

UDC 54.052, 54.058

DOI: 10.15372/CSD20202550

Investigation of the Nature of Functional Groups of Graphene Membranes by Means of IR Spectroscopy

M. A. SEITZHANOVA¹, S. A. YASHNIK², Z. R. ISMAGILOV³, S. R. KHAIRULIN², Z. A. MANSUROV^{1,4}, A. A. MONTAYEVA⁵

¹*Al-Farabi Kazakh National University,
Almaty, Kazakhstan*

E-mail: Seitzhanova.makpal@kaznu.kz

²*Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences,
Novosibirsk, Russia*

³*Federal Research Centre of Coal and Coal Chemistry, Siberian Branch, Russian Academy of Sciences,
Kemerovo, Russia*

⁴*Institute of Combustion Problems,
Almaty, Kazakhstan*

⁵*School-Gymnasium No. 136 named after M. Dulatov,
Almaty, Kazakhstan*

(Received February 21, 2020, revised September 02, 2020)

Abstract

Graphene membranes were manufactured for the purpose of developing efficient materials for the membrane technologies of water freshening. Investigation of the nature of their functional groups was carried out by means of IR spectroscopy. Graphene membranes were obtained using two methods: 1) vacuum filtration; 2) immersion precipitation. Graphene materials used in the study were graphene oxide (a commercial sample) and graphene (a laboratory sample obtained by means of stepwise carbonization of rice husks). The data of the FTIR spectra of diffuse reflection (DRIFT) from membranes manufactured using graphene point to the low defect content in its single-layer graphite structure, while membranes based on graphene oxide contain not only graphene layers but also amorphous carbon with sp^3 -hybridized atoms and oxygen-containing functional groups (mainly carboxylic and phenolic). The tests of the membranes were carried out with respect to the efficiency of filtration of salt-containing solutions (NaCl , KCl , MgCl_2 , CaSO_4 и MgSO_4) and salt removal. Analysis of desalinated solutions by means of atomic absorption flame emission spectrophotometry showed that purification efficiency was 74–80 % for membranes obtained by means of vacuum filtration.

Keywords: graphene, graphene oxide, rice husks, membrane, IR spectroscopy

INTRODUCTION

At present, the problem of seawater freshening is escalating by the rapid increase in the Earth's population (by more than 80 million persons per year), so by 2025, at least 2 milliard people will systematically suffer a sharp deficit of drinking water. The consumption of fresh water depending

on residential site varies from 19 to 380 L per one person per day. It is also known that 70 % of water resources are salty waters of seas and oceans. Each kilogram of seawater contains 35 g of various salts on average; the major components are Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} ions [1, 2]. Under the conditions of limited fresh water resources and an increase in its consumption, it is

very relevant to improve the technologies of water freshening.

Freshening implies the removal of dissolved salts to the parameters corresponding to the standards of drinking and industrial water supply. The use of membranes for water freshening increases every year [3–6] due to the development of nanotechnologies and nanomaterials allowing the improvement of the structure and properties of water-permeable membranes [7, 8]. Among nanomaterials, special outlooks for seawater freshening are held by graphene. This is a two-dimensional allotropic modification of carbon with hexagonal lattice one carbon atom thick; carbon atoms in sp^2 -hybrid state are connected with each other by σ - and π -bonds [9, 10]. Freshening membranes made of traditional materials, most frequently plastics, are usually made rather thick to achieve strength. The strength of graphene is several ten times higher than that of plastics, so eth membrane may be much thinner and let water pass much faster. Graphene is also able to retain larger molecules of pollutants including magnesium sulphate and dextrin [11]. The wide application of graphene is hindered by the high cost of its production and the absence of its manufacture on an industrial scale. To reduce the net cost of these membranes, graphene or graphene oxide are deposited in the form of a thin film onto a commercial membrane; in this case, the membrane provides filtration properties, and graphene is responsible for freshening characteristics of the membrane in general. The presence of surface functional groups in graphene oxide allows the manufacture of composite materials on its basis. As a result of the interaction, which includes the formation of hydrogen bonds and electrostatic attraction [12], graphene oxide on membrane surface gets bound mainly through carboxylic groups with amino or hydroxyl groups of the modifying component of the membrane [11, 12]. However, graphene fixation on the membrane surface is in the majority of cases provided by surface forces – hydrophobic interaction [11].

