Adsorption of heavy metal ions (Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{2+}) from aqueous solutions by natural zeolite

T.P. Belova *

Research Geotechnological Center, Far Eastern Branch of Russian Academy of Sciences, Russia

ABSTRACT

The process of remove copper, nickel, cobalt and iron ions by natural zeolite of the Yagodninsky deposits, Kamchatka region, from water resources within a concentration range of 0.5–3.5 mg-eq/L has been experimentally investigated. The specified concentrations range was chosen according the contents of heavy metals in the waste water of the mining enterprise of Kamchatka region The values of maximum sorption capacity have been determined. On the basis of studies using X-ray powder diffraction (XRD) it has been established by the Rietveld method of calculation that the zeolite tuff of the Yagodninsky deposit consists of clinoptilolite-Na (23.0 %), clinoptilolite-Ca (52.1 %) and modernite (12.9 %). It has been established that exchange cations are sodium, calcium, potassium and magnesium. The Gibbs free energy has been calculated which is equal for copper $\Delta G = -25.6$ kJ/mol, iron – $\Delta G = -23.7$ kJ/mol, nickel – $\Delta G = -21.5$ kJ/mol and cobalt – $\Delta G = -20.0$ kJ/mol. The obtained results show that natural zeolite can be used as an effective sorbent for extracting of ions Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{2+} from polluted waters. On the basis of the analysis of the parameters of the mordenite crystal lattice a decrease in sizes in the direction of the *a*- and *b*-axes and, consequently, of the elementary cell volume of the treated zeolite is observed as compared with the initial zeolite in the Cu > Ni > Co > Fe row. New knowledge about the sorption properties of the Yagodninsky deposit zeolites can be interesting for the industrial areas of South-Eastern Asia such as China, Japan, Korea, etc.

1. Introduction

Zeolites form a large family of aluminosilicates which have been studied by mineralogists for more than 200 years [1, 2]. The present-day understanding of the composition of silicate structures is based on the principles developed by Pauling. The primary unit is a tetrahedral complex consisting of cation Si^{4+} tetrahedrally coordinated with four oxygen ions. The isomorphous substitution of Al^{3+} for Si^{4+} causes a negative charge density in the zeolite lattice. Zeolites are alumosilicates consisting of a three-dimensional network of tetrahedrons SiO_4 and AlO_4^-, connected with one another by common oxygen atoms [2]. This charge is compensated by the exchanging ions of sodium, calcium and potassium.

Kamchatka region has a significant amount of mineral deposits: gold, platinum, silver, nickel, cobalt, copper, mercury, sulfur, gas, oil, zeolite-containing tuffs, pumice perlites, geothermal resources. This is a non-inclusive list of prospective mineral resources which can be extracted in the region. Lately Kamchatka ore-mining industry has been taken a great interest. Such factors as economic efficiency and ecological safety of enterprise should be taken into account to develop ore-mining industry

on the peninsula.

Technological scheme of bacterial-chemical leaching of sulfide cobalt-copper-nickel ores of Shanuch deposit with three-stage mode was carried out in the Research Geotechnological Center of Far Eastern Branch of Russian Academy of Sciences (RGC FEB RAS) [3]. The following indexes of nonferrous metal extraction were obtained: Ni – 73.3%, Co – 67.5%, Cu – 15.6%. However, there is not anything about waste water purification in the mentioned work. Both low-concentrated and high-concentrated washing solutions are formed during the bacterial-chemical leaching of sulfide cobalt-copper-nickel ores in a stirred tank. It happens under the cake blow of leaching from product solution at the end. Leaching cake is washed twice keeping the ratio S(solid):L(liquid) = 1:5. Thus, the volume of washing solutions is 2 times higher than the volume of product solution. A part of such water returns in a technological cycle, another part necessarily enters the waste. In accordance with chemical analytical data it was determined that in the first part of washing solutions a fraction of non-ferrous metals was in the range 6.0–8.5 % from the concentration of product solution. It seems advisable to remove valuable components from washing and waste

water.

