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# ИССЛЕДОВАНИЯ СОВМЕСТНОГО ПРИМЕНЕНИЯ УГЛЕРОДСОДЕРЖАЩИХ И АЛЮМИНИЙСОДЕРЖАЩИХ СОЕДИНЕНИЙ ДЛЯ ОЧИСТКИ СТОЧНЫХ ВОД

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***Исследование посвящено изучению адсорбционных свойств термически модифицированного углеродсодержащего материала шунгита в сочетании с коагулянтом оксихлорид алюминия для дальнейшей эксплуатации в комбинированной очистке сточных вод. Был изучен традиционно применяемый в сорбционной очистке воды углеродный сорбент – гидроантрацит, не обработанный измельченный природный минерал-шунгит. На основании полученных первичных экспериментальных данных по адсорбции на природном шунгите и гидроантраците была проведена его термическая модификация с целью увеличения удельной поверхности и суммарного объема пор для увеличения эффективности очистки. В ходе эксперимента получен термически модифицированный адсорбент на основе шунгита Зажогинского месторождения, Карелия. Проведено сравнительное изучение адсорбции железа (III) на адсорбентах: антрацит, природный шунгит, термически модифицированный шунгит, также получены изотермы адсорбции железа (III) от равновесной концентрации. Определена степень извлечения катиона металла из модельного раствора с применением исходного и модифицированного природных адсорбентов. Рассмотрено получение оксихлоридного коагулянта и его применение. Приведена предполагаемая схема очистки сточной воды с использованием модифицированного шунгита и коагулянта оксихлорида алюминия. По итогам экспериментов можно сделать вывод, что модифицированный шунгит адсорбирует по сравнению с антрацитом в 1,4 раз выше и в 2 раза выше, чем природный шунгит без термообработки. Значение максимальной адсорбции для модифицированного шунгита почти в 7 раз больше максимальной адсорбции, полученной для антрацита, и в 5,6 раза – для необработанного природного шунгита.***

**Ключевые слова:** адсорбция, природный адсорбент, шунгит, коагулянт, антрацит, сточная вода

# RESEARCH OF COMBINED USE OF CARBON AND ALUMINUM COMPOUNDS FOR WASTEWATER TREATMENT

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***The study is devoted to studying the adsorption properties of a thermally modified carbon-containing material of schungite in combination with a coagulant aluminum oxychloride for further operation in a combined wastewater treatment. The carbon sorbent traditionally used in water sorption treatment - hydroanthracite and untreated ground natural mineral shungite has been studied. Its thermal modification in order to increase the specific surface and total pore volume to increase the cleaning efficiency was carried out on the basis of the obtained experimental data on adsorption on natural shungite and hydroanthracite. In the course of the experiment, the thermal modification of natural adsorbent based on the schungite from Zazhoginsky deposit in Karelia was studied. A comparative study of the adsorption of iron (III) was made on the following adsorbents: anthracite, natural schungite, thermally modified schungite. The isotherms adsorption of iron (III) as a function of the equilibrium concentration were obtauned. The degree of extraction of the metal cations from standardized test solution using initial and modified natural adsorbents was determined. The use of oxychloride coagulant is suggested to clean the water up to the required indicators. On the basis of experimental data, a two-stage wastewater treatment scheme is proposed using the modified schungite and aluminum oxychloride coagulant. Following the results of experiments, it is possible to draw a conclusion that modified shungite adsorbs in comparison with anthracite 1.4 times higher and twice above, then natural shungite without heat treatment. The value of the maximum adsorption is of the great importance for the modified shungite, which almost in 7 times more the maximum adsorption received for anthracite and by 5.6 times – for not processed natural shungite.***

**Key words:** adsorption, natural adsorbent, shungite, coagulant, anthracite, waste water

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## INTRODUCTION

Water is a well-known and widely used material in the world. It plays a key role in our everyday human life and technology. Water consumption is increasing every year by tens of times, and the water quality standards, the maximum permissible concentrations of substances in drinking water, wastewater, water for technology and industrial needs become tougher every year. The ability to use various inorganic silicate and aluminate compounds, regional natural and man-made products for the purification of waste water from the toxic compounds is shown in [1].

