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Adsorption and mobility of Cu (II), Cd (II), Pb (II) ions adsorbed on (hydr)oxide polymer sorbents $M_xO_y·nH_2O$, M = Zr (IV), Ti (IV), Sn (IV), Mn (IV)

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ABSTRACT

Adsorption of K^+, Cu (II), Pb (II) and partly Cd (II) ions by (hydr)oxide adsorbents $M_xO_y·nH_2O$, where M – Zr (IV), Sn (IV), Ti (IV), Mn (IV), was studied. The Point of Zero Charges (PZC) of the (hydr)oxides varies from 2.7 ($MnO(OH)_2$) to 6.9 ($Al_2O_3·nH_2O$). Surface area is in the range 52–290 $m^2·g^{-1}$. The values of distribution coefficient which can be related to ion exchange are 15–62 for Cu (II) ions and 48–164 for Cd (II) and Pb (II) ions. The diffusion coefficient of adsorbed Cu (II) ions is influenced sufficiently by PZC and surface charge of (hydr)oxide. Presumable surface complexes for (hydr)oxide adsorbents are $(2SO^-)M^{2+}$ and $(SOH^o)…(HOM)^+$.

Keywords: (Hydr)oxide adsorbents; Point zero charge; Cu (II); Cd (II); Pb(II) ions; Selectivity; Diffusion coefficient

1. Introduction

The increasing interest towards ion-exchange and sorption properties of inorganic hydrous nanoporous materials is caused by the fact that these materials are chemically and thermally stable and are capable of selective ion sorption and ion transfer [1–3]. This paper presents the results of studies of selectivity and kinetics of adsorption of one- and two-charged cations by sol-gel precipitated (hydr)oxides of Zr, Al, Sn, Ti, and Mn. Within the above-mentioned row (hydr)oxides possess anion-exchange properties mainly ((hydr)oxides Zr, Al), as well as cation-exchange properties mainly ((hydr)oxides Sn and Mn).The point of zero charge (PZC) of manganous (hydr)oxides MnO_2 and MnO $(OH)_2$ is located in the range of 2.3–3.5 [4, 5]. It is known, that Zr and Ti (hydr)oxides can be considered as ampholitic, so they able to absorb as well as anions or cations (PZC values are in the range of pH = 5.7–7.0), and Sn (hydr)oxide can be considered cation exchanger (pH_{PZC} = 3.5–3.8), i.e., mainly adsorbs cations from the solutions with neutral pH values [4]. The task of the study was to compare adsorptive properties of above-mentioned (hydr)oxides towards one-charged and two-charged cations, namely, K^+, Cu (II), Cd (II), Pb (II).

2. Experimental

2.1. Materials and methods

(Hyrd)oxide adsorbents were synthesized by precipitation method from aqueous solutions of chlorides and oxychlorides of metals through the stage of sol-gel transformation. The preconditioning stage for all (hydr)oxide's treatment (removal of adsorbed ions during the synthesis) was to keep the samples in 0.2 M HNO_3 during 24 h. All samples of materials were then

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washed several times with distilled water and dried at 70°C. The raw of all materials was sieved to different fractions. The chemical composition of the (hydr)oxides was determined by analytical methods.

Potentiometric titration experiments for (hydr)oxide adsorbents were carried out with 0.12 M solution of KNO_3. To study the adsorption properties of all (hydr) oxides we used solutions of KNO_3, $CuCl_2$, $CdCl_2$ and Pb $(NO_3)_2$ as adsorbates in the range of concentration from 0.001 to 0.1 M. All adsorption experiments were performed at pH 5.0–5.5 at 20°C. The value of absorption was calculated from the value of the difference in the content of ions in solutions before and after adsorption which occured during 24 h. The concentrations of K^+, Cd (II), Pb (II) ions in the solutions were determined by atomic adsorption spectroscopy and Cu (II) ions – by spectrophotometry at the wavelength of 812 nm. Ion distribution coefficients K_{di} were calculated from the slope of linear initial part of isotherms, and selectivity coefficients K_S – as the ratio of distribution coefficients. To estimate the velocity of adsorption, we used the value of half exchange-time $t_{0.5}$ of the Cu (II) ions at adsorption from 0.05 M $CuCl_2$ solution. This concentration of solution was chosen because the limiting stage of sorption under these conditions is pore-diffusion kinetics [6].

