# Sorption of non-ferrous metal cations on hydrated titanium dioxide

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Adsorption properties of ion-exchange material based on spherical hydrous TiO<sub>2</sub> particles (HTD) in regards to non-ferrous metal cations has been investigated. TiO<sub>2</sub> particles were synthesized by the sol-gel method. The high stable titanium sol (IV) was obtained by the method of limited hydrolysis of ammonium titanyl sulfate  $(NH_4)_2 TiO(SO_4)_2 H_2O$  (ATS) solution without the usage of organometalic compounds. The presence of ammonium ion in sol prevents the polymerization of gels, which has a positive impact on porosity of the obtained compounds and, consequently, on ion-exchange properties. The synthesized material is weakly-acidic ion-exchanger, pK value of functional groups to be determined as  $pK_1 = 5.28$  and  $pK_2 = 7.88$ . The total ion-exchange capacity equals 4.0 mg-eq/g towards sodium cation. This article presents the adsorption behavior of non-ferrous metal cations using HTD during technological wastewater purification. The cations were selected based on their ubiquity in wastewater of different industrial processes. The maximum ion-exchange capacity of the researched cations as well as quantitative characteristics of the sorption process was estimated. According to the maximum exchange capacity the selectivity order of the metal ions on HTD is determined as follows: Pb<sup>2+</sup> >  $> Co^{2+} > Cu^{2+} > Ni^{2+} > Sn^{2+} > Cd^{2+} > Zn^{2+}$ . The obtained sorption data are best elucidated by the Freundlich model for cadmium and lead cations, and by Langmuir and Freundlich models in the case of sorption of zinc, copper and nickel cations. The sorption kinetics of these metal ions on HTD shows that the internal diffusion processes play a main role. The tests on purification of water from hardness salts and polyvalent metals in dynamic regime were performed to evaluate the functional properties of HTD. It was shown that HTD has an increased capacity in regards to divalent metal cations and low selectivity to hardness cations as compared to carboxylic cation exchanger C-104 ("Purolite"). In the case of wastewater treatment in tannery industry, the sorption of chrome cations by HTD exceeds 99% in all the researched systems, whilst the remaining concentration of chromium ions (III, VI) in the solution is lower than PMC.

*Key words:* hydrous titanium dioxide, adsorption properties, kinetics, sorption isotherms, wastewater treatment, chromium (III), chromium (VI), polyvalent metals.

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## Introduction

Now owadays, the most widespread method for deactivation of wastewater that contains non-ferrous toxic metals is chemical deposition. However, the application of this method increases the quantity of hard sludge, the costs of its disposal and, first and foremost, the ecological risks of the disposal. For that reason, the alternative processes for elimination of pollutants from wastewater are gaining importance. The most acceptable one is the sorption method, which is known for high productivity, simple mechanization and highly reliable purification.

Hydrated titanium dioxide (HTD) based inorganic materials are getting widely used for ion-exchange separations. They are resistant to chemical, thermal and radioactive influences, whilst they are also selective regarding several ions [1-5]. The selectiveness of ionexchangers is determined through the structure of matrix and the nature of functional groups with ion-exchanging capability.

When using HTD as a solvent, it is important, from economic point of view, how they are obtained, since inexpensive HTD's do not have to be regenerated and are thus economically justified.

The basic known methods of obtaining HTD include thermal hydrolysis, deposition and sol-gel synthesis. The first two have a serious shortcoming as they make it impossible to regulate the phase formation. An uncontrolled synthesis, performed without controlling the speed of hard phase coagulation, leads to irregularities of its phase and dispersive composition and, subsequently, has a negative impact on technical characteristics of end products. The sol-gel synthesis, however, has more perspective. In the sol-gel process the stages of obtaining sol and gel are done at different times and, as a result, gel-spheres are derived from formed primary particles, they are mechanically strong and elastically structured, which

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makes it possible to preserve the form of granules when cleaning and drying. The processes of hydrolysis need to be slowed down during formation of sols and, subsequently, gels. Titanium alkoxides or electrolysis of titanium salts are used for this purpose [6-9].

We propose a new version of HTD sol-gel synthesis, based on obtaining of stabile titanium sol (IV) by the method of limited hydrolysis of ammonium titanyl sulfate  $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$  (ATS) without the usage of organometalic compounds. We substantiated the optimal concentration parameters of the synthesis that enable high sorption properties of HTD [10].

