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Sorption of Heavy Metal Ions from Water by Natural  
Apatite Ore

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**Abstract**—The article shows the efficient use of natural apatite ore in purification of mining industrial wastewaters from heavy metal ions. The determination of adsorption constants, calculation of thermodynamic parameters at various pH of the medium were carried out. It was established that the sorbent based on apatite ore may be used in ecological and technological aims in water conditioning and water treatment.

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**Keywords:** apatite ore, adsorption isotherms, Fe<sup>3+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> ions, sorption concentration.

INTRODUCTION

Wastewater (WW) treatment of industrial enterprises is an important ecological problem. Natural and man-made water reservoirs are intensively polluted by WW of various industrial sections, therefore there is an acute deficit of clear water in many large cities of the world. Heavy metals ions (HM) belong to the most polluted agents of the environment their main sources are wastewaters of metallurgical, machine-building and metal-working enterprises. The most HM ions belong to I–II classes of danger; they are distinguished by any carcinogenic, mutagenic and teratogenic effects, they also possess a cumulative effect [1–2].

At present accessible and effective methods of purifying low-concentrated wastewaters of compounds of heavy metals are absent. In this connection the objective of the present research is a development of new, highly-efficient and cheap methods of water purification from HM. Adsorption purification of WW of ions of HM and fluorine on cheap and accessible adsorbents is one of the most promising methods making it possible to lower the content of toxic components to a safe level [3–4]. Materials capable in that or other measure of purifying water of polluting matter include a rather wide list of natural substances including of mineral nature [5–8].

EXPERIMENTAL

The ore mineral—natural apatite ore was taken as a sorbent with a relative humidity 7% and output of volatile substances 14%.

X-ray fluorescent analysis of the ore was carried out on an energy-dispersed X-ray fluorescence spectrometer EDX-800 Shimadzu, in this case the following data were obtained:

Mass fraction, %	Mass fraction, %
CaO..... 50.82	Na <sub>2</sub> O.....0.3
P <sub>2</sub> O <sub>2</sub> .....25.99	SrO.....0.19
SiO <sub>2</sub> .....17.41	MnO.....0.11
Al <sub>2</sub> O <sub>3</sub> .....1.52	TiO <sub>2</sub> .....0.11
MgO .....1.48	SO <sub>3</sub> .....0.06
Fe <sub>2</sub> O <sub>3</sub> .....1.45	ZrO <sub>2</sub> .....0.01
K <sub>2</sub> O .....0.49	

IR-spectroscopic analysis was carried out on an IR-Fourier FSM-1202 by means of averaging interferograms and their subsequent Fourier transformation in the range 400–4000 cm<sup>-1</sup> with specimens in tablets of spectrally pure KBr (1.5 : 3000) resolution—4 cm<sup>-1</sup>, scanings number—10.

Solutions of  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  were used as model samples, the solutions were prepared by dissolving exact weighted quantities in distilled water. For this purpose  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  of qualification “pure for analysis”  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ —“pure” and  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  were used. Tests for adsorption were conducted in a static mode according to conditions set in a three-factor 5-level matrix by the method of planning the experiment [9]. The weight of the sorbent constituted 1 g. The working interval of temperatures—298–318 K (a pitch 5 K), the pH of the medium was from 4 to 8. Sorption time—60 min. The initial concentration of  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions was varied from 20 to 100  $\text{mg}/\text{dm}^3$ . The residual concentration of metal ions in the solution after adsorption was registered on an AA 149 Varian spectrometer. Parameters of adsorption were calculated the Freundlich equation, thermodynamic parameters—based on Gibbs–Helmholtz equation. Experimental data were treated by the method of statistical treatment, all calculations were conducted in three parallels (standard deviation—not more than  $\pm 0.0065$ ).