At the same time, there is a large field of natural resources of zeolites in the Kamchatskiy region - the Yagodnisky deposit. The deposit area is 350 hectares. The thickness of the useful stratum is 80–100 m. The field belongs to the hydrothermal-metasomatic type of deposits. Natural zeolite of the Yagodnisky deposit has a high cation-exchange capacity, high mechanical strength, resistance to aggressive media, which allows their use in a wide range of pH. It is used in water treatment processes [4]. Zeolite tuffs of the Yagodninsky deposit can be used to extract heavy metals from waste waters. It increases economic efficiency of the mining industry due to recycling of heavy metals.

New knowledge about the sorption properties of the Yagodninsky deposit zeolites can be interesting in the mining enterprises of Kamchatka region and in the industrial areas of South-Eastern Asia such as China, Japan, Korea, etc.

The aim of this paper is to investigate the sorption properties of natural zeolite of the Yagodninsky deposit of the Kamchatka region with respect to nickel, copper, cobalt and iron as well as their mixtures.

2. Materials and methods

2.1. Sample description

The natural zeolite tuff used in the experiments was obtained from the Yagodninsky deposit of the Kamchatka region (Russia). This deposit is located 100 km from the city of Petropavlovsk-Kamchatsky. Zeolite tuff is a massive rock of greenish-gray color. According to the data of the X-ray phase studies carried out at the RGC FEB RAS the main minerals are mordenite and clinoptilolite. Zeolite preparation was carried out in the following way: the sample was comminuted in a jaw crusher, a fraction measuring 0.25–0.5 mm was disengaged on sieves, washed with distilled water; the solid and liquid phases were separated by centrifuging or filtering and dried in the air at the room temperature. The average sample of the prepared zeolite was subjected to chemical and mineralogical analyses. The photo of natural zeolite of the Yagodnisky deposit of the Kamchatka region (Russia) is shown in the picture (Fig. 1).

2.2. Adsorption of heavy metals by zeolites

The experiments to determine sorption characteristics were made by the method of limited volume at the room temperature ($20\pm2^\circ$C). Zeolite preparation was made as follows: the sample was grinded up in a roll-jaw crusher, the fraction of 0.25–0.5 mm was separated on the sieves, washed by distilled water by decantation, dried on the air under the room temperature. Sub-samples of air-dry zeolite were placed in Ehrlenmeyer's

Fig. 1. Natural zeolite of the Yagodnisky deposit of the Kamchatka region (Russia).

flasks, model solutions with different concentrations of heavy metals in the ratio S:L = 1:5 were added, and placed in the shaker. In 4 h the solution was separated by filtering, and the concentration of heavy metals were determined. The experimental researches of heavy metals sorption by zeolite of Yagodnisky deposit of Kamchatka region from model solutions in the concentrations range from 0.5 up to 3.5 mg-eq/l were made. Sulfate productive solutions are formed during the oxidation of sulfide ores. Therefore, heavy metal sulfates were chosen for modeling adsorption processes. $CoSO_4 \cdot 7H_2O$ (analytically pure, Federal Standard 4528-78); $CuSO_4 \cdot 5H_2O$ (analytically pure, Federal Standard 4165-78); $NiSO_4 \cdot 7H_2O$ (chemically pure, Federal Standard 4528-78), $FeSO_4 \cdot 7H_2O$ (chemically pure, Federal Standard) were used to prepare model solutions. Ferrous iron accumulates as a result of the oxidation of sulfide minerals with ferric iron. Ferrous iron was stabilized at low pH.

The content of copper, nickel, cobalt, iron magnesium cations and of the exchange cations of potassium, sodium in the solutions was determined by atomic absorption spectroscopy using the AA-6300 «Shimadzu» (Japan) [23] using WizAArd software operating on a personal computer. Calcium was titrated with 2Na-EDTA (Ethylenediamine-N,N, N'N'-tetraacetic acid, disodium salt). All the data reported are the mean of three replicates.

The characteristics of sorption properties of the material are described by the equations of Langmuir and Freundlich. Static exchange capacity (Q, mg-eq/g) was calculated by the equation:

$$Q = \frac{(C_0 - C_t)V}{m},\tag{1}$$

where C_0 and C_t are the initial and steady-state concentrations of the metal ions in the solution, mg-eq/l; V – the solution volume, l; m – the sub-sample of sorbent, g.

The equation of Langmuir was used to describe adsorption isotherm:

$$Q = Q_{max}\frac{kC_t}{1 + kC_t}\tag{2}$$

where Q_{max} is the maximum sorption capacity mg-eq/g, k – the constant of adsorption equilibrium.