The present article considers the possibility of using HDT, obtained from ATS, for purification of technological wastewater from cations  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ . The cations were selected based on their ubiquity in wastewater that result from different production processes, such as industrial painting, textile industry, electrochemical production and galvanizing chemistry, metallurgical production etc.

## **Experimental part**

The research on sorption of cations of the selected metals in statistical conditions was conducted by a 0.2 g ion-exchanger sample being poured over with chloride metal solution of a given concentration, with a 1:200 proportion between the hard and liquid phase, and aged at 22 °C and occasionally mixed to a state of balance; the balanced pH value was being recorded during the research. The initial pH value of solutions was ascertained by addition of KOH/HCl. After separation of the ion exchanger, the balanced liquid was analysed regarding the level of sorbate with the atomic-adsorption spectrometer AAnalist 400 Perkin-Elmer. Based on the obtained results, the capacity of the sorbent was calculated with respect to the specific ion (mg/g) according to the method [11].

In order to analyze the balance of interphase distribution, the concentration of metal ions was being changed within the range of 0.1-1 g/l, the volume of test samples was 200 ml, the sorbent sample was 0.5 g, the initial pH values of solutions were 4.5-5.0 in the case of Cu and Zn and 6.0-6.5 in the case of other metals, the contact period of phases was 2 weeks. During that time, the balance was being determined in the system. Departing from the results of the analyses, we established the dependencies of cation concentrations in the sorbent on balanced concentration in the solution.

In order to obtain quantitative properties of the sorption process, the experimental data were processed with the help of Langmuir (1) and Freundlich (2) isotherm equations:

$$\frac{1}{A} = \frac{1}{A_{\max}} + \left(\frac{1}{KA_{\max}}\right) \left(\frac{1}{C_p}\right),\tag{1}$$

$$\log A = \log K_f + 1/n \log C_p, \tag{2}$$

where  $C_p$  — balanced concentration mmmol/l; A — quantity of the sorbed substance, mmol/g;  $A_{max}$  — maximum level of sorption, mmol/g; K — concentration constant of the sorption balance or the Langmuir constant, which characterizes the intensity of the sorption process, l/mol;  $K_f$  — the Freundlich constant, which characterizes the adsorbent's relative capability to interact with the adsorbate; N — coefficient in the Freundlich equation, which indicates the intensity of the sorption process and distribution of active centres.

The kinetics of sorption of lead and copper cations was researched by a method of limited range. The experiments were performed from solutions with a 50 and 100 m/g concentration of the respective metals and a 1:200 hard/liquid proportion with mixing and thermostating the samples at temperatures of 25 and 45 °C. The initial pH value of the solutions equalled 6.5 for Pb<sup>2+</sup> and 4.5 for Cu<sup>2+</sup>.

In order to determine the limiting and defining speed of the phase's process, kinetic curves of metal sorption were processed with the help of diffusion-kinetics equation. In the case of external diffusion processes, the kinetic curve with coordinates  $-\lg(1 - F)$ , depending on "t", forms a straight line. If this condition is met, the diffusion in the film contributes to the overall speed of the process. If the sorption curves with coordinates  $F - \sqrt{t}$  are dependencies that, in the case of short contact time of the phases, form straight lines, but are then curved, this testifies that diffusion in the granule of the sorbent limits the overall speed of the process [10].

### **Results and discussion**

The synthesized material belongs to subacid cations, the values of dissociation constants in the case of cation-exchanging mechanism of functional groups equal  $pK_1 = 5.28$  and  $pK_2 = 7.88$ , respectively, whilst the full exchanging capacity equals 4.0 mg-eq/g in the case of sodium cation.

The first stage included an investigation of the researched cations' dependence on their pH environment. The maximum pH value of a working solution was lower than the initial values of deposition of metal hydroxide.

Evidently (Fig. 1), HTD has a capability to absorb metal cations in an acid environment, even though the level of sorption does not exceed 45% in this case. A significant enhancement of the level of cation sorption through increased pH is related to the enhancement of dissociation level of functional groups.

The investigation of HTD's sorption capacity showed that it has a rather high capacity as regards hard metal cations from solutions with a high initial concentration in the case of the analyzed elements (Table 1). The sorption was performed from salt solutions of respective metals in the water at hard/liquid = 1:200, pH of solutions was 4.5-6.5.

