

Article

Graphene Oxide-Chitosan Composites for Water Treatment from Copper Cations

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Abstract: This paper considers modern sorption materials for wastewater treatment. The literature data on wastewater treatment with materials based on graphene and chitosan are presented. The production and application of composite sorbents is discussed. It is shown that a promising application of graphene oxide (GO) as a filler enhances the mechanical and sorption properties of the polymer matrix. The biopolymer chitosan (Ch) is a challenging matrix for GO, having unique sorption, chelate-forming, ion-exchange, and complex-forming properties. Composite adsorbents based on graphene oxide and chitosan have a high extraction efficiency of heavy and radioactive metals, dyes, and pharmaceutical compounds dorzolamide and tetracycline. GO-Ch composites with various ratios of chitosan and graphene oxide (2–7%) were formed by drop granulation. The composites obtained were investigated in terms of the ability to extract copper cations from the effluents, and it was shown that the composite having the content of GO:Ch = 55.5:44.5% (by mass in dry granules) had the best sorption and mechanical properties. This sample had high purification efficiency from copper cations (96%) and the required mechanical properties (attrition ≤ 0.4%, grindability ≤ 4%). For this sample, the influence of various factors (pH, sorbent dosage, temperature, and time of sorption) on sorption processes were studied. The best conditions for the sorption processes by the GO-Ch sorbent were determined. The sorbent dosage was 20 g/L, the sorption time was 20 min, and the temperature was 20 ± 2 °C, pH = 7. The adsorption isotherm was plotted and the maximum sorption capacity of copper cations A = 58.5 mg/g was determined. Microstructural and infrared (IR) spectroscopy studies of GO-Ch composites showed the presence of a porous surface and OH- and C=O functional groups. A mechanism for the extraction of copper cations due to physical sorption of the porous surface by GO-Ch composites, and due to chemisorption processes by functional groups, was proposed. The sorption properties for methylene blue and iodine absorption, and the specific surface area of the GO-Ch samples, were determined. The spent sorbent is proposed to be used as a soil improver.

Keywords: graphene oxide; chitosan; adsorbents; water purification; heavy metal ions



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1. Introduction

With the development of world industry, nature is increasingly exposed to the negative impact, so the issues on preserving the environment and reducing the harm caused by

anthropogenic impact are highly relevant today. One of the current environmental problems is the discharge of wastewater into natural water bodies. Mechanical, chemical, biological, and physical-chemical methods are used for wastewater treatment. Physical-chemical methods include sorption, which is used for water purification from hazardous pollutants (petroleum products, heavy metals, etc.) [1]. Sorbents made from waste simultaneously solve the issues of waste disposal and water purification [2–11].

The application of sorbents based on two- and three-dimensional carbon materials is promising [12]. Fullerenes, and the waste from their production (soot, niello), are widely used for wastewater treatment. A sorbent made of fullerene soot and chitosan was used to remove heavy metal ions from effluents [13]; it was shown that the efficiency of purification from iron cations reached 83%.

Graphene derivatives are widely used as adsorbents for removing various pollutants from wastewater [14–16]. Graphene oxide kills harmful bacteria with the effectiveness of chlorine. Graphene oxide has been added to solutions containing cultures of the most dangerous contaminant of tap water (*Escherichia coli*) [17]. Laser-Induced Graphene (LIG) was studied by Barbhuiya, et al., [18]; graphene membranes were obtained from it, for water disinfection and purification. Laser-induced graphene-polymer composites were developed to increase the strength of the membranes.

Scientists from Russia and the United States have discovered that microscopic particles of graphene oxide can absorb radioactive substances [19]. It has been shown that microscopic plates of graphene oxide sorb uranium and plutonium salts regardless of temperature and pH. The scientists proposed utilizing the spent graphene oxide with toxic elements by incineration. A method to improve the dispersibility of graphene in polyethylene (PE) by mixing PE with oxidized graphene (OPE) was considered [20].

Sodium alginate/graphene oxide (SA/GO) nanocomposites were obtained in a variety of forms (fibers, balls, and hydrogels), and were used to adsorb dyes (methylene blue) from wastewater [21]. SA/GO fibers were formed by coagulating an aqueous solution of SA with GO. It was found that the solution pH does not greatly affect the adsorption process of methylene blue. The adsorption capacity increased with decreasing temperature, indicating an exothermic process. It was found that desorption is optimal at acidic pH due to the competition in H⁺ adsorption with positively charged molecules of methylene blue.

Ma, et al., [22] synthesized various nanocomposites (calcium alginate/graphene oxide (CAA/GO), calcium alginate/reduced graphene oxide (CAA/RGO), sodium alginate/graphene oxide (SA/GO), sodium alginate/reduced graphene oxide (SA/RGO)) in the form of porous hydrogels, and studied their adsorption capacity for methylene blue. The maximum adsorption capacity of methylene blue was found to be $Q = 833.3$ mg/g for SA/GO, and $Q = 192.3$ mg/g for SA/RGO at 30 °C. SA and GO-based porous beads were used for the adsorption of acridine orange dye. It was shown that the sorption capacity increased with the addition of GO [23].

