Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2021.26645

214 (2021) 49–55
February

Development of graphene oxide-coated membranes to support the process of removing pharmacological agents from water

Daniel Polak[a], Izabela Tonecka[a], Wojciech Fabianowski[b], Maciej Szwast[a,*]

[a]*Faculty of Chemical and Process Engineering, Warsaw University of Technology, Waryńskiego 1, 00-645, Warsaw, Poland, email: maciej.szwast@pw.edu.pl (M. Szwast)*
[b]*Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664, Warsaw, Poland*

Received 27 February 2020; Accepted 27 May 2020

ABSTRACT

Inefficient removal of pharmacological agents from water in sewage treatment plants leads to the introduction of pharmaceuticals, including antibiotics, into the hydrological cycle, and also contributes to the growth of antibiotic-resistant bacteria. This problem requires the development of new technologies that will support conventional treatment. One of the solutions is the use of membrane processes (microfiltration, ultrafiltration, membrane bioreactor) using membranes covered with materials with adsorptive and bactericidal properties. One of the substances that has these two properties is graphene oxide (GO). This paper presents the results of research on the modification of commercial microfiltration membranes involving the chemical attachment of graphene oxide to the membrane surface using a (3-aminopropyl)triethoxysilane (3-APTES) precursor and applying a GO-PEBAX 2533 (polyether block amide type 2533) layer in the dip-coating process. Using the scanning electron microscopy microscopic analysis, Fourier-transform infrared spectroscopy method and contact angle measurements, the presence of GO particles on the membrane surface and the change of membrane surface properties were confirmed. In the tests, aqueous solutions of sulfadiazine and amoxicillin were used. The amount of the adsorbed substances in a stationary system were: 31.03 and 4.77 mg/m^2, respectively. The membranes modified by GO are able to adsorb the pharmacological substances, which was confirmed in the flow system. In addition, the effects of modification on the membrane structure using a porosimeter and on water permeability based on the filtration coefficient were determined.

Keywords: Water treatment; Membrane modification; Graphene oxide; Pharmaceuticals

1. Introduction

One of the environmental hazards related to the development of society is the increasing number of the so–called pharmaceuticals and personal care products in the hydrological cycle, which include medicines, also veterinary drugs, antibiotics, hormones and cosmetics [1]. Although the concentrations of these substances in water are determined at the level of the nano- or micrograms per litre, their presence causes toxic effects on the environment and leads to the development of antibiotic-resistant bacteria [2]. This is due to the phenomenon of bioaccumulation. The source of these substances are plants which produce pharmacological substances, hospitals, refuse dumps as well as households and agricultural farms that use inefficiently operating sewage treatment plants [3].

The treatment of sewage containing pharmaceuticals uses biological methods (aerobic and anaerobic treatment), membrane techniques (RO, NF, membrane distillation), adsorption (e.g., on activated carbon) and oxidation processes (ozonisation, Fenton reaction, photocatalysis, electrochemical oxidation) or hybrid methods [4]. One of the

* Corresponding author.

methods used with a high potential of removing contaminants of this type are membrane bioreactors (MBR) [5,6]. This technique is a combination of the biological oxidation method with the process of membrane filtration. A wide choice of biological deposits used and the option to select the appropriate membrane process (microfiltration, ultrafiltration or nanofiltration) help to design an MBR intended for a specific type of contaminants. However, the great variety of pharmaceuticals in the water may reduce the effectiveness of the MBR used, and so some substances will enter the treated stream.

A solution proposed by the authors to improve the efficiency of the removal process for this type of contaminants with the use of MBR, is to develop membranes coated with graphene oxide, which allows for the adsorption of pharmacological substances from water. In addition, graphene oxide has bactericidal properties, which proves to be helpful in removing antibiotic resistant bacteria. The development of membranes coated with graphene oxide is the aim of this study.

1.1. Properties of graphene oxide

Graphene oxide (GO) has hydrophilic, adsorption and antibacterial properties. The first two characteristics are due to the presence of the epoxy, hydroxyl and carboxyl groups on the surface of GO, which develop as a result of strong oxidation of graphite at the production stage of GO [7]. What is particularly interesting is the fact that GO can adsorb a number of compounds such as gases (ammonia, hydrogen, carbon dioxide, nitrogen dioxide and carbon monoxide), metal ions (Cu, Zn, Pb, Au, Pt, Pb, Cd and Co), dyes (methylene blue, methyl violet, methyl orange, remazol black and neutral red) and pharmaceutical substances (antibiotics, anti-inflammatory drugs and hormones) [8–17]. The adsorption mechanism depends on the type of the functional group on the surface of GO and the type of the compound being adsorbed. The basic interactions that bond GO with a specific substance include: π–bond, hydrogen bond, hydrophobic interactions and electrostatic interactions [18].

