# Extraction of ions of zinc and copper by modified kaolinite forms

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**Abstract**. A study was made on the extraction of zinc and copper ions by modified forms of kaolinite. The quantitative characteristics of the adsorption of zinc and copper ions are obtained. It is shown that kaolinite after alkaline and salt treatment increases the exchange capacity with respect to zinc and copper ions. The adsorption equilibrium was described using Langmuir and Freundlich models. The degree of extraction of zinc and copper ions from solutions was determined depending on their concentration at a constant mass of the adsorbent. It is shown that when kaolinite is modified by solutions of sodium chloride and sodium hydroxide, the adsorption capacity with respect to zinc and copper ions increases.

## 1. Introduction

The greatest harm to the environment is caused by heavy industry. They are characterized by large indicators of discharged wastewater, as well as a high concentration of metal ions in water (up to 50-200 mg / l), which exceeds the permissible maximum permissible concentration PDK [1]. The sewage of galvanic production contains in its composition heavy metal ions – Cr (chromium), Cu (copper), Fe (iron), Zn (zinc), Pb (lead), Cd (cadmium), Ni (nickel). Metals Zn, Cu, Pb, Cd, Sr are the most common and dangerous substances that pollute the environment [2-5]. Heavy metals include more than 40 chemical elements with a relative density of more than 6 $g/cm^3$. The danger of contamination of the biosphere by heavy metals is that they are eternal. Unlike organic pollutants, they do not collapse, but only pass from one form to another, they can be part of oxides, salts, organometallic compounds, complex compounds [6-9].

For the purification of sewage containing heavy metals, the main physicochemical methods are reagent, electrochemical, biochemical, membrane and sorption methods [10-12]. Natural adsorbents have some advantages over industrial adsorption materials. To their dignity are low cost, radiation stability and environmental safety. Clay rocks are the most common inorganic adsorbents for water purification [13-16].

At the Department of General and Special Chemistry of the Tyumen Industrial University, research is being conducted on the adsorption properties of natural adsorbents with respect to heavy metals.

## 2. Materials and methods

The aim of the paper is to evaluate the adsorption properties of modified forms of kaolinite with respect to zinc and copper ions by the possible use of an adsorbent to solve environmental

problems.The choice of these metals was associated with their high toxicity and prevalence as pollution of natural and industrial waters.

In the work, kaolinite was used as an adsorbent.Kaolinite is a uniform distribution of highly disperse crystalline silicate particles. The crystal lattice consists of two-layered packets in which one grid of octahedra has one grid of silicon-oxygen tetrahedra. The distance between the tetrahedral and octahedral layers is constant and equal to 0.28 nm. The distance between the packets is 0.72 nm. Crystals of kaolinite have the form of well-defined hexagons up to 0.3-0.4 microns in size and 0.05-2.00 microns thick, which corresponds to the specific surface area 1-22 м$^2$/g.

A scanning electron microscope (SEM) determined the composition of kaolinite (table 1).

**Table 1.**Content of components in kaolinite.

| Content | $SiO_2$ | $Al_2O_3$ | $Na_2O$ | $K_2O$ | CaO | $Fe_2O_3$ |
|---|---|---|---|---|---|---|
| % mass. | 54.55 | 27.23 | 1.29 | 0.96 | 3.81 | 9.94 |
| the number of mol | 0.909 | 0.267 | 0.021 | 0.010 | 0.068 | 0.062 |

The presented data make it possible to determine the atomic ratio of aluminum oxide to silicon dioxide, which is ~ 1 / 2.1, which corresponds to the number of acid centers of the surface of the aluminosilicate kaolinite framework [17,18]. The active ions in kaolinite are the mobile ions $Na^+$ , $K^+$ and als $Ca^{2+}$ , which participate in the exchange of heavy metal ions.