Diffusion coefficients D for ions were calculated by following equation [7]:

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

where $t_{0.5}$ is the half exchange time, s; d is the effective diameter of particles of (hydr)oxide, m. Specific surface area and porous characteristic parameters were calculated from the data obtained by the method of thermal adsorption/desorption of nitrogen (TDN) after the removing of physically-adsorbed water at 150–190°C during 2 h with using the "AUTOSORB-NOVA-6" instrument by Quantachrome equipment. The specific surface area S_{BET} was determined according to the Brunauer–Emmett–Taylor method. The surface area with content of pore radius less then 1 nm $S_{r>1}$. The total pore volumes (V) were obtained from the amount of nitrogen adsorbed at relative pressure 0.99. The micropore volumes $(V_{r<1})$ were calculated from Dubinin–Radushkevich (D–R) equation [8] in the relative pressure range of less 0.2. Percentage content of volume of micropores to the total volume of pores were defined ($V_{r<1}\cdot V^{-1}$ 100 %).

3. Results and discussion

According to thermogravimetry, the content of structural bound water in (hydr)oxides was 10–30%.

Fig. 1 represents distribution of pore volume from pore radius for some (hydr)oxides. It can be concluded that in the row of hydroxides from low to neutral PZC the volume of micro- and mesopores increases while the volume of macropores decreases, with the exception $ZrO_2\cdot nH_2O$. All adsorbents content a sufficient quantity of pores with radius from 1 to 2 nm.

Potentiometric titration curves obtained for some (hydr)oxides are represented on Fig. 2. From these dependencies the PZC values were obtained.

The values of PZC, specific surface area, prevalent radius of pores and the proportion of micropores in the structure of (hydr)oxides are shown in Table 1.

Analysis of the data of the Table 1 allows concluding that increasing in micro pores percentage leads to growth of percentage of surface which related to pores with radius less than 1 nanometer. Most of (hydr)oxides can be classified as mesoporous adsorbents.

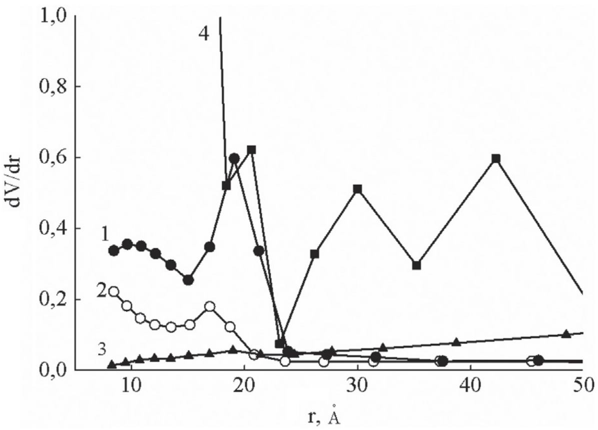


Fig. 1. Pore volume *vs* pore radius calculated for (hydr) oxides: 1 – $Al_2O_3\cdot nH_2O$; 2 – $TiO_2\cdot nH_2O$; 3 – $MnO_2\cdot nH_2O$; 4 – $ZrO_2\cdot nH_2O$.

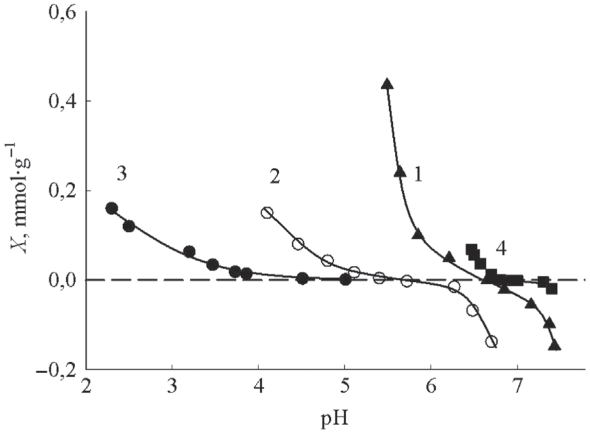


Fig. 2. Potentiometric titration curves of (hydr)oxides: 1 – $ZrO_2\cdot nH_2O$; 2 – $TiO_2\cdot nH_2O$; 3 – $SnO_2\cdot nH_2O$; 4 – $Al_2O_3\cdot nH_2O$.

