

SORPTION OF NON-FERROUS METAL CATIONS ON SPHEROGRANULATED AMOPTHOUS TITANIUM HYDROXIDE

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Abstract

The sorption properties of amorphous titanium hydroxide ion-exchanger (ATH) toward non-ferrous metal cations are investigated. The sol-gel synthesis of ATH is based on the method of limited hydrolysis of ammonium titanyl sulfate $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (ATS) without the usage of organometallic 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-exchanging characteristics. The sorption isotherms for five divalent metal ions including Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , and Ni^{2+} are built. 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 and nickel cations. The sorption kinetics of these metal ions on the ATH is limited by internal diffusion. The selectivity order of the metal ions on TiP1 is determined as follows: $\text{Pb}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. Additional sorption studies are carried on industrial water containing a mixture of divalent and hardness cations. The quality of water after the sorption on the ATH sorbent reaches the EU recommendations for drinking waters for most of the metal ions concentrations. In the case of wastewater treatment in tannery industry, the sorption of chrome cations on the ATH exceeds 99% for all types of wastewater and the remaining concentration of chrome ions (III, VI) in the solution is lower than maximum concentration limit.

Keywords: amorphous titanium hydroxide, sorption properties, kinetics, sorption isotherms, wastewater treatment, chrome (III), chrome (VI), polyvalent metals

1. INTRODUCTION

Nowadays, the most widespread method for treatment of wastewater with non-ferrous toxic metals is chemical precipitation. 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 as high productivity and highly reliable purification method.

Amorphous titanium hydroxide (ATH) is widely used for ion-exchange separations. ATH resistant to chemical, thermal and radioactive influences, whilst it is also has high selectivity regarding to several ions [1–5]. The selectivity of ion-exchangers is determined through the structure of matrix and the nature of functional groups with ion-exchanging capability.

When ATH use as a sorbent, it is important, from economic point of view, how it is obtained. Inexpensive ATH do not have to be regenerated and are thus economically justified.

The common methods of ATH obtaining include thermal hydrolysis, chemical precipitation and sol-gel synthesis. The first two methods have a serious shortcoming as they make it impossible to regulate the phase formation. An uncontrolled synthesis, performed without controlling the speed of solid phase coagulation, leads to irregularities of its phase and dispersive composition and, subsequently, has a negative impact on technical characteristics of final products. The sol-gel synthesis, however, has more perspective. In the sol-gel process the stages of obtaining sol and gel are separated in time and, as a result, gel-spheres are formed from initial particles, they are mechanically strong which makes it possible to preserve the form of granules after cleaning and drying procedure. 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 method of ATH sol-gel synthesis, based on obtaining of stabile titanium sol (IV) by the method of limited hydrolysis of ammonium titanyl sulfate solution $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (ATS) without the usage of organometallic 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 ATH, 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.

2. MATERIALS AND METHODS

2.1. Materials

Crystalline ammonium titanyl sulfate $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (ATS) was obtained from a titanium sulphate solution according to the procedure as described by Fang [11]. The XRD analysis confirmed that the final product is ATS. The chemical composition of the obtained solid was TiO_2 – 19.5, NH_4^+ – 9.7, SO_4^{2-} – 52.3 (wt.%).

2.2. Synthesis

Synthesis of the amorphous titanium hydroxide included the following stages: 25 g of ATS was loaded into 100 ml of distilled water and kept for one hour under stirring. The resulting solution contained 50 g/L TiO_2 was used for synthesis of ATH.

Titanium sol was obtained using 10% ammonia solution, which was gradually added with stirring to titanium solution until $\text{H}_2\text{SO}_4/\text{TiO}_2$ weight ratio reached 0.1–0.5, which corresponds to pH 2.0–3.5. The resultant colloidal system mainly consists of titanium sol of variable composition $\text{TiO}_{1+x}(\text{OH})_{2(1-x)}$ with particle size of 1–100 nm [12,13]. To obtain narrow fractional composition, the sol was peptized by slow heating to 65–70°C for 1 h, the prepared colloidal solution was stabilized by keeping for 2 h, and then the solution was quickly cooled to ambient temperature. Under these conditions, olation and oxolation reactions between nonmicellar titanium hydroxide species occur [14]. The content of disperse phase in sol (%) was determined by the introduction of concentrated HCl into sol aliquot until volume ratio of the components of 1 : 1. The resultant suspension was filtered to remove precipitate and residual titanium(IV) concentration was determined. The concentration was calculated by the formula

$$A = (C_f/C_0) \times 100 \text{ [14]},$$

where A is amount of titanium disperse phase in sol, %; C_0 is TiO_2 concentration in initial titanium solution, g/L; C_f is TiO_2 concentration in filtrate, g/L.

