cdot nH_2O$. M: (*1*) Zr, (*2*) Al, (*3*) Sn, and (*4*) Ti; the same for Figs. 2 and 3.

From the results of the kinetic experiments, using the Nernst–Einstein equation, we calculated the mobility of the adsorbed ions $\bar{u}_i$. To determine the mobility of the adsorbed cations, we also used data on the specific electrical conductivity of the oxyhydrates saturated with Cu(II) ions from 0.05 M $CuCl_2$ solutions. The resistance of oxyhydrate samples was measured in a capacitor-type cell with platinized titanium electrodes in the ac mode in the frequency range 10–100 kHz in the presence of an equilibrium solution. Then the solution concentration was made many times lower, and the measurements were repeated. The dependences of the specific electrical conductivity of the oxyhydrate on that of the solution were extrapolated to the ordinate to obtain the limiting specific electrical conductivity. The effective mobilities of ions absorbed by the oxyhydrates were calculated by the equation

$$\bar{u}_i = k/(z_i F X_i), \quad (2)$$

where $\bar{u}_i$ is the mobility of ith ion in the oxyhydrate phase (m^2 V^{-1} s^{-1}); k, specific electrical conductivity of the oxyhydrate (limiting value) (S m^{-1}); z_i, ion charge; F, Faraday constant (C mol^{-1}); X_i, volumetric concentration of ith ion in the oxyhydrate phase (mol m^{-3}), determined by the formula

$$X_i = A\rho, \quad (3)$$

where A is the amount of absorbed cations (mol g^{-1}) and ρ is the bulk density of the oxyhydrate (kg m^{-3}).

In studying the properties of double oxyhydrates, we first examined the effect of the proton-donor component on ZCP. Figure 1 shows the ZCP values (pH^0) of the

surface of individual and double oxyhydrates in relation to the content of MnO_2 introduced in synthesis. As can be seen, an increase in the amount of the proton-donor component leads to a shift of ZCP toward lower pH values and to an increase in the acidity of surface functional groups and in the share of cations in the total adsorption. The most pronounced changes in ZCP on introducing MnO_2 were observed with ampholytes (ZrO_2, TiO_2), whereas ZCP of the cation-exchange oxyhydrate SnO_2 was not noticeably affected by introducing MnO_2. The ZCP values and distribution coefficients of ions are given in Table 1.

It can be seen that the distribution coefficients of Cu(II) ions under experimental conditions were 20–40, and those of Cd(II) ions were 10–20% higher with all the oxyhydrates. The highest distribution coefficients were obtained with Pb(II) ions: 91 and 78 in sorption with Al_2O_3-based oxyhydrates containing MnO_2. For the majority of adsorption materials, the selectivity coefficient with respect to Cu(II) and Pb(II) ions is within 10–15, but for three adsorbents, $Al_{0.5}Mn_{0.5}\cdot nH_2O$, $Al_{0.75}Mn_{0.25}\cdot nH_2O$, and $Sn_{0.75}Mn_{0.25}\cdot nH_2O$, it increases to 30 with respect to lead ions. The close values of K_s toward both metals for the majority of adsorbents can probably be attributed to the microporous structure.

The results of studying the sorption interaction are presented in more detail in Fig. 2. These results allowed calculation of the stoichiometry of the ion-exchange reaction with Cu(II) cations. From the dependences obtained, we calculated the proton exchange constants for low and high degrees of filling of adsorption centers (Table 1). As can be seen, the majority of the results obtained are indicative of the high share of anion exchange in the total uptake. Exceptions are Sn : Mn = 1 : 1 and Ti : Mn = 1 : 1 sorbents which predominantly exhibit cation-exchange properties. It is known [9] that the mechanism of the uptake of transition metal ions by oxyhydrate adsorbents can involve adsorption of hydrolyzed species ($MeOH^+$) and surface hydrolysis of cations at low degrees of filling. Therefore, high selectivity of uptake of the examined ions by oxyhydrates with zero total charge and zero coefficients of proton exchange is most likely due to adsorption of hydrolyzed species. For oxyhydrates having negative surface charge under the conditions of the sorption experiment, this process is improbable, and the following reaction prevails:

$$2S{-}O^- + M^+ \leftrightarrows (S{-}O^-)_2M^{2+}. \qquad (4)$$

Apparently, in this case the charge of the external plate of the electrical double layer (EDL) is fully neutralized by cations from solution. With positively charged exchangeable groups, the anion uptake occurs simultaneously with the cation uptake:

$$(2S{-}OH^2)_n + A^- \leftrightarrows \begin{matrix}(SOH_2^+A^-)\\ |\\ (SOH_2^+)_{n-1}\end{matrix} \qquad (5)$$

As a result, the external plate of the EDL contains a large amount of anions. Considering the data shown in Fig. 2, it should be noted that, as the component ratio in the synthesis of double oxyhydrates is changed from 1 : 3 to 1 : 1, the cation-exchange function is enhanced, which leads to an increase in the stoichiometric coefficients of proton exchange for all the adsorbents.