## RESULTS AND DISCUSSIONS

From the data [10] it is known that a sample of natural phosphates studied by us mainly contains fluoroapatite  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , quartz  $\text{SiO}_2$ , dolomite  $\text{CaCO}_3 \cdot \text{MgCO}_3$ , magnesite  $\text{MgCO}_3$ .

The spectrum obtained as a result of IR-Fourier spectroscopic investigation of apatite ore is characterized by absorption bands shown in Fig. 1. The absorption band at  $520.78 \text{ cm}^{-1}$  may be referred to asymmetric oscillations P–O in  $\text{PO}_4^{3-}$ . Absorption in the region  $1647.21 \text{ cm}^{-1}$  may be linked with various physical components—water molecules, OH-groupings and carbonate-ions  $\text{CO}_3^{2-}$  [11]. The band on absorption at  $935.67 \text{ cm}^{-1}$  refers to asymmetric valence oscillations C–O being matched with the group  $\text{CO}_3^{2-}$ . The bands being observed at  $3402.44$  and  $3395.62 \text{ cm}^{-1}$  characterize valence oscillations of various types of hydroxyl-groups of  $\text{OH}^-$ . Supposedly, absorption band registered at  $3695.62 \text{ cm}^{-1}$  may be referred both with the isolated groups C–O–, C–O–H and to silane groups Si–O–H which may effectively connect heavy metals by the type of ionic exchange.

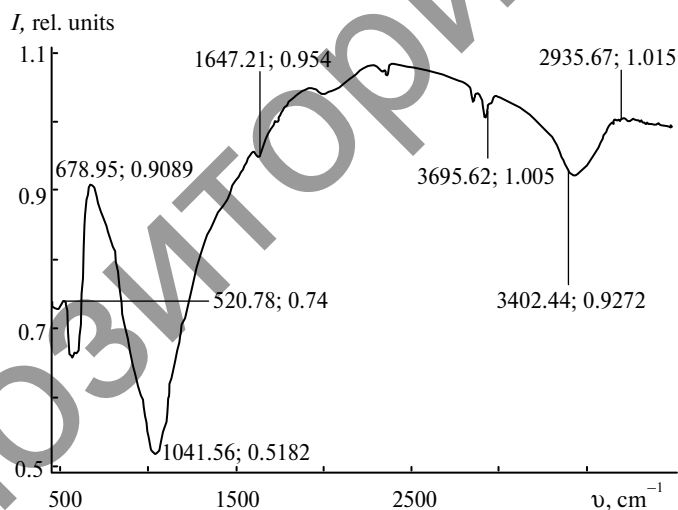


Fig. 1. IR-Fourier spectrum of the initial sorbent.

It should be noted that mineral sorbent based on the basis of apatite ore may be used as a sorbent for purification of industrial wastewater from heavy metal ions as it is characterized by the presence of reactive functional groups on the sorbent surface.

Sorption experiments were conducted in static conditions, adsorption value ( $a$ ,  $\text{mg}/\text{g}$ ) was calculated according to the equation

$$a = \frac{(C_{\text{ini}} - C_{\text{res}}) \cdot V}{m_{\text{ads}}},$$

where  $C_{\text{ini}}$  and  $C_{\text{res}}$  are concentrations of ions of metals before and after adsorption,  $\text{mg}/\text{dm}^3$ ;  $V$ —the volume of the solution,  $\text{dm}^3$ ;  $m_{\text{ads}}$ —weight of the adsorbent, g.

As a result we obtained particular relationships of adsorption from different factors describing the influence of temperature, pH, contact time of the sorbent with the solution and initial concentration of metal ions.

From Table 1 it is seen that all factors in question affect the sorption value with the correlation coefficient being in the interval 0.96–1.00. Table 2 shows optimal conditions of sorption concentration of Fe(III), Co(II) and Ni(II) ions.