Sol gelation was conducted without heating by its dropwise dispersing into concentrated ammonia solution to produce precipitate as gel spheres. The precipitate was separated from liquid phase, mother liquor was removed by washing first with 5% NH_4OH solution, next with water, and then the precipitate was dried in air to give the product as ATH.

2.3. Methods

For all sorption experiments, commercial sulfate salts were used as sources of metal ions. The pH of the starting solutions was between 4.5 and 6.5. To determine the sorption capacity of the ATH sorbent towards Cd^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} and Pb^{2+} sorption studies were performed using 40 mL of metal solutions with 0.2 g of ATH. For each case, the suspensions were stirred continuously for 24 hours to ensure that equilibrium was reached and were then filtered. The pH of the filtrates (pH ~ 4.1–6.5) were measured and found in the same range as the starting pHs. The final metal concentrations remaining in the filtrates were determined using atomic-adsorption spectrometer AAnalyst 400 Perkin-Elmer. The amount of each metal ion adsorbed by ATH, q_e ($\text{mg} \cdot \text{g}^{-1}$), was calculated by the following equation:

$$q_e = \frac{C_0 - C_e}{m} * V \quad (1)$$

where C_0 is the initial concentration of the metal ion in solution (mg.L^{-1}), C_e is the concentration of the metal ion at equilibrium (mg.L^{-1}) and V/m (L.g^{-1}) is the volume to mass ratio of the solution to ATH used in the sorption experiments.

In order to analyze the equilibrium distribution, the concentration of metal ions was being changed within the range of 0.1–1 g/L, the volume of metal solution 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 time was 2 weeks. During that time, the equilibrium was being determined in the system.

Adsorption data for metal ions were analyzed and were modeled using Langmuir (2) and Freundlich (3) isotherm equations:

$$\frac{1}{A} = \frac{1}{A_{\max}} + \left(\frac{1}{K A_{\max}}\right) \left(\frac{1}{C_p}\right), \quad (2)$$

$$\log A = \log K_f + \frac{1}{n} \log C_p \quad (3)$$

where C_p — equilibrium concentration mmol/L; A — is the maximum monolayer coverage mmol/g; $A_{\max}$ — maximum sorption capacity mmol/g; K — is the affinity constant (also called Langmuir isotherm constant) which characterizes the intensity of the sorption process, l/mol; K_f — is a constant related to the adsorption capacity in (mg/g) (L/mg) $^{1/n}$; n — coefficient in the Freundlich equation, the parameter indicating the system heterogeneity.

The kinetics of sorption of lead and copper cations was studied by a method of limited volume. The experiments were performed using solutions with a 50 and 100 m/g concentration of the metals and a 1:200 solid/liquid ratio. The resulting suspensions were thermostated at 25 and 45 °C. The initial pH value of the solutions was 6.5 for Pb^{2+} and 4.5 for Cu^{2+} .

The experimental data obtained were fitted to the diffusion models in order to validate the most probable sorption mechanism. In the case of external diffusion processes, the kinetic curve with coordinates $-\lg(1 - F)/t$, forms a straight line and the diffusion in the film contributes to the overall kinetics of the process. If the sorption curves with coordinates $F - \sqrt{t}$ form straight lines at initial contact time and then warped this confirmed that diffusion in the granule of the sorbent limits the overall kinetic of the process [15].

3. RESULTS AND DISCUSSION

The synthesized ATH belongs to weakly acid ion-exchanger, the values of dissociation constants in the case of cation exchanging mechanism of functional groups equal $pK1 = 5.28$ and $pK2 = 7.88$, respectively, whilst the full ion-exchange capacity equals 4.0 mg-eq/g for sodium cation.

The first stage included an investigation the sorption capacity of ATH depend on pH medium. The maximum pH value of a starting solution was lower than the initial values of deposition of metal hydroxide pH precipitation. Evidently (Fig. 1), ATH has a sorption affinity to the metal cations in an acid solution, even though the level of sorption does not exceed 45% in this case. A significant increase in sorption capacity with increase of pH is related to increase in dissociated degree of functional groups.

