Graphene – the Nanomaterial for Preparation of Next Generation Semipermeable Membranes

Michał Bodzek[1], Krystyna Konieczny[2]*
[1]Institute of Environmental Engineering
of Polish Academy of Sciences, Zabrze, Poland
[2]The Cardinal Wyszynski University in Warsaw, Poland
[*]corresponding author's e-mail: michal.bodzek@ipis.zabrze.pl

1. Introduction

Water is essential for any form of life on Earth. The continuous population growth (from current 7 to predicted 10 billion of people in 2050, urbanization and intensive industrialization as well as climate change and limited fresh water resources are key factors resulting in a number of stresses in global water demand. 98% of all water resources appears in the form of saline water, whereas only 2% corresponds to freshwater, among which almost 70% is cumulated in snow and ice, while 30% appears in the form of ground waters (Yang et al. 2018). More than 1.2 billion of people suffers due to the limited access to clean and sanitary safe freshwater, and the water scarcity will continue to increase in next decades (Montgomery & Elimelech 2007).

Nowadays, reverse osmosis (RO) is the main process used to water, especially seawater, desalination, as it is well recognized and corresponds to market demands. As of June 30, 2016 the total number of desalination plants worldwide was 18,983 and these plants have cumulative fresh water production capacity of 95.6 million m^3/day (Voulkov 2018). Nevertheless, despite a number of features of this desalination process, its economy, environmental impacts, feed water preparation issues and utilization of used membranes. Most of commercial RO membranes are based on thin film composite (TFC) polyamide and polyamide derivatives membranes. Their main disadvantage is related to relatively low water permeability (from 2 to 8 $L/m^2 \cdot h \cdot bar$ for brackish- and 1 to 2.2 $L/m^2 \cdot h \cdot bar$ for seawater desalination), insufficient selectivity and high fouling affinity as well as poor chemical and mechanical stability (Werber et al. 2016). The energy demand, which has been significantly improved since 1990s, when it was 5 kWh/m^3

to current 1.8-2.0 kWh/m^3), is still much lower than for other desalination methods, especially thermal ones (Elimelech & Phillip, 2011). Nevertheless, conventional polymeric membranes used in RO systems suffer due to severe fouling, highly undesired phenomenon responsible for membranes' capacity decrease (Matin et al. 2011). The similar problems are connected with membranes from other membrane techniques (Basile et al. 2015).

Next generation of membranes should overcome limits related to water and wastewater treatment by improvement of structural and physico-chemical features and introduction of antibacterial, photocatalytic or adsorption properties. Recent analyses have indicated that the use of RO membranes of three times higher water permeability results in 15% energy demand decrease and 44% decrease in number of pressurized tanks required for seawater desalination process, as well as 45% energy demand decrease and 63% pressurized tank number decrease in wastewater treatment (Cohen-Tanugi et al., 2014).

In recent years, the growing interest in the use of nanomaterials for development of next generation of membranes of advanced antifouling properties to be used in water desalination and wastewater treatment, has been observed (Werber et al. 2016a). The development of nanomaterials and nanotechnologies enables the improvement of a structure and transport properties of membranes. Among available nanostructures, the most of attention is given to fullerene, carbon nanotubes (CNTs) and graphene based materials (Manawi et al. 2016, Goh et al. 2016).

A number of recent research in the field of water desalination and wastewater treatment is dedicated to the use of graphene-based materials (Goh et al. 2016; Cohen-Tanugi et al. 2012), what is confirmed by latest articles discussing the positive role of graphene oxide (GO) in membranes' manufacturing. In this paper methods of synthesis of membranes containing graphene and its derivatives, their properties and application areas are discussed.

2. Graphene and graphene oxide

Graphene is a thin layer sheet of densely packed carbon atoms, which are bonded with each other in the form of uniform hexagonal structures, similar to honeycomb lattice (Fig. 1). As the thickness of a single graphene sheet corresponds to the thickness of single carbon atom (i.e. 0.3 nm), its special structure is simplified to 2D (Suk & Aluru 2010) (Fig. 1a). Carbon atoms within graphene structure are bonded by means of strong sigma bonds of sp^2 hybridization and very short length (0.142 nm) (Cohen-Tanugi et al. 2014). Graphene characterizes with a large specific surface area, very low weight (1 m^2 sheet of graphene weights ca. 0.77 mg), outstanding heat transfer (from $4.84 \cdot 10^3$ to $5.3 \cdot 10^3$ W/m·K at room temperature), exceptional flexibility, relatively high conductivity

(from 10^2 S/m) and mechanical strength (from 100 to 300 times higher than steel, tensile strength – 130 GPa, Young module – 1 TPa), is also excellent, mobile charge carrier (Marinho et al. 2012, Lee et al. 2008).

Despite negligible thickness of a graphene monolayer accompanied with unique durability, defect-free graphene sheets are not permeable to all gaseous and liquids (Wang & Karnik 2012). It is caused by repulsing forces generated by dense and delocalized electron clouds of π orbitals, which fill gaps in aromatic graphene rings and are able to block the permeation of the smallest particles, such as hydrogen of helium, even at high pressure (Koenig et al. 2012). In order to enable graphene use if membrane separation, nanoporous graphene (NPG) permeable to water and other fluids needs to be obtained. For this purpose, in the monolayer of unsaturated carbon atoms, nanopores of different diameters, geometry, edge quality and density, which are simultaneously neutral to surface structure, need to be formed (Wang et al. 2013, Becton et al. 2014). These pores have to be properly large to allow for water particles permeation, while on the other hand they should enable rejection of ions and other undesired chemical compounds. In last years a number of techniques, which are usually based on high-energy bombarding of graphene structure targeted at dislocation of thousands of neighborhooding carbon atoms, have been investigated. The formation of nanopores of various sizes in monolayer graphene can be obtained using electrons/ions beams, ultraviolet digestive oxidation and ionic helium beam (Lee et al. 2011, Hung et al. 2014, Fischbein et al. 2008). The size of nanopores and their chemical character as well as on the method used for their functionalization significantly influences on separation effectiveness (Han et al. 2013). Nanopores of NPG are most often functionalized with hydrogen, hydroxyl groups and sometimes with nitrogen, and this action is carried out for the improvement of separation effectiveness (Cohen-Tanugi & Grossman 2012).