According to the values of the maximum exchanging capacity, the sequence of the selected metal cations may be depicted as  $Pb^{2+} > Co^{2+} > Cu^{2+} > Ni^{2+} > Sn^{2+} > Cd^{2+} > > Zn^{2+}$ . The sorption isotherms for divalent cations, as presented in Fig. 2, belong to high-affinity isotherms, which allows us to prognosticate an effective purification at low initial concentrations of cations to comply with PMC norms.

The Langmuir model presupposes an equipotential adsorbent surface, that is, an energetic equivalency of adsorption centres. Each of the adsorption centres thus interacts with only one adsorbate molecule, which results in a formation of a mononuclear layer. The Freundlich model is characterized by exponent distribution of adsorption centres across energies that presuppose an enhanced concentration of adsorbate on the sorbent's surface through enhancement of the adsorbate' concentration in the solution [12, 13].

The proposed isotherm equations were linearized through coordinates  $(1/C_p) - (1/A)$  for the Langmuir model and log  $C_p - \log A$  for the Freundlich model. The analysis of the straight lines allowed us to calculate the parameters of isotherm equations (Table 2).

Departing from the correlation coefficient values, the sorption isotherms of cadmium and lead cations are best



**Fig. 1.** Dependency of the level of sorption (S, %) of cations Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> on pH of the environment, initial concentration of metals in the solution 0.001 mol/l, hard: liquid = 1:200

#### Table 1 HTD sorption properties

Cations	Initial concentration of metal in the solution, mg/l	Level of sorption, %	Capacity, mg/g
Cu <sup>2+</sup>	510	99.7	101.7
Co <sup>2+</sup>	519	98.4	100.1
Ni <sup>2+</sup>	490	96.3	94.4
Cd <sup>2+</sup>	640	60.2	76.9
Pb <sup>2+</sup>	735	96.6	142.3
Zn <sup>2+</sup>	400	45.0	36.3
Sn <sup>2+</sup>	410	99.5	81.0

described with the Freundlich model, whilst sorption of lead, zinc, copper and nickel cations is best described with the Langmuir and Freundlich models. The coefficient "n" of the Freundlich isotherm was over 2 with all the researched cations, which proves that the connection energy diminishes as the surface gets filled. No threshold values are given by Freundlich isotherms at saturation. The analysis of the  $A_{\text{max}}$  Langmuir isotherm values showed that, in the case of copper, zinc and nickel cations, the obtained values of maximum sorption are close to the experimental values, as opposed to  $Pb^{2+}$  and  $Cd^{2+}$  where estimated values exceed the experimental ones. It is evident that HTD's surface is chemically non-homogenous, that is, there are sorption groups with various chemical activities. In this case, we can observe constant changing of sorption energy as, first of all, the most active sorption centres are getting filled and the surface is constantly filled until the positions with least energy are occupied.

At a low concentration of metal in the solution, the temperature has a bigger influence on the sorption speed than with high concentrations (Fig. 3). As regards  $Pb^{2+}$  cations, the sorption balance is reached in approximately 60 minutes with the selected metal concentrations and in 120 minutes in the case of  $Cu^{2+}$ .

The processing of kinetic curves in the given coordinate systems showed that the sorption process can



Fig. 2. Sorption isotherms of cations  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ 

Sorption parameters of equations and correlation coefficients (A
for Langmuir and Freundlich models

Table 2

Isotherms	Cations				
Langmuir	Pb <sup>2+</sup>	Cd <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Ni <sup>2+</sup>
A <sub>max</sub> , mol/g	1.30·10 <sup>-3</sup>	1.11.10-3	1.69.10 <sup>-3</sup>	0.52.10-3	1.38·10 <sup>-3</sup>
<i>K</i> ·10 <sup>-2</sup> , l/mol	13.7	11.5	8.4	6.1	3.4
R	0.975	0.974	0.986	0.992	0.995
Freundlich					
<i>K<sub>f</sub></i> , mg/g	350	168	92	58	23
п	4.5	2.7	2.9	2.5	2.2
R	0,996	0.997	0.972	0.984	0.989

be controlled with gel (internal) diffusion (Fig. 4). The final conclusion regarding the limiting stage of sorption of HTD hard metal ions was made according to the results of the research on kinetic sorption with interruption of contact of solution phases and the sorbent.