The removal of cations and anions from water occurs according to the mechanisms of ion exchange, chemisorption or physical adsorption with the formation of anion-cation pairs or through the formation of covalent, hydrogen, Van der Waals and electrostatic interactions with the functional groups of graphene. The sorption capacity of graphene membranes in seawater freshening is directly dependent on the type and concentration of functional groups on its surface. Because of this, the

information on the nature of functional groups of graphene and its derivatives (graphene oxide and reduced graphene oxide) is important for predicting their sorption properties and the reasonableness of the use of graphene membrane to freshen waters of definite composition.

Infrared (IR) spectroscopy is a rapid and non-destructing method to obtain the data on the chemical structure of the material. Reliable identification of separate functional groups in the IR spectra is based on the specific frequency of vibrations characteristic of each chemical bond. Pure graphene is considered to have no characteristic absorption bands related to the graphene structure [13, 14], which is formed by carbon in sp^2 -hybridization, while materials based on graphene – graphene oxide and reduced graphene oxide – contain oxygenated groups and absorb in the region of IR radiation [13–22]. Graphene oxide contains mainly hydroxyl [17], phenol [18], carbonyl [17, 19], carboxyl [15, 19–22], aryl [15, 20, 21], ether [15, 17], phosphorus-containing and other functional groups depending on the method of synthesis. It is assumed that oxygenated functional groups are connected with sp^3 -hybrid carbon atoms and differ from each other in the positions with respect to the graphite plane, for example, hydroxyl and ether-epoxy groups are located above and behind it [17], while carbonyl and carboxyl groups are situated at the edges or inside the plane [21]. Hydrogen bonds may be formed between the graphene layers [19]. A detailed discussion of the assignment of absorption bands observed in carbon-containing materials was published in reviews [23, 24].

In the present work, we carried out a detailed investigation of the nature of functional groups on the surface of graphene and graphene membranes obtained on the basis of this material using two different methods. The investigation was carried out by means of IR diffuse reflectance spectroscopy. Functional groups were identified relying on published data. The efficiency of membranes in the removal of some salts (NaCl, KCl, $MgCl_2$, $CaSO_4$ and $MgSO_4$) from aqueous solutions was evaluated.

EXPERIMENTAL

Materials and methods

Commercial graphene oxide powder (GO) manufactured by XFNANO (Nanjing XFNANO

Materials Tech Co., Ltd., China) was used in the work. The GO powder has a side size of 1 μm with a thickness of 0.8–1.2 nm, its purity is more than 99 %.

Graphene was obtained from rice husks using a four-stage method [25, 26], which included preliminary carbonization, desilication, activation with KOH, and exfoliation. According to the data of elemental analysis, the synthesized graphene powder contained carbon ~70 mass % and inorganic substances 0–30 mass % including K, Fe, Si. To remove the inorganic substances, the stage of purification and functionalization was then carried out.

Graphene membranes were deposited on the commercial Vladipor microfiltration membranes of the MFAS-SPA type (CC STC Vladipor, Russia) based on cellulose acetate, 47 mm in diameter, with pore size 1.5–3 μm , total porosity 80–85 % (Table 1, sample No. 1, Fig. 1).

Obtaining graphene membranes

The conditions of membrane preparation and the general characteristics of membranes are listed in Table 1.

Membranes based on graphene materials were obtained using two methods: vacuum filtration

TABLE 1

General characteristics of the obtained graphene membranes

Sample No.	Title	Characteristics	Conditions of preparation
1	Commercial membrane	Vladipor membrane MFAS-SPA type	Initial material
2	Membrane based on commercial graphene oxide (GO)	Microporous membrane modified with graphene oxide (commercial)	Membrane was prepared by means of vacuum filtration
3	Membrane based on graphene	Microporous membrane modified with graphene (prepared from rice husks)	Membrane was prepared by means of vacuum filtration. Graphene was obtained by the activation of rice husks with KOH at 850 °C
4	PVDF filter based on a mixture of graphene oxide and graphene	Macroporous filter. The particles of the same size and fragile aggregates. Leaf-shaped particles	The filter was prepared by immersion precipitation (NIPS) using GO and graphene

Note. PVDF is polyvinylidene difluoride.