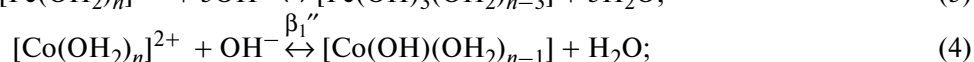
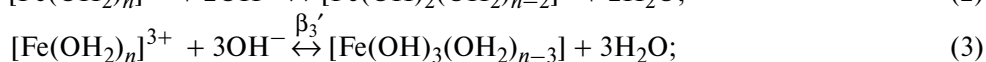
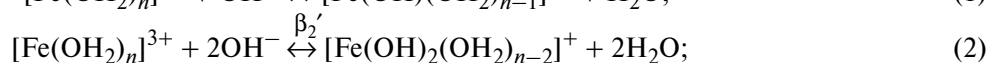
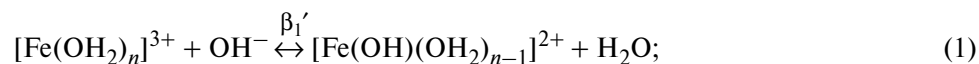
**Table 1.** Equation of the particular relationship between adsorption of heavy metals and different indicators

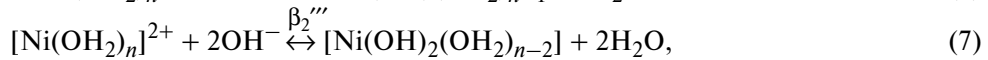
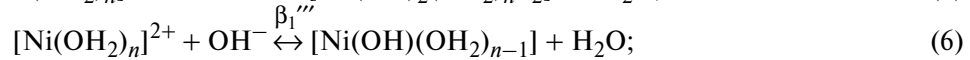
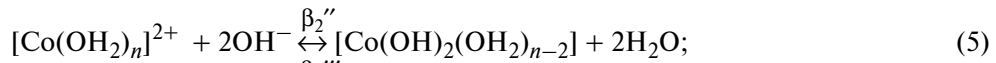
Ion of metal	Factors	Equation	R
Fe <sup>3+</sup>	T, K	$a = \frac{-0.03T + 10.59}{1.99}$	0.98
	C, mg/dm <sup>3</sup>	$a = \frac{0.04C - 0.14}{1.99}$	0.99
	τ, min	$a = \frac{-0.002\tau^2 + 0.24\tau - 0.14}{1.99}$	0.99
Co <sup>2+</sup>	T, K	$a = \frac{-0.01T^2 + 6.102T - 924.4}{1.99}$	0.99
	C, mg/dm <sup>3</sup>	$a = \frac{0.03C - 0.06}{1.93}$	0.99
	τ, min	$a = \frac{-0.004\tau^2 + 0.34\tau - 4.66}{1.93}$	0.99
Ni <sup>2+</sup>	T, K	$a = \frac{-0.01T + 5.36}{1.72}$	0.96
	C, mg/dm <sup>3</sup>	$a = \frac{0.04C - 0.54}{1.72}$	0.99
	τ, min	$a = \frac{-0.004\tau^2 + 0.45\tau - 6.82}{1.72}$	0.99

**Table 2.** Optimal conditions of concentration of Fe(III), Co(II), Ni(II) ions ( $C_{ini}$ —100 mg/g) on the sorbent of model solutions corresponding to the maximum value of sorption

Ions	pH	T, K	τ, min	a, mol/g
Fe(III)	4	298	45	$1.8 \times 10^{-4}$
	8			$1.2 \times 10^{-4}$
Co(II)	4	308	60	$1.12 \times 10^{-4}$
	8			$1.49 \times 10^{-4}$
Ni(II)	4	308	60	$1.97 \times 10^{-4}$
	8			$2.00 \times 10^{-4}$

When studying the influence of the pH on the sorption value it is necessary to allow for the fact that in changing the acidity of the environment ions of metals form similar in composition ion complexes in the all range of the pH:





where  $\beta_1' - \beta_3'$  are constants of stability of Fe(III) hydrocomplexes,  $\beta_1''$ ,  $\beta_2''$ —the same for Co(II),  $\beta_1'''$ ,  $\beta_2'''$ —the same for Ni(II) (12).