For example, the industrial waste of chemical, steel, limestone and other productions can be used as reagents: under-burnt limestone, dolomitic limestone, dolomite and limestone dust and lime sludge from nepheline concentrate production, sludge from the bauxite processing, sludge from blast and open-hearth furnaces, lime sludge from thermal power plants, and other kaolinite compounds [2].

Therefore, in connection with the modernization of the sorption areas of water purification and the related synthesis of inorganic compounds with desired physical and chemical properties, it is required to perform and obtain new experimental data that complement the existing scientific statements about the chemistry and mechanism of this process.

Schungite mineral can be used as an adsorbent for purification of household waste water by settling tanks which are filled with granular material in the filters of various designs. This is particularly important in water treatment process for structural type adsorption systems containing natural silicate forms of silicon dioxide (sand – $SiO_2$) as a precipitation material. Therefore, when filtering «toxic» water through the schungite filter, the water color is significantly reduced and microflora is almost completely removed. The practically zero coli index can be achieved by adjusting the water flow rate through the schungite filter [3]. In accordance with the above, it should be recognized that the schungite mineral reacts with water due to the unique surface so that it can be used not only as a filter material but also as an active adsorbent due to its catalytic and cation-exchange properties.

For wastewater treatment, the authors suggest using the oxychloride coagulant produced by the method of complex processing of copper-ammonia solutions using aluminum waste, the use of modified schungite and recommend process flow design with preliminary water treatment.

## EXPERIMENTAL PART

Schungite density of 2.1-2.4 g/cm$^3$; porosity – 5%; compressive strength – CCC 1000-1200 ktf/cm$^3$; conductivity – 1500 Sim/m; thermal conductivity – 3.8 W/m·K. Natural schungites differ in the composition of mineral bases (aluminosilicate, siliceous, carbonate), and the amount of schungite carbon. Schungite rocks with silicate mineral base are divided into low-carbon schungite (5% C), medium-carbon schungite (5-25% C) and high-carbon shungite (25-80% C) [4].

To achieve the goal the following experimental procedures were conducted in the process of thermal modification of natural schungite adsorbent, including its crushing, screening and heat treatment. Thermal influence on schungite was performed according to the authors' invention: heat treatment of schungite was carried out at a temperature 500-550 °C for 2-3 h [5, 19]. The schungite thermal modification that was made according to the patent allowed to increase the surface area and total pore volume of the schungite mineral, which made it possible to improve the quality of water purification compared with anthracite.

The adsorption properties of the adsorbents were determined by a statistical method. To conduct the experiment, the standardized test solutions were prepared from a solution of iron sulfate (III)-ammonium using dilution method with various concentrations of $Fe^{3+}$ cations from 3 mg/l to 150 mg/l. 1 g of an adsorbent was added to the standardized test solution, then the solution was stirred for 15 min and filtered. The 0.2 cm$^3$ of concentrated sulfuric acid, 1 cm$^3$ 2 M ammonium chloride, 1 cm$^3$ 20% sulfosalicylic acid, 1 cm$^3$ ammonia solution 1:1 were added to the resulting filtrate. The solution was thoroughly stirred and the absorbance at λ = 400 μm in 50 mm cell against water on Promekolab PE-5400 UV spectrophotometer [6, 18].

The adsorption (T) is quantitatively determined by an interfacial excess of the substance compared to the equilibrium amount of the substance in solution. Comparing the initial values of the cation concentration in the solution with a residual concentration of metal ions after solution contacts with the adsorbent, we can deduce the adsorption capacity of the ion for the studied adsorbent itself and its properties. The Fig. 1 shows the experimental data: statistically processed direct dependence «specific adsorption – equilibrium concentration».

Adsorption (Г, g/g) was calculated by the formula:

$$\Gamma = \frac{(C_{base} - C_{end}) \cdot V \cdot M}{m} \qquad (1)$$

where $C_{base}$ – the initial concentration of iron cations (III) in the solution in mol/l; $C_{end}$ – the equilibrium concentration of iron cations in the solution after adsorption process, mol/l; V – the volume of the solution, l; M – the molar mass of the test compound; m - the mass of an adsorbent used for the adsorption process, g.