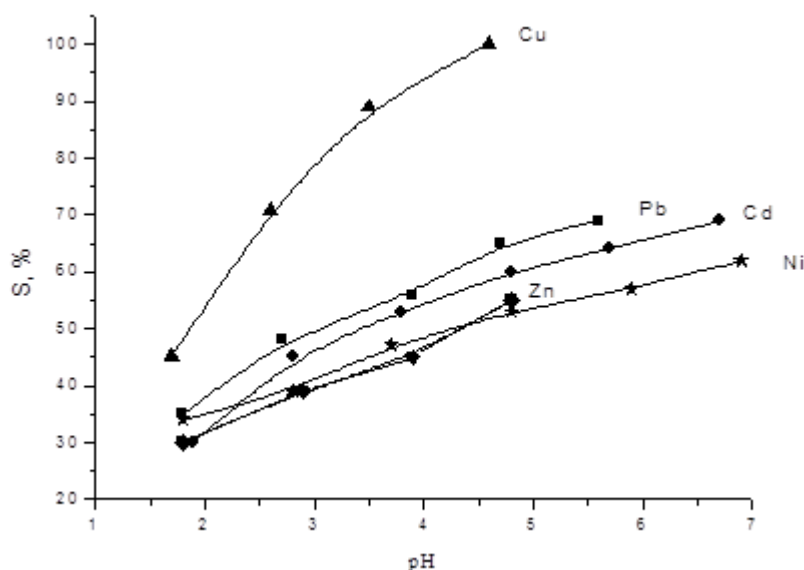


Fig. 1. Dependence the sorption affinity (S, %) of cations Pb^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} on pH. Initial concentration of metals in the solution 0.001 mol/L, T:V = 1:200

The calculated sorption capacity of HTD showed that it has a rather high capacity as regards to divalent metal cations from solutions with a high initial concentration of the metals (Table 1). The sorption was performed from water solutions of respective metals at solid/liquid = 1:200, pH of solutions was 4.5–6.5.

Cations	Initial concentration of metal in the solution, mg/l	Sorption degree, %	Sorption capacity, mg/g
Cu^{2+}	510	99.7	101.7
Co^{2+}	519	98.4	100.1
Ni^{2+}	490	96.3	94.4
Cd^{2+}	640	60.2	76.9
Pb^{2+}	735	96.6	142.3
Zn^{2+}	400	45.0	36.3

Table 1. ATH sorption properties

According to the maximum of ion-exchange capacity, the selectivity order of the metal ions on ATH is determined as follows $\text{Pb}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Sn}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. The sorption isotherms for divalent cations presented in Fig. 2, belong to high-affinity isotherms, which allows us to predict an effective purification of sewage water with low initial concentrations of cations to MCL norms.

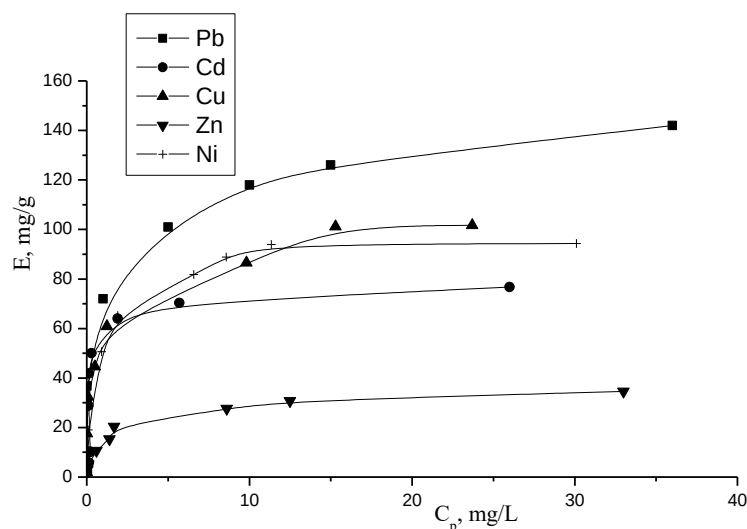


Fig. 2. Sorption isotherms of cations Pb^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+}

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 increase in concentration of adsorbate on the sorbent's surface with increase in adsorbate' concentration in the solution [16, 17].

