Extracting copper (II) ions from model solutions with carbon containing adsorption material

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Abstract. A method for purifying model aqueous solutions from Cu\(^{2+}\) ions with carbon-containing adsorption material obtained by thermal modification of kieselghur sludge is proposed. Waste kieselghur sludge is characterized by an organic-mineral composition, which is formed in the technology of refining vegetable oil at the winterization stage i.e. removing waxes and wax-like substances at a temperature corresponding to their crystallization. As a result of heat treatment of the sludge at a temperature of 500 °C, carbonization of organic substances occurs with the formation of a carbon layer on the surface of diatomite particles and the formation of a carbon-containing adsorption material. The concentrations of Cu\(^{2+}\) ions in model aqueous solutions was determined out by photometric method. It was shown that the maximum sorption of copper ions occurs in the range of pH 6-7 and at the consumption of the adsorbent 1 g per 100 cm\(^3\) of solution. The kinetic dependences of the adsorption process are studied - the maximum efficiency of extracting copper ions reaches 15 and 30 minutes at the initial concentration of solutions 10 and 25 mg / dm\(^3\), respectively. The adsorption capacity of the carbon-containing material was 14.3 mg / g, the nature of the process is monomolecular.

1. Introduction

With increasing development of industrial production, its anthropogenic impact on the environment is increasing. In 2010, according to the data [1], 16.5 billion m\(^3\) of polluted sewage was discharged into the water bodies of the Russian Federation. In subsequent years, this figure has steadily decreased in 2014 and 2015, remained relatively stable and amounted to about 1/3 of the total volume of sewage. It should also be noted that there was a reduction in the volume of dumping of many substances, including heavy metal ions. Thus, the decrease in the discharge of copper and nickel ions into the surface natural water bodies of Russia in 2016 compared to 2005 was 60.93% and 67.38%, respectively (table 1).

Based on the above mentioned data, one would expect an improvement in the water quality of water bodies. However, in most river basins, water quality remains unsatisfactory and does not meet regulatory requirements. This fact requires increasing the efficiency of sewage treatment and reducing the flow of pollutants into water bodies.
Table 1. Some key indicators of water use in the Central Federal District of the Russian Federation, (million m³) [1].

| Year | Water intake from natural water objects | Losses water during transportation | Discharge of sewage into surface water bodies | Volume of recycling and reuse |
|------|----------------------------------------|-----------------------------------|-----------------------------------------------|----------------------------|
|      |                                        |                                   | Total                                         |                            |
|      |                                        |                                   | Polluted sewage among them Total In % to the total volume of discharge |
| 2014 | 12140                                  | 607                               | 7912                                         | 3328                       | 42.1                           | 37451                           |
| 2015 | 11348                                  | 606                               | 7215                                         | 3203                       | 44.4                           | 38061                           |
| 2016 | 11652                                  | 549                               | 7378                                         | 3187                       | 43.2                           | 37779                           |

Among a number of pollutants, heavy metal ions (HM) are among the most dangerous. HM includes the chemical elements of the D.I. Mendeleev table with the properties of metals and with an atomic mass greater than 50 atomic units [2]. According to another classification, this group includes metals with a density of more than 8 g / cm³.

All sources of HM in the environment can be divided into two large groups: natural and man-made ones. Currently, the main technogenic "suppliers" of HM are industrial enterprises and especially galvanic production, whose contribution is about 80%. Every year, up to 1 km³ of toxic sewage from galvanic plants containing 50 thousand tons of heavy metals enters the environment [3]. Only when washing products after coating, 3300 tons of zinc, 2400 tons of nickel, 460 tons of copper and 500 tons of chromium per year get into the sewage of metalworking enterprises of non-ferrous metallurgy [4].

Copper is also a heavy metal. Copper ions fall from natural and anthropogenic sources into all components of the biosphere - the atmosphere, hydrosphere and soil [5]. Copper enters the environment during the extraction and enrichment of ore, the smelting of metals and alloys, as well as when introduced into the soil as micronutrients or using fungicides and toxic chemicals in agriculture [6].