Figure 3 shows the kinetic dependences of the adsorption of Cu(II) ions by double oxyhydrates, and Table 2 presents the mobilities of the adsorbed ions $\bar{u}$, calculated by formula (1) and by the Nernst–Einstein

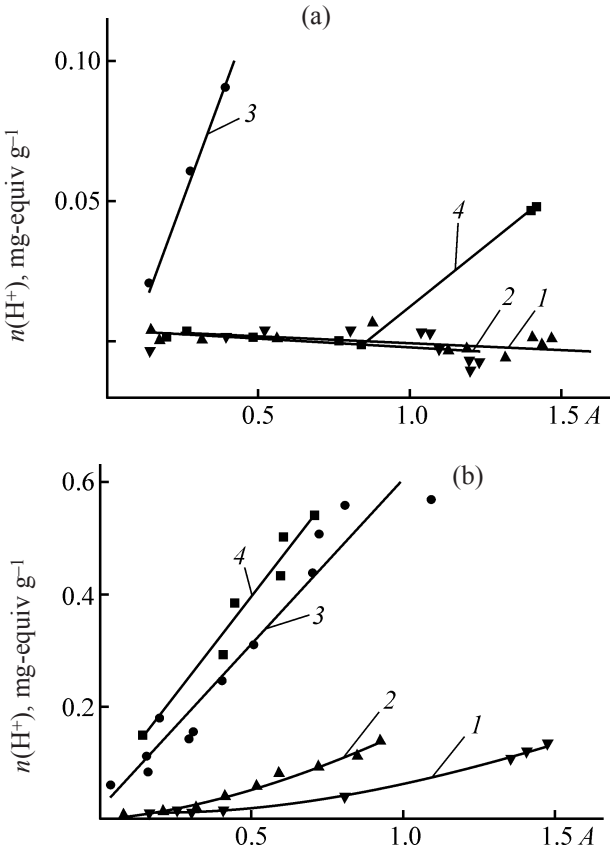

Fig. 2. Specific amount of H_3O^+ ions n(H^+) as a function of the degree of adsorption A of Cu(II) ions with oxyhydrates (a) $M_{0.75}Mn_{0.25}\cdot nH_2O$ and (b) $M_{0.5}Mn_{0.5}\cdot nH_2O$.

Table 2. Half-exchange time $t_{0.5}$, diameter of oxyhydrate particles d, and mobility of adsorbed Cu(II) ions $\bar{u}$

Oxyhydrate composition	$t_{0.5}$, min	$d \times 10^3$, m	$u \times 10^{-11}$, $m^2\ V^{-1}\ s^{-1}$
$ZrO_2 \cdot MnO_2 \cdot nH_2O$ (1:1)	110	0.2	0.5
$Al_2O_3 \cdot MnO_2 \cdot nH_2O$ (1:1)	11	0.1–0.2	0.9–3.6
$SnO_2 \cdot MnO_2 \cdot nH_2O$ (1:1)	52	0.2	0.7
$TiO_2 \cdot nMnO_2 \cdot nH_2O$ (1:1)	23	0.2	1.7
$ZrO_2 \cdot MnO_2 \cdot nH_2O$ (3:1)	8	0.2	4.8
$Al_2O_3 \cdot MnO_2 \cdot nH_2O$ (3:1)	3	0.1–0.2	3.1–12.4
$SnO_2 \cdot MnO_2 \cdot nH_2O$ (3:1)	23	0.20	1.7
$TiO_2 \cdot nMnO_2 \cdot nH_2O$ (3:1)	4	0.2	9.6

Table 3. Specific electrical conductivity σ and mobility of Cu(II) ions $\bar{u}$

