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СОРБЦИЯ КАТИОНОВ МЕДИ (II) ИЗ ВОДНЫХ РАСТВОРОВ ТЕРМОВОССТАНОВЛЕННЫМ ОКСИДОМ ГРАФЕНА

Е.В. Яковлева, С.В. Брудник, А.В. Яковлев, Т.О. Рябухова,
О.Г. Неверная, А.С. Мостовой, Л.Н. Ольшанская

Елена Владимировна Яковлева (ORCID 0000-0002-8489-9804), Любовь Николаевна Ольшанская (ORCID 0000-0002-8449-9368)

Кафедра экологии и техносферной безопасности, Саратовский государственный технический университет им. Ю.А. Гагарина, ул. Политехническая, 77, Саратов, Российская Федерация, 410054
E-mail: elenayakovleva1977@list.ru, ecos123@mail.ru

Сергей Витальевич Брудник (ORCID 0000-0001-7093-6494), Андрей Васильевич Яковлев (ORCID 0000-0002-3542-1927)*

Кафедра химии и химической технологии материалов, Саратовский государственный технический университет им. Ю.А. Гагарина, ул. Политехническая, 77, Саратов, Российская Федерация, 410054
E-mail: sbrud@mail.ru, aw_71@mail.ru *

Татьяна Олеговна Рябухова (ORCID 0000-0001-9099-8158)

Кафедра общей, биоорганической и фармацевтической химии, Саратовский государственный медицинский университет имени В.И. Разумовского, ул. Большая Казачья, 112, Саратов, Российская Федерация, 410012
E-mail: eng34@list.ru

Ольга Геннадьевна Неверная (ORCID 0000-0001-7644-7747), Антон Станиславович Мостовой (ORCID 0000-0003-2828-9988)

Кафедра естественных и математических наук, Энгельсский технологический институт (филиал) Саратовского государственного технического университета им. Ю.А. Гагарина, пл. Свободы, 17, Энгельс, Российская Федерация, 413100
E-mail: olga19081969@yandex.ru, mostovoy19@rambler.ru

Электрохимическим методом синтезированы образцы многослойного оксида графена в электролитах на основе H_2SO_4. Результаты дифференциальной сканирующей калориметрии и термогравиметрического анализа полученных образцов выявляют эндотермический пик в интервале сканирования до 100 °С, сопровождающийся потерей массы порядка 7%. Этот эффект может быть обусловлен десорбцией и испарением некоторого количества удерживаемой воды в образцах. Другой эндотермический пик появляется при 252 °С на кривой ДТА и потерю массы 15%, можно объяснить разложением лабильных гидроксильных, эпоксидных и карбоксильных кислородсодержащих функциональных групп. Термическая эксфолиация при 250 °С многослойного оксида графена приводит к удалению кислородсодержащих функциональных групп, значительному увеличению размера частиц (K_V = 1490 см^3·г$^{-1}$) и формированию червеобразных структур с большим количеством V-образных пор с размером 1-10 мкм и толщиной полиграфеновых плоскостей до 0,01 мкм. Удельная поверхность порошка термовосстановленного оксида графена составляет 400-500 м^{2}г$^{-1}$, диапазон распределения частиц в воде составляет 0,3-1400 мкм, модальный размер 211 мкм. При ультразвуковом воздействии на водную дисперсию оксида графена размер частиц дисперсной фазы значительно уменьшается до 0,2-400 мкм, с модальным размером 143 мкм. По ИК спектрам термовосстановленного оксида графена установлено наличие sp^2-гибридизации С=С в структуре графена (пик при 1627 см$^{-1}$), эпоксигрупп -С-О-С- (полоса между 1106 см$^{-1}$ и 1005 см$^{-1}$), карбоксильных групп -СООН- (полоса при 1384 см$^{-1}$). Пик при 2300 см$^{-1}$ соответствует пику поглощенных молекул CO_2. После экспонирования термовосстановленного оксида графена в растворах, содержащих катионы меди, на ИК спектрах в области 690 - 1130 см$^{-1}$ наблюдаются полосы поглощения,