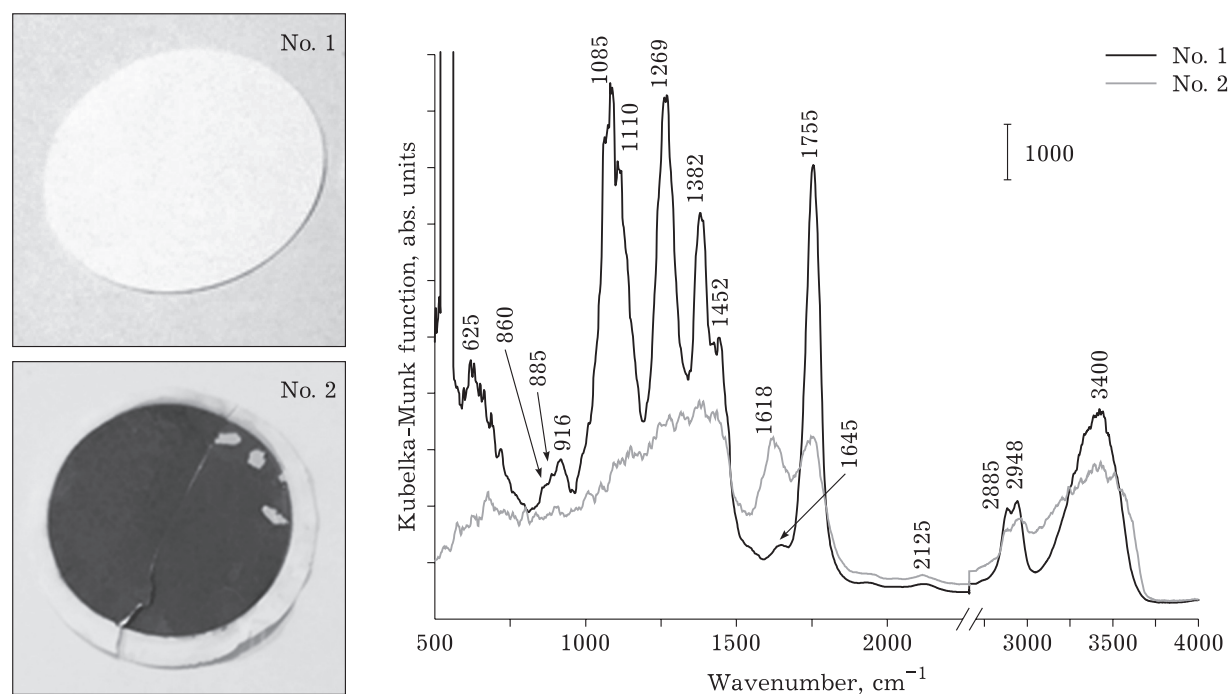


Fig. 1. DRIFT of membranes No. 1 (commercial membrane based on a mixture of acetates) and No. 2 (commercial membrane with deposited commercial graphene oxide).

