

Graphene nanocomposites modified with organic polymers as effective heavy metal sorbents in aqueous media

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Abstract: The sorption materials based on graphene oxide (GO) modified with a chitosan coating (GO/CS) and a lignin derivative, lignosulfonate (GO/LS), were developed by the authors to remove heavy metal ions from aqueous media. The technology for obtaining sorbents involved the formation of a hydrogel and its subsequent lyophilization in order to preserve the porous space. The synthesized nanostructured sorbents were characterized on the basis of transmission electron microscopy with the elemental analysis, the surface area measurement and the thermogravimetric analysis (BET). The thermogravimetric analysis showed that nanocomposites decompose in two stages: 3–5 % weight loss at temperatures up to 250–270 °C and 40–50 % weight loss at temperatures up to 750–770 °C. The measured BET surface area for GO/LS and GO/CS was 85.34 and 73.256 m²·g⁻¹, respectively. Batch sorption experiments were carried out at pH = 6, followed by the quantitative adsorption of Cu²⁺ and Pb²⁺ using atomic absorption spectrometry. According to the results of the experimental studies, the best ratio of the initial components of the nanocomposites was established. For the GO/LS nanocomposite, the ratio of 2 : 1 was chosen for further studies, and 100 : 1 for the GO/CS nanocomposite. The value of the adsorption capacity for these compositions for lead was: 178.1 mg·g⁻¹ for GO/LS; 197.38 mg·g⁻¹ for GO/CS; and for copper: 162.39 mg·g⁻¹ for GO/LS, 186.17 mg·g⁻¹ for GO/CS.

Keywords: graphene oxide; lignosulfonate; chitosan; organic polymers; liquid phase adsorption; heavy metal ions; lead; copper.

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Графеновые нанокомпозиты, модифицированные органическими полимерами, как эффективный инструмент для удаления тяжелых металлов из водных сред

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Аннотация: Сорбционные материалы на основе оксида графена (ОГ), модифицированного хитозаном (ОГ/Х) и производным лигнина – лигносульфонатом (ОГ/ЛС), разработаны для удаления тяжелых металлов из водных сред. Технологии получения нанокомпозитов включали стадии формирования гидрогеля и его последующей лиофилизации в целях сохранения структуры пористого пространства. Синтезированные наноструктурированные сорбенты охарактеризованы с использованием просвечивающей электронной микроскопией с элементным анализом, метода термогравиметрического анализа и путем измерения площади поверхности (БЭТ). Термогравиметрический анализ показал наличие двух температурных интервалов потери массы нанокомпозитов: 3–5 % при температуре до 250...270 °C и 40–50% – до 750...770 °C. Измеренная площадь поверхности по БЭТ

для ОГ/ЛС и ОГ/Х составила 85,34 и 73,256 м²/г соответственно. Адсорбционные исследования методом ограниченного объема проводили в буферных модельных системах для Cu²⁺ и Pb²⁺ при значениях pH = 6 с использованием атомно-абсорбционной спектроскопии. По результатам проведенных экспериментальных исследований установлены эффективные составы нанокмпозитов с наилучшим соотношением исходных компонентов. Для нанокмпозита ОГ/ЛС наиболее результативным является соотношение 2 : 1, для ОГ/Х – 100 : 1. Величина адсорбционной емкости для указанных соотношений составила по свинцу: для ОГ/ЛС – 178,1 мг/г, для ОГ/Х – 197,38 мг/г; по меди: для ОГ/ЛС – 162,39 мг/г, для ОГ/Х – 186,17 мг/г.

Ключевые слова: оксид графена; лигносульфонат; хитозан; органические полимеры; жидкофазная адсорбция; ионы тяжелых металлов; свинец; медь.

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1. Introduction

The possibility of global pollution of the environment, and especially water resources, with heavy metals causes serious concern around the world due to their significant toxicity, ubiquitous distribution, easy migration and the ability to penetrate into the human body with subsequent accumulation, bringing serious harm. Ingested heavy metals are generally carcinogenic and non-biodegradable.