The mineralogical composition of kaolinite was determined by X-ray phase analysis.In Fig. 1 shows the X-ray diffraction pattern taken with a DRON-7 diffractometer with a copper anode ($\lambda$ = 1.5406 Å).The results of X-ray phase analysis give additional grounds for the assumption of high mobility and exchange capacity of $Na^+$ , $K^+$ , $Ca^{2+}$ cations retained on the surface of kaolinite.
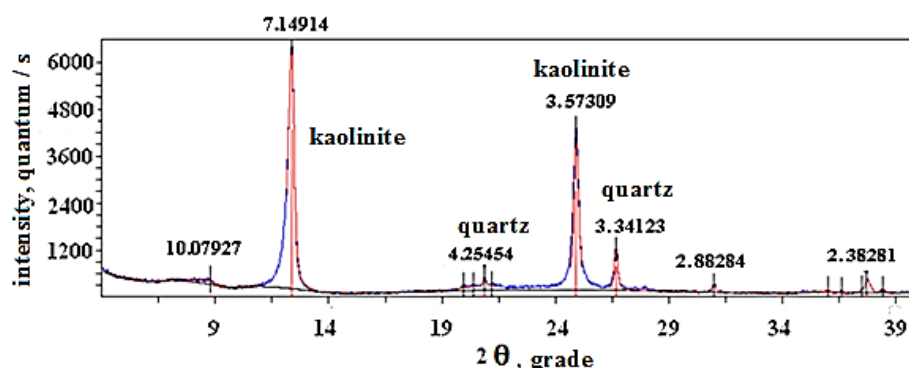


**Figure1**. X-ray pattern of the kaolinite sample.

The sorption process was studied using 4 forms of kaolinite: kaolinite in native (initial) form, Na-form (treated with NaCl solution), OH-form (treated with NaOH solution), H-form (treated with HCl solution). In this processing, natural clay sorbents an increase of the pore spaces, specific surface area and correspondingly increased sorption capacity [9]. The objects of the studies were model aqueous solutions of zinc sulfate and copper with concentrations from 0.01 to 0.10 mmol / ml.Adsorption equilibrium was studied at a temperature of 298 K under static conditions using the variable concentration method [17].A sample of kaolinite 1.0 g in air-dry state was brought into contact with 50 ml of a solution of zinc sulfate and zinc at a given temperature.Equilibrium in the system was achieved within 5 days. Then, the equilibrium phases were separated by filtration and the concentration of zinc and copper ions was determined in the filtrate by complexometric titration.

Based on the obtained data, the static capacity of sorption of zinc and copper ions $A$, (mmol/g):

$$A = \frac{C_0 - C_p}{m} \cdot V, mmol/\text{g} \tag{1}$$

and degree of sorption $\alpha$ (%)

$$\alpha = \frac{C_0 - C_P}{C_0} \cdot 100\% \qquad (2)$$

where $C_0$ - concentration of zinc and copper ions in the initial solution, mmol/ml; $C_P$ - equilibrium (residual) concentration of the extracted ion in solution, mmol/ml; $V$ - volume of solution, ml; $m$ – mass of adsorbent, $g$.

## 3. Results

Based on the experimental results of the study, isotherms of adsorption of zinc and copper ions on kaolinite (figure 2).
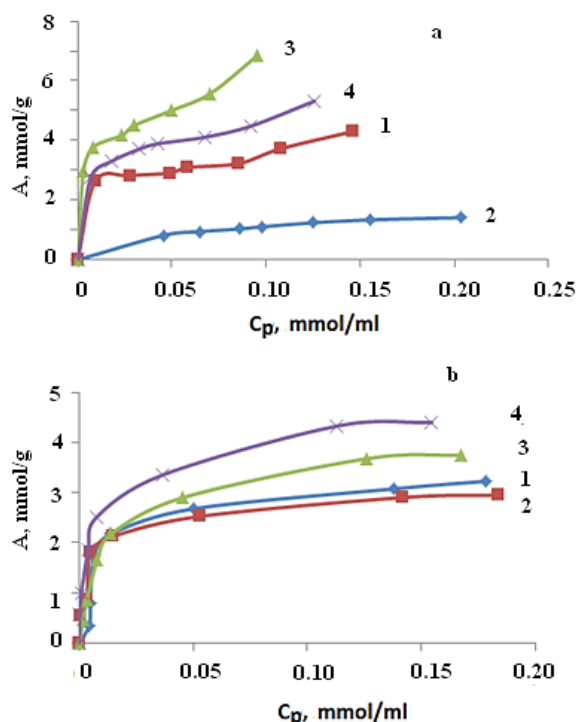


**Figure2**.Isotherms of sorption of zinc ions (a) and copper (b) by various forms of kaolinite: 1-H-form, 2-kaolinite in native form, 3-Na-form, 4-OH form.