Chitosan is a promising matrix for graphene oxide. Chitosan is a biopolymer with unique sorption, chelate-forming, ion-exchange, and complex-forming properties [24]. Chitosan is highly efficient for the extraction of heavy [24] and radioactive [25] metal ions from wastewater. It has been shown that the optimum sorption of uranium takes place at pH = 3–5 [25]. A patented technology [26] presented a method for purifying lignin-containing wastewater, from the pulp and paper industry, with chitosan solutions.

To improve the properties of biopolymers, carbon (graphene, nanotubes) materials can be used to create composites; their properties and methods of preparation are presented in the literature [27,28]. The addition of carbon materials (graphene and its oxides) to biopolymers improved the mechanical, thermal, and electrical properties [29]. The authors developed graphene nanocomposites with chitosan, which showed high removal of dyes [30,31], heavy metal ions [32], and pharmaceutical dorzolamide compounds from biomedical wastewater [33]. Composite based on graphene oxide-chitosan effectively removed tetracycline (1.13×10^3 mg/g) from pharmaceutical industry waters [34].

Han, et al., studied the influence of GO on the properties of Ch films prepared by mixing solutions [35]. Strong interactions between the functional groups of the two components were confirmed by IR spectra. The addition of GO increased the mechanical strength and thermal stability of Ch films. Composites based on chitosan and GO completely inhibited the growth of *P. aeruginosa*, thus enhancing the antimicrobial character of Ch [36,37].

This work aimed to select the optimum percentage of graphene oxide additive for creating mechanically strong and highly effective graphene oxide-chitosan sorbents, and to examine them as a sorbent for highly effective removal of copper ions from wastewater.

2. Materials and Methods

Electrochemical synthesis of multilayer graphene oxide and the mechanism of dispersion of natural graphite powder in sulfuric acid electrolytes are described in detail in [38,39]. Electrochemical synthesis of multilayer graphene oxide was carried out using 83% H₂SO₄, obtained by sequential dilution with bidistilled water of concentrated H₂SO₄ (ultra-high purity, AO “ECOS-1”). The natural graphite powder of the 160–200 µm fraction (GB/T 3518-95 Sunshine Resources Holdings Limited Beijing, China), and IPC Pro MF potentiostat (NTF “Volta”) with a mercury-sulfate reference electrode, were also used.

Electrochemically oxidized graphite in the galvanostatic mode under 700 mA·h·g^{−1} was washed in bidistilled water (T = 15–18 °C) for 15 min to remove residual sulfuric acid compounds. The aqueous dispersion of oxidized graphite was filtered through a polypropylene filter cloth (item No. 56306, CJSC “SYNTEX”). Thermal reduction and exfoliation of oxidized graphite were carried out under static conditions for 5 s at 250 °C (muffle furnace SNOL-1,6,2,5.1/9-I4). The swelling coefficient of thermally reduced graphite oxide (K_V, cm³·g^{−1}) was determined using the formula:

$$K_V = V/m,$$

where V is the volume of thermally expanded graphite, cm³; m is the weight of oxidized graphite, g.

The particle size distribution in aqueous suspensions was studied using the Analysette 22 NanoTec (Fritsch GmbH, Idar-Oberstein, Germany) laser particle size analyzer with a measuring range of 0.01–2100 µm. The surface and structure of nanostructured graphite particles were investigated using the EXplorer (Aspex Corporation, Reston, VA, USA) scanning electron microscope with built-in energy dispersive analysis. The FTIR spectroscopy of nanostructured graphite particles was studied using the IRTracer-100 (Shimadzu, Kyoto, Japan) using KBr pellet.

Biopolymer chitosan obtained from the waste of processing the crustaceans (the shell of the walking limbs of the Kamchatka king crab) was used as a binder. Biopolymer was purchased from OOO “Chitosan Technologies” (Engels, Russia). The chitosan obtained had the following characteristics: bulk density of 0.2738 g/m³, moisture content of 13.8%, viscosity-average molecular weight u.a.m. of 420 kDa, deacetylation ratio DR = 80% [40].

To obtain granulated composites of graphene oxide-chitosan (GO-Ch), the method of droplet granulation was used [41]. In this method, chitosan binder, a 4% solution of chitosan in 3% acetic acid solution was first prepared [42]. 40 g of chitosan was added to 960 g of 3% acetic acid. The mixture was stirred for 4–5 h until the chitosan completely dissolved, and a homogeneous gel-like mass was obtained. Then, GO-Ch mixtures were prepared. For this purpose, different contents (by mass) of GO (2, 3, 4, 5, 6, 7%) were added to the homogeneous gel-like mass of chitosan in acetic acid. The mixtures were poured dropwise through a syringe into 5% NaOH solution of 500 mL. The NaOH solution was stirred using the Capacity magnetic stirrer at a speed of 1000 rpm. The formed granules were kept for 24 h in NaOH solution, and were then separated from the NaOH solution by being filtered through a paper filter “white tape” with a diameter of 5 cm, and washed with distilled water to pH = 7.0–7.5. The granules were dried naturally in the air for 24 h. Amounts of 100 g of each sample of dry GO-Ch granules were obtained.