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).

Isotherms	Cations				
	Pb^{2+}	Cd^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}
Langmuir					
$A_{max}, \text{mol/g}$	$1.30 \cdot 10^{-3}$	$1.11 \cdot 10^{-3}$	$1.69 \cdot 10^{-3}$	$0.52 \cdot 10^{-3}$	$1.38 \cdot 10^{-3}$
$K \cdot 10^{-2}, \text{L/mol}$	13.7	11.5	8.4	6.1	3.4
R	0.975	0.974	0.986	0.992	0.995
Freundlich					
$K_f, \text{mg/g}$	350	168	92	58	23
n	4.5	2.7	2.9	2.5	2.2
R	0,996	0.997	0.972	0.984	0.989

Table 2. Sorption parameters of equations and correlation coefficients (R) for Langmuir and Freundlich models

According to the correlation coefficient values, the sorption isotherms of cadmium and lead cations are best described with the Freundlich model, whilst sorption of zinc, copper and nickel cations is best described with the Langmuir and Freundlich models. The coefficient "n" of the Freundlich isotherm was over 2 for all the cations, which proves that the interaction energy diminishes as the surface gets

filled. No maximum values are given by Freundlich isotherms at saturation. The analysis of the A_{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. For Pb^{2+} and Cd^{2+} cations estimated values exceed the experimental ones. It is evident that ATH's surface is chemically non-homogenous and there are sorption functional groups with various chemical activities. In this case, the constant changing of sorption energy take place and 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 large influence on the sorption kinetic than at high concentrations (Fig. 3). For Pb^{2+} cation, the sorption equilibrium is reached in approximately 60 minutes with the selected metal concentrations and in 120 minutes in the case of Cu^{2+} .

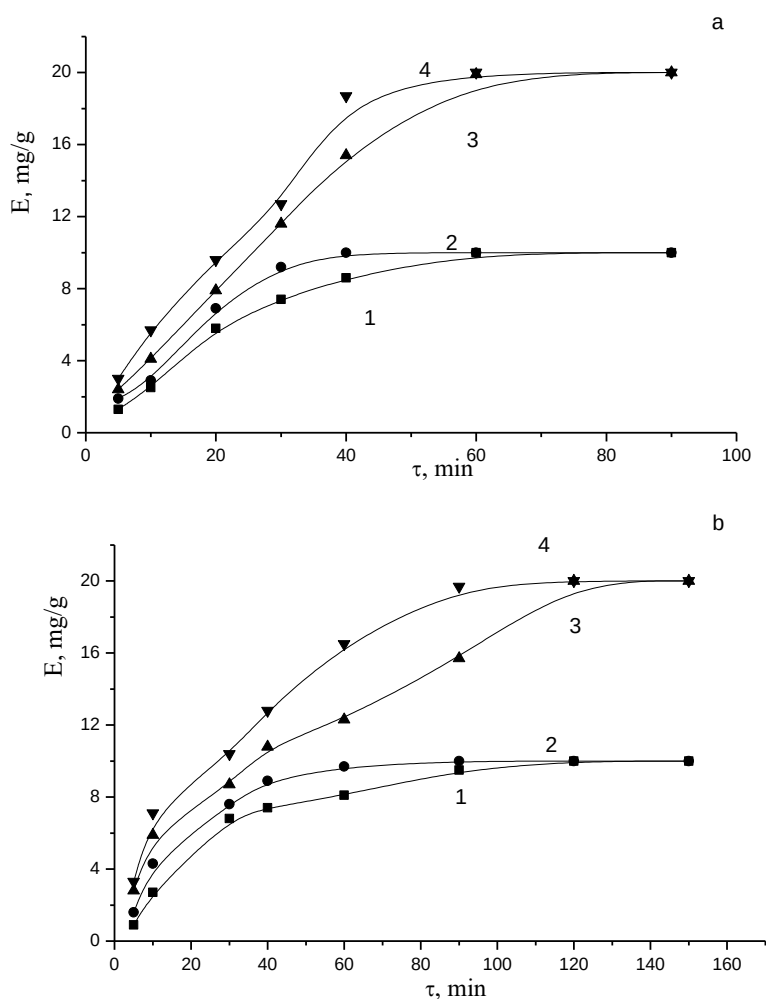


Fig. 3. Kinetic curves of sorption of Pb^{2+} (a) and Cu^{2+} (b) on ATH
at initial concentration of metal in the solution of 50 mg/l (curves 1, 2) and 100 mg/l (3, 4)
at the temperature of 25 °C (1, 3) and 45 °C (2, 4)

The processing of kinetic curves in the given coordinate systems showed that the sorption process can be controlled with gel (internal) diffusion (Fig. 4). The final conclusion regarding the limiting stage of sorption divalent metal ions on ATH was made according to the results of the kinetic sorption with interruption of contact between the solution and the sorbent.