Copper ions have a high toxic effect on living organisms due to their influence on iron transport and hemoglobin formation [7]. Excessive copper content in the human body contributes to the disruption of the liver, the gastrointestinal tract and the cardiovascular system, leading to Wilson's disease [8]. A fatal dose of copper salts for humans is 200 mg / kg per body weight [9].

For removal and disposal of sewage from heavy metal ions, various methods are used such as mechanical, including membrane, chemical (reagent), physico-chemical (sorption, ion exchange, reverse osmosis, extraction), electrochemical, and biological ones. But the most common method is reagent, based on the transfer of HM ions into poorly soluble substances - hydroxides, sulfates and phosphates, which form sludge. However, this method is characterized by a high consumption of reagents and a significant amount of sludge formation, which reduces the economic efficiency of the cleaning system.

The most promising method of purifying water from heavy metal ions is sorption, characterized by high efficiency, the ability to purify multicomponent sewage to low concentrations of pollutants, which allows reuse of treated water in closed water circulation systems of enterprises [10].

Such traditional materials as activated carbons of the type AG-OV-5, SKD-515, DAK, KAD, MIUS [10-12] are used as sorbents. They have high sorption properties and efficiency, but are characterized by high ash content (3–10%) and remain expensive [13].

We know the use of natural materials such as clays, zeolite-containing and shungite rocks, flasks, peat, etc., the cost of which is several times lower compared to activated carbons with comparable sorption characteristics [14-17].


In recent years, much attention has been paid to the use of industrial and agricultural wastes as sorbents for the treatment of sewage from various pollutants, including HM ions. This allows us to solve two problems at once - to purify sewage and dispose of waste. We know the use of waste from steel-making production [18] from enterprises of the construction complex [19] and agricultural and food industry waste [20-22].

Combined or composite materials consisting of components of different origin are also widely used as sorbents [23].

But in some cases, both natural materials and wastes of various industries do not have sufficient sorption properties, which dictate the need to modify them to increase the porous structure and change the chemical nature of the surface of the particles. To intensify the sorption characteristics, various methods are used such as physical, chemical, and combined methods, the purpose of which is to create active adsorption centers in the structure and on the surface of the sorption materials, allowing increasing the sorption capacity with respect to various pollutants.

For the activation of natural clays, chemical methods are actively used e.g. the action of solutions of acids and alkalis. It is known that increasing the concentration of H$_2$SO$_4$ solutions in the process of acid modification of natural aluminosilicates increases the volume of micro- and mesopores.

In the work [24], as a result of acid-base modification of diatomite, its specific surface increases two to three times and the ions of hydroxyl groups are localized on the surface of the particles, which gives the resulting material its basic properties. As a result, the modified diatomite is characterized as a universal adsorbent for many HM ions.

In the papers [25, 26], it was shown that as a result of thermal modification of the saturation sludge of sugar production, a carbon layer forms on the surface of the particles, which causes an increased sorption properties of the resulting product with respect to heavy metal ions and other pollutants.

Studies presented in the paper [27] showed the effectiveness of ultraviolet irradiation of natural clays, which leads to a change in the electro kinetic properties of the surface of the particles and increases the efficiency of sewage treatment from heavy metal ions with their use.

Recently, in the sewage treatment system from HM ions, more and more attention has been paid to the use of carbon-containing adsorption materials obtained from waste from various industries [28-30].

The purpose of this work is to study the kinetic regularities and effectiveness of adsorption extraction of copper ions from aqueous media by carbon-containing sorbent, obtained as a result of thermal modification of the sludge waste of oil-extraction production. To achieve this goal, the following tasks were solved:

- assessment of the influence of the pH level of the medium on the efficiency of extraction of copper ions from model solutions;
- determination of the optimal parameters of the adsorption process - the mass of the adsorbent and the duration of mixing;
- determination of the sorption capacity of the carbon-containing sorbent for Cu$^{2+}$ ions.

2. Materials and research methods

As an adsorbent for the extraction of copper (II) ions, carbon-containing material obtained as a result of thermal modification of kieselghur sludge from oil extraction production was used.

The essence of the method of obtaining carbon-containing sorbent is as follows. To obtain an adsorption material, waste Kieselghur sludge (WKS) was used, which is formed in the technology of refining vegetable oil at the stage of winterization — removing waxes and wax-like substances at a lower temperature, corresponding to their crystallization, and filtering them from natural powdery materials (kieselghur, zeolite & others). WKS is a greasy mass of dusty white color with the content of fat-and-oil mixture in the amount of 60-70%.