The linear form of the Langmuir equation is as follows:

$$\frac{C_t}{Q} = \frac{1}{Q_{max}C_t} + \frac{1}{Q_{max}k}\tag{3}$$

The dependence of sorption capacity on the concentration for sorption isotherms of parabolic character can be described by the Freundlich equation:

$$Q = k^{'}C^{1/n}\tag{4}$$

where $1/n$ is the constant, index of power depending on the temperature and adsorbate nature.

It is a straight-line equation in logarithmical coordinates.

$$lgQ = lgk^{'} + \frac{1}{n}lgC\tag{5}$$

The coefficients in the Eqs. (3) and (5) were determined by a graphical method (Figs. 2 and 3).

The Gibbs free energy ΔG was measured by the formula:

$$\Delta G = -RTln1000k,$$

where

R – the absolute gas constant equaled 8.314 J/mol·K;

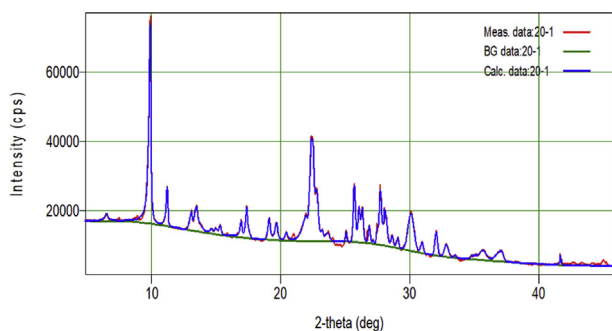T – Kelvin temperature;

k – the constant of sorption equilibrium.

Fig. 2. X-ray diffraction pattern for the natural zeolite of the Yagodninsky deposits, Kamchatka region (Russia).
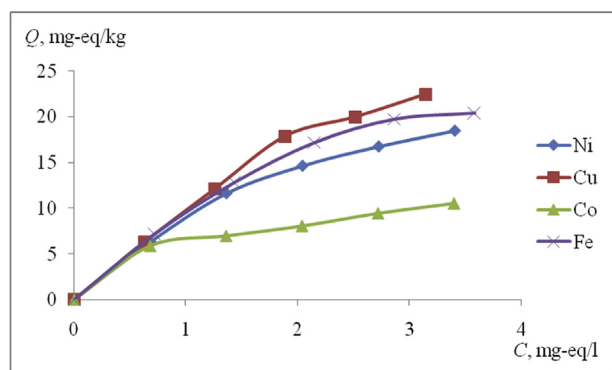

Fig. 3. Sorption isotherm of heavy metals from model solutions by zeolite of the Yagodnisky deposit of the Kamchatka region.

2.3. Powder X-ray diffraction analysis (XRD)

Before performing the analysis all specimens of the initial zeolite and zeolites obtained after saturating with heavy metal ions were first dried in the air, then abraded in an agate mortar and after that dried at 65–70 C during 8 h. Diffractograms were registered to assess mineralogical and structural changes.

The X-ray diffraction analysis (XRD) was performed on Rigaku Ultima IV diffractometer (Japan) (Cu Kα). The X-ray generator operated at a power of 40 kW and 30 mA, the scanning speed was 1.0°/min, with a pitch of 0.02°, in an angular range of 3–50° (2 theta). The obtained diffractograms were analyzed in accordance with the Rietveld method [5] using PDXL software operating on a personal computer. The crystal phases were identified using the ICDD data base – International Center of Diffraction Data for Inorganic Substances.

3. Results and discussion

3.1. Sorbent characteristic

Natural zeolites are referred to a middle class of sorbents with ion-exchange and shape selective properties. In accordance with mineral composition the zeolite tuffs of the Yagodnisky deposit of Kamchatka are presented by clinoptilolite (up to 70%) and mordenite (up to 10%). The share of cristobalite, quartz, mica(biotite) and clay minerals is up to 20%. In accordance with mineral composition the zeolite raw of the deposit is referred to a clinoptilolite type, clinoptilolite and mordenite-clinoptilolite subtype. Chemical composition varies, mass fraction %: SiO_2 – 66–72; Al_2O_3 – 11–14; Fe_2O_3 – 0.6–1.7; CaO – 0.5–2.0; MgO – 0.1–0.5; MnO – 0.06; K_2O – 2.8–4.8; Na_2O – 1.34–3.55; TiO_2 – 0.23–0.45; P_2O_5 – 0.01; H_2O – 3.7–13.5. By chemical composition zeolites are referred to a high-silica and strongly alkaline aluminosilicates, silica module SiO_2/Al_2O_3 is 5.0–6.0.