To obtain highly efficient samples of GO-Ch composite, the optimal ratio of the binder (chitosan acid solution) and filler (graphene oxide) was selected. To determine the best composition, six experimental samples were prepared with different ratios of chitosan and graphene oxide.

Stock solutions containing copper cations, with an initial concentration of 10 mg/L, were used to examine the adsorption properties of the GO-Ch composites. The GO-Ch composites were added to the stock solution, in amounts of 20 g per liter. Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was used to prepare the solution containing copper cations.

The sorption was performed for 20 min under constant stirring. The GO-Ch composites were separated from the water by filtration. The final concentration of copper cations in the solution was determined by the photometric method, using the KFK-3-01 spectrophotometer. This method is based on the formation of a complex compound of copper ions with ammonia, which has an intense blue-violet color. The analyzed solution, after purification with sorbents, was placed in a 50 mL volumetric flask; 10 mL of ammonia 1:1 solution were added and diluted to the mark, and the solution was stirred thoroughly. The optical density was measured at $\alpha = 640 \text{ nm}$ [43].

To assess copper content in the wastewater, a calibration graph was preliminarily constructed (Figure 1, the relationship between the optical density D and the concentration of the solution C by which the concentration of the metal in the analyzed sample was determined). To determine the concentration in the sample, a “zero” sample was used for comparison. The device error of measurements of final concentrations did not exceed 15%.

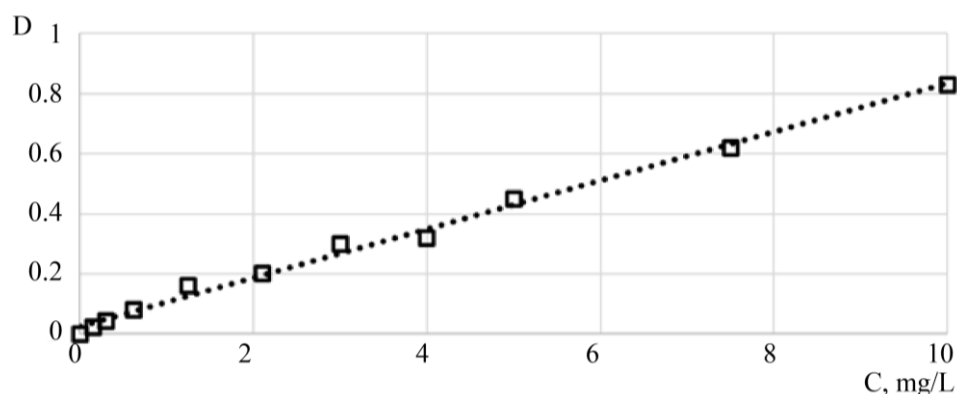


Figure 1. Calibration graph for determining the concentration of copper cations.

The degree of purification of stock solution (E) was calculated using the final (C_{fin}) and initial (C_{ini}) concentrations according to the formula:

$$E = \frac{C_{\text{ini}} - C_{\text{fin}}}{C_{\text{ini}}} \times 100\%$$

To study the influence of solution pH on purification efficiency, the required pH value of the solution was obtained with HNO_3 (7%) and NaOH (7%) solutions, and controlled using the I-160MI laboratory ionometer (OOO “Izmeritelnaya tekhnika”).

The studies were performed in a temperature range from 10 to 40 °C. Thermostating at 30–50 °C was performed using the LOIP LB-140 water bath. To achieve and maintain the temperature of 10 °C, the samples were placed in a cooling chamber. The sorption temperature was controlled using the thermometer.

To construct sorption isotherms, 20 g/L portions of GO-Ch sorbent were placed in a series of test tubes with solutions containing copper cations at initial concentrations (from 1 to 200 mg/L), and incubated until equilibrium was reached. The sorption temperature was $T = 20 \pm 2$ °C. The solution was then separated from the sorbent by filtration, and the final concentration of copper within it was determined.

The mechanical properties (grindability, attrition) of the obtained granules were determined according to the requirements of the Russian State Standard GOST R 51641-2000.

Microstructural studies were performed using the JSM-7001F (Jeol) scanning electron microscope.

The specific surface area of the materials was determined by low-temperature nitrogen adsorption ($-196\text{ }^{\circ}\text{C}$), by the BET method, using the TriStar II 3020 automated sorption unit (Micromeritics, Norcross, GA 30093-2901, USA.). The volumetric version of the sorption method was used.

Adsorption activity for methylene blue (which characterizes the presence of pores with a diameter of 1.5 nm) was determined according to GOST 4453-74 "Active clarifying charcoal powder".

Adsorption activity for iodine (which characterizes the presence of pores with a diameter of 1.0 nm) was determined according to GOST 6217-74 "Active crushed charcoal. Technical conditions".

The IR spectra of the residual biomass and sorbents were recorded using the FSM 1201 spectrometer. A KBr tablet obtained by pressing a crystalline powder upon vacuum pumping was used as a reference sample. Samples were obtained by pressing a mixture of the test powder (5 mg) and KBr. The total weight of the tablet with the test sample was 300 mg.