As a result of intensive anthropogenic activity, polluted surface and ground waters as well as industrial wastewater contain dangerously high concentrations of nickel, arsenic, cadmium, mercury, chromium, zinc, copper and lead. The presence of these heavy metals in the used water resources creates an obvious threat to humans and other living organisms [1–3].

Lead (Pb) is the most common heavy metal contaminant found in contaminated water systems, particularly industrial wastewater. This element is bioaccumulative, non-biodegradable and poses serious health problems to living organisms, causing kidney failure, anemia, hemolysis, liver dysfunction, neuronal damage and cancer [4, 5].

The specific toxicity of lead is confirmed by the fact that the permissible limit for lead in drinking water established according to the World Health Organization (WHO) is 0.01 mg·L⁻¹, while for other heavy metals such as chromium, manganese, arsenic, nickel and copper the permissible content in drinking water is less than 0.20 mg·L⁻¹ [6].

Another common and dangerous heavy metal is copper (II), which is mostly abundant in wastewater from electroplating, paint and varnish industries, oil refineries, in the production of fertilizers and pesticides, in the mining and metallurgical industries and in the production of explosives. Copper can cause irritation of the mucous membrane, kidney failure, neurotoxicity, disruption of the gastrointestinal tract, Wilson's disease, inhibit cell metabolism [7, 8].

Thus, using these two elements as an example, it is clear how toxic and dangerous representatives of a number of heavy metals are, and it is obvious that environmental organizations around the world are concerned about the quality of treatment of wastewater discharged into the environment, calling for acceptable limits for the concentrations of these pollutants in operated water systems [9].

However, purification and remediation of water resources from heavy metals contained in them is a rather difficult problem. To solve it, traditional technologies for removing target pollutants are widely used – chemical and electrochemical precipitation, solvent extraction, reduction, ion exchange, membrane separation, cementation, foaming, evaporation, etc. At the same time, these cleaning methods have a number of significant drawbacks that limit the scope of their use and reduce the efficiency of the achieved result, namely, high energy and chemical (reagent) costs, incomplete removal of pollutants, the formation of secondary pollution and toxic sludge [10–12].

The adsorption process, in comparison with other purification methods, has a number of significant advantages, such as easy implementation, high functional efficiency, lower comparative cost, a small amount of reagents used, and the possibility of regenerating adsorbents after the completion of the purification process [13, 14].

One of the most promising and highly efficient adsorbents for cleaning and restoring polluted hydro- and geosystems are materials based on graphene oxide (GO). This material, which is a highly oxidized form of graphene, is of great interest to researchers due to the presence of a large number of oxygen-containing functional groups (epoxy, carboxyl and hydroxyl), the high surface area to volume ratio, excellent solubility in water, etc. [15, 16].

However, when traditional GO is used in liquid-phase adsorption processes, a number of significant disadvantages appear, in particular, a decrease in the

adsorption efficiency due to the compaction of GO sheets as a result of interplanar attraction; difficult and often impossible removal from aqueous media [17].

The rational solution of these problems is the use of various methods for the functionalization of graphene oxide with the subsequent formation of graphene composites. Such materials retain advantages of the main initial component (for example, a developed surface), but have a large number and variety of active sorption sites as well as excellent chemical stability [18].

In the past few years various organic polymers have been used as highly effective modifiers of graphene materials for the adsorption of heavy metals [19].

Among many existing organic polymers such as cellulose, sodium alginate, polyvinyl alcohol, rubber, etc., chitosan is a popular and effective biosorbent [20].

Chitosan (CS) is a deacetylated product of chitin, a nitrogen-containing natural polysaccharide, the second most abundant in nature after cellulose. This material has important functional properties such as biocompatibility, biodegradability and bioadhesiveness. Chitosan has an excellent adsorption capacity due to the high content of amino and hydroxyl groups in the molecular structure; in particular, in a neutral aqueous solution, the amino groups of chitosan tend to adsorb cations [20, 21].