In the given case at the ascension of the pH of the solution there occurs the formation of hydrocomplexes. Therefore further on diagrams of distribution of molar fractions of metal complexes in the solution [13] were calculated. It was shown that at the pH 2–4.5 the main form of Fe(III) ions is  $[\text{Fe}(\text{OH})(\text{OH}_2)_{n-2}]^+$ , at the pH 8— $[\text{Fe}(\text{OH})_3(\text{OH}_2)_{n-3}]$ . The main form of Co(II), Ni(II) ions in the interval pH 1–8 is  $[\text{Co}(\text{OH}_2)_n]^{2+}$ ,  $[\text{Ni}(\text{OH}_2)_n]^{2+}$ .

From the data of Table 2 one can see that for Fe(III) ions at pH 4 one may observe maximum of sorption. It is connected with the participation of silanol groups with the formation of complexes [14]. A decrease of sorption at pH 8 is determined by the formation of neutral hydroxides [15], which are attached to phosphate groups through hydrogen bonds, which is characteristic of physical sorption [16].

Sorption of Co(II) ions is reached maximum in a weakly alkaline medium (pH 8), which is determined by coordination of aquacomplexes Co(II) with phosphate groups through atoms of oxygen [17]; Ni(II) ions coordinate in a similar way.

A real constant of stability of phosphate complexes of metals were calculated in the following way;

$$K_{KtL_2}^r = K_{KtL_2}^\beta \cdot x_{Kt} x_L^2, \quad (8)$$

where  $x_{Kt}$  is a molar fraction of free ions of metals;  $x_L$  is a molar fraction of ligands not bound in a complex;  $K_{KtL_2}^\beta$  is a constant of stability of the phosphate complex of metal (II)  $\log\beta(\text{Fe}(\text{HPO}_4)^+) = 21.0$ ,  $\log\beta(\text{CoHPO}_4) = 13.9$ ,  $\log\beta(\text{NiHPO}_4) = 13.8$  [18].

From the data of Fig. 2 one can see that Fe(III), Co(II) and Ni(II) ions in a weakly alkaline environment form hydrophosphate complexes for which real constant of stability ( $\log K_n^r$ ) are equal respectively 8.26; 13.82 and 13.62. A decrease of the constant of stability of specified complexes at high values of pH is determined by the formation of hydrocomplexes of metals. In particular, at pH 11 the real constant of stability of hydrophosphate complexes Fe(III) acquires negative values (–0.67) whereas for ions Co(II) and Ni(II)—positive (respectively 10.68 and 10.98) [13]. Specified above relationships of real constants of stability correlate with indicators of sorption at high values of the pH of the environment. It was found that sorption of metal ions most fully proceeds at pH 8, in this case of Fe(III) ions form the less stable hydrophosphate complexes than of Co(II) and Ni(II) ions. Since the solubility product (SP) of potassium phosphate constitutes 5 [19] and that of iron phosphate 21.9 [18], the sorption mechanism at precipitation of phosphates is not realized. On the other hand, the sorption mechanism at precipitation of hydroxides for Fe(III) ions in the form of hydroxide Fe(III) (SP—37.2) [12] is realized only through the formation of hydrogen bonds with phosphate groups of the sorbent. Whereas Co(II) and Ni(II) ions do not form hydroxides in the interval pH 4–8.