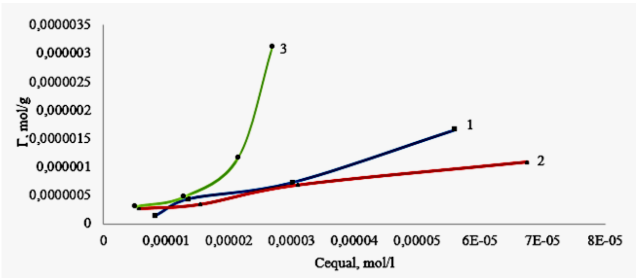


Fig. 1. Isotherms of adsorption of iron (III) (Г) vs the equilibrium concentration (C) on adsorbents studied: 1. natural schungite; 2. hydro anthracite; 3. modified schungite

Рис. 1. Изотермы адсорбции железа (III) (Г) от равновесной концентрации (С) на исследуемых адсорбентах: 1. шунгит природный; 2. гидроантроцит; 3. шунгит модифицированный

The value of the specified confidence level, P = 0.95. The total number of determinations, n = 4. Knowing the limit adsorption $\Gamma_{max}$, it is possible to calculate the surface area occupied by a molecule on the adsorbent according to the formula:

$$S_0 = \frac{1}{N_a \cdot \Gamma_{max}} \qquad (2)$$

Table 1 shows the results of calculations for the adsorption of iron cations (III) on the surface of the adsorbent.

With increasing concentration of the source solution the extraction rate of $Fe^{3+}$ cation from the solutions decreases.

To study the effectiveness of wastewater treatment with modified adsorbent, authors conducted an experiment to determine the index of total hardness of tap water (the norm for drinking water is 7 mg eq/l [7]) with the addition of 2-4 mm fraction of natural and modified schungite.

***Table 1***

**Comparison of quantitative characteristics of iron cations adsorption, depending on the adsorbent kind**

***Таблица 1.* Сравнение количественных характеристик процесса адсорбции катионов железа в зависимости от вида адсорбента**

| Sorbent type | The degree of adsorption, % | Freundlich equation | G, mmol/g ($C_{equal}$ = 1 mmol/l) | G, mmol/g ($C_{equal}$ = 0.1 mmol/l) | $G_{max}$, mmol/g | $S_0 \cdot 10^{-20}$, $m^2$ |
|---|---|---|---|---|---|---|
| Anthracite | 24-49 | $G = 0.0003 \cdot C^{0.5796}$ | 0.0003 | $7.9^{-5}$ | $9.2 \cdot 10^{-4}$ | 0.152 |
| Natural schungite | 25-37 | $G = 0.1885 \cdot C^{1.1875}$ | 0.01885 | 0.012 | $1.2 \cdot 10^{-3}$ | 0.199 |
| Modified schungite | 55-70 | $G = 1.0083 \cdot C^{1.2505}$ | 1.0083 | 0.057 | $6.7 \cdot 10^{-3}$ | 1.11 |

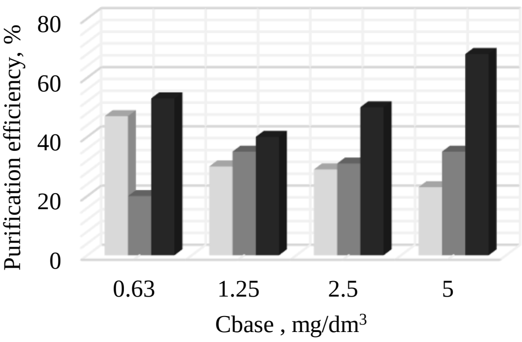


Fig. 2. Changing the degree of extraction of iron cations (III) as a function of the adsorbent type and initial concentration: hydro anthracite (white column), natural schungite (grey column), modified schungite (black column)

Рис. 2. Изменение степени извлечения катионов железа (III) в зависимости от вида адсорбента и исходной концентрации: гидроантроцит (белый столбец), шунгит природный (серый столбец), шунгит модифицированный (черный столбец)