However, the use of chitosan is limited by a very serious drawback - it has extremely poor mechanical properties. To overcome this limitation, some researchers have studied the possibility of crosslinking GO with chitosan to form a stable, cost-effective and environmentally friendly composite material with improved sorption characteristics, in particular, due to the amidation reaction [22–24].

In recent years the use of various biomass wastes as effective sorbents or their modifiers has become an effective strategy for obtaining valuable functional carbon products [25, 26].

In the pulp industry the extraction of cellulose from wood, the largest biomass resource on Earth, produces a large amount of lignin-rich residue [27].

Despite the huge quantities generated as a by-product of wood processing industries, lignin is still not used much, usually in minor applications, for example, budgetary fuel.

Lignin is a complex heterogeneous polymer consisting mainly of *p*-coumaryl, coniferyl, and sinapyl building blocks that form a molecular chain with a large number of phenyl rings [28].

Being a renewable and environmentally friendly resource, and due to its good biocompatibility,

biodegradability, lignin-based materials have been effectively used to remove various pollutants from wastewater. Their excellent adsorption capacity has been attributed to functional groups abundant in lignin, such as phenolic, methoxy, hydroxyl, carbonyl, and aldehyde groups [29, 30].

The aim of the research in this paper was to study the adsorption potential of new sorption materials based on GO modified with organic polymers chitosan and lignin – lignosulfonate. Nanostructured sorbents are characterized by low cost compared to other graphene nanomaterials, easy production and operation, and will be effective in the removal of heavy metals from wastewater.

2. Materials and Methods

2.1. Chemicals

Reagents for obtaining nanocomposites are GO suspension (LLC «NanoTechCenter», Tambov, Russia) with the dry matter content of 1 % by weight; distilled water (demineralized); sodium hydroxide (LLC «REACHIM» Moscow, Russia); acetic acid (chemically pure, RM Engineering, Russia); Chitosan Powder $C_6H_{12}NO_4$ (Fengchen Group Co., Ltd., China); technical powdered lignosulfonate (LLC «AQUAKHIM» Kazan, Russia). Sorption experiments were carried out using metal nitrates $Cu(NO_3)_2 \cdot 3H_2O$ (pure for analysis) and $Pb(NO_3)_2$ (chemically pure) (LLC «REACHIM» Moscow, Russia).

2.2. Synthesis of nanocomposites

2.2.1. Obtaining the GO/LS nanocomposite

To obtain the GO/LS nanocomposite the following steps were taken: 1 M NaOH solution was added into the original GO suspension to bring the mixture to pH=10; then the LS powder was dissolved in distilled water, preheated to 70 °C for 30 min. The cooled LS was added into the GO suspension and stirring was continued for 10 min. To form a hydrogel, the resulting mixture was heated for 24 h at 90 °C. The final stage of the synthesis was the loading of the GO/LS hydrogel into the Scientz-10n freeze dryer (Scientz, China) to freeze the sample to –30 °C and subsequent lyophilization for 48 h which contributed to the formation of a porous framework due to the solvent sublimation. To identify the best ratio of GO and LS, the following mixture proportions were chosen: 100 : 1, 20 : 1, 10 : 1, 5 : 1, 2 : 1, 1 : 1.

2.2.2. Obtaining the GO/CS nanocomposite

At the first stage the aqueous solution of chitosan was obtained. To do this chitosan powder was added to the aqueous solution of acetic acid (2.5 wt. %), then the resulting mixture was stirred until the complete dissolution of chitosan. The next step was mixing the suspension of graphene oxide ($1 \text{ mg}\cdot\text{mL}^{-1}$) with the solution of chitosan at the GO suspension pH equal to 10 (by adding the required amount of NaOH). The resulting mixture was heated to 95°C for 24 h, resulting in the formation of a hydrogel (GO/CS). The obtained hydrogel was subjected to lyophilization in the dryer (Scientz-10N, Scientz, China) to preserve the porous structure ($t = -55^\circ\text{C}$, $P = 10 \text{ Pa}$). To determine the best ratio of GO and CS, the following mixture proportions were chosen: 200 : 1, 100 : 1, 20 : 1, 10 : 1, 5 : 1, 2 : 1, 1 : 1.