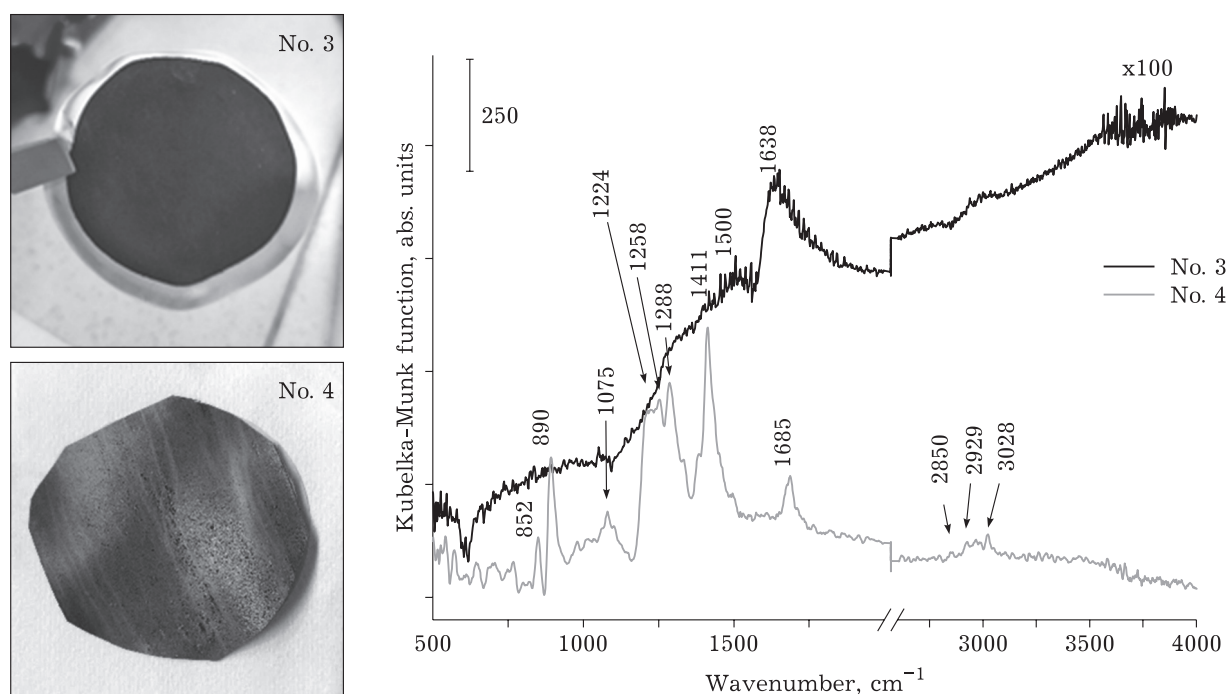


Fig. 2. DRIFT of membranes No. 3 (membrane with deposited graphene prepared from rice husks) and No. 4 (filter based on a mixture of polyvinylidene difluoride (PVDF), polyvinylpyrrolidone with graphene oxide and graphene).

and immersion precipitation (NIPS) [27]. In the former case, GO powder (see Table 1, sample No. 2, Fig. 1) or graphene (see Table 1, sample No. 3, Fig. 2) was dispersed in deionized water and treated with ultrasound for 2 h. Then 40 mL of the resulting suspension (0.01 mg/mL) was filtered through the membrane (filtration area 38 mm²) at a pressure of 0.8 bar and room temperature, resulting in the formation of a thin GO or graphene layer on the surface of the membrane. The resulting membranes based on graphene materials were dried in vacuum (pressure 0.95 bar) at 40 °C for 40 h.

According to the second method, 0.5 g of polyvinylidene difluoride (PVDF) and 4 mL of 1-methyl-2-pyrrolidone were placed in a heat-resistant glass beaker, heated to 50 °C, and mixed for 1 h to obtain a homogeneous solution of the polymer. Then 0.1 g of the mixture of graphene with GO (at the mass ratio of 1 : 1) was dispersed with the help of ultrasound in a small amount of 1-methyl-2-pyrrolidone (2 mL). The duration of the ultrasonic treatment was 30 min. The resulting uniform dispersion was added to the homogeneous solution of PVDF. Then 0.1 g of polyvinyl pyrrolidone (PVP) was introduced into the dispersed suspension PVDF/GO/graphene and mixed carefully for 1 h till the homogeneous suspension was formed. The suspension was treated

with ultrasound for degassing. The homogeneous foundry solution was poured onto a glass plate (with the adjustment of thickness 400 μm) and immersed into a coagulation bath containing water as a non-dissolving agent. The resulting membrane (see Table 1, sample No. 4, Fig. 2) was kept in the coagulation bath for 24 h to provide complete phase inversion.

Investigation by means of IR spectroscopy

The nature of functional groups on the surface of membranes was studied by means of IR spectroscopy with the help of a Cary-660 FTIR spectrometer (Agilent Technologies, USA) in the diffuse reflection mode using a DiffusIR™ attachment (Pike Technology, USA) within wavenumber range 4500–500 cm⁻¹ with the resolution of 4 cm⁻¹ and accumulation of 256 scans (to improve the quality of spectra and the signal to noise ratio). The diffuse reflection infrared fourier transform (DRIFT) spectra are represented in the coordinates: Kubelka-Munk function, $F(R)$, – wavenumber, without baseline correction.

Procedure to study water freshening with the help of membranes

The tests of membranes for the efficiency of filtration of salt-containing solutions and salt removal from the solutions were carried out using

the laboratory vacuum filtration apparatus at a pressure of 0.8 bar. For this purpose, the salts NaCl, KCl, MgCl_2 , CaSO_4 and MgSO_4 were dissolved in distilled water. Initial concentrations of the salts were, g/L: 27.3 (NaCl), 0.7 (KCl), 2.275 (MgCl_2), 1.225 (CaSO_4), 2.275 (MgSO_4). The composition of the solutions filtered through the membranes was studied with the help of atomic absorption flame ionization spectrophotometer AA-6200 (Shimadzu, Japan) at the Centre of Physicochemical Investigations and Analysis (Almaty, Kazakhstan) using the following discretization modes: optical system – two-ray, monochromator – Czerny-Turner, spectral range – 190–900 nm, spectral region – 0.2, 0.7 nm (switched by hand), background corrector – deuterium, simultaneous switching on (one works, another warms).