которые можно рассматривать как колебания группировок, образовавшихся на поверхности в результате взаимодействия катионов меди с атомами кислорода в составе функциональных групп. Изотермы адсорбции Cu^{2+} на термовосстановленном оксиде многослойного графена имеют вид характерный для изотерм класса H_2 и характеризуются прямолинейным крутовосходящим начальным участком, что свидетельствует о большом сродстве адсорбата к адсорбенту и образовании химичсеких соединений. Вероятно, происходит взаимодействие ионов Cu^{2+} с карбоксильными функциональными группами, что подтверждается незначительным понижением pH раствора. Изотерма аппроксимирована прямой линией, что позволяет использовать для описания процесса адсорбции модель Ленгмюра. Максимальная сорбционная способность термовосстановленного оксида многослойного графена к Cu^{2+} составила ≈ 25 мг $г^{-1}$, что заметно выше, чем сорбционная способность активированных углеродных волокон.

Ключевые слова: оксид графена, термовосстановленный оксид графена, окисленный графит, сорбция, катион

SORPTION OF COPPER (II) CATIONS FROM AQUEOUS SOLUTIONS BY THERMALLY REDUCED GRAPHENE OXIDE

E.V. Yakovleva, S.V. Brudnik, A.V. Yakovlev, T.O. Ryabukhova,
O.G. Nevernaya, A.S. Mostovoy, L.N. Olshanskaya

Elena V. Yakovleva (ORCID 0000-0002-8489-9804), Lyubov N. Olshanskaya (ORCID 0000-0002-8449-9368)

Department of Ecology and Technogenic Safety, Saratov State Technical University named after Yu.A. Gagarin, Polytekhnicheskaya st., 77, Saratov, 410054, Russia
E-mail: elenayakovleva1977@list.ru, ecos123@mail.ru

Sergey V. Brudnik (ORCID 0000-0001-7093-6494), Andrey V. Yakovlev (ORCID 0000-0002-3542-1927)*

Department of Chemistry and Chemical Engineering of Materials, Saratov State Technical University named after Yu.A. Gagarin, Polytekhnicheskaya st., 77, Saratov, 410054, Russia
E-mail: sbrud@mail.ru, aw_71@mail.ru *

Tatiana O. Ryabukhova (ORCID 0000-0001-9099-8158)

Department of General, Bioorganic and Pharmaceutical Chemistry, Saratov State Medical University named after V.I. Razumovsky, Bolshaya Kazachya st., 112, Saratov, 410012, Russia
E-mail: eng34@list.ru

Ol'ga G. Nevernaya (ORCID 0000-0001-7644-7747), Anton S. Mostovoy (ORCID 0000-0003-2828-9988)

Department of Natural and Mathematical Sciences, Engels Technolodical Institute (Branch) Yuri Gagarin State Technical University, Svobody sq., 17, Engels, 413100, Russia
E-mail: olga19081969@yandex.ru, mostovoy19@rambler.ru

Samples of multilayer graphene oxide in electrolytes based on H_2SO_4 have been synthesized by the electrochemical method. The results of differential scanning calorimetry and thermogravimetric analysis reveal an endothermic peak in the scanning interval up to 100 °C accompanied by the weight loss of about 7%, which may be caused by desorption and evaporation of a certain amount of retained water in the samples. Another endothermic peak appears at 252 °C on the DTA curve and the weight loss of 15% that can be explained by decomposition of labile hydroxyl, epoxy, and carboxyl oxygen-containing functional groups, including those between the layers of polygraphene planes. Thermal exfoliation of multilayer graphene oxide at 250 °C leads to removal of oxygen-containing functional groups, a significant increase in the particle size (K_V = 1490 cm^3 g^{-1}), and formation of worm-like structures with a large number of V-shaped pores with a size of 1-10 µm and thickness of polygraphene planes up to 0.01 µm. A specific surface area of the heat-treated