Antibacterial properties, on the other hand, result from the possible damage to cell membranes as a result of the contact of the cell with the edges of the nanolayers of GO and oxidative stress that is also connected with the presence of the functional groups on the surface of GO [19].

2. Experimental

2.1. Materials and methods

The study involved commercial microfiltration polypropylene membranes (S6/4 3M™ Capillary Membrane MF-PP Series, Type S6/2) with the external/internal capillary diameter of 2.7/1.8 mm, average pore diameter of 0.2 μm and porosity of 55%. The membranes were modified with two methods: dip-coating method and chemical method. For the dip-coating method, a modifying solution was a 2% polyether block amide type 2533 – PEBAX 2533 (Arkema, France) solution in ethanol (Sigma-Aldrich, Germany) containing 5 % of GO (WUT laboratory [20], Poland) in relation to the polymer weight, while for the chemical modification with a precursor, perhydride (Sigma-Aldrich), 10% solution of (3-aminopropyl)triethoxysilane – 3-APTES (Sigma-Aldrich) in ethanol and 0.1% suspended matter of GO in ethanol were used.

The adsorption properties of the prepared materials were tested using aqueous solutions of pharmacological substances such as: amoxicillin (Sigma-Aldrich) and sulphadiazine (Sigma-Aldrich).

The KSV NIMA Dip Coater was used for dip-coating to control the parameters of the membrane emergence from the modifying solution. A constant rate of emergence was used, which was 450 mm/min. The evaporation temperature of the solvent was 25°C.

The process of chemical modification of a precursor was carried out by dipping membranes in appropriate solutions one by one, at a stabilised temperature of 25°C. The membranes were dipped in perhydride for 4 h, in solution 3-APTES for 24 h and finally in the suspended matter of GO for 24 h. After each stage, the membranes were dried at 25°C for a period of at least 24 h.

Twelve membranes of a specific type were prepared and ten of them were used for the construction of membrane modules, while the other two were subjected to an instrumental analysis.

To analyse the surface of modified membranes a contact angle measurement was used as well as Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and porosimetry. The contact angle was measured with the sessile drop method using the OCA 25 DataPhysics goniometer. Ultrapure water was used in the tests as the liquid with the drop volume of 0.5 μl. The tests were carried out at the temperature of 25°C. The FTIR analysis was conducted with the attenuated total reflectance (ATR) technique and the Nicolet iS10 (Thermo Scientific) apparatus. The sample was scanned 32 times within the wavenumbers of 4,000–800 cm^{-1}. The SEM analysis was carried out with the PhenomWord microscope taking photos of the external surface of the membrane. To determine the pore size distribution the PMI Capillary Flow Porometer iPore –1200A was used.

The adsorption properties of the materials containing GO were tested in the fixed and flow systems. The fixed system was used for testing flat samples of the material containing GO. A weighed amount of the material (in one piece) was placed in the beaker including the test solution, and after 10, 15, 30 and 45 min from the start of the experiment a sample of the solution was taken and the concentration of the test pharmacological substance was determined. The mass of the sample was 0.4 g and its surface area was 0.0290 m^2 and the volume of solution was 0.01 L. The flow system was used to test the adsorptibility of the membranes in the module. This was a typical system for conducting the process of microfiltration of closed-circuit of the feed. The feed pressure was 0.5 bar. The total area of the membranes in the module was 0.058 m^2 (10 membranes with a length of 41 cm each were in the module; the area of sorption is the sum of the inner and outer surface of the membranes). Permeate and retentate were turned back to the feed tank. After 10, 15, 30 and 45 min from the start of the process a sample of the feed was taken and the concentration of the test pharmacological substance was determined. The volume of the feed solution was 0.5 L. To determine the

concentration of the pharmacological substances UV-Vis spectroscopy was used. For this purpose, for each substance calibration curves of the test substances were prepared and on their basis the concentration was determined. The wavelength of maximum absorbance for amoxicillin and for sulfadiazine is 283 and 288 nm, respectively. The flow system was also used to determine ultrafiltration coefficient (UFC) (Eq. (1)).

$$\mathrm{UFC} = \frac{Q_p}{p \cdot A} \tag{1}$$

where Q_p is the permeate volumetric flow (m^3/s); p is the feed pressure (Pa); A is the filtration area (m^2).