There are many examples of using different deposits zeolites to purify waste waters from heavy metals ions. The sorption of heavy metals Ni, Cd, Cr, Zn, Cu from surface water on natural and modified clinoptilolites of Kholinsky (Russia) deposit was investigated [6], cobalt sorption was studied by clinoptilolite of Mexican deposit [7], sorption mechanism of heavy metals Pb, Cu, Ni, Cd from individual and multicomponents solutions by clinoptilolite of one of the Ukraine deposits were considered [8], a set of experimental researches to remove metal ions from polluted (contaminated) waters by Bulgarian natural and modified zeolites was made [9]. The sorption properties of the activated carbon-zeolite composite prepared from coal fly ash for Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} were studied by V.K. Jha etc [10]. Shaobin Wang, Yuelian Peng [11] reported that natural zeolites are used as effective adsorbents in water and wastewater treatment. P. Castaldi, etc. [12] studied natural zeolite from a formation in northern Sardinia (Italy), the adsorption capacity of the three cations decreases in the series Zn > Pb > Cd. G. Du etc. [13] were shown that the adsorption capacity for Cr(VI) increases with the processing ions Fe(III) of natural zeolite. I.A.M. Ahmed, etc. [14] were studied the sorption characteristics of cadmium absorption by clinoptilolite and zeolite-Y. S. Slivović, etc. analyzed [15] the influences of the initial temperature, size and particle size on copper ions sorption on zeolite 13X in a batch reactor. G. Purna Chandra Rao, etc. were studied the sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite [16]. The sorption properties are arranged in a row in the following order: zeolite 4A> zeolite 13X > bentonite. Bahia Meroufel, etc. [17] were studied of zinc recovery from water solutions using kaolin in batch reactors. The adsorbed amount of Zn (II) ions increased with an increase in the initial concentration of adsorbate, pH and temperature. Obaid, Shamsan S., et al. [18], Zamzow M.J., et al. [19] were studied the removal of heavy metals and other cations from wastewater using zeolites.

Earlier [20, 21, 22] the authors were studied the sorption of nonferrous metals from low concentration solutions by natural and modified zeolites. The prospects of their application were shown. To reduce pollution by mining wastes, filters with dried marine alga Saccharina bongardiana in combination with zeolite and pumice are recommended. Sorbents based on Kamchatka aluminosilicates were shown to be effective for the purification of sewage waters of mining factories from heavy metals. Besides cleaning industrial waters, their utilization appeared to be a promising technique for the extraction of non-ferrous metals from natural waters. The method was further modernized with the addition of components derived from marine organisms, in particular, from brown algae [20]. The mutual influence on the kinetics of the sorption of copper (II), nickel (II) and cobalt (II) ions (under their compresence) by natural zeolite of theYagodninsky deposit (Kamchatka) was experimentally investigated. The coefficient of internal diffusion, the rate constant of exchange reaction according to the models of pseudo-first and pseudo-second order were calculated for each ion. The calculated diffusion coefficients $n \cdot 10^{-9}$ sm·c^{-1}, reaction rate constants $k_1=(0.46 \div 1.10) \cdot 10^{-4}$ (pseudo-first-order model, c^{-1}) and $k2=n \cdot 10^{-12} \div n \cdot 10^{-7}$ (pseudosecond-order model, g·mmol-eq^{-1}·s^{-1}), high correlation coefficients confirm that the diffusion of exchangeable ions in the crystal lattice of minerals is the limiting factor [21]. The sorption of metals (Mn^{2+} and Pb^{2+}) from aqueous solutions by natural zeolite of the Yagodninsky deposits (Kamchatka) has been experimentally studied. Estimated values of the Gibbs energy are equaled, kJ/mol: for manganese (II) ΔG = -15.4; lead (II) – ΔG = -24.9 [22].