RESULTS AND DISCUSSION

The salt-removing characteristics of the resulting membranes were studied relying on their ability to remove salts (NaCl, KCl, MgCl_2 , CaSO_4 and MgSO_4) from solutions. After the filtration of initial solutions through membrane samples No. 2 and No. 3, salt concentrations decreased to 6.64 (NaCl), 0.18 (KCl), 0.19 (MgCl_2), 0.28 (CaSO_4), 0.46 g/L (MgSO_4). Analysis of freshened solutions by means of atomic absorption flame ionization spectrophotometry showed that the efficiency of water purification with the help of membranes prepared by means of vacuum filtration was 74–80 % with respect to the listed salts. In the case of the membrane obtained by means of immersion precipitation, this parameter does not exceed 50 %. Relying on these data, we may conclude that it is much more promising to prepare membranes by means of vacuum filtration (both for commercial GO and for graphene from rice husks).

The appearance and DRIFT of membrane samples are shown in Fig. 1 and 2. For the convenience of analysis, the spectra are grouped taking into account the intensity of the observed absorption bands (a. b.).

The DRIFT spectrum of the initial membrane (No. 1) contains intense a. b. at 3400, 2948, 2885, 1755, 1452, 1382, 1269, 1085–1110, 860–916, 625 cm^{-1} , which completely describe the vibrations of separate carboxylate (R-COOH) groups [28]. For instance, the a. b. at 1755 cm^{-1} relates to the stretching vibrations of C=O in non-ionized carboxylic groups (–COOH), and the fraction of ionized –COO– groups is very small in this case

(a. b. at 1645 cm^{-1} [29]). The bands at 2885 and 2948 cm^{-1} , characteristic of symmetrical and asymmetrical stretching vibrations of C–H bonds in CH_3 fragments [30–32] of organic acids also point to the presence of carboxylate groups in the membrane material. Additional a. b. at 1452, 1382 and 1085–1110 cm^{-1} in the spectrum of the material relate to asymmetrical, symmetrical and rotational bending vibrations of H–C–H in CH_3 fragments of carboxylates, respectively. The bands at 3400 (broad) and 1385 cm^{-1} correspond to the stretching and bending vibrations of O–H bonds in free –COOH groups of acetic acid, and a. b. at 915–885 cm^{-1} (broad) – in hydrogen-bonded –COOH groups. The bands at 1265–1205 and 1190–1075 cm^{-1} are due to the stretching and bending vibrations of C–O bonds in –COO groups, respectively, a. b. at 665–590 cm^{-1} are due to the bending vibrations of C=O [28].

The DRIFT spectrum of the microporous membrane with deposited graphene oxide (see Fig. 1, sample No. 2) contains a. b. characteristic of the initial membrane (see Fig. 1, sample No. 1): 3400, 2885, 2948, 1755, 1452–1050 and 625 cm^{-1} , but their intensity decreases substantially, and band splitting in the region of 1452–1050 cm^{-1} disappears. This may point to the interaction of graphene oxide deposited on the membrane surface with its functional groups. However, we failed to improve the quality of DRIFT and clearly detect the characteristic bands of graphene oxide functional groups described in [13–22]. Among all a. b. listed in review [23], only the band at 1618 cm^{-1} and asymmetry of the band with the centre at about 3400 cm^{-1} are observed in the spectrum of sample No. 2. According to [33], the band in the region of 1560–1600 cm^{-1} corresponds to the E_{1u} mode in graphite structures; however, the spectrum of sample No. 2 does not contain the second a. b. in the region of 820–860 cm^{-1} , related to the vibration mode A_{2u} of graphite. The absorption band at 1618 cm^{-1} may also be related to the functional groups of graphene oxide, for example, with the stretching vibrations of –C=C bond in aromatic or polyaromatic structures (graphite or graphene layers [15, 20, 22], naphthalene, anthracene [28]) or –C=O bonds in quinolone-like structures [28]. According to literature data, the mentioned functional groups manifest themselves in the regions of 1618–1620 [15, 20], 1620–1580 [28] and 1690–1655 cm^{-1} [24, 28]. The asymmetry of the band at 3400 cm^{-1} toward smaller wavenumbers may be due to the contribution from the stretching vibrations of O–H bonds within

carboxylic groups ($3300\text{--}2500\text{ cm}^{-1}$ [17]) or phenol groups (3214 cm^{-1} [17, 18]) of graphene oxide used for membrane preparation; their bending vibrations could not be distinguished due to the poor resolution of bands in the region $<1500\text{ cm}^{-1}$.