2.2. Modification of microfiltration membranes

To modify the commercial polypropylene microfiltration membranes dip-coating and chemical modification with a precursor were used. The purpose of both modifications was to create a layer containing graphene oxide on the surface of the membranes.

Coating processes are commonly used in many industries. They are used to provide protective and anticorrosive layers as well as layers that facilitate washing or improve the appearance. These are relatively simple techniques used on an industrial scale [21]. The dip-coating method consists in dipping an element in a solution from which a new layer will be created following evaporation of the solvent. In the case of coating polypropylene membranes, the suspended matter of graphene oxide in the solution of the polymer is the modifying liquid. The polymer is the base and connects inorganic fill to the surface of the membrane [22,23]. By controlling the rate of withdrawing the element from the solution, the surface tension and the viscosity of the solution as well as the number of repetitions of the process a layer of the required thickness may be achieved.

The second test method was the chemical connection of GO to the surface of the membrane with the use of a precursor. In this study, 3-aminopropyltriethoxysilane was used as the precursor [24–26]). The presence of alkoxy groups in the 3-APTES molecule makes it possible to connect to the hydrophilic surfaces having OH groups [27]. Reactive amine groups connect with functional groups that are on the surface of GO [28]. Since the polypropylene membranes used in the tests are hydrophobic in nature, the first stage of the modification process was oxidation in perhydride to generate OH groups on the surface. The process of the chemical modification is schematically shown in Fig. 1. The quality of the resulting layer is affected by the duration of the reaction, the temperature and the concentrations of the individual components [29].

3. Results and discussion

The first part of the research confirmed the adsorptibility of the pharmacological substances by materials containing GO. For this purpose flat samples of materials made of PEBAX 2533 and GO were used, which were tested in the fixed system. The results of changes in the concentration of the test substances during the process are shown in Table 1. The results are presented as the mass of antibiotics adsorbed per one unit of the surface area of adsorbent q_t in the time of adsorption t. Because the adsorption process takes place only on the surface of the material, the amount of the adsorption substance is presented in the relation to the unit of the surface area.

On the basis of the results it can be concluded that the concentration of the substance in the solution decreases, hence the quantity of the adsorbed substance by the test samples increases with time aiming at the specified value, which determines the adsorptibility of the material under given conditions. Similar results were obtained by authors of other studies, who examined the adsorption properties of GO [15,30]. Since the PEBAX 2533 copolymer does not have adsorption properties, it can be concluded that GO is responsible for the whole effect of removing the substance, which is confirmed by its properties. The amount

Table 1
Change in the concentration of pharmaceutical substance during the adsorption process

	Amoxicillin	Sulfadiazine
t (min)	q_t (mg/m^2)	
10	3.45	3.39
15	20.69	4.42
30	26.55	4.60
45	31.03	4.77

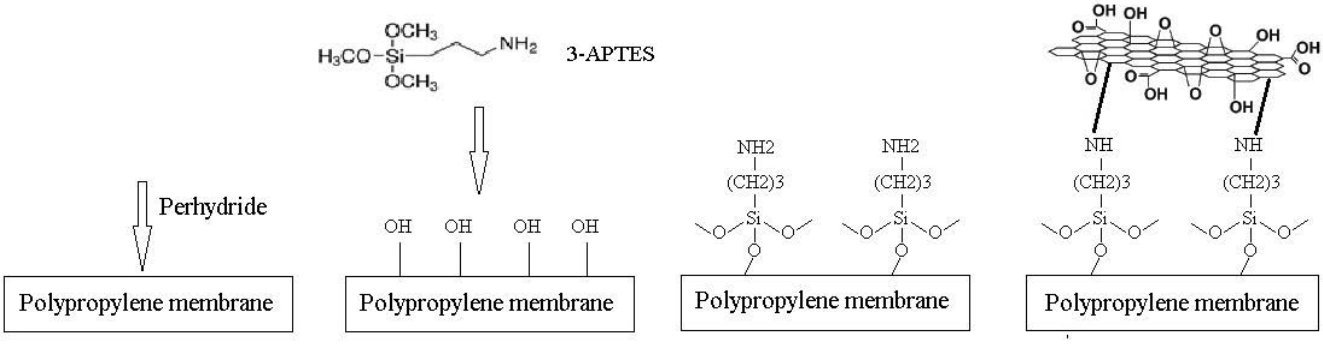

Fig. 1. Modification process of the membranes with the use of 3-APTES precursor.

of adsorbed substances for the materials without GO was lower than 0.1 mg/m^2.