2.3. Characterization

To assess the graphene structure of the obtained materials and the elemental composition, the transmission electron microscope (TEM) JEM-2010 instrument (JEOL Ltd., Tokyo, Japan) was used. The specific surface area, volume, and pore size were determined using the Autosobr-1 analyzer (Quantachrome, Odelzhausen, Germany). The thermal stability of the sorbent was determined using the NETZSCH STA 449 F3 Jupiter® synchronous thermal analyzer (NETZSCH-Feinmahltechnik

GmbH, Selb, Germany) which makes it possible to measure mass changes (TG) and calorimetric effects (DSC) in a sample.

2.4. Adsorption experiments

To determine the sorption efficiency of the synthesized batches of GO/CS and GO/LS nanocomposites with respect to heavy metal ions, comparative liquid-phase adsorption experiments were carried out under static conditions. To do this 0.01 g of the sorbent from each batch was added to 30 ml of buffer solutions ($\text{pH} = 6$) of heavy metals with the concentration of $100 \text{ mg}\cdot\text{L}^{-1}$. Samples were taken every 60 min. In the course of experimental studies, solutions were continuously mixed at the room temperature using programmable rotators Multi Bio RS-24 (Biosan, Riga, Latvia) at the frequency of 100 rpm. The determination of the residual concentration of metals in the liquid phase was carried out using the method of atomic absorption spectrometry and the MGA-915MD spectrometer (Atompribor, St. Petersburg, Russia).

3. Results and Discussion

3.1. Nanocomposite characterization

According to the transmission electron microscopy (Figs. 1. and 2), nanocomposites have a complex structure of folded translucent GO sheets