The shape of the curves has a convex character, which indicates a high affinity of copper ions to kaolinite.On the curves there are no excesses, hence all the molecules of the initial substance are in a dissociated state.The amount of absorbed ions naturally increases with the increase in their content in the initial solution.The statistical exchange capacity of kaolinite, depending on the form, is (mmol/g): native (initial) form – 1.42 (Zn), 3.23 (Cu); H – form– 4.3 (Zn), 2.95 (Cu); Na–form – 5.32 (Zn), 3.75 (Cu); OH– form – 6.84 (Zn), 4.40 (Cu).An analysis of the obtained data shows that activation of kaolinite by solutions of sodium chloride and sodium hydroxide increases the adsorption capacity in 1.2 (NaCl), 1.4 times (NaOH), aH- form reduces by 0.9 times for copper and increases for zinc in 4.8 (NaOH), 3.75 (NaCl), 3.03 (HCl) in comparison with the native form.

It can be seen from the experimental data that kaolinite after alkaline and salt treatment increases the exchange capacity with respect to zinc and copper ions. In an acidic environment, the exchange capacity of kaolinite with respect to copper is reduced by blocking its active sites, which leads to a decrease in the extraction effect.

The adsorption process on kaolinite is due to the nature of the interaction of heavy metal ions by two mechanisms: the type of substitution of the exchange cation complex on the surface of the particles and with hydroxyl groups of the adsorbent. The total content of oxides $Na_2O$ и $K_2O$ in kaolinite in molar expression is 2.25 mol/kg and determines the limiting value of adsorption of copper

ions by the first type of mechanism. Ion exchange capacity is related to the reactivity of silane groups ($\equiv$ Si - OH) and their amount, which depends on the degree of hydration of silica. The adsorption properties of siliceous rocks are directly dependent on the specific surface area and volume of the adsorption space represented by the macropores of the mineral [19].

For the quantitative description of the adsorption equilibrium, several models:

Langmuir:

$$A = A_\infty \frac{k_L \cdot C_P}{1 + k_L \cdot C_P} \tag{3}$$

or in a linear form:

$$\frac{C_P}{A} = \frac{C_P}{A_\infty} + \frac{1}{A_\infty \cdot k_L} \tag{4}$$

where A is the amount of sorbed copper and $A_\infty$ - is the value of limiting sorption (mmol/g), $C_P$ - equilibrium concentration of zinc and copper ions in solution (mmol/ml), $k_L$ - concentration constant of sorption equilibrium, characterizing the intensity of the sorption process, ml/mmol;

Freindlich:

$$A = k_L \cdot C_P^{1/n} \tag{5}$$

or in the logarithmic form

$$\lg A = \lg k_F + \frac{1}{n} \cdot \lg C_P \tag{6}$$

where $k_F$ and n - are Freundlich constants.

The Langmuir isotherm model is based on the formation of a monomolecular adsorption layer on the adsorbent surface and all active sites have the same energy and enthalpy of adsorption [20]. The Freundlich model is used to describe adsorption on a heterogeneous surface [20]. The relative adsorption capacity is reflected by the constant $k_F$, and the intensity of the adsorption process and the distribution of active sites are characterized by the constant $n$. If n = 1, then all adsorption centers in the adsorbent will be equivalent, for n> 1 the binding energy between the adsorbent and the sorbed ion decreases as the surface becomes filled, and for n <1 the binding energy increases. In this case, first of all, the active adsorption positions with the lowest energy are filled, which is accompanied by a continuous change in the adsorption energy [21]. The adsorption energy in the Freundlich isotherm is in the logarithmic dependence on the degree of filling of the surface.