Sample No. 3 turned out to be the poorest for the analysis of its functional groups by means of IR spectroscopy. Its spectrum has the lowest intensity and only two a. b. at 1638 and 1500 cm^{-1} that could be analyzed. The observed manifestations agree with membrane composition. That membrane was prepared using graphene obtained by the activation of rice husks with KOH at a temperature of $850\text{ }^{\circ}\text{C}$. In the opinion of the authors of [13, 14], pure graphene does not have characteristic peaks corresponding to the graphene structure in IR spectroscopy. On the other hand, a. b. at 1638 and 1500 cm^{-1} are likely to be due to the stretching vibration of --C=C bonds in aromatic [15, 20], polyaromatic [28] or graphite-like [33] structures. The high synthesis temperature is likely to lead to the low defect content in graphene.

The DRIFT spectrum of membrane No. 4, obtained by mixing graphene oxide and graphene with PVP, contains intense a. b. at 852 , 890 , 1025 , 1224 , 1258 , 1288 , 1411 , 1685 , 2850 , 2929 , 2965 and 3028 cm^{-1} . As indicated above, the bands at 1685 and $852\text{--}890\text{ cm}^{-1}$ are in the region of vibrational modes $E1u$ and $A2u$ of graphite-like structures [33]. The a. b. at 1224 , 1258 and 1288 cm^{-1} may be due to defects in graphite-like structures. A broad band at $1220\text{--}1290\text{ cm}^{-1}$ was observed in the spectrum of N-containing carbon nanotubes [33] and nanofibres [34] and was related by the authors to the distortions of the translation symmetry of defect-bearing graphite-like structure. The couple of a. b. at 2850 and 2965 cm^{-1} is characteristic of CH_3 groups and corresponds to the symmetrical and asymmetrical (respectively) stretching vibrations of C--H bonds in them. In this case, additional bands at 1411 and 1025 cm^{-1} in the spectrum of membrane No. 4 relate to bending and rotational vibrations of H--C--H in CH_3 groups, respectively. These bands point to the presence of carbon with sp^3 -hybridization in the composition of the membrane. The couple of a. b. at 2929 and 3028 cm^{-1} is characteristic of $\text{CH}_2\text{--}$ and =C--H -groups in acyclic and aromatic compounds, respectively. On the other hand, some bands in the spectrum of sample No. 4 may be related to the characteristic a. b. of C=O , C--O and O--H bands from oxygen-containing groups of graphene oxide, for example, epoxide ($852\text{--}890$, $1215\text{--}1230$ and 1280 cm^{-1} – deformation,

asymmetrical and symmetrical stretching vibrations of C--O--C bonds, respectively [15]), carboxylic (1025 and 1411 cm^{-1} – stretching vibrations of C--O [15]) and alcohol and phenol groups ($1405\text{--}1415\text{ cm}^{-1}$ – deformation vibrations of O--H bonds, 1220 cm^{-1} – stretching vibrations of O--H and ArO--H [19]).

CONCLUSION

The effect of the method of synthesis of graphene membranes (vacuum filtration and immersion precipitation) and the type of graphene material (graphene oxide and/or graphene) on the composition of functional groups of the surface and on the efficiency of the membrane in water freshening was studied.

As a result of the investigation by means of IR spectroscopy, it was revealed that the spectra of graphene membranes obtained by vacuum filtration contain the bands indicating the interaction of graphene oxide through the functional groups with the surface of the membrane onto which it is deposited. It is highly probable that the bands observed in the IR spectra are due to the stretching vibration of --C=C bonds in polyaromatic, graphite-like or graphene-like structures of graphene and its oxide. Graphene membranes obtained by means of immersion precipitation have the bands characteristic of $\text{CH}_2\text{--}$ and =C--H -groups in acyclic and aromatic compounds. For membranes obtained using both methods and containing graphene oxide in their composition, the vibrations of functional oxygen-containing groups (mainly carboxyl and phenol) are detected.