The adsorbent was placed in laboratory columns with a supporting load of quartz sand, drinking water was passed at a predetermined flow rate of 19.4 ml/min, the analysis of purified water was carried out at 24, 53, 153, 250, 345 h. The solution pH was not adjusted during the study. Following the experiments, it can be concluded that the modified schungite adsorption is 1.4 times higher and 2 times higher compared to anthracite than the natural schungite without heat treatment. The maximum absorption ($\Gamma_{max}$) has the highest value for the modified schungite, which is almost 7 times greater than the maximum absorption obtained for the anthracite and 5.6 times for non-processed natural schungite. The carbonaceous materials may contain crystals of 1000 μm classes and +40 – -40 μm classes, representing a fine particulate mineral – an element which determines the turbidity of the treated water. In this regard, there is a problem of aggregation based on the proposed and developed oxychloride coagulant of the copper-ammonia solution [8].

Schungite allows you to get only 70% of cleaning and, therefore, it is necessary to raise the efficiency of cleaning to the parameters required by GOST. In accordance with the GOST requirements, the authors of this paper developed a method of obtaining the oxychloride coagulant which is added in the second stage of the process, after the water will be cleaned using a modified adsorbent. The preparation of oxychloride coagulant was described in [9, 17]. Electroplating is one of the most dangerous sources of pollution, mainly the surface and underground water bodies, due to the formation of a large volume of wastewater containing toxic impurities of heavy metals ($Cu^{2+}$) with hazard class 3, 0.5 mg/l MPC [20].

The processed copper-ammonium solution with a concentration of dissolved substances of copper-ammonia complex $[Cu(NH_3)_4]Cl_2$ of 350-400 g/l is diluted to a concentration of 30 g/l by copper. The diluted copper-ammonium solution is placed in the installation, consisting of a glass with an agitator. The agitator is driven by an electric motor; the speed is regulated by the motor. We destroy the copper-ammonia complex using the hydrochloric acid and then add the portions of aluminum shavings. The process of obtaining oxychloride coagulant is carried by the reaction:

$$2Al + 3[Cu(NH_3)_4]Cl_2 + 4HCl + 5H_2O =$$
$$3Cu + Al_2(OH)_5Cl + 4NH_4Cl + 2.5H_2 + \Delta H$$

The changes in the temperature of the solution were determined using a thermometer. Sampling for the analysis was carried out every five minutes. The content of copper and aluminum in the samples was defined. The solution was stirred for 30 min. Then the precipitated copper is filtered, readings for filtration are taken (filtrate volume, the amount of water for washing, to a negative reaction on $Al_3^+$ and $H^+$). The copper precipitate is dried at a temperature of 100 °C [10].

The aluminum oxychloride solution is used as a coagulant to intensify and accelerate the flocculation and precipitation of coagulated slurry during wastewater treatment [11]. The combined water purification scheme that is shown in Fig. 3 involves the following sequence of water purification.

The oxychloride coagulant (OCA reagent) is introduced in the treated water that contains the toxic components. OCA in accordance with chemical reaction $Al(OH)_2Cl + H_2O \Leftrightarrow Al(OH)_3 + HCl$ is hydrolyzed resulting in the formation of amorphous aluminum hydroxide flakes which are the active adsorbent [12].

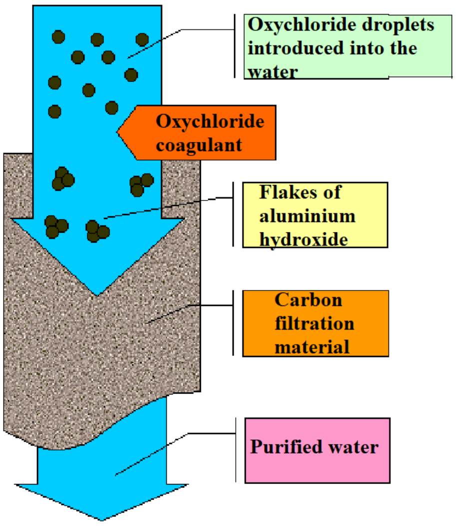


Fig. 3. Scheme of combined water purification using an oxychloride coagulant and a carbon-containing adsorbent
Рис. 3. Схема комбинированной очистки воды с применением оксихлоридного коагулянта и углеродсодержащего адсорбента