The data obtained during the experiment were statistically processed using Microsoft Excel 2010 using the "Descriptive statistics" tool. Each single experiment was repeated 6 times, and was then subjected to statistical processing at a confidence level of 0.95.

3. Results

In the earlier studies of the thermolysis of the multilayer graphene oxide obtained by the electrochemical method, thermal exfoliation was carried out at $250\text{ }^{\circ}\text{C}$. Thermal exfoliation at this temperature led to the modification of the oxygen-containing functional groups, a significant increase in the particle size ($K_V = 1490\text{ cm}^3\cdot\text{g}^{-1}$), and the formation of worm-like structures with a large number of V-shaped pores with the size $1\text{--}10\text{ }\mu\text{m}$ and the thickness of the polyhedral planes up to $0.01\text{ }\mu\text{m}$ (Figure 2). The specific surface area of the heat-treated graphene oxide powder was $400\text{--}500\text{ m}^2\text{g}^{-1}$. The particle distribution range of the heat-treated multilayer graphene oxide in water was $0.3\text{--}1400\text{ }\mu\text{m}$; the modal size was $211\text{ }\mu\text{m}$ (Figure 3).

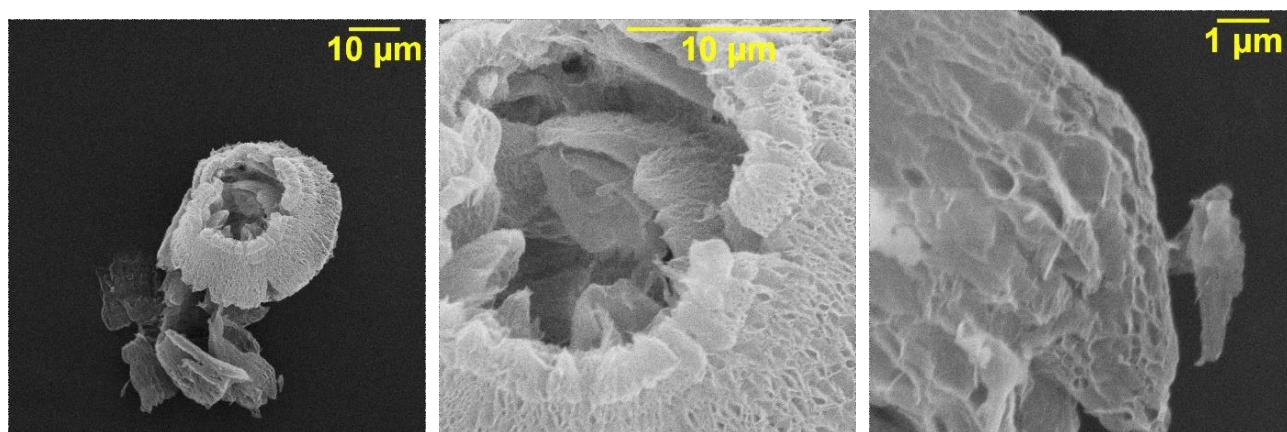


Figure 2. Scanning electron microscopy of thermally reduced graphene oxide.

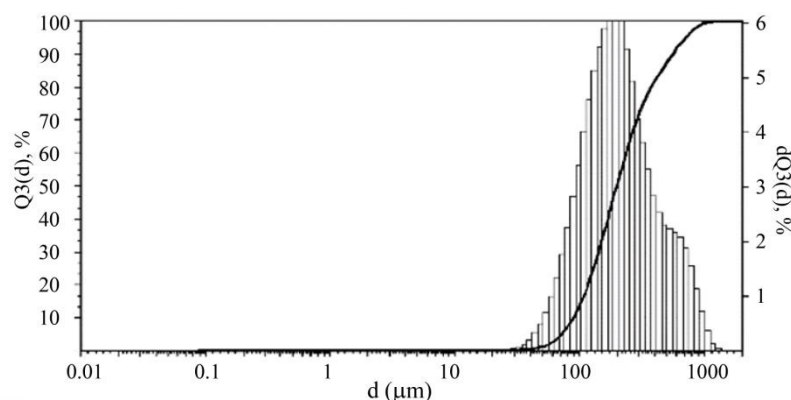


Figure 3. Size distribution of thermally reduced graphene oxide particles in the aqueous suspension.

The qualitative composition of the surface functional groups in the process of thermal reduction did not change (Figure 4). There was a marked decrease in the intensity of the peak at 3417 cm^{-1} and the band between 2800 cm^{-1} and 3100 cm^{-1} , compared to the original multilayer graphene oxide. The sp^2 -hybridization of $\text{C}=\text{C}$ in the graphene structure (peak at 1627 cm^{-1}), epoxy groups $-\text{C}-\text{O}-\text{C}-$ (band between 1106 cm^{-1} and 1005 cm^{-1}), and carboxylic groups $-\text{COOH}-$ (band at 1384 cm^{-1}) were also registered. The peak at 2300 cm^{-1} corresponded to the peak of absorbed CO_2 molecules.