The tests of graphene membranes for the efficiency of filtration of the solutions containing salts (NaCl , KCl , MgCl_2 , CaSO_4 and MgSO_4) followed by the analysis of freshened solutions by means of atomic absorption flame emission spectrophotometry revealed the dependence of filtration rate and freshening efficiency on the method of membrane synthesis. It was revealed that the efficiency of freshening with the help of the membrane prepared by means of immersion precipitation is not more than 50 %, while the efficiency of membranes obtained by means of vacuum filtration is 74–80 %. In addition, the use of vacuum filtration for the production of filtering membranes made of graphene oxide and graphene ensures a high filtration rate, which points to the high potential of the use of this method for the development of efficient materials for the membrane technology of water freshening.

IR studies of the membranes were carried out within the State Assignment to the BIC SB RAS (Project No. AAAA-A17-117041710086-6).

REFERENCES

- Nayar K. G., Sharqawy M. H., Banchik L. D., Lienhard J. H., Thermophysical properties of seawater: A review and new correlations that include pressure dependence, *Desalination*, 2016, Vol. 390, P. 1–24.
- Panagopoulos A., Haralambous K. J., Loizidou M., Desalination brine disposal methods and treatment technologies, *The Science of the Total Environment*, 2019, Vol. 693, Article 133545.
- Elimelech M., Phillip W. A., The future of seawater desalination: Energy, technology, and environment, *Science*, 2011, Vol. 333, P. 712–717.
- Yang Z., Ma X.-H., Tang C. Y., Recent development of novel membranes for desalination, *Desalination*, 2018, Vol. 434, P. 37–59.
- Boretti A., Al-Zubaidy S., Vaclavikova M., Al-Abri M., Castelletto S., Mikhalevsky S., Outlook for graphene-based desalination membranes, *NPJ Clean Water*, 2018, Vol. 1, Article 5.
- Shen Y.-X., Saboe P. O., Sines I. T., Erbakan M., Kumar M., Biomimetic membranes: A review, *Journal of Membrane Science*, 2014, Vol. 454, P. 359–381.
- Werber J. R., Osuji C. O., Elimelech M., Materials for next-generation desalination and water purification membranes, *Nature Reviews Materials*, 2016, Article 16018.
- Humphik T., Lee J., O'Hern S. C., Fellman B. A., Baig M. A., Hassan S. F., Atieh M. A., Rahman F., Laoui T., Karnik R., Wang E. N., Nanostructured materials for water desalination, *Nanotechnology*, 2011, Vol. 22, No. 29, Article 292001.
- Wang E. N., Karnik R., Graphene cleans up water, *Nature Nanotechnology*, 2012, Vol. 7, P. 552–554.
- Geim A., Novoselov K., The rise of graphene, *Nature Materials*, 2007, Vol. 6, P. 183–191.
- Mahmoud K. A., Mansoor B., Mansour A., Khraisheh M., Functional graphene nanosheets: The next generation membranes for water desalination, *Desalination*, 2015, Vol. 356, P. 208–225.
- Song N., Gao X., Ma Z., Wang X., Wei Y., Gao C., A review of graphene-based separation membrane: Materials, characteristics, preparation and applications, *Desalination*, 2018, Vol. 437, P. 59–72.
- Sangermano M., Marchi S., Valentini L., Bon S. B., Fabbri P., Transparent and conductive graphene oxide/Poly(ethylene glycol) diacrylate coatings obtained by photopolymerization, *Macromol. Mater. Eng.*, 2011, Vol. 296, Ed. 5, P. 401–407.
- Kumar P. A., Singh K., Hussain S., Hui K. N., Hui K. S., Eom J., Jung J., Singh J., Graphene: Synthesis, properties and application in transparent electronic devices, *Rev. Adv. Sci. Eng.*, 2013, Vol. 2, No. 4, P. 238–258.
- Obreja A. C., Cristea D., Gavrilă R., Schiopu V., Dinescu A., Danila M., Comanescu F., Isocyanate functionalized graphene/P3HT based nanocomposites, *Appl. Surf. Sci.*, 2013, Vol. 276, P. 458–467.