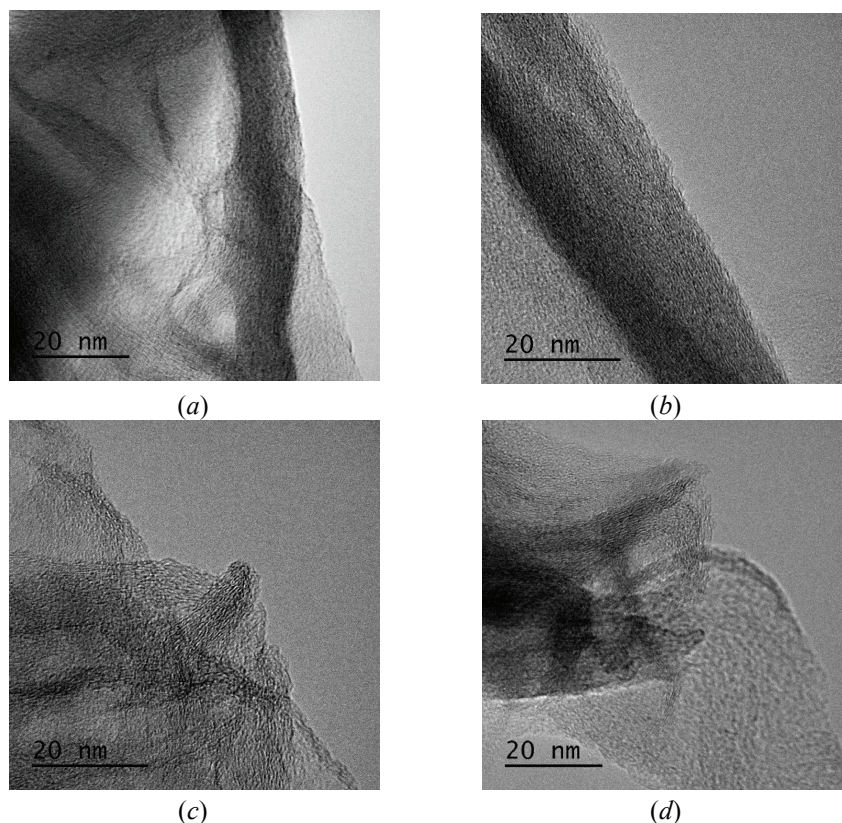


Fig. 1 TEM images of the GO/LS nanocomposite

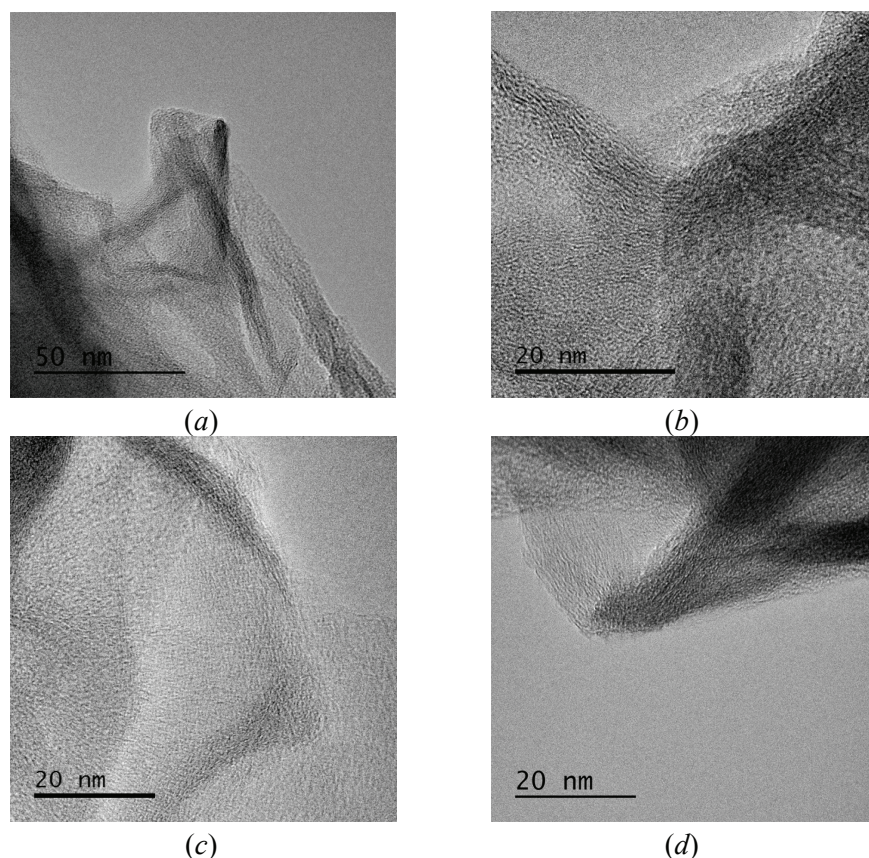


Fig. 2. TEM images of the GO/CS nanocomposite

with the admixture of darker multilayer accumulations and unfolded lighter-colored monolayers, for example, those shown in Fig. 1d, Fig. 2a, c. The darker areas in all images appear to be the local overlap of the sheets and the arrangement of individual sheets parallel to the electron beam.

Rounded and elliptical transparent shapes appear along the edges of some sheets of GO, possibly resulting from the modification of GO during processing, as shown in Fig. 1b, c, d and Fig. 2a, d.

The results of the elemental analysis are given in Table 1.

According to Table 1 nanocomposites are a carbon material (with C content of approximately 82 – 94 wt. %). Oxygen is the main impurity in the material. The results of measuring the parameters of the porous space are given in Table 2.

Based on the obtained data on the parameters of the porous space, it should be concluded that nanocomposites have a predominantly mesoporous structure.