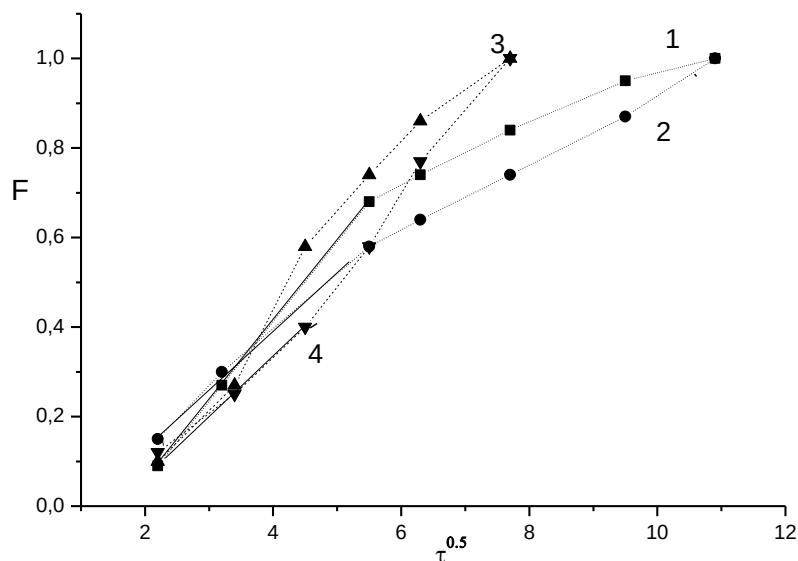


Fig. 4. Kinetics of sorption of Cu^{2+} (curves 1, 2) and Pb^{2+} (curves 3, 4) on ATH. The initial concentration of metal ions in the solution is 50 mg/l (1, 3) and 100 mg/l (2, 4) (F- degree sorption equilibrium)

It is known 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 is increased, whilst in the case of external diffusion kinetics the sorption is not increased after interruption. The test show that for Pb^{2+} and Cu^{2+} cations after interrupted contact between the phase for 2 hours the curves built in F- τ coordinate (Fig.5) do not concur. This proves that sorption kinetics is limited by diffusion of ions inside the sorbent's granules, that is, an internal diffusion kinetics is take place.

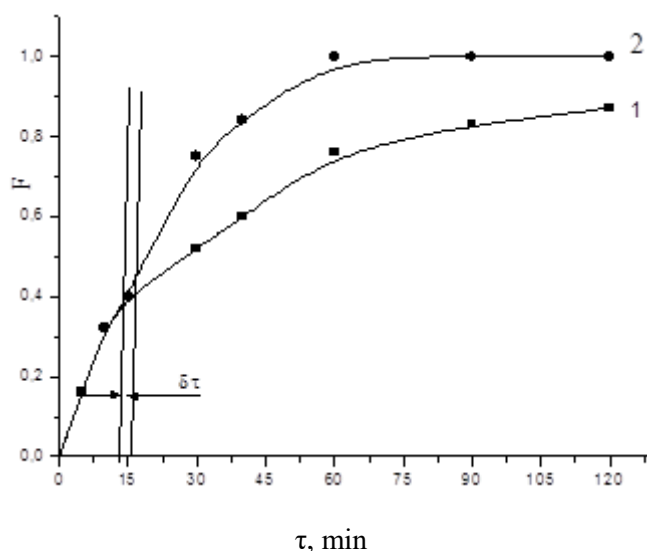


Fig. 5. Kinetic curves of sorption of copper cations from the solution with a 50 mg/l concentration without interrupting the contact of phases (1) and with interruption (2)

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 ATH and industrial cation exchanger Purolite C104, which is used for softening of water and selective uptake of non-ferrous metals from sewage water. The technical properties of the studied ion-exchangers are presented in Table 3.