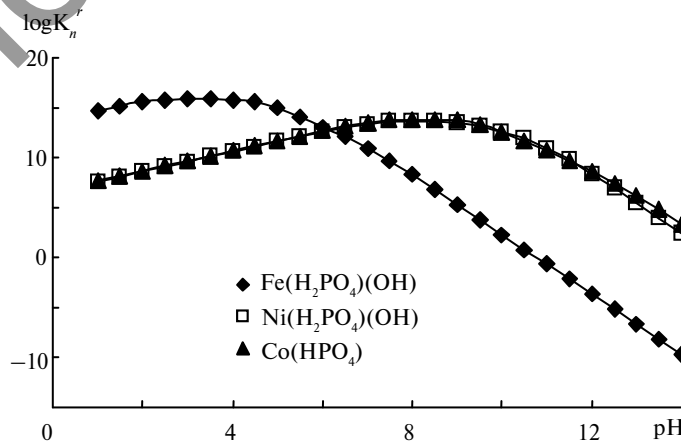


Fig. 2. Relationship between logarithms of real constants of stability ( $T=298$  K)  $\log K_n^r$  from pH of the aqueous solution in the case of the systems  $[\text{Fe}(\text{OH}_2)_n]^{3+} - \text{HPO}_4^{2-}$ ,  $[\text{Co}(\text{OH}_2)_n]^{2+} - \text{HPO}_4^{2-}$ ,  $[\text{Ni}(\text{OH}_2)_n]^{2+} - \text{HPO}_4^{2-}$ .

Consequently, the specified sorbent containing orthophosphate and silane groups at different pH of the environment may be used for sorption concentration of ions of heavy metals.

However, only Ni(II) and Co(II) ions are characterized by the formation of strong coordination links therefore the investigation of the sorption of ions of heavy metals was conducted using the specified ions as an example. Then we built sorption isotherms (at optimal values of the pH) at 298–318 K (pitch 10 K), which are shown in Figs. 3a–3c. It is seen that for Fe(III), Co(II) and Ni(II) ions the observable value of sorption with the growth of temperature is determined by a decrease of constants of hydrolysis of ions of metals ( $pK_{th}$ ) with Fe(III) ions the difference in constants of hydrolysis ( $pK_{th}$ ) is 1.5–2 times higher than for Co(II) and Ni(II) [15]. On the other hand, at high temperatures one also observes the destruction of hydrogen bonds between phosphate groups and hydrocomplexes of metals [20].

Then for conducting a qualitative assessment of effects considered above the sorption isotherms were treated in accordance with the Freundlich equation in a rectangular form and calculated sorption constants at 298; 308 and 318 K. Based on temperature dependence of adsorption constants calculation of the thermo-