The hydrolysis of oxychloride compound with water molecules occurs according to the reaction $Al_2(OH)_5Cl + H_2O_{aq} = 2Al(OH)_3$, amorphous $+ HCl_{aq}$ and comprises the aluminum complex and the chlorine ion reacting with water molecules. The dissociation of water molecules occurs $H_2O + H_2O = OH^- + H_3O^+$ and the increase in the concentration of hydroxide ions or hydronium ions is observed depending on the environment [15, 16]. When using the oxychloride coagulant in water treatment systems, the following indicators are unique to the compounds formed with a strong acid and weak base $Al(OH)_mCl_{n-m}$: 1. the high-efficiency removal of toxic compounds, slurries, color from the water; 2. low costs of reagents (1-6 $Al_2O_3$ mg/dm$^3$) [13, 14].

When introduced into water, the dissolution and electrolytic dissociation of the coagulant occur, followed by the formation of aluminum hydroxide precipitates in the form of flakes that are acting as a complexing agent. Setting-out of the treated water was carried out in closed containers at a temperature of 20-24 °C and atmospheric pressure, and then the settled water was passed through the adsorbent layer. The quality of raw and purified water was determined photometrically in terms of the iron content and the evaluation of the effectiveness of the combined treatment was calculated, the experimental results are shown in Table 2.

*Table 2*

**The experimental results for the adsorbents used in combined water treatment**

***Таблица 2.* Результаты экспериментальных исследований применяемых адсорбентов в комбинированной очистке воды**

| Ion of metal | Cleaning method | | | |
|---|---|---|---|---|
| | Without OCA coagulant | The OCA coagulant + anthracite | The OCA coagulant + natural schungite | The OCA coagulant + modified schungite |
| | The degree of purification, % | | | |
| Fe (total) | 69.84 | 75.86 | 78.79 | 92.89 |

## RESULTS AND DISCUSSION

As a result of studies, it was found that a better quality of clarified water was provided using the oxychloride coagulant and thermally modified schungite.

The degree of extraction of iron cations (III) on the modified shungite is higher in compared with other adsorbents. The ionic strength of solutions increases with increasing initial concentration, and the activity of iron cations (III) decreases. Therefore, free ions $Fe^{3+}$ in the solution become less, therefore, the degree of adsorption of iron cations should decrease. The adsorption value and the degree of extraction of $Fe^{3+}$ cations on adsorbents hydroanthracite and natural schungite are much lower compared to the modified schungite process. According to the calculations, the maximum adsorption value is in keeping with to the complete saturation of the surface layer.

Based on the results of the experiment, it can be concluded that the modified shungite adsorbs 1.4 times higher and 2 times higher than natural shungite without heat treatment compared to hydroanthracite. The use of combined (oxychloride, adsorbent) purification with preliminary clarification of water with an oxychloride coagulant purifies water 1.3 times better than using an adsorbent without preliminary clarification of water.

## CONCLUSION

The developed technology of combined water treatment has the following advantages:

1. Adding the oxychloride coagulant before the adsorption iron ions process on the modified material will allow to intensify the process of water treatment and improve water quality.

2. Adding the oxychloride coagulant prior to the water supply in the adsorption filter will increase the service life of the adsorbent until replacement, and thermal modification of the schungite adsorbent to increase pore quantity will significantly improve the quality of treated water compared to traditionally used anthracite.

Mandatory conditions for this cleaning are:

During adsorption on the adsorbent (coal, schungite, anthracite, fuel shale [21]), the water containing suspended and colloidal material that will shield the pores of the adsorbent should not be treated.

The material that exhausted its adsorption capacity is regenerated or replaced completely.

The developed method of water treatment should be recommended for industrial waters of cogeneration plants, hydroelectric power stations, thermoelectric power station and other enterprises that require a purification rate of 93% based on the content of iron ions.

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