Table 1. Elemental composition of nanocomposites

Element	Weight, %	Atomic, %
GO/LS		
C	81.96	85.82
O	18.04	14.18
GO/CS		
C	93.74	95.23
O	6.26	4.77

Table 2. Parameters of the porous space of the GO/LS and GO/CS nanocomposites

Indicator Nanocomposite	Specific surface area by nitrogen S_{BET} , $\text{m}^2 \cdot \text{g}^{-1}$	Total pore volume, DFT, $\text{cm}^3 \cdot \text{g}^{-1}$	The average pore diameter (DFT), nm
GO/LS	85.34	0.144	34.56
GO/CS	73.256	0.079	26.87

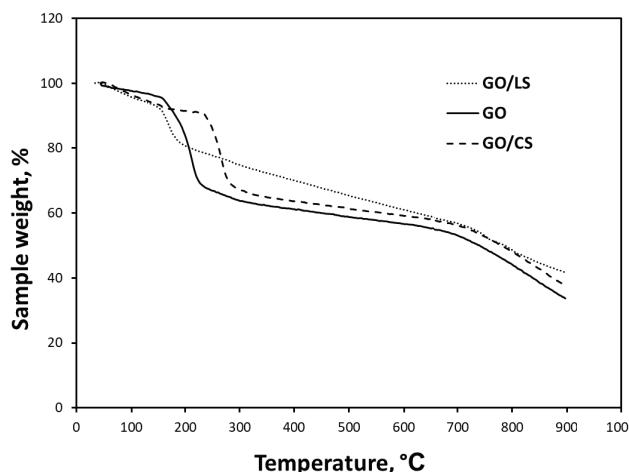


Fig. 3. Thermogravimetric analysis of the GO/LS and GO/CS nanocomposites in comparison with initial graphene oxide

The lignin-containing nanocomposite and the original GO at the initial stage (up to 180 °C) gradually lose 3 % of the mass for GO and 5 % for

GO/LS (Fig. 3). This is due to the evaporation of adsorbed water molecules on the GO sheets. GO/CS has a wider initial temperature range of weight loss (250 – 270 °C), where the thermal decomposition of chitosan also occurs [20], followed by a slow weight loss up to ~750 °C. The second stage of weight loss (40–50 %) in the samples can be traced at the temperatures of 700 – 750 °C, which is probably associated with the decomposition of GO functional groups [21].

3.2. Determination of sorption characteristics

To select the effective ratio of graphene composites containing chitosan and liginosulfonate, the following compositions were obtained: GO/CS – 200 : 1, 100 : 1, 20 : 1, 10 : 1, 5 : 1, 2 : 1, 1 : 1 and GO /LS – 100 : 1, 20 : 1, 10 : 1, 5 : 1, 2 : 1, 1 : 1. As a result of studying the sorption of Pb^{2+} and Cu^{2+} by the synthesized nanocomposites, the adsorption capacity values shown in Figs. 4 and 5 were obtained.