The FTIR analysis failed to confirm unequivocally the presence of GO on the surface of the produced materials. The results of the measurement are shown in Fig. 2. The characteristic absorption bands for GO are connected with the functional groups on its surface and correspond to the stretching vibrations of the O–H group (3,200–3,600 cm^{-1}), stretching vibrations of the C=O group (1,710–1,740 cm^{-1}) and stretching vibrations of the C–O–C group (1,050–1,150 cm^{-1}) [31]. However, vibrations connected with the C=O and C–O–C groups also occur in the spectrum PEBAX 2533 [32], while vibrations connected with the OH group correspond to the stretching vibrations of the NH group, which impedes an unambiguous identification of the groups on the surface of the material originating from GO. Only the intensity of the absorption of individual bands for the material containing GO increases, which proves that there is a modification in relation to the pure PEBAX 2533.

The tests of wettability of the material containing GO showed a decreased contact angle from 83.21° for PEBAX 2533 to 40.84°. The results confirm the presence of hydrophilic GO on the surface of the material.

Later the study presents the results obtained using modified polypropylene membranes.

The surface of polypropylene membranes modified by dip-coating underwent the FTIR analysis, and the results are shown in Fig. 3.

The characteristic bands corresponding to the bands obtained in the case of the material containing PEBAX and GO prove the presence of a new layer on the surface of the membranes. Bands corresponding to the stretching vibrations of CH (2,800–3,000 cm^{-1}) and asymmetric and non-asymmetric deformation vibrations of the CH groups (1,400–1,500 cm^{-1}) are connected both with polypropylene [33] and with PEBAX 2533.

Also the contact angle of new membranes was tested, which for the unmodified membranes is approximately 110°. For membranes coated with material containing GO,

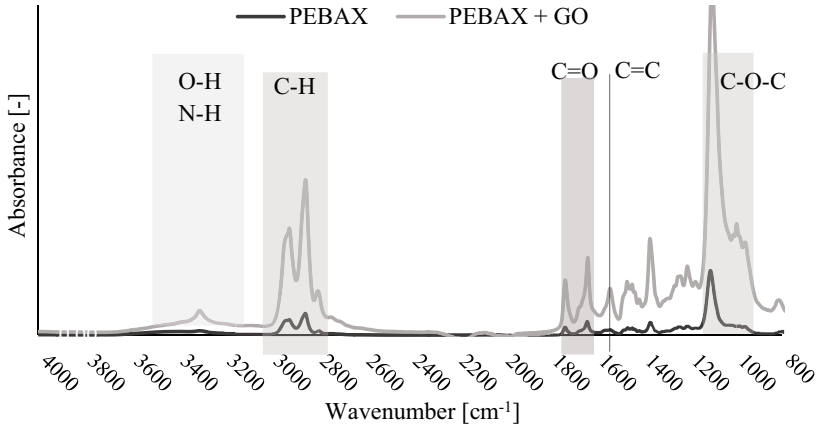

Fig. 2. FTIR analysis of a sample of material created from PEBAX 2533 (PEBAX) and PEBAX 2533 + GO (PEBAX GO).

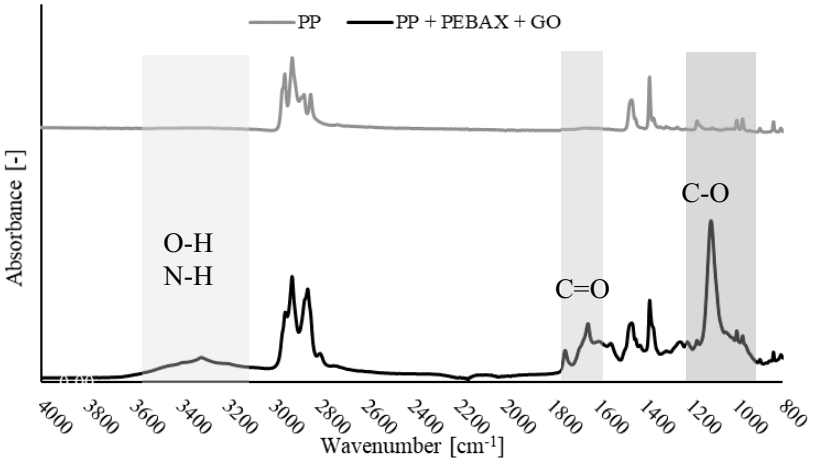

Fig. 3. FTIR analysis of unmodified membranes (PP) covered with the PEBAX + GO (PP + PEBAX + GO) material in the dip-coating process.

the contact angle of 89° was obtained. The decreased contact angle reflects the improved wettability of modified membranes, which can be related to the presence of new material on the surface of the membrane.