Linear processing of isotherms of adsorption of zinc and copper ions from aqueous solutions on all forms of kaolinite is presented in Table 2.

**Table 2.** Processing of isotherms of sorption of zinc and copper ions by models

| Formof kaolinite | The Langmuir model | | | The Freindlich model | | |
|---|---|---|---|---|---|---|
| | $A_\infty$, mmoll/l | $k_L$ | $R^2$ | $k_F$ | n | $R^2$ |
| | | | zinc | | | |
| native | $0.4 \cdot 10^{-2}$ | 1.72 | 0.962 | 2.66 | 0,38 | 0,991 |
| H- | $1.9 \cdot 10^{-2}$ | 2,04 | 0.947 | 5.13 | 0,16 | 0,896 |
| Na- | $2,7 \cdot 10^{-2}$ | 2.18 | 0.921 | 7.60 | 0,206 | 0,962 |
| OH- | $4.8 \cdot 10^{-2}$ | 2.63 | 0.918 | 4.96 | 0,148 | 0,962 |
| | | | copper | | | |
| native | 0,50 | $1.5 \cdot 10^3$ | 0,998 | 3,78 | 0,14 | 0,998 |
| H- | 0,25 | $0.7 \cdot 10^3$ | 0,997 | 3,53 | 0,11 | 0,941 |
| Na- | 3,33 | $1.65 \cdot 10^3$ | 0,995 | 7,51 | 0,26 | 0,984 |
| OH- | 0,50 | $1.68 \cdot 10^3$ | 0,999 | 4,54 | 0,17 | 0,968 |

The larger the adsorption equilibrium constant $k_L$, the stronger the interaction of adsorbent-adsorbate systems (zinc and copper ions in solution).

The obtained data on the adsorption of zinc and copper ions indicate a high adsorption activity of kaolinite. The extraction rate to 0.06 M solution is close to 100%. Figure 3 shows the results of the extraction of zinc and copper ions.
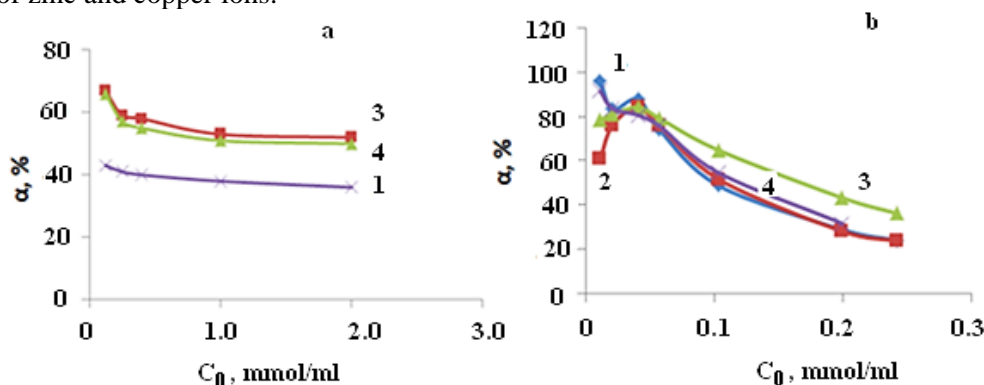


**Figure3**. Change in the recovery of zinc ions (a) and copper (b) upon adsorption on kaolinite: 1-H form, 2-kaolinite in native form, 3-Na-form, 4-OH form.

It can be seen from the graphical dependence that with an increase in the initialconcentration, the degree of purification of solutions from zinc and copper ions decreases. This can be explained by the fact that as the concentration of the initial solution increases, the ionic strength of the solutions increases, while the ion activity decreases. Thus, the free ions of copper in the solution become smaller and the degree of adsorption should decrease.

From a practical point of view, the efficiency of cleaning solutions depends on the ratio of the adsorbent consumption and the volume of the solution to be cleaned. It is known that the value of adsorption (A, mmol/g) is determined by the ratio of the mass of the adsorbent and the content of ions in the solution being purified, that is, its concentration and volume.