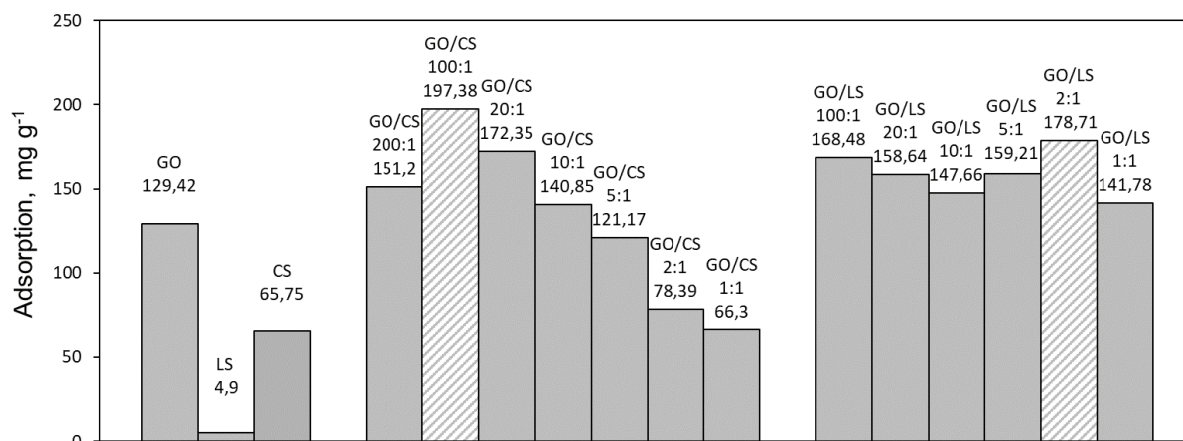


Fig. 4. Comparative adsorption capacity of various nanocomposites with respect to Pb^{2+} ions

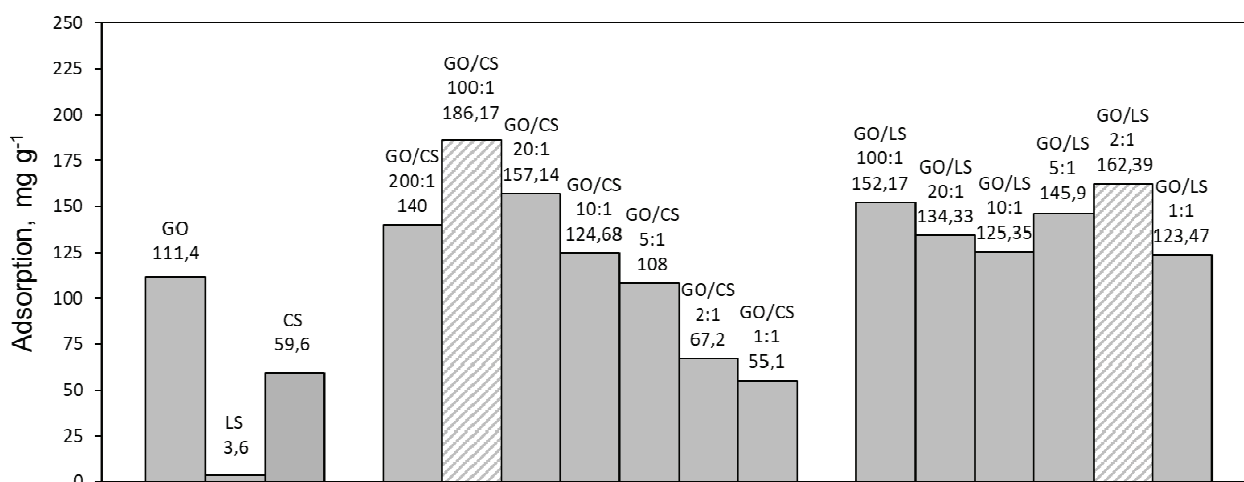


Fig. 5. Comparative adsorption capacity of various nanocomposites with respect to Cu^{2+} ions

Thus, Figs. 4 and 5 show that the most effective compositions are GO/CS (100:1) and GO/LS (2:1). The adsorption capacity of the initial GO, the suspension of which was dried in the lyophilic dryer, is $129.24 \text{ mg}\cdot\text{g}^{-1}$ for lead and $111.4 \text{ mg}\cdot\text{g}^{-1}$ for copper. The selected nanocomposite compositions exhibit better adsorption capacity than the initial GO.

The results obtained for the GO/CS nanocomposite are presumably explained by the rational amount of introduced chitosan, which is sufficient for effective crosslinking of oxidized graphene sheets, while enhancing its functional properties. A further increase in the amount of introduced chitosan worsens the sorption properties of the formed composite, possibly distorting its structure, destroying and making it less permeable, reducing the number of available active centers [24].