A similar analysis was carried out for chemically modified membranes. In this case in order to confirm the overlapping of individual phenomena, the FTIR analysis was carried out (Fig. 4) and the contact angle was measured after each stage of the process (Table 2), that is, after the stage of oxidation with perhydride (PP + H_2O_2), modification with a precursor (PP + H_2O_2 + 3-APTES) and modification with the use of GO (PP + H_2O_2 + 3-APTES + GO).

The purpose of the oxidation stage was to create OH groups on the surface of the polypropylene membrane. The improved wettability of the membrane PP + H_2O_2 (decreasing the contact angle in relation to the unmodified membrane) and the occurrence of the band (of low intensity) within the range of 3,600–3,200 cm^{-1} confirm the presence of the OH groups. At the next stage, 3-APTES is connected to the hydroxyl groups. The presence of the precursor is confirmed by the occurrence of the band corresponding to the vibrations of the Si–O–Si groups (1,050–1,200 cm^{-1}) and the peak connected with the NH vibration group (1,630 cm^{-1}). The lack of visible peaks corresponding to the vibrations of the group –CH (2,930–2,890 cm^{-1}) and –NH_2 (3,400 cm^{-1}) that occur in the structure of 3-APTES [34] results from their overlapping with the peaks that are typical of polypropylene, or the number of these groups on the surface is too low, which causes slight absorbance. On the other hand, decreasing the contact angle on the surface of the membrane below 90° results from the presence of the hydrophilic groups NH_2 on the surface of the membrane [35]. At the final stage of the modification process, GO is connected to the amine groups connected with molecules 3-APTES by the functional groups on its surface. The presence of GO on the surface of the membrane is confirmed by bands of vibrations connected with the C=O and C–O groups and the change in the contact angle. The increased wetting may be due to a small quantity of GO which covered the surfaces of the membranes, but the value of the contact angle after the modification is still lower than that for the unmodified membrane. In addition, some bonds were created between oxygen groups on the GO surface and groups of the modifiers. This effect could also influence the increase in the contact angle. Creating a new layer is also confirmed by microscopic photos of the surface of the membranes (Fig. 5). On the basis of the photos it is possible to confirm the presence of a small quantity of GO as a result of using low concentrations of GO and the fact that as thin layer as possible was attempted to be made. In addition, it can be noted that some of the pores of the membrane covered with the dip coating method is covered up by a new layer of the material.

The fact that the pores are blocked is confirmed by a porosimetric analysis and values of filtration coefficient UFC (Fig. 6). On the basis of the results it can be concluded that for the modified membranes UFC decreases. It is related to the change of pores size distribution. The modified membranes are characterized by higher number of pores with a lower diameter. It is the result of the blocking pores with higher diameter by the new layer, particularly pores with a diameter between 0.20–0.24 μm.

In the final part of the tests, the possibility of adsorption of the pharmacological substance, amoxicillin, by modified membranes in the flow systems was specified. The results are shown in Table 3. On their basis it can be concluded that the concentration of the pharmacological substance decreases during the process. However, in the case of using chemically modified membranes, the change in the concentration is quite low, which may result from the insufficiently small quantity of GO located on the surface of the

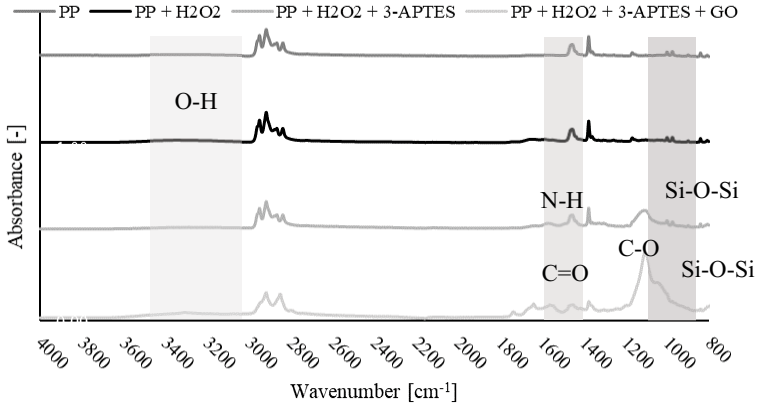

Fig. 4. FTIR analysis of unmodified membranes (PP) and chemically modified membranes after each stage of the process.