- Ramachandran R., Mani V., Chen S. M., Saraswathi R., Lou B. S., Recent trends in graphene based electrode materials for energy storage devices and sensors applications, *Int. J. Electrochem. Sci.*, 2013, Vol. 8, P. 11680–11694.
- Chhabra V. A., Deep A., Kaur R., Kumar R., Functionalization of graphene using carboxylation process, *International Journal for Science and Emerging Technologies with Latest Trends*, 2012, Vol. 4, No. 1, P. 13–19.
- Xu C., Li J., Wang X., Wang J., Wan L., Li Y., Zhang M., Shang X., Yang Y., Synthesis of hemin functionalized graphene and its application as a counter electrode in dye-sensitized solar cells, *Materials Chemistry and Physics*, 2012, Vol. 132, P. 858–864.
- Thakur S., Karak N., Green reduction of graphene oxide by aqueous phytoextracts, *Carbon*, 2012, Vol. 50, No. 14, P. 5331–5339.
- Chang D. W., Lee E. K., Park E., Yu Y. H., Choi H. J., Jeon I. Y., Sohn G. J., Shin D., Park N., Oh J. H., Dai L., Baek J. B., Nitrogen-doped graphene nanoplatelets from simple solution edge-functionalization for N-type field-effect transistors, *J. Am. Chem. Soc.*, 2013, Vol. 135, P. 8981–8988.
- Zhang H., Han X., Yang Z., Zou J., Tang H., Enhanced adsorption of methylene blue on graphene oxide by tuning the oxidation degree of graphene oxide, *J. Nanomater. Mol. Nanotechnol.*, 2013, Vol. S1, Article 003.
- Stankovich S., Piner R. D., Nguyen S. T., Ruoff R. S., Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets, *Carbon*, 2006, Vol. 44, No. 15, P. 3342–3347.
- Țucureanu V., Matei A., Avram A. M., FTIR spectroscopy for carbon family study, *Critical Reviews in Analytical Chemistry*, 2016, Vol. 46, No. 6, P. 502–520.
- Yan P., Zhang B., Wu K.-H., Su D., Qi W., Surface chemistry of nanocarbon: Characterization strategies from the viewpoint of catalysis and energy conversion, *Carbon*, 2019, Vol. 143, P. 915–936.
- Seitzhanova M. A., Chenchik D. I., Mansurov Z. A., Di Capua R., Development of a method of obtaining graphene layers from rice husk, *Functional Nanostructures Proceedings*, 2017, Vol. 1 (3), P. 6–8.
- Seitzhanova M. A., Chenchik D. I., Yeleuov M. A., Mansurov Z. A., Di Capua R., Elibaeva N. S., Synthesis and characterization of graphene layers from rice husks, *Chemical Bulletin of Kazakh National University*, 2018, Vol. 2, P. 12–18.
- Hebbbar R. S., Isloor A. M., Prabhu B., Inamuddin, Asiri A. M., Ismail A. F., Removal of metal ions and humic acids through polyetherimide membrane with grafted bentonite clay, *Scientific Reports*, 2018, Vol. 8, Article 4665.
- Socrates G., Infrared and Raman Characteristic Group Frequencies: Tables and Charts, John Wiley & Sons Ltd., 3d Ed., 2004. 366 p.
- Nakamoto K., Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, 2009. 419 p.
- Zielke U., Huttinger K. J., Hoffman W. P., Surface-oxidized carbon fibers: I. Surface structure and chemistry, *Carbon*, 1996, Vol. 34, No. 8, P. 983–998.
- Mckinnon J. T., Meyer E., Howard J. B., Infrared analysis of flame-generated PAH samples, *Combustion and Flame*, 1996, Vol. 105, No. 1–2, P. 161–166.
- Wang L., Song C., Song J., Lv G., Pang H., Zhang W., Aliphatic C–H and oxygenated surface functional groups of diesel in-cylinder soot: Characterizations and impact on soot oxidation behaviour, *Proceedings of the Combustion Institute*, 2013, Vol. 34, No. 2, P. 3099–3106.
- Ismagilov Z. R., Shalagina A. E., Podyacheva O. Yu., Ischenko A. V., Kibis L. S., Boronin A. I., Chesalov Y. A., Kochubey D. I., Romanenko A. I., Anikeeva O. B., Buryakov T. I., Tkachev E. N. Structure and electrical conductivity of nitrogen-doped carbon nanofibres, *Carbon*, 2009, Vol. 47, No. 8, P. 1922–1929.
- Shaffer M. S. P., Fan X., Windle A. H., Dispersion and packing of carbon nanotubes, *Carbon*, 1998, Vol. 36, No. 11, P. 1603–1612.