graphene oxide powder is 400-500 m^2g^{-1}. The distribution range of thermally reduced multilayer graphene oxide particles in water is 0.3-1400 μm, and the modal size is 211 μm. Under ultrasonic action on an aqueous dispersion, the particle size of the dispersed phase reduces significantly to 0.2-400 μm, with the modal size of 143 μm, which allows a more uniform distribution of carbon material particles in the volume of water. FTIR spectroscopy of thermally reduced graphene oxide reveals the presence of sp2-hybridization C = C in the structure of graphene (its peak at 1627 cm^{-1}), epoxy groups -COC- (band between 1106 cm^{-1} and 1005 cm^{-1}), and carboxyl groups -COOH- (the band at 1384 cm^{-1}). The peak at 2300 cm^{-1} corresponds to the peak of absorbed CO_2 molecules. After exposure of thermally reduced graphene oxide in the solutions containing copper cations, the absorption bands are observed in the FTIR range of 690 - 1130 cm^{-1}, which can be considered as vibrations of groups formed on the surface as a result of interaction of copper cations with oxygen atoms in the composition of functional groups. The Cu^{2+} adsorption isotherms on a thermally reduced multilayer oxide graphene have the form typical for isotherms of H_2 class, and are characterized by a straight steeply ascending initial segment, which indicates a high affinity of the adsorbate to the adsorbent with formation of chemical compounds. A likely explanation is that there is an interaction of Cu^{2+} ions with carboxyl functional groups, which is confirmed by a slight decrease in the pH of the solution. The isotherm is approximated by a straight line, which allows us to use it to describe the adsorption process of the Langmuir model. The maximum sorption capacity of thermally reduced multilayer graphene oxide to Cu^{2+} was 25 mg g^{-1}, which is noticeably higher than the sorption capacity of activated carbon fibers.

Key words: graphene oxide, thermally reduced graphene oxide, oxidized graphite, sorption, cation

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INTRODUCTION

Heavy metals are a common waste contaminant and their recovery is an important environmental and technological challenge. [1]. The following methods are used to remove heavy metal ions, including adsorption, coagulation, ion exchange, etc. Among these methods, adsorption is considered the most practical method and is widely used in various industries. Traditionally, carbon materials are used as sorbents in water purification. Emergence of new forms of carbon nanomaterials, such as graphene, graphene oxide (GO) and its precursors, initiated the study of sorbents based on them [2], including removal of metal cations and various petroleum products [3]. Compared to other carbon-containing sorbents, graphene oxide is considered the most promising material for adsorption of various heavy metal ions [4] based on its large specific surface area, hydrophilicity, and negative charge density [5]. The ability of graphene oxide to adsorb various particles is determined by its structure, nature, and concentration of surface reactive groups. GO can effectively adsorb on the surface such heavy metal cations as: Pt (IV) [6], Pb (II) [7,8], Cu (II) [9,10], Zn (II) [11,12], Cd (II) [13], Co (II) [14]. The adsorptive affinity of exhaust gas for many metal ions is high and varies with the type of heavy metal cation. Here we observe the following dependency: the higher the electronegativity of heavy metal cations, the stronger the attraction of ions to the negatively charged surface of GO. One of the possible options for adsorption is the process of complexation of heavy metals with the surface oxygen-containing functional groups (for example, –OH and –COOH). It should be noted that GO is a bifunctional material, i.e. it can sorb both cations and anions [15]. By obtaining graphene oxides modified by organic molecules, it is possible to achieve an increase in the sorption properties and selectivity for certain types of ions. [16, 17]. Graphene oxide is able to form stable dispersions in water and polar organic solvents, due to various oxygen-containing functional groups (carboxyl, hydroxyl, phenolic, epoxy, etc.) saturating free bonds of carbon atoms that make up the structure of graphene [18-20]. Carboxyl and hydroxyl groups found both on the edges and on the basal plane of the GO oxide, lead to a negatively charged surface in a certain pH range, which can be explained by deprotonization in the solution [21]. These groups are formed during graphene oxidation in a strongly acidic medium; therefore, in aqueous solutions they can participate in ion exchange processes. In our previous works, we showed a possibility for obtaining a multilayer graphene oxide by electrochemical oxidation of graphite in the sulfuric acid [22,23] and nitric acid [24] electrolytes. This method is less environmentally hazardous compared to the traditional Hammers method [25].