## 4. Conclusion
Based on the results of the study, the following conclusions can be drawn:

The main regularities of extraction of copper ions from aqueous solutions by kaolinite and its modified forms under static conditions are established. It was found that the processed kaolinite with sodium chloride increases the exchange capacity to 5.32 (Zn), 3.75 (Cu) mmol / ml, and sodium hydroxide to 6.84 (Zn), 4.4 (Cu) mmol / ml.

A sorption mechanism is proposed for two types of substitution of the exchange cation complex on the surface of particles and with hydroxyl groups of the adsorbent.

**Reference**
[1]   Zubarev G I, Gurinovich A V 2008 Deep sewage treatment of galvanic production *Ecology and Industry of Russia* December 16
[2]   Lupandina N S, Sverguzova Zh A 2012 Wastewater treatment from heavy metals as a factor of increasing environmental safety *Life safety* **4** 19
[3]   Garipova S A 2011 Wastewater treatment of galvanic production from heavy metals *Ecologyofproduction* **10** 66
[4]   Akhobadze G N 2011 Methods of sewage treatment from heavy metals and petroleum products *Ecologyofproduction* **2** 45
[5]   Kostyukevich G V, Brazovsky I I, Evseenko T I 2011 Technology of purification of washings of galvanic production *Ecologyandindustry Russia* January 16
[6]   Frumin G T 2013 *Ecological Toxicology (ecotoxicology)* (Petersburg: RSHU) p 179

[7]     Voronov Yu V 2009 *Wastewater and Sewage Treatment Textbook for High Schools* (Moscow) p 761

[8]     Lozhnichenko O V, Volkova V F 2008 *Ecological Chemistry* (Moscow Academy) p 272

[9]     Topalova O V, Pimneva L A 2013 *Chemistry of the Environment*: *textbook* (Petersburg: Lan) p 160

[10]    Burenin V V 2009 New designs of filters and devices for cleaning and neutralizing wastewaters of industrial enterprises *Safety of vital activity* **1** 30

[11]    Shchuklin P V, Romakhina E Yu 2011 Analysis of the main directions of industrial wastewater treatment from heavy metal ions *Bulletin of PSTU.Urbanistics* **3** 108

[12]    Shcherbakov A V 2014 Cleaning of sewage from salts of heavy metals *Ecology and production* **5** 56

[13]    Sikorska A V, Sikorski A V, Sivolobova B U T, Kruchina E A 2017 Waste water treatment from heavy metals by natural sorbents *Ecology and safety in the technosphere*: *modern problems and solutions: a collection of works of the All- practical conference of young scientists, graduate students and students Yurga November 23-25* (Tomsk: TPU) 125

[14]    Korolev V A, Samarin E N, Panfilov V A, Romanova I V 2016 Sorption properties of brucite and clay mixtures on its basis *Ekologiyai Promyshlennost Rossii* **20** 18

[15]    Deineka L A, Chulkov A N, Deineka V I 2009 Sorption of anthocyanins by natural clays: dependence on the structure of anthocyanins and the composition of extractants *J. Prikl. Chemistry* **5** 742

[16]    Chulkov A N, Deinek V I, Tikhov A A 2012 Effect of surface modification of clay berberine on the sorption of anthocyanins *Zh. physical chemistry* 86 **3** 500

[17]    Pimneva L A 2017 Adsorption of copper ions of natural montmorillonite clay *MATEC Web of Conferences* **106**

[18]    Shchumyatsky Yu I, Afanasyev Yu M, Shchumyatsky Yu I 1998 *Adsorption: a Process with Unlimited Possibilities* (Moscow: High School) p 76

[19]    Belenova S V, Vigdorovich V I, Shel N V et al. 2015 Sorption capacity of natural sorbents *Bulletin of TSU* **20 (2)** 388

[20]    Voyutskiy S S 1976 *Course of Colloid Chemistry* (Moscow: Chemistry) p 512

[21]    Pimneva L A, Nesterova E L 2008 Sorption isotherms of barium, copper and yttrium ions on the carboxyl cation exchange KB-4px2 *Modern high technology* **4** 15