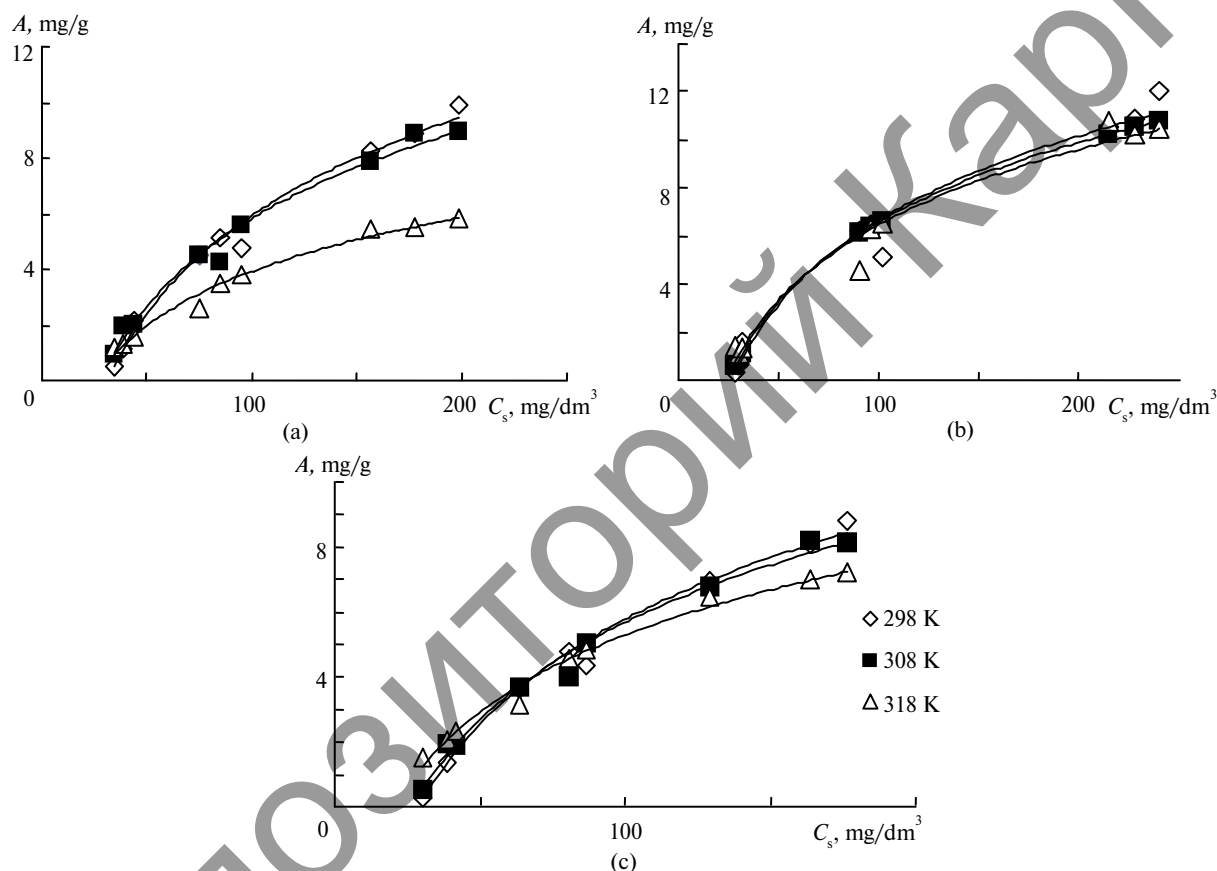


Fig. 3. Adsorption isotherms of ions Fe(III) (a), Ni(II) (b), Co(II) (c).

dynamic characteristics of sorption—the change of enthalpy  $\Delta H$ , Gibbs's free energy  $\Delta G$  and entropy  $\Delta S$  (Table 3) was carried out:

$$\Delta H = \frac{RT_i T_k \ln \frac{K_i}{K_k}}{T_i - T_k}; \Delta G_i = -RT_i \ln K_i; \Delta S_i = \frac{\Delta H - \Delta G_i}{T_i}.$$

From the table in question it is seen that adsorption of Co(II) ions at pH 4 proceeds with a release of heat, consequently, cobalt phosphate complexes being formed on the surface have high strength. At pH 8 binding of Co(II) ions is done via ion exchange [21]. Whereas for Ni(II) ions the intensity of the reaction of ion exchange decreases with an increase of pH of the medium and the probability of the formation of strong phosphate complexes increases.

**Table 3.** Constants and thermodynamic parameters of adsorption of heavy metals

Parameter	T, K	Co (II)			Ni(II)		
		pH 4	pH 6	pH 8	pH 4	pH 6	pH 8
K	298	226.77	200.16	185.57	162.06	184.87	182.15
	308	166.52	193.84	177.45	195.41	184.51	183.41
	318	165.79	211.37	214.10	213.09	202.85	201.58
$\Delta G$ , kJ/mol	298	-13.44	-13.13	-12.94	-12.61	-12.93	-12.89
	308	-13.10	-13.49	-13.26	-13.51	-13.36	-13.35
	318	-13.51	-14.15	-14.19	-14.18	-14.04	-14.03
$\Delta H$ , kJ/mol	298–318	-239.02	41.58	109.11	208.90	70.80	77.25
$\Delta S$ , J/(mol·K)	298	-756.98	183.61	409.57	743.33	280.99	302.50
	308	-733.50	178.81	397.32	722.12	273.26	294.14
	318	-709.14	175.28	387.74	701.51	266.82	287.04

According to the data of Table 3 ore rather effectively removes heavy metal ions from water. In this case there forms the formation of strong adsorption complexes. The value of adsorption of Ni(II) ions constitutes ~ 10.8, and for Co(II) ion—~ 8.5 mg/g, which allows us to remove from water rather great amounts of these metals.