The aim of this work is to study the process of thermal reduction of the multilayer graphene oxide, its structure and composition of surface compounds, as well as to assess the sorption properties of the obtained material by the Cu^{2+} cations from aqueous solutions.

MATERIALS AND METHODS

The work used a fraction of 160-200 μm of natural graphite powder (GB/T 3518-95 Sunshine Resources Holdings Limited Beijing, China). For the electrolyte, we used the 83% H_2SO_4 obtained by successive dilution of the concentrated H_2SO_4 with bidistilled water (high purity grade, AO «EKOS-1»). A double-distilled water was obtained using the BE-2 double distiller (PF Livam).

Electrochemical measurements were carried out using the IPC Pro MF potentiostat (NTF "Volta") with a mercury sulfate reference electrode. Electrochemically oxidized graphite with a reported amount of electricity of 700 $mAh{\cdot}hg^{-1}$ in the galvanostatic mode was washed in bidistilled water (t = 15-18 °C) for 15 min to remove the residual sulfuric acid compounds. An aqueous dispersion of oxidized graphite was filtered through a polypropylene filter cloth (art: 56306, SINTEKS). Thermal reduction and exfoliation of oxidized graphite was carried out under static conditions for 5-10 s at the temperature of 250 °C (muffle furnace SNOL-1,6.2,5.1/9-I4). The exfoliation coefficient of thermally reduced graphite oxide K_V ($см^3{\cdot}г^{-1}$) was determined by the formula:

$$K_V = V/m,$$

where Vis the volume of thermally expanded graphite, cm^3; and m is the weight of a sample of oxidized graphite, g.

The particle size distribution in aqueous suspensions was studied using the Analysette-22 NanoTech (Fritsch GmbH) laser particle size analyzer with the measurement range of 0.01-2100 μm. Investigation of the surface and structure of nanostructured graphite particles was carried out using a scanning electron microscope with a built-in energy dispersive analysis EXplorer (Aspex Corporation). Simultaneous thermal analysis (Thermogravimetry and DSC) was carried out on the STA 449 F3 Jupiter, NETZSCH with the heating rate of 10 deg min^{-1}. FTIR spectroscopy of nanostructured graphite particles was performed on the IRTracer-100 (Shimadzu).

To prepare Cu^{2+} solutions, bidistilled water and state standard samples of Cu^{2+} were used (OOO TsSOVV 3K-1 MED'GSO 7998-93, lot 27/3K-1-TsSO. 06.2020/07.2023). For accurate measurement of GSO aliquots, pipet-dispensers were used, such as Ekohim OP-500-5000 μl (ID470142), Ecohim OP-100-1000 μl (IH461801), and a "termo scientific" pipette, single-channel, Light DPOP-1-5-50 (TU 9443-007-33189998-2007). To determine the sorption capacity of thermally reduced graphene oxide, a sample of sorbent 0.0065 g was exposed in 10 ml of Cu^{2+} solution of various concentrations for 3 h until a constant value of Cu^{2+} concentration was reached.

Upon completion of the sorption process, the solutions were filtered through an ashless filter for the analysis "White Ribbon" d = 11.0 cm (TU 2642-001-68085491-2011, LLC "MELIOR XXI"). Concentration of Cu^{2+} in aqueous solutions was determined by the stripping voltammetry on the TA-Lab voltammetric analyzer (NPP Tom'analit). The equilibrium adsorption capacity for copper ions was calculated by the formula:

$$q_e = (C_0 – C_e)\ V/m,$$

where C_0 is the initial concentration of Cu^{2+}, mg l^{-1}; C_e is the equilibrium concentration of Cu^{2+}, mg l^{-1}; V is the volume of the solution, l; and m is the sorbent weight, g.