At the same time, for GO/LS composites, the composition of 2 : 1 is rational, which demonstrates a high adsorption capacity, while also being economically feasible. The effectiveness of this ratio can be explained by the fact that the introduced lignosulfonate forms a uniform modifying structure

on the surface of oxidized graphene planes, significantly enhancing the functionality of the target nanocomposite due to carbonyl, hydroxyl (phenolic and alcohol), carboxyl, and sulfo groups [30].

3.3. Comparison of adsorption capacity with analogues

The authors analyzed international research papers to compare the effectiveness of the developed nanocomposites with other sorption materials in relation to the removed Cu^{2+} , Pb^{2+} ions.

Analyzing Table 3 we can conclude that the nanocomposites developed by the authors show higher adsorption characteristics than the existing graphene complex materials, all other things being equal for the adsorption of heavy metals (initial concentration, contact time, mass of the adsorbent). In the overwhelming majority of cases, the adsorption of metal contaminants using GO/LS and GO/CS is faster than the process of removing these particles using other adsorbents. This ensures very high values of adsorption capacity.

Table 3. The Cu^{2+} and Pb^{2+} adsorption parameters for various graphene nanomaterials

Adsorbent	Metal ion	Experimental conditions					Q_e , $\text{mg}\cdot\text{g}^{-1}$
		pH	T , K	Initial concentration, $\text{mg}\cdot\text{L}^{-1}$	Adsorbent weight, g	Time, min	
MWCNTs (oxidized)	Pb^{2+}	5	Room temperature	40	1	150	50
GO		5		–	0.02	90	44.56
rGONF (ferrite-reduced GO) nanocomposite		5		–	0.02	30	25.78
GO/chitosan		–		50	–	–	100
GO/ Fe_3O_4 /chitozan		5		–	$0.2 \text{ g}\cdot\text{L}^{-1}$	60	77
GO	Cu^{2+}	5	303	3.2	$0.5 \text{ g}\cdot\text{L}^{-1}$	720	47
GO/MWCNTs/ Fe_3O_4 nanocomposite		7	Room temperature	25	25	–	20.83
Chitosan-coated carbon nanotubes (CNTs) composites		7		10	–	60	115.8
GO		5.3		50	$1 \text{ g}\cdot\text{L}^{-1}$	150	118
GO/Chitosan		6	303	19.2	$0.6 \text{ g}\cdot\text{L}^{-1}$	480	25.4
GO/ Fe_3O_4		5.3	Room temperature	10	$0.4 \text{ g}\cdot\text{L}^{-1}$	1440	18
LS-functionalized nGO/gelatin aerogel		7		0,006 M	0.01	40	69

4. Conclusions

The authors developed a method for obtaining new adsorption materials based on graphene oxide modified with promising and economically attractive organic polymers – derivatives of lignin and chitin. In order to provide a developed structure of the porous space of nanocomposites, the preliminarily obtained hydrogel was subjected to lyophilic treatment. According to the analysis of the porous space parameters for nitrogen adsorption, the measured specific surface area for GO/LS and GO/CS was 85.34 and 73.256 m²·g⁻¹, respectively. The resulting sorbents are predominantly mesoporous materials with pore sizes up to 50 nm. To determine the effective composition of nanocomposites, a series of samples were synthesized with different ratios of the initial components – GO/CS and GO/LS. The rational composition was determined from the results of adsorption studies by the limited volume method when Cu²⁺ and Pb²⁺ ions were removed from aqueous solutions. It was found that the composition with the ratio of 2 : 1 showed the maximum absorption capacity for the GO/LS nanocomposite and 100 : 1 for GO/CS. The adsorption capacity for these compositions was 178.1 mg·g⁻¹ for GO/LS, 197.38 mg·g⁻¹ for GO/CS with respect to Pb²⁺; and 162.39 mg·g⁻¹ for GO/LS, 186.17 mg·g⁻¹ for GO/CS with respect to Cu²⁺. Thus, the synthesized nanocomposites proved to be effective in the removal of heavy metals from aqueous solutions in comparison with existing analogues.

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7. Conflict of interests

The authors declare no conflict of interest.

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