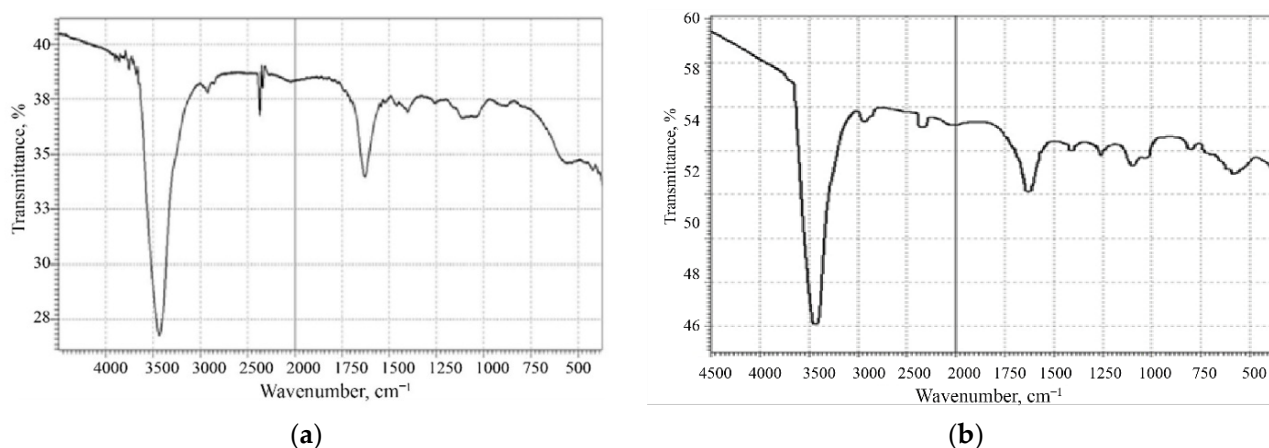


Figure 4. FTIR spectroscopy of: (a) thermally reduced graphene oxide, (b) graphene oxide.

Analysis of the effectiveness of the purification of stock solution from copper cations by the obtained GO-Ch sorbents of various compositions is presented in Table 1.

Table 1. Relationship between the effectiveness of copper cations recovery and the composition of the initial mixture and dry granules of the experimental samples of the GO-Ch composite.

Sample No.	GO:Binder (Acidic Chitosan Solution) Content (by Weight), %	GO:Ch Content (by Weight), % in Dry Granules	$E_{\text{Cu}^{2+}}$, %
1	2:98	33.3:66.7	92
2	3:97	42.8:58.2	94
3	4:96	50.0:50.0	95
4	5:95	55.5:44.5	96
5	6:94	60.0:40.0	96
6	7:93	63.6:46.4	96

The final and initial concentrations were used to determine the purification efficiency ($E_{\text{Cu}^{2+}}$) of samples, which increased in the following order: sample No. 1 (92%) < sample

No. 2 (94%) < sample No. 3 (95%) < sample No. 4 (96%) < sample No. 5 (96%) < sample No. 6 (96%) (Table 1). The maximum efficiency (96%) was achieved for the experimental samples Nos. 4, 5, and 6. For the graphene oxide content exceeding 55.5%, the mechanical strength of the granules decreased. Visually, it can be seen that samples Nos. 5 and 6 did not have a clear granular shape (Figure 5). Sorbent samples Nos. 5 and 6 decayed in water, and did not have clear granule shapes, but formed agglomerates. This material has no toxic effect on water, but technically it is inconvenient to use, since it is necessary to remove its small particles. When drying samples Nos. 5 and 6, particles of uneven and unequal shape were formed, which went to pieces during purification. Samples Nos. 1–4 were of a clear, solidified drop shape, therefore granules of even and equal shape were formed when dried.



Figure 5. Freshly prepared GO-Ch composites with different GO contents: 1—63% (sample No. 1); 2—50% (sample No. 4); 3—60% (sample No. 5); 4—63.6% (sample No. 6).

To confirm the visual observations, the mechanical properties (attrition and grindability) of the obtained experimental samples of GO-Ch composites with different contents of graphene oxide were investigated. The results are presented in Table 2.

Table 2. Mechanical characteristics of the experimental samples of the granulated GO-Ch composites.

Sample No.	Attrition, %	Grindability, %
1	0.3	3
2	0.3	3
3	0.3	3
4	0.4	4
5	0.5	5
6	0.6	6

Table 2 shows that the experimental samples of sorption material (sample No. 4) met the requirements of the Russian State standard GOST R 51641-2000 (attrition $\leq 0.5\%$, grindability $\leq 4\%$).

Analyzing the data obtained, it can be concluded that experimental sample No. 4, with the percentage ratio graphene oxide:chitosan = 55.5:44.5 (by weight in dry granules), had the most acceptable parameters, namely high cleaning efficiency (96%), attrition (0.4%), and grindability (4%). Therefore, it is proposed to use this composite (GO:Ch = 55.5:44.5) for wastewater treatment.

For the best sample, No. 4, the influence of the sorbent dosage, pH, and temperature were studied, and the adsorption isotherm was constructed. The results are presented in Table 3.