Table 1
The values of PZC, specific surface area, prevalent radius of pores and the proportion of micropores in the structure of individual and double (hydr)oxides

(Hydr)oxide	PZC	$S_{BET}/S_{r>1}$, $m^2 \cdot g^{-1}$	r, nm	Micro pores, DR-methods %
$ZrO_2 \cdot nH_2O$	6.7	52/48	2.3	3
$Al_2O_3 \cdot nH_2O$	6.9	133/98	2.1	33
$SnO_2 \cdot nH_2O$	3.7	112/81	–	28
$TiO_2 \cdot nH_2O$	6.2	289/55	0.8;1.7	66
$MnO(OH)_2$	2.7	78/74	–	4

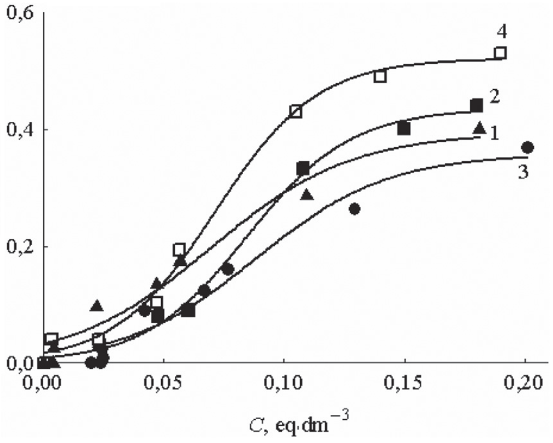
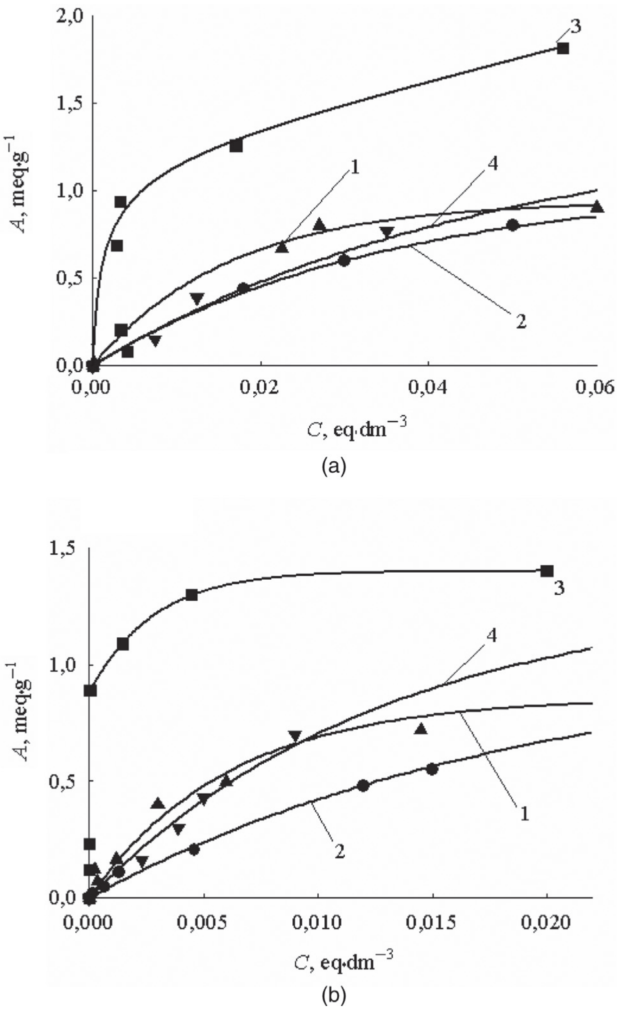


Fig. 3. Adsorption of K^+ ions by (hydr)oxides: 1 – $ZrO_2 \cdot nH_2O$; 2 – $Al_2O_3 \cdot nH_2O$; 3 – $SnO_2 \cdot nH_2O$; 4 – $TiO_2 \cdot nH_2O$.