Table 2
Contact angle for the membranes after each stage of the modification process

Non-modified membrane PP	PP + H_2O_2	PP + H_2O_2 + 3-APTES	PP + H_2O_2 + 3-APTES + GO
110.68°	42.91°	62.96°	85.15°

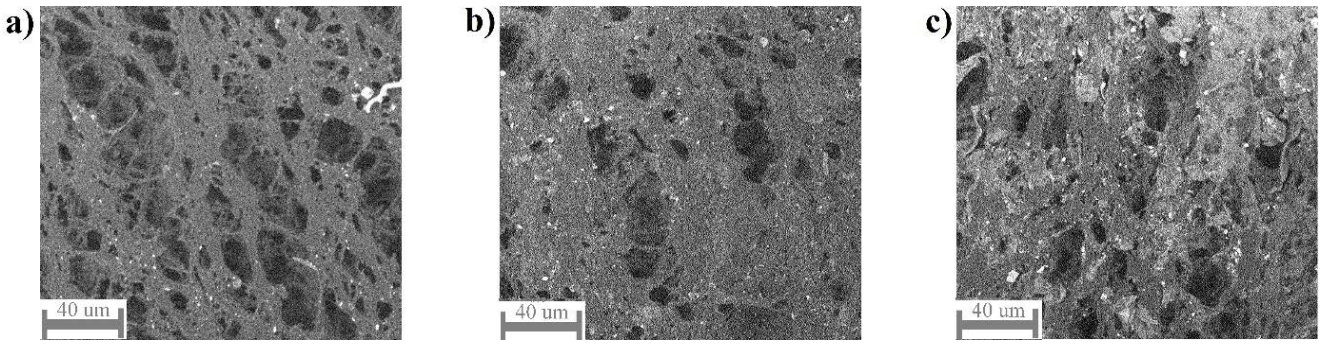

Fig. 5. SEM images of the surface: (a) the unmodified membrane, (b) the membrane modified with the dip-coating method and (c) the chemically modified with a precursor.

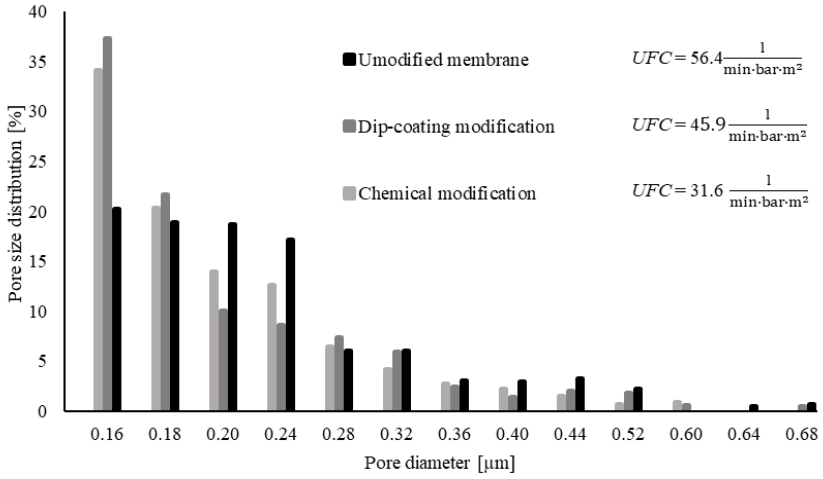

Fig. 6. Pore size distribution and UFC for unmodified and modified membranes.

Table 3
Change in the concentration of amoxicillin during the adsorption process

	Dip-coating	Chemical modification
t (min)	q_t (mg/m^2)	
10	43.10	0.86
15	86.21	4.31
30	94.83	8.62
45	103.45	17.79

membrane. It should be noted that the layer created with dip-coating has a thickness of a dozen or so micrometres, while the layer created chemically has a thickness corresponding to the thickness of one layer of graphene oxide.

4. Summary

The study confirms the possible adsorption of pharmacological substances using materials containing GO. Layers containing GO on the surface of the polypropylene membranes were effectively created on the polypropylene membranes using dip-coating and chemical modification with a precursor. It was demonstrated that such membranes have adsorption properties and are characterised by better wettability. The contact angle decreased from 110° for the unmodified membrane to about 85°–90° for the modified membranes. In the case of membranes modified by dip-coating, better adsorption properties are noticed. The amount of adsorbed substance was 103.45 and 17.79 mg/m^2 for the membranes modified by the dip-coating method and the chemical method, respectively. The difference between the results is related to the amount of GO that covers the membrane in the modification process. However, after the modification process membranes have lower UFC. It is related to the blocking of pores by a new layer.