RESULTS AND DISCUSSION

The route of electrochemical synthesis of a multilayer graphene oxide, including certain physical and chemical properties are described in detail in [23]. The results of differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) (Fig. 1) reveal an endothermic peak in the scanning range up to 100 °C, accompanied by the weight loss of about 7%, and may be due to desorption and evaporation of a certain amount of retained water in the samples. The obtained results are consistent with the TG data of oxidized graphite obtained by the Hammers method [6] and differ by 2% in the weight loss. Another endothermic peak appears at 252 °C on the DTA curve and the weight loss of 15% can be explained by decomposition of labile hydroxyl, epoxy and carboxyl oxygen-containing functional groups, including those between the layers of polygraphene planes. The subsequent weight loss of graphite oxide is probably due to pyrolysis of residual oxygen-containing groups and carbon atoms of polygraphene planes. It should be noted that compared to the results presented in [26], the weight loss of the oxidized graphite in the temperature range under study is less by 10% (200 °C) and 25% (400 °C), which may indicate a lower concentration of oxygen-containing functional groups in the electrochemically oxidized graphite. Thermal exfoliation at 250 °C of multilayer graphene oxide leads to the removal of oxygen-containing functional groups [26, 27], a significant increase in the particle size (K_V = 1490 cm^3 g^{-1}) and formation of worm-like structures with a large number of V-shaped pores (Fig. 2) with 1-10 µm in size and thickness of poly graphene planes up to 0.01 µm. The specific surface area of the heat-treated graphene oxide powder is 400-500 m^{2}g^{-1}. The particle distribution range of a thermally reduced multilayer graphene oxide in the water is 0.3-1400 µm, modal size is 211 µm (Fig. 3a). Under ultrasonic treatment of the water dispersion, the particle size of the dispersed phase significantly decreases to 0.2-400 µm, with the modal size of 143 µm (Fig. 3b), which allows a more uniform distribution of carbon material particles in the volume of water. The particle distribution range of the thermally reduced multilayer graphene oxide in the water is 0.3-1400 µm, the modal size is 211 µm (Fig. 3a). Under ultrasonic influence on the water dispersion, the particle size of the dispersed phase decreases significantly to 0.2-400 µm, with the modal size of 143 µm (Fig. 3b), which allows a more uniform distribution of the carbon material particles in the volume of water.