The best conditions for sorption processes by GO-Ch sorbent No. 4 were established, namely: sorbent dosage of 20 g/L, sorption time of 20 min, and temperature of 20 ± 2 °C.

When studying the influence of temperature on sorption processes, it was shown that with an increase in temperature, the purification efficiency reached its maximum at 20 °C, and then decreased. Possibly, at temperatures above 20 °C, chemisorption processes predominate. This effect can be explained by the activation energy required for the sorption process. Increasing the sorption dosage for more than 20 g/L is not economically profitable, because the efficiency does not increase significantly, and spending a large amount of

sorbent is not rational. Kinetic studies showed that the sorption time of 20 min was sufficient to obtain high efficiency of purification.

Table 3. Relationship between the sorbent dosage, time, and temperature of sorption and the efficiency of purification of copper cations by the GO-Ch sorbent (sample No. 4).

* Sorbent Dosage, g/L	Efficiency E, %	** Sorption Time, min *	Efficiency E, %	*** Solution Temperature T, °C	Efficiency E, %
5	90.5 ± 0.4	10	94.5 ± 0.5	10 ± 1	90.3 ± 0.4
10	92.3 ± 0.5	20	96.0 ± 0.5	20 ± 2	96.2 ± 0.5
20	96.0 ± 0.5	40	96.0 ± 0.5	30 ± 2	96.0 ± 0.5
30	96.5 ± 0.5	60	96.0 ± 0.5	40 ± 2	94.6 ± 0.5
40	96.5 ± 0.5	120	96.0 ± 0.5	50 ± 2	90.4 ± 0.4

* The effect of the sorbent dosage was studied for 20 min at room temperature of 20 ± 2 °C; ** The sorption kinetics (time effect) was studied at a sorbent dosage of 20 g/L at room temperature of 20 ± 2 °C; *** The effect of temperature was studied for 20 min at a sorbent dosage of 20 g/L.

To study the effect of pH solutions on purification efficiency, we used copper solutions with $C_{\text{ini}} = 10$ mg/L and with different pH = 2; 4; 6; 8; other sorption conditions were not changed. The results obtained are presented in Figure 6. Figure 6 shows that purification efficiency increased with increasing pH, and the optimal purification conditions corresponded to pH close to neutral (pH = 7). It is not rational to increase pH above 8 for sorption purification, since at pH = 8–10 precipitation of copper cations in the form of hydroxides occurs.

Isotherm of copper cation [44] sorption was constructed for sample No. 4 (Figure 7).

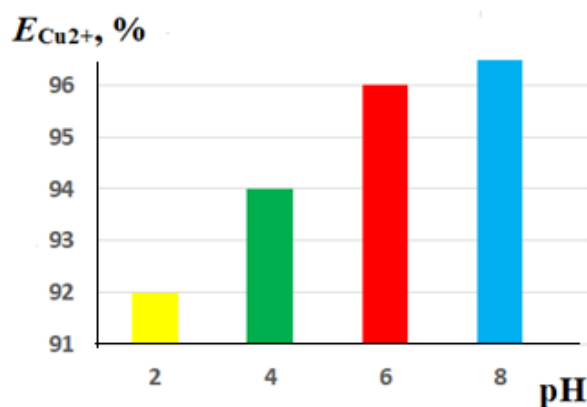


Figure 6. Effect of solution pH on the efficiency of copper cations sorption by GO-Ch sorbent No. 4.

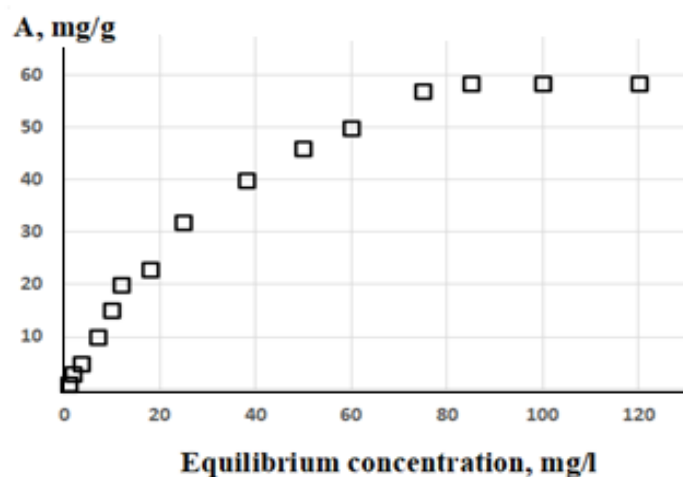


Figure 7. Isotherm of copper cation sorption by GO-Ch composite (sample No. 4).

The sorption isotherm of copper cations by the GO-Ch composite (sample No. 4) had a convex shape, and belonged to the first classification according to the BET theory, which is typical for microporous sorbents. According to Giles' [44] sorption isotherm classification, the constructed isotherms belonged to the L-type (Langmuir) class, which is characterized by the parallel orientation of the adsorbate molecules, and weak interactions in the adsorption layers. The initial section of the low-concentration region of the isotherm is described by the Henry equation. Then the adsorbent is saturated, which is characterized by the maximum adsorption capacity.