Acknowledgments

This research was supported by the National Centre for Research and Development, M.Era-Net Programme, project HyprSTEP.

References

[1] L. Cizmas, V.K. Sharma, C.M. Gray, T.J. McDonald, Pharmaceuticals and personal care products in waters: occurrence, toxicity, and risk, Environ. Chem. Lett., 13 (2015) 381–394.

[2] B. Huerta, S. Rodríguez-Mozaz, D. Barceló, Pharmaceuticals in biota in the aquatic environment: analytical methods and environmental implications, Anal. Bioanal. Chem., 404 (2012) 2611–2624.
[3] A.M. Deegan, B. Shaik, K. Nolan, K. Urell, M. Oelgemöller, J. Tobin, A. Morrissey, Treatment options for wastewater effluents from pharmaceutical companies, Int. J. Environ. Sci. Technol., 8 (2011) 649–666.
[4] C. Gadipelly, A. Pérez-González, G.D. Yadav, I. Ortiz, R. Ibáñez, V.K. Rathod, K.V. Marathe, Pharmaceutical industry wastewater: review of the technologies for water treatment and reuse, Ind. Eng. Chem. Res., 53 (2014) 11571–11592.
[5] J. Radjenovic, M. Petrovic, D. Barceló, Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor, Anal. Bioanal. Chem., 387 (2007) 1365–1377.
[6] J. Radjenović, M. Petrović, D. Barceló, Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, Water Res., 43 (2009) 831–841.
[7] Y. Gao, Y. Li, L. Zhang, H. Huang, J.J. Hu, S.M. Shah, X.G. Su, Adsorption and removal of tetracycline antibiotics from aqueous solution by graphene oxide, J. Colloid Interface Sci., 368 (2012) 540–546.
[8] M. Seredych, T.J. Bandosz, Adsorption of ammonia on graphite oxide/aluminium polycation and graphite oxide/zirconium–aluminium polyoxycation composites, J. Colloid Interface Sci., 324 (2018) 25–35.
[9] B.H. Kim, W.G. Hong, H.Y. Yu, Y.-K. Han, S.M. Lee, S.J. Chang, H.R. Moon, Y.S. Jun, H.J. Kim, Thermally modulated multilayered graphene oxide for hydrogen storage, Phys. Chem. Chem. Phys., 14 (2012) 1480–1484.
[10] C. Chen, K. Xu, X. Ji, L. Miao, J.J. Jiang, Enhanced adsorption of acidic gases (CO_2, NO_2 and SO_2) on light metal decorated graphene oxide, Phys. Chem. Chem. Phys., 16 (2014) 11031–11036.
[11] R. Sitko, E. Turek, B. Zawisza, E. Malicka, E. Talik, J. Heimann, A. Gagor, B. Feist, R. Wrzalik, Adsorption of divalent metal ions from aqueous solutions using graphene oxide, Dalton Trans., 42 (2013) 5682–5689.
[12] W.J. Peng, H.Q. Li, Y.Y. Liu, S.X. Song, A review on heavy metal ions adsorption from water by graphene oxide and its composites, J. Mol. Liq., 230 (2017) 496–504.
[13] G.K. Ramesha, A.V. Kumara, H.B. Muralidhara, S. Sampath, Graphene and graphene oxide as effective adsorbents toward anionic and cationic dyes, J. Colloid Interface Sci., 361 (2011) 270–277.
[14] J.A. González, M.E. Villanueva, L.L. Piehl, G.J. Copello, Development of a chitin/graphene oxide hybrid composite for the removal of pollutant dyes: adsorption and desorption study, Chem. Eng. J., 280 (2015) 41–48.
[15] B.Q. Peng, L. Chen, C.J. Que, K. Yang, F. Deng, X.Y. Deng, G.S. Shi, G. Xu, M.H. Wu, Adsorption of antibiotics on graphene and biochar in aqueous solutions induced by π-π interactions, Sci. Rep., 6 (2016) 31920.
[16] S.-W. Nam, C. Jung, H. Li, M. Yu, J.R. Flora, L.K. Boateng, N. Her, K.-D. Zoh, Y.M. Yoon, Adsorption characteristics of diclofenac and sulfamethoxazole to graphene oxide in aqueous solution, Chemosphere, 136 (2015) 20–26.
[17] L.-H. Jiang, Y.-G. Liu, G.-M. Zeng, F.-Y. Xiao, X.-J. Hu, X. Hu, H. Wang, T.-T. Li, L. Zhou, X.-F. Tan, Removal of 17β-estradiol by few-layered graphene oxide nanosheets from aqueous solutions: external influence and adsorption mechanism, Chem. Eng. J., 284 (2016) 93–102.