It was determined that in the case of internal diffusion kinetics the sorption curves do not concur in experiments where phases are interrupted and where they are uninterrupted: the moment the contact between phases is restored, the sorption proceeds with a higher



Fig. 3. Kinetic curves of sorption of  $Pb^{2+}(a)$  and  $Cu^{2+}(b)$  on HTD at initial concentration of metal in the solution of 50 mg/l (curves *1*, *2*) and 100 mg/l (*3*, *4*) at the temperature of 25 °C (*1*, *3*) and 45 °C (*2*, *4*)



**Fig. 4.** Kinetics of sorption of  $Cu^{2+}$  (curves *1*, *2*) and  $Pb^{2+}$  (curves *3*, *4*) on HTD. The initial concentration of metal ions in the solution is 50 mg/l (*1*, *3*) and 100 mg/l (*2*, *4*) (*F* = level of sorption balance)

speed, whilst in the case of external diffusion kinetics the sorption speed is not increased after interruption. The dependencies of sorption of ions Pb<sup>2+</sup> and Cu<sup>2+</sup> do not concur when phases are interrupted for 2 hours after 20 minutes from the beginning of the process, and when there is no separation of phases, determined by the coordinates "the level of completeness of the process" (F) – "time" ( $\tau$ ). This proves that sorption speed of the definable ion is limited by diffusion of ions inside the sorbent's granules, that is, an internal diffusion kinetics is taking place.

One of the fields where cation exchanger can be used is softening and purification of water. For purposes of comparison of sorption properties, the water was purified by application of HTD and industrial subacid carboxyl cation exchanger Purolite C104, which is used for softening of water and selective extraction of transition metal from aquatic environment. The basic technical properties of the researched ion exchanger are presented in Table 3.

The experiments were performed on real water in dynamic conditions, the filtering load of the ion exchanger was 400 ml, and the flow rate was 5 turn/h. The composition of incoming water (mg/l) was as follows: 30 Ca; 15 Pb; 7 Mn; 36 Cu; 24 Ni; 75 Fe; 19 Zn; 12 Cr.

The basic goal of the experiments was to evaluate the exploitation properties of sorption materials in the case of non-ferrous metal ions and hard salts. 250 dm<sup>3</sup> of water was purified over the course of the experiments (Table 4).

Based on the results of the experiment, it was determined that HTD enables an effective purification of water from hard cations in polyvalent metals. In comparison with C-104, hydrated titanium oxide has an increased capacity as regards polyvalent metal cations and selectivity to hard cations. When 250 dm<sup>3</sup> of water was run through, none of the controlled ions caused an increase of concentration in the filtrate in the case of HTD, whilst in the case of C-104 the concentration of polyvalent metals started to grow when 75 dm<sup>3</sup> of solution was run through.

The most toxic water discharge components in tannery industry are chrome compounds, which enter the sewage

Tab	ole	3		
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Technical	l characteristic	s and stand	dard workin	g conditions
of ion exc	hangers			

Parameters	Purolite C104	HTD
Appearance	Non-transparent s	pherical particles
Functional groups	R-COOH	R-OH
lon form	$H^+$	$H^+$
Particle size, mm	0.3-1.2	0.5-1.0
Reversible swelling, %	85	-
Bulk mass, g/cm <sup>3</sup>	0.74-0.77	0.85-0.90
Full exchangeable capacity, mg-eq/l	Not less than 4.2	Not less than 3.6
Stability in pH range	0-14	2-14
Working range of pH	5-14	6-12

Table 4

Results of experiments on cation exchangers

Definable estions	Concentration of metal in the filtrate, mg/l			
Definable cations	Purolite C-104	HTD		
Ca	64	4		
Pb	4.37	N/D		
Mn	1.8721	N/D		
Cu	0.3418	N/D		
Ni	0.0677	0.0021		
Fe	-	-		
Zn	0.5911	0.0452		
Cr	N/D	N/D		

Table 5

Results of experiments on purification of tannery industry wastewater from chrome compounds

Parameters	Before purification, mg/l	After purification, mg/l	Level of sorption, %	Capacity of sorbent, mg/g	
Common wastewater at the plant					
Cr <sup>3+</sup>	59.6	0.14	99.8	11.9	
Cr <sup>6+</sup>	6.1	0.038	99.4	1.2	
рН	8.11	-	-	-	
Wastewater, released during tannery and washing					
Chlorides	1000	-	-	-	
Cr <sup>3+</sup>	28.9	0.01	99.9	5.8	
Cr <sup>6+</sup>	3.7	0.02	99.5	0.7	
Hq	4.4	_	_	_	