The quantitative analysis by the Rietveld method has shown that the zeolite tuff of the Yagodninsky deposit consists of 88% of clinoptilolite-Na, clinoptilolite-Ca and mordenite. Mordenite has an orthorhombic structure, while clinoptilolite-Na and clinoptilolite-Ca have a monoclinic structure. Other phases are represented by anorthite, albite, cristobalite, while the share of secondary phases accounts for about 12%. Biotite and muscovite are determined in the form of single inclusions. A diffractogram of the pattern of initial zeolite tuff and quantitative ratio of the main phases calculated by the Rietveld method is presented in Fig. 2 and

in Table 1. The parameters of the crystal lattice of the main zeolite tuff minerals and minerals treated with heavy metal solutions are presented in Table 2.

On the basis of the analysis of the parameters of the mordenite crystal lattice (Table 2) a decrease in sizes in the direction of the *a*- and *b*-axes and, consequently, of the elementary cell volume of the treated zeolite is observed as compared with the initial zeolite in the Cu > Ni > Co > Fe row. At the same time no changes occur in the direction of the *c*-axis. This is probably due to the ion exchange occurring predominantly according to the scheme: $2Na^+ \overset{\rightarrow}{\underset{\leftarrow}{}} Me^{2+}$ and $Ca^{2+} \overset{\rightarrow}{\underset{\leftarrow}{}} Me^{2+}$ Such a trend has not been revealed with regard to clinoptilolite-Na and clinoptilolite-Ca.

3.2. Zeolite adsorption isotherms

The experimental researches of heavy metals sorption by zeolite of the Yagodnisky deposit of the Kamchatka region from model solutions in the concentrations range from 0.5 up to 3.5 mg-eq/L were made. The specified range of concentrations was taking into account the content of heavy metals in the wastewater of the mining enterprise of Kamchatka region. Sorption isotherms are presented in Fig. 3. The sorption capacity of zeolite increases with metal ions concentration The ions of heavy metals in the order of sorption capacity increasing are as follows: $Cu^{2+} > Fe^{2+} > Ni^{2+} > Co^{2+}$. The calculation of sorption characteristics for every studied ion was made by the equations of Langmuir (2) and Freundlich (4). Sorption isotherms built as coordinates of linear equation of Langmuir (3) and Freundlich (5) are presented on the plot (Figs. 4 and 5 and Table 3), respectively.

It should be pointed out that sorption isotherms of non-ferrous metals are lionized in the coordinates ($C_t - C_t/SE$) of Langmuir equation in the concentrations range as follows, mg-eq/l: C_{cu} from 0.63 up to 3.15; C_{Ni} – 0.68–3.41; C_{Co} – 0.68–3.39; C_{Fe} – 0.72–3.58. The table presents the values of maximum sorption, the constant of adsorption equilibrium, the Gibbs free energy, index values in Freundlich equation.

Values of the correlation coefficient R^2 are about one using the equation of Langmuir, but they are (slightly below) some lower if it is calculated by the equation of Freundlich. For copper the plot linearity in the coordinates ($lg\ C_t - lg\ SE$) of the Freundlich equation keeps up to the equilibrium concentration from 0.045 up to 0.9 mg-eq/L, the correlation coefficient $R^2 = 0.846$.

For nickel and iron the linearity keeps up to throughout the range equilibrium concentration, $R^2 = 0.948$. For cobalt there is the correlation coefficient $R^2 = 0.866$. Thus, using the equation of Langmuir is more preferred in the range of studied concentrations of non-ferrous metal.

Estimated values of the Gibbs energy give the possibility to suppose that the ions of copper – $\Delta G = -25.6$ kJ/mol, iron – $\Delta G = -23.7$ kJ/mol, nickel – $\Delta G = -21.5$ kJ/mol, cobalt – $\Delta G = -20.0$ kJ/mol are fixed steadily on the zeolite surface, the sorption takes place (develops) surely. Zeolite of the Yagodnisky deposit of the Kamchatka region can be used for the sorption of heavy metals such as copper, iron, nickel and cobalt

Table 1
Mineral composition of the natural zeolite of the Yagodninsky deposits, Kamchatka region (Russia).

