Analysis of kinetic and equilibrium adsorption of heavy metals by natural materials

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Abstract. One of the effective methods of cleaning up water is an adsorption method. The adsorption treatment is effectively used as a post-treatment after using treatment chemicals precipitators. You can use natural porous carbon-containing materials as obtained sorbents, as industrial waste, or cheap carbon raw modified by humans: ash, fines coconut, peat, activated carbon, active clay, bio- and phyto-sorbents, agricultural wastes (rice, barley, wheat husk, nutshell, bagasse, etc.). In this regard, there is a question of finding cheap natural sorbents with a high adsorption capacity. In this article we studied the regularity of extraction of heavy metal cations Cu$^{2+}$, Co$^{3+}$, Ni$^{2+}$, Fe$^{3+}$ from aqueous solutions, using natural sorbents: husk cedar cones, pine nut meal, walnut partitions, pectin. Constancy of the concentration of heavy metal ions in the solution corresponds to the time of adsorption equilibrium (from 10 to 40 minutes). High adsorption capacity with respect to heavy metal ions showed pectin and proteinaceous materials. It is shown that the adsorption capacity of natural raw materials in relation to heavy metal ions increases by 20-30% due to modification of the surface of biosorbents. The degree of metals extraction from solution using a composition based on a peel cedar cones and pectin increases by 20-30% in comparison with pure husk of a cedar cone. According to the degree of extraction from the aqueous solution, metal ions are arranged in the row Fe$^{3+}$>Co$^{3+}$>Ni$^{2+}$>Cu$^{2+}$.

1. Introduction
Pollution with heavy toxic metals is harmful to the earth's biosphere entailing the most severe biological consequences for both living organisms and humans.

The toxicity of "metal poisons" is due to the formation of strong chemical bonds with functional sulfur-, phosphorus-, nitrogen-containing groups of vital protein and biologically active compounds in the body. At the same time, the resulting organometallic complexes with various cell components block the biological functions of enzymes, damage cell membranes. As a result, the life cycles of cells and tissues in the body are disrupted, the mechanisms of vital redox processes with the formation of free radicals are changed, and poisoning occurs, which in some cases leads to death.

Heavy metals, whose compounds are used in various technological processes, enter reservoirs and soil in the form of ions with the effluents of industrial enterprises: mining, metallurgical, chemical and light industry.

Another modern problem of mankind is waste disposal. Some substances are potentially dangerous to all living things in the environment. Others are subject to decomposition, which can naturally last more than a hundred years.

In the modern world, the amount of waste produced is huge. The anthropogenic load on nature has increased. Industrial waste and garbage should be converted into raw materials through recycling and
reuse. In this regard, special attention has recently been paid to the creation of technologies for processing industrial waste generated as a result of production.

One of the effective methods of cleaning up water is an adsorption method. Adsorption treatment is effectively used as a posttreatment after effluent treatment chemicals precipitators. Sorbents can be natural and porous carbon materials are obtained as waste of production or cheap natural raw materials, modified by man: ash, coconut trifle, activated carbons, peat, active clay, bio- and phytosorbents, waste from agricultural production (rice, barley, wheat husks, nut shells, bagasse, etc.). In this regard, there is a question of finding cheap natural sorbents with a high adsorption capacity.

A large number of studies are devoted to adsorption waste water from heavy metal ions using a porous carbonaceous materials. For porous materials of different nature characteristic we developed specific surface, high absorption capacity in relation to liquids and dissolved substances. On their surface we fixed modifying various compounds using them as a template. Demand modified mineral sorbent materials caused by their specific properties. Modification increases the rate of establishment of equilibrium adsorption, chemical resistance to aggressive environment, the mechanical strength, selectivity and completeness of the ion binding toxicants. A study of the kinetic parameters of adsorption processes determines the time to reach adsorption equilibrium, required to provide engineering calculation process parameters. We previously studied the possibility of using as the adsorbent mineral material - burnt rock are waste coal industry [1].

Calorimetrically and sorption methods investigated enthalpy and kinetics of interaction of acids and alkalis with weakly ionizing fibrous chemisorbing. The sorption process of Cu\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\) Na-salt form of the cation exchanger and the enthalpy are an endothermic process depending on the nature of the metal cations and their concentrations in solution [2]. There is the use of ion-exchange of the synthetic fibers to extract ions from wastewater electroplating [3].

Wood industry is the main in the amount of waste produced. Its waste accounts for over fifty percent of the finished production.

Currently, one of the promising methods of waste disposal plant is bioconversion, the essence of which consists in splitting complex polysaccharides into simple with subsequent production based on their carbohydrate and protein fodder and fodder additives. Another equally effective process for treating vegetable waste production plant adsorbents can be used for water purification or adsorbents capable of absorbing and excrete harmful substances: toxins, metabolites, pathogens, toxic, allergens, heavy metal salts.

Biosorption becomes a potential alternative to existing technologies removal and recovery of toxic metals from waste waters. The main advantages of bio-sorption technology are its effectiveness in reducing the concentration of heavy metal ion to very low levels and using of cheap biosorbent materials. There are many factors to consider for a complex adsorption process for recovering metals agricultural wastes, since the processes are complicated mechanisms complexation, chemisorption, physisorption not only on the surface but also in the pores. We will appreciate ion exchange, microprecipitation, condensation of hydroxides of heavy metals on the adsorbent surface.