Experiments were conducted for wastewaters purification from toxic substances by sorbent. Wastewater samples from JSC Arselor Mittal Temirtau (town of Temirtau) and etching manufactory of galvanic production were chosen as objects.

Sorption purification was done under the static conditions at 298 K, the contact time of the adsorbent with the adsorbate is 2 h, sorbent weight—5 g, the volume of the solution—50 cm<sup>3</sup>. The obtained information was processed by the statistical method.

Determination results of indicators of wastewaters and quantitative content of the main chemical components in them are given in Table 4. For comparison the data from San PiN 2.1.4.559-96 were used.

**Table 4.** Limited permissible concentrations, indicators of wastewaters content before and after sorption

Composition of wastewaters	LPC, mg/dm <sup>3</sup> (SanPinN 2.1.4.1074-01)	1*		2**	
		C <sub>ini</sub> , mg/dm <sup>3</sup>	Degree of purification, %	C <sub>ini</sub> , mg/dm <sup>3</sup>	Degree of purification, %
Ca <sup>2+</sup>	30–140	1352	96.45	1160	97.50
Mg <sup>2+</sup>	20–85	116	87.07	356	97.19
Na <sup>+</sup>	200	250	90.00	220	97.73
K <sup>+</sup>	–	550	99.45	500	99.00
NH <sub>4</sub> <sup>+</sup>	0.50	900	99.44	750	98.80
Cl <sup>-</sup>	350	100	0	116	43.10
SO <sub>4</sub> <sup>2-</sup>	500	6531	98.47	8179	79.02
NO <sub>3</sub> <sup>-</sup>	45	4	0	13	15.38
NO <sub>2</sub> <sup>-</sup>	3	–	–	0,55	1.0
Fe <sup>3+</sup>	0.30	50	100.00	150	100.00
Co <sup>2+</sup>	0.10	0.006	–	1.06	94.84
Ni <sup>2+</sup>	0.10	0.08	95.00	11.3	91.05
Hardness total, mg-equ/dm <sup>3</sup>	7–10	77.25	3.61	87.68	2.28
pH	6–9	3.61	4.20	3.00	3.70

\* Wastewater of JSC Arselor Mittal, Temirtau

\*\* Wastewater of galvanic production

It should be noted that in both samples of wastewaters many components exceed LPC, in particular they include  $\text{Ca}^{2+}$  ions (135 and 116 times),  $\text{NH}_4^+$  ion (1800 and 1500 times),  $\text{SO}_4^{2-}$  ion (13.06 and 16.36 times),  $\text{Fe}^{3+}$  ion (166.66 and 500 times),  $\text{Co}^{2+}$  ion (10.6 times, sample 2),  $\text{Ni}^{2+}$  ion (113 times, sample 2).

### CONCLUSIONS

It was established that the average degree of wastewater purification for both samples reached to 96.97% for  $\text{Ca}^{2+}$  ion, 99.12% for  $\text{NH}_4^+$  ion, 88.75% for  $\text{SO}_4^{2-}$  ion, 100% for  $\text{Fe}^{3+}$  ion, 94.84% for  $\text{Co}^{2+}$  in sample 2, 93.03% for  $\text{Ni}^{2+}$  ion as a result of sorption concentration using apatite ore. Thus, one may draw a conclusion that the sorbent based on apatite ore is rather effective for sorption removal of heavy metal ions and may be used in ecological and technological aims in water conditioning and water purification.

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