(a)

(b)

Fig. 4. Adsorption of Cu (II) (a) and Pb (II) (b) ions ions by (hydr)oxides: 1– $ZrO_2 \cdot nH_2O$; 2 – $SnO_2 \cdot nH_2O$; 3 – $TiO_2 \cdot nH_2O$; 4 – $MnO(OH)_2$.

To study the adsorption properties of (hydr)oxides, primarily, we studied the adsorption of K^+ . Fig. 3 illustrates the dependence of adsorption obtained for ion K^+.

Fig. 4 illustrate the adsorption of Cu (II) and Pb (II) ions by (hydr)oxides from the solution with the range of concentration up to 0.06 $eq \cdot dm^3$.

All the curves obtained for $TiO_2 \cdot nH_2O$ can be considered isotherms of high affinity. The distribution coefficients of ions, calculated for very dilute solutions ($TiO_2 \cdot nH_2O$) are: for Cu (II) – 270, Cd (II) –5590, Pb (II) – 18150. According to literature such high values of adsorption on (hydr)oxides with zero and positive surface charge can be caused by surface hydrolysis (SH) of metal ions, if a pH-static adsorption mode can be observed [9].

Changing pH values during absorption process gives additional information that helps determine the mechanism of ion adsorption. A pH-static adsorption mode of the studied ions was revealed for (hydr)oxides Zr and Ti for the adsorption from very dilute solutions in the range of equilibrium concentrations of solutions up to $2 \cdot 10^{-4}$ M. If adsorption is accompanied by changing of pH, the adsorption process can be considered as ion exchange (IE).

In Table 2 we represent changing of pH value during adsorption, coefficient of proton exchange (eq/eq), surface charge and mechanism of ion uptake from solution.

In Table 3 the values of K_{di} calculated from adsorption isotherms are represented for ion exchange only. For example, for (hydr)oxides TiO_2 at equilibrium concentrations 0.02–0.05 M K_H is changing from 0 to 0.2, which demonstrates the predominance of cation-exchange mechanism.

The distribution coefficients of the studied ions by cation-exchange (hydr)oxides namely SnO_2 and MnO_2 are quite high, but significantly lower than coefficients obtained for $TiO_2 \cdot nH_2O$.

For SnO_2 and MnO_2 (hydr)oxide sorbents in the solutions with neutral pH due to the predominance of

Table 2
PH values and proton exchange coefficient for adsorption from 10^{-3} and 10^{-2}M solutions

(Hydr)oxide, adsorbate	pH_1; pH_2	K_H	Surface charge, adsorption mechanism
ZrO_2, Cu (II)	4.6–4.2; 3.8	0.0; 0.0	$–S–OH_2^+$, (SH); $–S–O^-$, (IE)
ZrO_2, Pb (II)	3.2–3.1; 2.5	0.0; 0.2	
TiO_2, Cu (II)	7.0–6.9; 2.7	0.0; 0.1	$–S–OH_2^+$, (SH); $–S–O^-$, (IE)
TiO_2, Cd (II)	7.2–7.0; 3.3	0.0; 0.2	
TiO_2, Pb (II)	6.1–6.4; 2.8	0.0; 0.2	
Al_2O_3, Cu (II)	4.9–4.3; 4.0	0.0; 0.0	$–S–O^-$, (IE)
Al_2O_3, Pb (II)	3.3–3.4; 3.1	0.0; 0.1	
SnO_2, Cu (II)	2.2–1.9; 1.7	0.6; 0.6	$–S–O^-$, (IE)
SnO_2, Cd (II)	2.5–2.3; 1.8	1.0; 1.0	
SnO_2, Pb (II)	2.7–2.5; 2.1	1.0; 1.0	
MnO_2, Cu (II)	2.5–1.9	1.0; 1.0	$–S–O^-$, (IE)
MnO_2, Cd (II)	3.9–2.5	1.0; 1.0	
MnO_2, Pb (II)	3.3–2.0	1.0; 1.0	

Table 3
The values of K_{di} calculated from adsorption isotherms

(Hydr)oxide	K_{di}		
	K^+	Cu (II)/Cd(II)	Pb (II)
$ZrO_2 \cdot nH_2O$	3	62	164
$Al_2O_3 \cdot nH_2O$	3	15	48
$SnO_2 \cdot nH_2O$	2	22/50	52
$TiO_2 \cdot nH_2O$	4	72	142
$MnO(OH)_2$	3	20/82	78