Fig. 5. Kinetic curves of sorption of copper cations from the solution with a 50 mg/l concentration without interrupting the contact of phases (1) and with interruption (2)

system through processed solutions and then — through wastewater — end up in natural water resources. Chrome compounds are toxic due to their basic acid components Cr (III) and Cr (VI). It is known that chrome (VI) is more poisonous than chrome (III). In the wastewater, released by tannery industry, the main part of chrome (over 95%) is present as chrome (III). The level of the more toxic chrome (VI) usually equals around 1% of the overall level of chrome in the wastewater. We purified common wastewater from tannery industry that was released during the processes of tanning and washing. Apart from chrome cations, subject to removal, the water contains chlorides (1.0-1.5 g/l) and nitrogen (70-100 mg/l). The sorption was performed in static conditions, the mass ratio of ion ecxhanger to solution was 1:200. The results of the research are shown in Table 5.

The sorption of HTD chrome cations exceeds 99% with all of the researched systems. The remaining concentration of chrome ions in the solution is lower than PMC. Evidently, HTD can be successfully applied for purification of tannery industry wastewater from Cr (III) and Cr (VI) cations.

## Conclusions

1. A research was conducted on sorption capability of HTD with respect to cations of non-ferrous and hard metals. According to the values of the maximum exchanging capacity, the sequence of the selected metal cations may be depicted as  $Pb^{2+} > Co^{2+} > Cu^{2+} > Ni^{2+} >$  $> Sn^{2+} > Cd^{2+} > Zn^{2+}$ .

2. The statistical exchanging capacity regarding the researched cations as well as quantitative characteristics of the sorption process were calculated. The isotherms are best described with the Freundlich model in the case of sorption of cadmium and lead cations, and with the Langmuir and Freundlich models in the case of sorption of zinc, copper in nickel cations.

3. By researching the kinetic properties of sorption of lead and copper cations, it was shown that sorption kinetics of the selected cations is limited by internal diffusion.

4. The experiments on the usage of HTD in a water purification system showed that HTD enables an effective purification of water from hard cations and polyvalent metals. In comparison with carboxylic cation-exchanger C-104, HTD has an increased capacity as regards polyvalent metal cations and selectivity to hard cations. We tested the possibility of elimination of chrome ions from water discharges, released by tannery industry. It was shown that HTD can be successfully applied for purification of wastewater from Cr (III) and Cr (VI).

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# Synthesis of a titanium (IV)-based sorbent and potentialities of its usage for extracting cations of non-ferrous metals

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Studied are conditions of synthesizing frame-structured titanium-containing exchanger with a structure similar to ivanyukite out of  $(NH_4)_2 TiO(SO_4)_2 \cdot H_2O$  salt. To increase hydrolysis stability, partial reduction of initial solution has been fulfilled by electrochemical method with Ti<sup>4+</sup> conversion to Ti<sup>3+</sup>. This expedient allows avoiding an amorphous phase generation and directing the process to creation of crystalline ivanyukite in a form of two structural modifications: trigonal  $(Na_4(TiO)_4(SiO_4)_{3.6}H_2O)$  and cubic  $(Na_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O)$ ; the precipitate crystallinity degree is 90–95%. Crystallization proceeds under five times system oversaturation by sodium silicate. Determined have been optimal conditions for titanium- siliceous precursor sol-gel obtaining and consequent hydrothermal transformation of the obtained gel to crystalline phase: content of Ti<sub>2</sub>O<sub>3</sub> in the solution after reduction is 30–45 g/l, molar ratio TiO<sub>2</sub>:SiO<sub>2</sub> = 1:4.

It has been shown that the pore system (total volume of pores) of crystalline ivanyukite particles is approximately 1.5 times larger than that of *X*-ray amorphous samples and that it is mainly represented by mesopores of medium size, which are characterized by the most activity in sorption processes. Natrium and potassium ions situated in the ivanyukite frame space along with water provide high exchange velocity of cations absorption in sorption processes due to minimal diffusive obstacles.

The reported preliminary data on sorption allow to describe the frame-structured crystalline alkaline titanosilicates as effective sorbents of cations of non-ferrous metals, strontium, as well as univalent cations, caesium in particular.

*Key words:* titanium-containing sorbents, titanosilicates, synthesis, sol-gel process, crystallization, surface behaviour, sorption kinetics, uni- and bivalent cations.

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