Mineralogical phase	Chemical formula	ω, %	Card number
Mordenite	$K_{2.77} Ca_{1.86} Na_{1.90} (Al_{7.89} Si_{40.15} O_{96}) (H_2O)_{28.72}$	12.9	01-074-3676
Clinoptilolite- Na	$(Ca_{1.8} Mg_{.16} Na_{4.24} K_{.28}) (Al_{8.16} Si_{27.84}O_{72}) (H_2O)_{24.88}$	23.0	01-079-1461
Clinoptilolite-Ca	$(Na_{1.32} K_{1.28} Ca_{1.72} Mg_{0.52}) (Al_{6.77} Si_{29.23} O_{72}) (H_2O)_{26.84}$	52.1	01-089-7538
Anorthite	$Ca(Al_2Si_2O_8)$	10.7	01-076-0948
Albite	$NaAlSi_3O_8$	0.84	00-020-0572
Cristobalite	SiO_2	0.46	00-003-0257

Table 2
Lattice parameters of the mordenite, clinoptilolite-Na and clinoptilolite-Ca.

| Phase name	initial	Cu	Ni	Co	Fe	Mix
Mordenite						
a(A)	18.14	18.12	18.08	18.02	17.93	18.02
b(A)	20.57	20.44	20.47	20.39	20.35	20.46
c(A)	7.54	7.52	7.51	7.51	7.51	7.53
beta(deg)	90.0	90.0	90.0	90.0	90.0	90.0
V(A^3)	2814	2784	2781	2758	2740	2775
Clinoptilolite-Na						
a(A)	17.67	17.65	17.66	17.62	17.61	17.66
b(A)	17.94	17.93	17.93	17.89	17.88	17.93
c(A)	7.42	7.41	7.42	7.40	7.39	7.42
beta(deg)	116.5	116.5	116.5	116.5	116.5	116.5
V(A^3)	2104	2099	2102	2088	2083	2102
Clinoptilolite-Ca						
a(A)	17.68	17.67	17.70	17.62	17.61	17.67
b(A)	17.96	17.95	17.98	17.90	17.89	17.95
c(A)	7.41	7.41	7.42	7.38	7.38	7.41
beta(deg)	116.3	116.3	116.3	116.3	116.3	116.3
V(A^3)	2109	2104	2118	2088	2085	2106
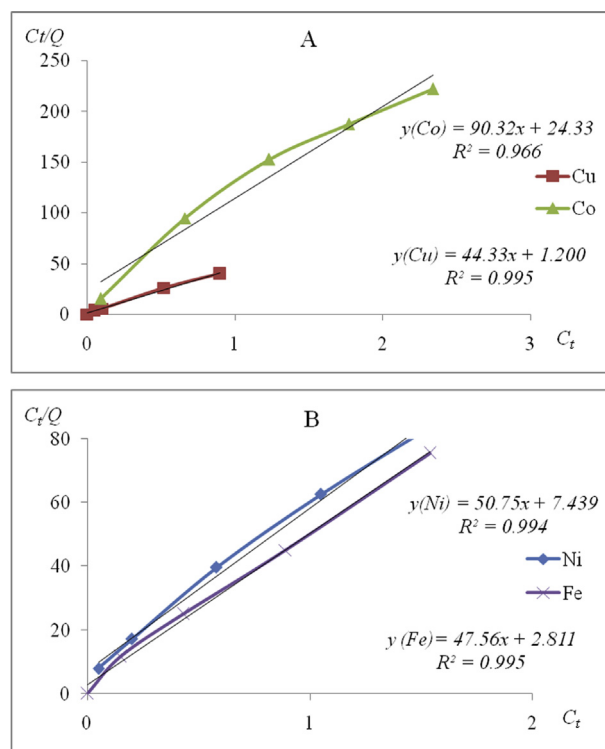
Fig. 4. Dependence of steady-state concentration ratio to the sorption zeolite capacity on the value of steady-state concentration of heavy metals in the solution (The Langmuir model). A – Cu^{2+} and Co^{2+}; B – Ni^{2+} and Fe^{2+}.

from aqueous solutions.