Parameters	Purolite C104	ATH
Appearance	spherical particles	
Functional groups	R-COOH	R-OH
Ion-exchanger form	H ⁺	H ⁺
Particle size, mm	0.3-1.2	0.5-1.0
Reversible swelling, %	85	-
Bulk mass, g/cm ³	0.74-0.77	0.85-0.90
Total ion-exchange capacity, mg-eq/L	Not less than 4.2	Not less than 3.6
Stability in pH range	0-14	2-14
pH working range	5-14	6-12

Table 3. Technical characteristics and working conditions of ion exchangers

The experiments were performed on industrial water in dynamic conditions, the load of the ion exchanger was 400 ml, and the flow rate was 5 C.V/h. The water composition was (mg/l) Ca-30; Pb-15; Mn-7; Cu-36; Ni-24; Fe-75; Zn-19; Cr-12. The main goal of the experiments was to evaluate the exploitation properties of the sorption materials in the case of non-ferrous metal ions and Ca. 250 dm³ of water was purified over the experiments (Table 4).

Cations	Concentration of the metal in the filtrate, mg/l	
	«Purolite» C-104	ATH
Ca ²⁺	64	4
Pb ²⁺	4.37	n/f
Mn ²⁺	1.8721	n/f
Cu ²⁺	0.3418	n/f
Ni ²⁺	0.0677	0.0021
Fe ²⁺	-	-
Zn ²⁺	0.5911	0.0452
Cr ³⁺	n/f	n/f

Table 4. Results of experiments of water purification

Based on the results of the experiment, it was found that ATH is a good material for purification water from Ca and polyvalent metals. In comparison with C-104, ATH has higher capacity as regards to polyvalent metal cations and selectivity to Ca cations. When 250 dm³ of water was pass through the column, the metals concentration in the filtrate for ATH were low than the EU recommendations for

drinking waters, whilst in the case of C-104 the concentration of polyvalent metals started to grow when 75 dm³ of solution was pass through the column.

The most toxic water discharge components in tannery industry are chromium compounds, which enter the sewage system through processed solutions and then — through wastewater — end up in natural water resources. Chromium compounds of Cr (III) and Cr (VI) are toxic. It is known that chromium (VI) is more poisonous than chromium (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 3-5% of the overall level of chrome in the wastewater.

We purified wastewater from tannery industry that was released during the processes of tanning and washing. Apart from chromium 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 batch condition, the mass ratio T:V was 1:200. The results of the study are shown in Table 5.

Parameters	Before purification, mg/l	After purification, mg/l	Sorption degree, %	Sorption capacity, mg/g
Common wastewater at the plant				
Cr ³⁺	59.6	0.14	99.8	11.9
Cr ⁶⁺	6.1	0.038	99.4	1.2
pH	8.11			
Wastewater, released during tannery and washing				
Chlorides	1000			
Cr ³⁺	28.9	0.01	99.9	5.8
Cr ⁶⁺	3.7	0.02	99.5	0.7
pH	4.4			

Table 5. Results of experiments on purification of tannery industry wastewater from chrome compounds

The sorption of chromium cations by ATH exceeds 99% with all of the investigated systems. The remaining concentration of chromium ions in the solution is lower than MPC in water. Evidently, ATH can be successfully applied for purification of tannery industry wastewater from Cr (III) and Cr (VI) cations.

4. CONCLUSIONS

The sorption capability of ATH with respect to cations of non-ferrous metals have been studied. According to the maximum of ion-exchange capacity, the selectivity order can be presents as follow: Pb²⁺ > Co²⁺ > Cu²⁺ > Ni²⁺ >> Sn²⁺ > Cd²⁺ > Zn²⁺. The ion-exchange capacities toward divalent cations as well as quantitative characteristics of the sorption process were calculated. The sorption isotherms are best described with the Freundlich model in the case of cadmium and lead cations, and with the Langmuir and Freundlich models in the case of zinc, copper in nickel cations. The kinetics properties of ATH was studied and shown that sorption kinetics of lead and copper cations is limited by internal diffusion. The experiments on the usage of ATH in a water purification system showed that ATH is a good sorbent for polyvalent metals and can be applied for multicomponent sewage water. Also it was shown that ATH can be successfully applied for purification of wastewater from Cr (III) and Cr (VI).

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