To describe the sorption process using Langmuir sorption models, the following expression is used:

$$A = A_{\infty} \cdot K \cdot C_p / (1 + K \cdot C_p),$$

where K is the concentration constant of sorption equilibrium characterizing the intensity of the sorption process; C_p is the equilibrium concentration of metal ions in solution; and A_{∞} is the maximum sorption capacity of the sorbent.

This equation describes the isotherm of monomolecular adsorption well, giving approximately linear sections at small and large concentrations. The K constant and the limiting capacity of the sorbent A_{∞} were determined by plotting the isotherm in $1/A-1/C_p$ coordinates [45], $K = 0.8$, $A_{\infty} = 58.5$ mg/g. Approximation coefficient was $R^2 = 0.995$.

For sample No. 4, the basic sorption characteristics were determined: maximum sorption capacity of copper cations, sorption properties for methylene blue and iodine absorption, and specific surface. Comparative analysis of the characteristics obtained, with those of DAK-grade coal (activated charcoal, which has industrial applications), is presented in Table 4.

Table 4. Characteristics of GO-Ch composite (sample No. 4) and DAK-grade coals.

Sorbent	GO-Ch 55.5:44.5	DAK-Grade Coal	Ch-TEG-BM *	OG-P **	Ch _a *** mole/kg	Ch _f *** mole/kg
Adsorption activity for methylene blue, mg/g	42.0	225.0	10	-	-	-
Iodine adsorption, %	8.1	30.0	9.8	-	-	-
Bulk density, g/dm ³	58 ± 1	240 ± 2	60	-	-	-
Moisture, %	8	10	5.6	-	-	-
Specific surface, m ² /g	232.2	700	148.2	-	-	-
Attrition, %	0.4	-	0.3	-	-	-
Grindability, %	4	-	3	-	-	-
Sorption capacity for Cu ²⁺ , A, mg/g	58.5	-	8.6	45	1.8	5.1
Specific surface, m ² /g	520	700				

* Ch-TEG-BM is Chitosan–thermoexpanded graphite–microalgae biomass [46]; ** OG-P is Graphene oxide modified with polyhydroquinone [47]; *** Ch_a is Chitosan air drying; Ch_f is Chitosan freeze-drying (mole/kg) [48].

Table 4 shows that the obtained composites were not inferior in sorption properties to the considered materials, but had a lower adsorption activity with respect to methylene blue and iodine than DAK grade coal (wood-active crushed, GOST 4453-74; 6217-74). This is explained by the fact that the composite pore sizes exceeded 1–1.5 nm, determined by microstructural studies.

Microstructural studies of samples of the initial chitosan and GO-Ch (sample No. 4) were performed (Figure 8). Microstructural studies of the initial chitosan showed the presence of a layered structure typical for chitosan. The addition of 44.5% graphene oxide (sample No. 4) showed the presence of a porous structure, typical for graphene oxide, located between the layers of chitosan. The main pore size varied from 4 to 12 nm (mesopores). Pores smaller than 1.5 nm were observed in an insignificant amount.

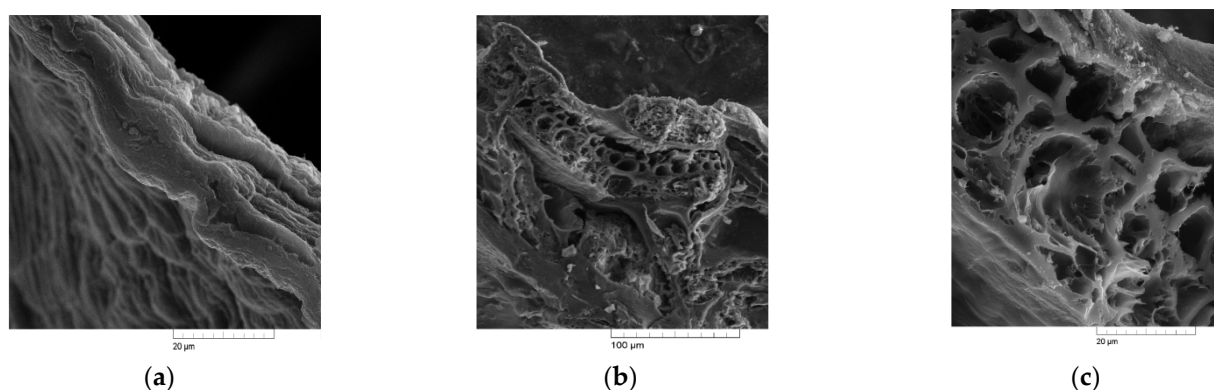


Figure 8. Surface morphology of: (a)—initial chitosan, $\times 200$; (b)—GO-Ch (sample No.4), $\times 100$; (c)—GO-Ch (sample No.4), $\times 200$.

The study of GO-Ch composites with different GO contents by infrared spectroscopy (Figure 9) showed the presence of absorption bands in the region of $3200\text{--}3500\text{ cm}^{-1}$, indicating the presence of hydrogen-bonded OH-groups. Valence vibrations of the C=O group at $1765\text{--}1645\text{ cm}^{-1}$ were also detected. It can be assumed that the extraction of copper cations can occur not only due to physical sorption of the porous surface by GO-Ch composites but also due to chemisorption processes caused by functional groups.