There are various sorbents of natural origin that differ in origin, sorption characteristics and efficiency. The composition of such adsorbents include cellulose, lignin, chitin, cellulose.

Biosorbents show high efficiency and selectivity. One of these includes pectin. Thus, pectins investigated complex ability towards copper ions and iron, proving its unique properties to bind and remove from the living body of harmful substances: antibiotics, radionuclides, toxic metal ions, and pesticides [4].

In [5] we studied the adsorption of ions Cu\(^{2+}\), Zn\(^{2+}\) and Ni\(^{2+}\) from solution using wheat straw. There is a mechanism of ion exchange of the alkaline earth metal wheat straw heavy metal ions and protons. In [6] we investigated removing ions Cd (II) from aqueous solutions of anhydrous carbon husk hazelnut. To remove the lead and cadmium from aqueous solutions in sunflower agricultural waste we used a nature of the sorbent [7].
2. Objectives of the study
The aim of this work was to study the adsorption properties of natural sorption materials. The research task was: learning patterns of extraction from aqueous solutions of heavy metal cations via natural sorbents: husk cedar cones, pine nut meal, walnut partitions, pectin; an increase in the adsorption capacity of natural resources in relation to the heavy metal ions due to the modification of biosorbents.

3. Objects of the study
Objects of the research study: husk cedar cones, pine nut oil cake, baffle walnut, pectin, Ni salt solutions (II), Cu (II), Fe (III), Co (III).

4. Research Methods
The content of heavy metal ions in solution was determined photometrically in the visible area.

Measurement of absorbance was performed in solutions by spectro-photocolorimeter KFK-3 with a layer thickness of 1 cm and a wavelength of maximum light absorption for the sample solution.

Study of the adsorption of heavy metal ions for the test adsorbents is based on determining the concentration of the solution prior to contact with the adsorbent \( c_0 \) and after the adsorption equilibrium \( c \). The amount of adsorbed substance was calculated from the difference in the metal ion concentration in solution before and after adsorption, considering the volume of solution from which goes adsorption. The specific adsorption capacity was expressed as the amount of substance adsorbed by one gram of adsorbent.

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a = \frac{n}{m} = \frac{(c_0 - c)V}{m},
\]

Ion adsorption was investigated under static and dynamic conditions. The studied concentrations were obtained as adsorption kinetics and adsorption isotherm curves (Figure 1).

The cleaning efficiency was calculated as the ratio of the difference of the concentrations of heavy metal ions in the solution before and after adsorption to the initial content of the metal ion.

Adsorptive materials surface modification was carried out by sintering the samples.

5. Discussion of the results
Constancy of the concentration of heavy metal ions in the solution corresponds to the time for establishing adsorption equilibria, which ranged from 10 to 40 minutes. Figure 1 shows the kinetic curves for adsorption of nickel ions in various types of natural adsorption materials.

![Figure 1. Kinetic curves of adsorption of nickel ions.](image-url)
Absorbent effect of any adsorbent is due to its large specific surface, which allows using adsorbents removing foreign substances from solutions of absorbing gases, liquids and discolor.

Table 1 presents data on the degree of extraction of metal ions in various types of adsorptive materials.

| Adsorbent material                  | Recovery rate, % |
|-------------------------------------|-----------------|
|                                     | Ni\(^{2+}\) | Fe\(^{3+}\) | Co\(^{3+}\) | Cu\(^{2+}\) |
| Husk pine cones                     | 76.0           | 84.6         | 82.4         | 72.0         |
| Partitions walnut                   | 88.4           | 64.0         | 44.0         | 74.4         |
| Pine cones after sintering          | 100            | 100          | 100          | 100          |
| Pine nut oilcake                    | 100            | 100          | 100          | 100          |
| Pectin                              | 100            | 100          | 100          | 100          |
| Briquette cedar husks and pectin    | 100            | 100          | 100          | 100          |

The research results revealed a high binding capacity pectin and protein-containing raw material relative to heavy metal ions. Increase in the adsorption capacity of the natural materials can be achieved by modifying the feedstock surface. Physical modification by sintering allows one to increase the degree of purification of aqueous solutions by 20-30%. We located the feedstock carbon during decarbonization which partially burns due to the formation of the maximum amount of micropores and formed a developed porous structure, formed of a new material.

Figure 2 shows the adsorption isotherms of nickel ions, cobalt, iron and copper on cedar cone after sintering.

![Figure 2. The isotherm adsorption of metal ions on cedar cone after sintering.](image)

The binding of heavy metals pectin proceeds by chemisorption type [4]. As a result of ion-coordinating functional interactions with the carboxylate groups of pectin is an additional retention of metal ions, which increases the degree of extraction. The high degree of extraction of heavy metals pine nut oil cake is due to their binding to complex with proteins of raw material.
The degree of extraction of metals from solution using a composition based on a peel cedar cones and pectin increases by 20-30% compared to pure husk cedar cones. According to the degree of extraction of the aqueous solution of metal ions are arranged in the row Fe$^{3+}$$>$Co$^{3+}$$>$Ni$^{2+}$$>$Cu$^{2+}$.

6. Conclusion
The obtained kinetic and equilibrium data for the adsorption of heavy metal ions showed that natural waste from the processing of vegetable carbon and pectin-containing raw materials are promising resource for cheap production of adsorption material. Using modifications can increase the adsorption capacity of natural materials by creating additional active adsorption centers and by the introduction of functional groups capable of ion-coordinating reaction with heavy metal ions.

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