WKS was subjected to heat treatment at a temperature of 500°C for 1 hour with a lack of oxygen. As a result of the carbonization of organic substances, a carbon layer forms on the surface of diatomite particles and a carbon-containing adsorption material is formed as well [21].
The sorption of copper (II) ions on a carbon-containing sorbent was carried out under static conditions at a constant temperature (20°C) from model aqueous solutions of CuSO₄ • 5H₂O “analytical grade” (pure for analysis), manufactured by the Kyshtym copper electrolyte plant with an Cu²⁺ ion concentration from 3 to 200 mg/dm³. The sorbent was taken in the amount of 0.5 g per 50 cm³ of solution. The sorption process was carried out for 24 hours. Determining the concentration of copper ions in the initial solutions and in the filtrates was carried out using a photo colorimetric method based on the interaction of Cu²⁺ ions with sodium diethyl dithiocarbamate in a weak ammonia solution to form diethyl dithiocarbamate copper colored in yellow-brown. Photo colorimeter KFK-3-01 was used.

A medium with different pH values was created by adding solutions of 0.1 mol/dm³ of HCl or NaOH solutions. The pH value was controlled on an I-130 ionomer.

3. Results and their discussion

One of the important factors influencing the process of sorption is the pH of the solution. The dependence of extracting copper ions degree on pH was investigated in the pH range from 1 to 10. The initial concentration of copper ions was 10 and 25 mg/dm³. Graphs of the dependence of the purification efficiency of model solutions on pH are given in Figure 1. The results showed that the maximum sorption of copper ions occurs at pH 6-7.

![Figure 1. The dependence of extracting copper ions degree on pH.](image)

The research to determine the rational amount of material needed for effective cleaning of model solutions was carried out. The research results presented in Figure 2, showed that when using TKS in an amount of from 0.1 to 1 g per 100 cm³ of model solution, the extraction efficiency of Cu²⁺ ions increases and reaches a maximum of 92%. With a further increase in the mass of carbon-mineral material, the cleaning efficiency increases slightly, which is not purposeful.

The efficiency of sorption is also determined by the kinetics of this process. Changes in the efficiency of purification of model solutions from copper ions (with an initial concentration of 10 and 25 mg/dm³) were studied with the duration of contact with the adsorbent from 5 to 60 minutes under static conditions. The results presented in Figure 3, showed that the equilibrium in the distribution of copper ions between the solution and the sorbent is achieved rather quickly. Thus, the maximum efficiency of copper extraction reaches 15 and 30 minutes at an initial concentration of 10 and 25 mg/dm³, respectively.

The isotherm of adsorption and desorption of copper ions on a carbon-containing adsorbent is shown in Figure 4.
The shape of the adsorption isotherm indicates the monomolecular nature of the process & the presence of micro pores and mesopores. The sorption capacity was 14.3 mg / g. The position of the desorption isotherm indicates the specific nature of the adsorption interaction.

**Figure 2.** Dependence of the cleaning efficiency of model solutions containing Cu$^{2+}$ ions on the mass of the TKS.

**Figure 3.** Kinetic curves of sorption of Cu$^{2+}$ ions on the TKS.

**Figure 4.** Isotherms of adsorption and desorption of Cu$^{2+}$ ions on surface particles of TKS.

### 4. Conclusion

According to the research results, the following conclusions can be drawn:
- it is shown the promise of adsorption of Cu$^{2+}$ ions from aqueous solutions with carbon-containing adsorbent obtained by thermal modification of the spent kieselghur sludge from oil extraction production;
- as the optimal parameters of the adsorption process, you can take the following: the consumption of the adsorbent is 1 g per 100 cm$^3$ of solution, the duration of mixing is 30 minutes, the pH is 6-7;
- the sorption capacity of the carbon-containing adsorbent was 14.3 mg / g, the adsorbent is characterized by the presence of micro- and mesopores, the nature of the process is monomolecular,
the position of the adsorption isotherm and desorption indicates the specific nature of the adsorption interaction.

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