Oxyhydrate composition	σ_2 ($\sigma_1 = 0$), S m^{-1}	ρ, g cm^{-3}	A, g-equiv g^{-1}	$u_{app} \times 10^{-11}$, $m^2\ V^{-1}\ s^{-1}$
$MnO_2 \cdot nH_2O$	0.001	0.9	2.1	0.5
$SnO_2 \cdot MnO_2 \cdot nH_2O$ (1:1)	0.001	1.3	0.9	0.9
$TiO_2 \cdot nMnO_2 \cdot nH_2O$ (1:1)	0.002	1.0	1.0	2.1
$ZrO_2 \cdot MnO_2 \cdot nH_2O$ (3:1)	0.004	1.1	1.2	3.1
$Al_2O_3 \cdot MnO_2 \cdot nH_2O$ (3:1)	0.004	0.6	1.0	6.7
$SnO_2 \cdot MnO_2 \cdot nH_2O$ (3:1)	0.003	1.6	1.3	1.5
$TiO_2 \cdot nMnO_2 \cdot nH_2O$ (3:1)	0.006	0.5	1.4	8.9

equation. The $\bar{u}_{app}$ values calculated from the specific electrical conductivity by Eq. (2) are given in Table 3. Our interesting finding was high mobility of ions adsorbed by double Al, Zr, and Ti oxyhydrates synthesized at 1 : 3 component ratio. This may be due to hydrogen bonding of the adsorbed hydrolyzed forms of the cations with the surface groups.

It should be noted that comparison of the mobilities of Cu(II) ions calculated by the two procedures (Tables 2, 3) shows that the values virtually coincide for the samples with high selectivity, but for the samples with relatively low selectivity the differences reach 30%. Most probably, this is due to the fact that the highest

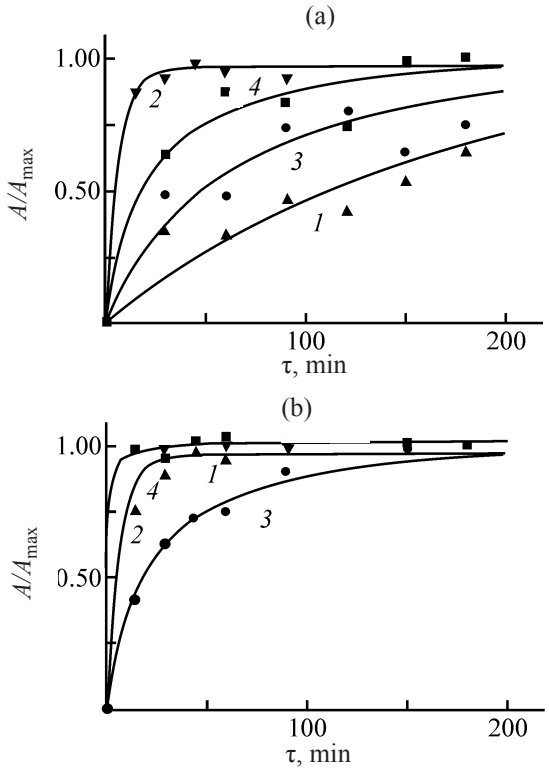

Fig. 3. Degree of adsorption completeness A/A_{max} vs. time τ of sorption of Cu(II) ions with double oxyhydrates (a) $M_{0.5}Mn_{0.5} \cdot nH_2O$ and (b) $M_{0.75}Mn_{0.25} \cdot nH_2O$.

selectivity is observed for microporous samples, and the lowest selectivity, for mesoporous samples. As the mean pore radius is increased, the contribution of the solution to the specific electrical conductivity of the oxyhydrate–solution system becomes more significant. Therefore, the limiting conductivity corresponds to an equilibrium of the oxyhydrate with distilled water, which leads to a decrease in the calculated conductivity of the oxyhydrate by 30%. Nevertheless, even in this case the general trend toward a decrease in the mobility with increasing selectivity of the uptake is preserved.

Thus, oxyhydrates take up Cu(II), Cd(II), and Pb(II) ions by the mechanism of both cation exchange and adsorption of hydrolyzed species. The sorbed ions are mobile in the matrix, and their mobility depends most probably on the pore radius of the adsorbed material, which, in turn, determines the selectivity of the ion uptake.

CONCLUSIONS

(1) Introduction of MnO_2 into Al, Zr, Sn, and Ti oxyhydrates increases the relative contribution of cation-exchange surface reactions.

(2) The materials prepared show promise for selective recovery of Cu(II), Cd(II), and Pb(II) ions by electrodeionization.

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