[18] A. Khan, J. Wang, J. Li, X.X. Wang, Z.S. Chen, A. Alsaedi, T. Hayat, Y.T. Chen, X.K. Wang, The role of graphene oxide and graphene oxide-based nanomaterials in the removal of pharmaceuticals from aqueous media: a review, Environ. Sci. Pollut. Res., 24 (2017) 7938–7958.
[19] S.B. Liu, T.H. Zeng, M. Hofmann, E. Burcombe, J. Wei, R.R. Jiang, J. Kong, Y. Chen, Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: membrane and oxidative stress. ACS Nano, 5 (2011) 6971–6980.
[20] M. Mazurkiewicz-Pawlicka, M. Nowak, A. Malolepszy, A. Witowski, D. Wasik, Y. Hu, L. Stobinski, Graphene oxide with controlled content of oxygen groups as a filler for polymer composites used for infrared radiation shielding, Nanomaterials, 10 (2020) 32.
[21] P.M. Schweizer, S.F. Kistler, Eds., Liquid Film Coating: Scientific Principles and Their Technological Implications, Springer Science & Business Media, 2012.
[22] M. Szwast, D. Polak, M. Zalewski, Novel gas separation membrane for energy, Desal. Water Treat., 64 (2017) 255–259.
[23] T. Schneller, R. Waser, M. Kosec, D. Payne, Eds., Chemical Solution Deposition of Functional Oxide Thin Films, Springer Vienna, 2013.
[24] A. Simon, T. Cohen-Bouhacina, M.C. Porté, J.P. Aimé, C. Baquey, Study of two grafting methods for obtaining a 3-aminopropyltriethoxysilane monolayer on silica surface, J. Colloid Interface Sci., 251 (2002) 278–283.
[25] J. Kathi, K.Y. Rhee, Surface modification of multi-walled carbon nanotubes using 3-aminopropyltriethoxysilane, J. Mater. Sci., 43 (2008) 33–37.
[26] M. Ostwal, R.P. Singh, S.F. Dec, M.T. Lusk, J.D. Way, 3-Aminopropyltriethoxysilane functionalized inorganic membranes for high temperature CO_2/N_2 separation, J. Membr. Sci., 369 (2011) 139–147.
[27] R.M. Pasternack, S. Rivillon Amy, Y.J. Chabal, Attachment of 3-(aminopropyl)triethoxysilane on silicon oxide surfaces: dependence on solution temperature, Langmuir, 24 (2008) 12963–12971.
[28] Y. Matsuo, Y. Nishino, T. Fukutsuka, Y. Sugie, Introduction of amino groups into the interlayer space of graphite oxide using 3-aminopropylethoxysilanes, Carbon, 45 (2007) 1384–1390.
[29] J.A. Howarter, J.P. Youngblood, Optimization of silica silanization by 3-aminopropyltriethoxysilane, Langmuir, 22 (2006) 11142–11147.
[30] C.J. Madadrang, H.Y. Kim, G.H. Gao, N. Wang, J. Zhu, H. Feng, M. Gorring, M.L. Kasner, S.F. Hou, Adsorption behavior of EDTA-graphene oxide for Pb(II) removal, ACS Appl. Mater. Interfaces, 4 (2012) 1186–1193.
[31] Z. Bojarska, M. Mazurkiewicz-Pawlicka, L. Makowski, Graphene oxide-based nano-materials as catalysts for oxygen reduction reaction, Chem. Process Eng., 40 (2019) 361–376.
[32] N. Azizi, M.R. Hojjati, M.M. Zarei, Study of CO_2 and CH_4 permeation properties through prepared and characterized blended PEBAX-2533/PEG-200 membranes, Silicon, 10 (2018) 1461–1467.
[33] B.R. Souza, R.M. Di Benedetto, D. Hirayama, O. de Andrade Raponi, L.C.M. Barbosa, A.C. Ancelotti Jr., Manufacturing and characterization of jute/pp thermoplastic commingled composite, Mater. Res., 20 (2017) 458–465.
[34] K.S. Aneja, S. Bohm, A.S. Khanna, H.L. Mallika Bohm, Graphene based anticorrosive coatings for Cr(VI) replacement, Nanoscale, 7 (2015) 17879–17888.
[35] H.H. Kyaw, S.H. Al-Harthi, A. Sellai, J. Dutta, Self-organization of gold nanoparticles on silanated surfaces, Beilstein J. Nanotechnol., 6 (2015) 2345–2353.