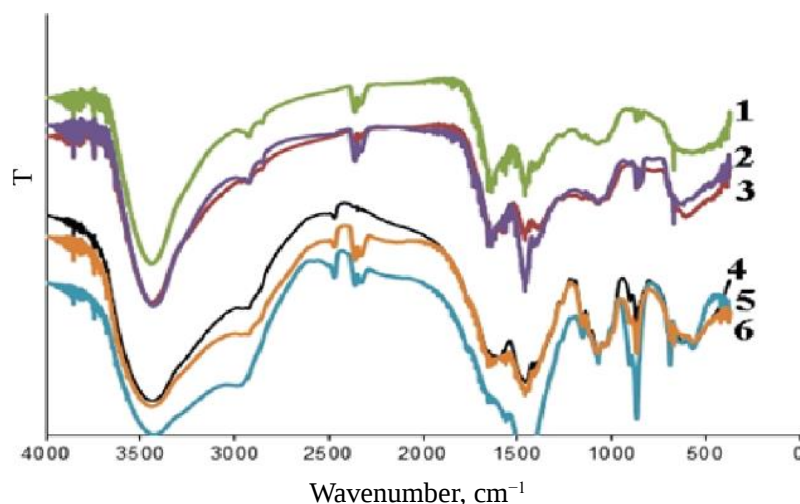
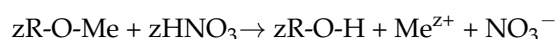


Figure 9. IR- spectra of GO-Ch samples: 1—No. 1; 2—No. 2; 3—No. 3; 4—No. 4; 5—No. 5; 6—No. 6.

4. Discussion

A problem of regeneration and the disposal of spent sorbents appeared after water treatment. For the regeneration of spent GO-Ch sorbents after wastewater purification from copper cations (Cu^{2+}), they were treated with nitric acid (1:1). After acid treatment, copper cations located in the pores of the sorbent passed into the solution in the form of nitrates. The sorption properties of the adsorbent were restored according to the scheme:



After the subsequent washing of the sorbents with distilled water to $\text{pH} = 7$ (1 g of GO-Ch sorbent needs 0.3 L of water), and drying at $103\text{ }^\circ\text{C}$, the sorbent was ready for the next cycle. After regeneration, the GO-Ch sorbent was able to work for about seven cycles. The cleaning efficiency after seven cycles was 80%. Regeneration is not always economically profitable and/or environmentally justified, since a large amount of clean water is needed for washing. Therefore, we propose to utilize the used sorbent.

It is known that when chitosan is added to the soil during its treatment, the release of CO₂ increases noticeably, which indicates that when chitosan is in the soil, it decomposes at a high rate. In modern agriculture, preparations based on chitosan are widely used, in particular to combat fungal infection. Chitosan-based materials have a stimulating effect on the growth of plants, and their resistance to adverse environmental factors; the introduction of chitosan into the soil accelerates the fight against rot [49].

Copper is a micronutrient for plant development, and participates in redox processes; it increases the intensity of photosynthesis and chlorophyll formation, and promotes the activation of carbohydrate and nitrogen metabolism. Sufficient copper content in crops improves plant resistance to fungal and bacterial diseases, and increases drought- and frost-resistance and lodging-resistance. The presence of this element in plant nutrition contributes to the increase of protein content in grain, starch in potato tubers, sugar in root crops, fats in oilseed grains, ascorbic acid, and sugars in berry and fruit plants [50].

In [51] it was shown that graphene can be used as a fertilizer carrier, which increases the rate of nutrient uptake by plants. If the sorbent is used to remove toxic elements, it is possible to burn it to generate heat.

Therefore, we propose to use the spent sorbents to improve the quality of soils when growing industrial crops.

5. Conclusions

The performed work showed that the developed composite graphene oxide: chitosan = 55.5:44.5% (by mass in dry granules) had the optimal sorption and mechanical properties. This sample had a high efficiency of water purification from copper cations (96%), and the required mechanical properties (attrition not exceeding 0.4%, grindability not exceeding 4%).

For the best sample, the influence of various factors (pH, sorbent dosage, temperature, and time of sorption) on sorption processes were studied. The best conditions for the sorption processes by the GO-Ch sorbent were determined. The sorbent dosage was 20 g/L, the sorption time was 20 min, and the temperature was 20 ± 2 °C, pH = 7. The adsorption isotherm was plotted, and the maximum sorption capacity of copper cations, $A = 58.5$ mg/g, was determined.

Microstructural studies and infrared spectroscopy of GO-Ch composites showed the presence of porous surface and functional groups OH- and C=O. The mechanism of copper cations extraction by physical sorption of porous surface by GO-Ch composites, and by chemisorption processes due to functional groups, was proposed.

The sorption properties for methylene blue and iodine absorption, and specific surfaces of GO-Ch samples, were determined. The spent sorbent is proposed to be used as a soil improver.

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