Table 4
The values of K_S (M/K^+) calculated from ratio $K_{d\,M}$ and $K_{d\,K}$

(Hydr)oxide	K_S	
	Cu (II)/K^+	Pb (II)/K^+
$ZrO_2 \cdot nH_2O$	21	55
$Al_2O_3 \cdot nH_2O$	5	16
$SnO_2 \cdot nH_2O$	12	26
$TiO_2 \cdot nH_2O$	18	36
$MnO(OH)_2$	7	26

negative surface charge surface hydrolysis and anion exchange are not possible, and the main surface reaction is cation exchange.

As can be seen from Table 3, the greatest values of distribution coefficient and adsorption selectivity of studied ions are observed for individual (hydr)oxide $TiO_2 \cdot nH_2O$. We observed the pH-static mode of sorption, based on this, the adsorption of double-charge cations from very dilute solutions occurs without changing the pH of the solution. So, it can be concluded, that in this case, the predominant mechanism of absorption of studied ions is surface heterogeneous hydrolysis.

The results of calculation of selectivity coefficients are summarized in Table 4.

It can be concluded from this presentation that only $Al_2O_3 \cdot nH_2O$ possesses relatively weak selectivity of adsorption towards two-charged cations. Perhaps, predominant mechanism is anion-exchange, and cations adsorb in small part of surface only.

The value of the mobility of absorbed ions, that strongly depend on interaction energy of "adsorbent–adsorbate", can be used to calculate the energy consumption for at electro-membrane processes with the (hydr) oxide's application for purification of contaminated water solutions from valuable or toxic ionic components [2, 3]. The value of mobility is proportional to coefficient of diffusion in accordance to Nernst–Einstein equation.

Diffusion coefficients values for (hydr)oxides with "acid" surfaces ($MnO_2 \cdot nH_2O$; $SnO_2 \cdot nH_2O$) are 0.3–0.4 $m^2 \cdot s^{-1}$ and this is due to the basic surface complex of it: two negative charge centers and one copper ion. Diffusion coefficients values $0.8–1.1 \cdot 10^{-12}$ $m^2 \cdot s^{-1}$ for anion-exchangers due to the high proportion of positively charged or neutral centers, which form the metal hydrolysis, can be linked by a hydrogen bond.

The highest values for (hydr)oxides titanium, as well as high selectivity coefficients can be related to a higher content of structural bound water – up to 30%.

Table 5
Diameter of (hydr)oxide particles (*d*), half-exchange time ($t_{0.5}$), diffusion coefficient (*D*) and equilibrium pH

(Hydr)oxide	$d \cdot 10^3$, m	$T_{0.5}$, min	$D \cdot 10^{12}$, $m^2 \cdot s^{-1}$	pH
$ZrO_2 \cdot nH_2O$	0.8–1.1	146	0.8	3.3
$Al_2O_3 \cdot nH_2O$	0.6–1.2	92	1.1	3.8
$SnO_2 \cdot nH_2O$	0.4–0.5	55	0.4	4.3
$TiO_2 \cdot nH_2O$	0.5–0.7	18	2.5	3.1
$MnO_2 \cdot nH_2O$	0.4–0.5	79	0.3	2.8

4. Conclusions

Simple (hydr)oxides $M_xO_y \cdot nH_2O$, where M – Zr (IV), Sn (IV), Ti (IV), Mn (IV) synthesized by sol-gel method are ion-exchange materials. These materials are characterized both microporous structure and high specific surface area. As had been show, obtained materials are able to sorption toxic cations from diluted aqua solutions. Materials have good kinetics, high ion-exchange capacity and selectivity towards some toxic cations (e.g., Cu(II), Cd(II), Pb(II)). Studied materials (hydr)oxides are very promising for water treatment processes such as separation by ion-exchange.

Symbols

D — Diffusion coefficients
d — the effective diameter of particles of (hydr) oxide
$t_{0.5}$ — the Half exchange time
PZC — Point Zero Charge
r — Prevalent pore radius
K_d — Ion distribution coefficient
K_S — Selectivity coefficient

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