4. Conclusion

On the basis of the above-mentioned studies and obtained results one can draw the following conclusions:

1. The zeolites of the Yagodninsky deposit of the Kamchatka region are promising sorbents for extracting heavy metal ions from aqueous solutions.
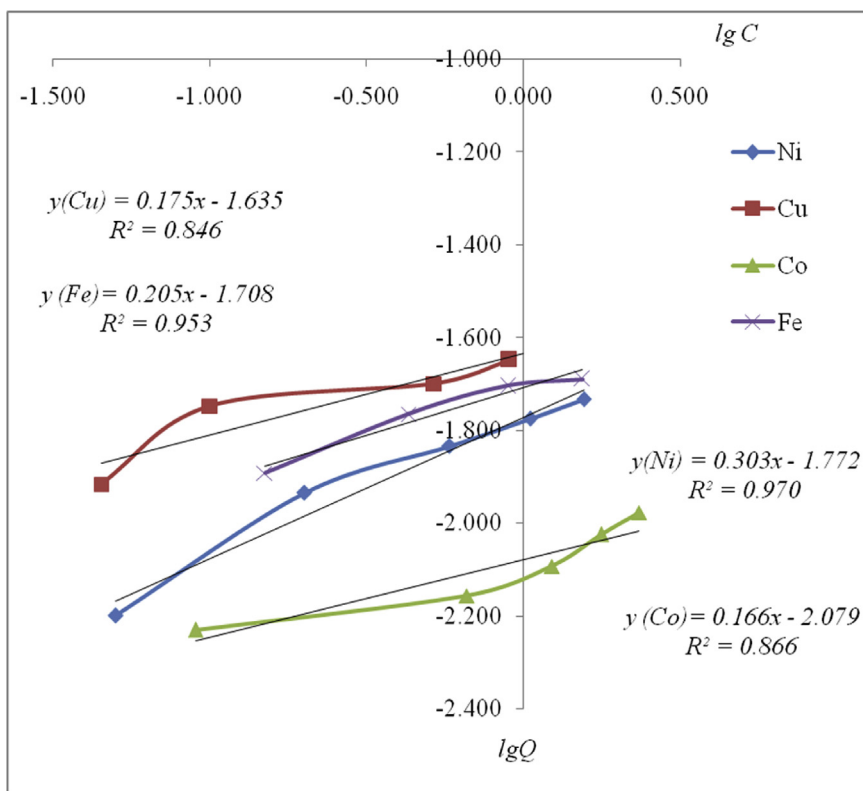
Fig. 5. The dependence of logarithm of sorption zeolite capacity on logarithm of steady-state concentration of heavy metals (The Freundlich model).

Table 3
Sorption characteristics of heavy metals ions uptake by zeolite calculated by the equations of Langmuir and Freundlich.

Ions	Langmuir			Freundlich		
	Q_{max}	k	R^2	k'	n	R^2
Cu	0.023	36.9	0.966	0.023	5.7	0.846
Fe	0.021	16.9	0.995	0.020	4.9	0.953
Ni	0.020	6.82	0.994	0.017	3.3	0.970
Co	0.011	3.71	0.966	0.008	6.0	0.866

where Q_{max} is the maximum sorption capacity, mg-eq/g.
k – is the constant of adsorption equilibrium (the Langmuir model).
k' – is the constant of adsorption equilibrium (the Freundlich model).
n – is the constant, index of power depending on the temperature and adsorbate nature.
R^2 – is the correlation coefficient.

2. Within the concentration ranges of heavy metals relevant to this study, from 0.5 to 3.5 mg-equ/L, sorption is described satisfactorily by the Lengmur equation.
3. The values of the maximum sorption capacity of the zeolites of the Yagodninsk deposit of the Kamchatka region have been determined. They are, in mg-equ/L,: for copper – 0.023; for iron – 0.021; for nickel – 0.020; for cobalt – 0.011.
4. The calculated values of the Gibbs energy which are equal to for copper $\Delta G = -25.6$ кJ/mol, for iron – $\Delta G = -23.7$ kJ/mol, for nickel – $\Delta G = -21.5$ kJ/mol and for cobalt – $\Delta G = -20.0$ kJ/mol corroborate the assumption about the steady attaching of nonferrous metal ions on the zeolite surface.
5. On the basis of the analysis of the parameters of the mordenite crystal lattice a decrease in sizes in the direction of the *a*- and *b*-axes and, consequently, of the elementary cell volume of the treated zeolite is observed as compared with the initial zeolite in the Cu > Ni > Co > Fe row.

6. New knowledge about the sorption properties of the Yagodninsky deposit zeolites can be interesting for the industrial areas of South-Eastern Asia such as China, Japan, Korea, etc.

Declarations

Author contribution statement

Tatiana P Belova: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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