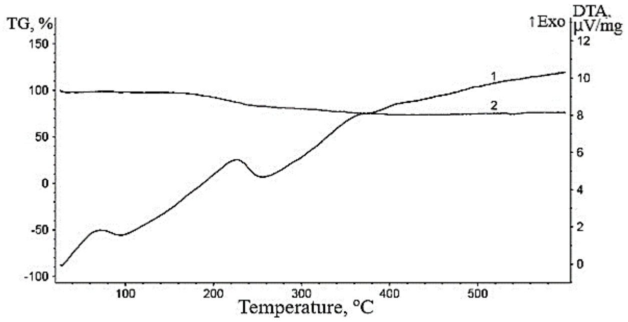
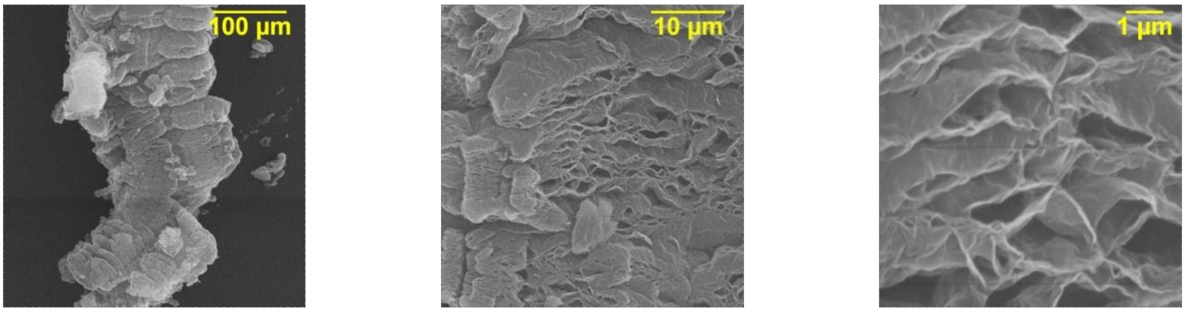
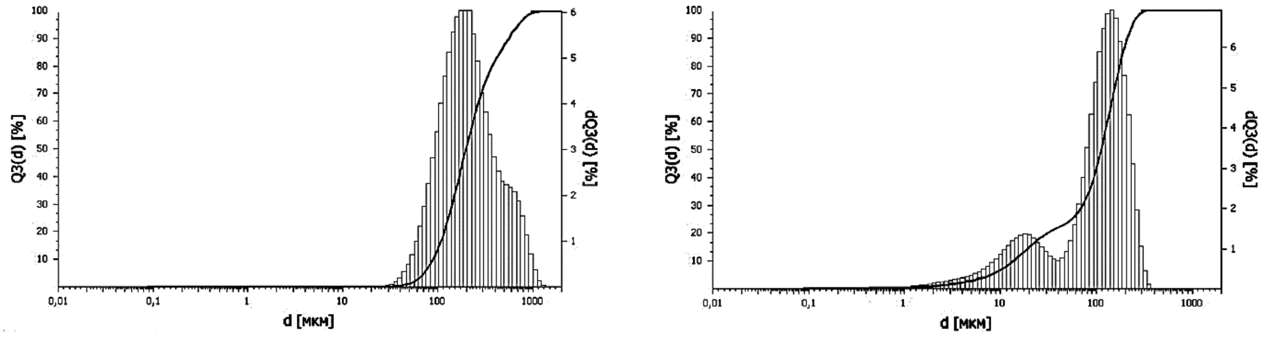


Fig. 1. TG-DTA of electrochemically oxidized graphite: 1 - differential thermal curve, 2 - thermogravimetric curve
Рис. 1. ТГ-ДТА электрохимически окисленного графита: 1- кривая дифферинциально-термическая, 2- кривая термогравиметрическая



a b c

Fig. 2. Scanning electron microscopy of thermally reduced graphene oxide a) ×500, b) ×5000, c) ×25000
Рис. 2. Сканирующая электронная микроскопия термовосстановленного оксида графена a) ×500, b) ×5000, c) ×25000



a b

Fig. 3. Distribution of particles of thermally reduced graphene oxide by size in an aqueous suspension (a) with ultrasonic action (b)
Рис. 3. Распределение частиц термовосстановленного оксида графена по размерам в водной суспензии (a) с ультразвуковым воздействием (b)

The qualitative composition of surface functional groups practically does not change during the thermal reduction (Fig. 4). There is a noticeable decrease in the peak intensity at 3417 cm^{-1} and the band between 2800 cm^{-1} and 3100 cm^{-1} compared to the initial multilayer graphene oxide [22]. We also found the presence of sp^2 hybridization of C=C in the graphene structure (peak at 1627 cm^{-1}), epoxy groups -COC- (band between 1106 cm^{-1} and 1005 cm^{-1}), and carboxyl groups -COOH- (band at 1384 cm^{-1}). The peak at 2300 cm^{-1} corresponds to the peak of absorbed CO_2 molecules.

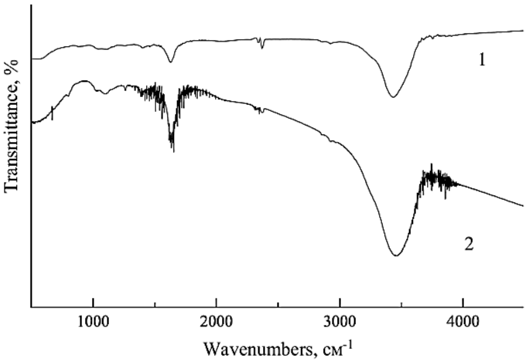


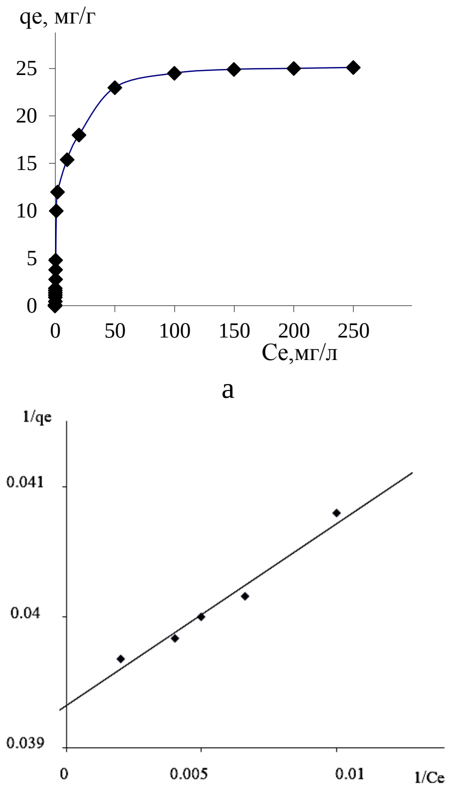
Fig. 4. FTIR spectroscopy of thermally reduced graphene oxide 1- original; 2- modified with Cu^{2+}

Рис. 4. ИК-Фурье спектроскопия термовосстановленного оксида графена. 1- исходный; 2- модифицированный Cu^{2+}

The developed porous structure, a large specific surface area, and the presence of acidic functional groups create the prerequisites for the use of thermally reduced oxide of a multilayer graphene for the sorption of metal cations from aqueous solutions.

According to the obtained results, the adsorption isotherms of Cu^{2+} on a thermally reduced multilayer graphene oxide (Fig. 5) have the form typical for the isotherms of H2 class, and are characterized by a straight steep rising initial segment, which indicates a high affinity of adsorbate to adsorbent with the formation of chemical compounds. Therefore, the interaction of Cu^{2+} ions with carboxyl functional groups is likely to occur, which is confirmed by a slight decrease in the pH of the solution. The isotherm is approximated by a straight line, which makes it possible to use it to describe the adsorption process of the Langmuir model. The maximum sorption capacity of a thermally reduced multilayer graphene oxide for Cu^{2+} was ≈25 mg g^{-1}, which is noticeably higher than the sorption capacity of activated carbon fibers [8].

After exposure of thermally reduced graphene oxide in the solutions containing copper cations, the absorption bands are observed in the FTIR spectroscopy (Fig. 4) in the region of 690-1130 cm^{-1}, which can be considered as vibrations of groups formed on the surface as a result of interaction of copper cations with oxygen atoms as part of functional groups. Carbon material modified with copper cations can be used to obtain composite electrochemical coatings according to the methods described in [28, 29].



b

Fig. 5. Isotherms of Cu^{2+} adsorption by thermally reduced oxide of multilayer graphene. a - experimental, b - Langmuir

Рис. 5. Изотермы адсорбции Cu^{2+} термовосстановленным оксидом многослойного графена. a - экспериментальная, b - Ленгмюра

CONCLUSIONS

The electrochemical method is used to synthesize the samples of a multilayer graphene oxide, which under thermal reduction at the temperature of 250 °C leads to formation of foam-like worm-like structures with V-shaped pores and a specific surface area of 400-500 m^{2}g^{-1}. The sorption capacity of a thermally reduced multilayer graphene oxide to Cu^{2+} was ≈25 mg g^{-1}.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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