Despite huge applicability potential of NPG in production of membranes for water desalination (Cohen-Tanugi & Grossman 2012) and other environmental techniques (Wang et al. 2012b), the transfer of the technology to industrial scale is an open issue, that needs to be solved (Aghigh et al. 2015). On the other hand, membranes formed from graphene oxide (GO) overcome this barrier and make the material more suitable candidate for manufacturing of membranes dedicated to separation of ions and particles. Even though GO nanopores characterize with high hydrophobicity, GO nanosheets are hydrophilic (Hu & Mi 2013; Han et al. 2013). GO is modified form of graphene and oxygen and hydrogen atoms, which are all connected via carbon atoms (Fig. 1b). GO reveals properties similar to graphene, except for asymmetry of its sheets, which results from the presence of oxygen base functional groups localized at the edges and in the basal plane (Fig. 1b) (Perreault et al. 2014, Cho & Lee 2011, Compton & Nguyen 2010,).

The presence of functional groups containing oxygen and hydrogen favors dispersion in aquatic environment, but also in other solvents and thus, the use of surface active agents or other stabilizing compounds is not required and formation of thin GO film from the solution is enabled (Perreault et al. 2014). This functional groups also allow for performance of a various surface modifications, which may be used in preparation of functionalized GO-based membranes utilized to separation processes.
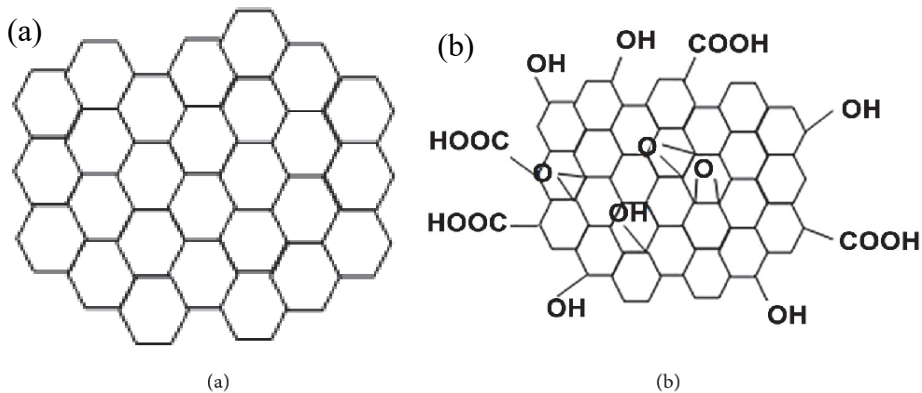

(a)   (b)

Fig. 1. An exemplary structure of graphene (a) and graphene oxide (b)

GO is usually obtained by oxidation of graphene with strong acids and oxidants (Hu and Mi 2013) as well as by chemical exfoliation and oxidation of graphite. During oxidation, functional groups, i.e. hydroxyl, carboxyl and epoxide one may be introduced to the compound structure (Cohen-Tanugi & Grossman, 2012, Han et al. 2013). Oxidation of cheap graphite results in formation of GO nanosheets of 2D dimension composed only from C, O and H, which possess a lot of hydrophilic functional groups.

The presence of oxygen-based functional groups in GO structure modifies its character and favors its reactivity, allowing the reactions to be performer on the surface of the material (Huang et al. 2014). Additionally, nanopores may also be introduced to GO structure. Such functionalized and porous GO sheets used as a membrane reveal the ability of selective separation of ions and particles, improve capacity and antifouling character (Hu & Mi 2013). Another important aspect is the possibility of production of GO nanosheets piles. The pile like structure of GO characterizes with the thickness ranging from 1 to 30 μm and possesses a number of functional groups reach in oxygen localized at edges and on the surface (Dikin et. al. 2007). Amorphous character of epoxide, hydroxyl and carboxyl groups cause the tendency of the material to curving, thus basal place

of GO nanosheets can be defected, however it results in enhanced water permeation through GO nanosheets piles. Even hydrophobic character of GO sheet piles may form frictionless surface allowing for efficient permeation of water through the formed membrane. Contiguous GO nanosheets form nanochannels and nanocapillaries, which also favor water/solvent transport, while dissolved substances are retained (Fig. 2) (Yang et al. 2018). The presence of functional groups also favors the formation of nanochannels (Dai et al. 2016). The distance between GO nanosheets is also important and it may change in dependence of external/operational environment (Mi, 2014). It is assumed, that hydrated ions and particles of other dissolved substances of radius greater than 0.45 nm are rejected by hydrophobic nanochannels, whereas ions of radius below 0.45 nm permeate through (Mi, 2014). Due to amphiphilic GO nature, water particles are adsorbed by hydrophilic spots, and thus their diffusion though hydrophobic carbon place is enabled. Simulation studies by means of molecular dynamics of GO membranes (Nicolai et al., 2014) suggest that water permeability may be regulated in the range from 208 to 16,640 L/bar·h·m^2 by modifying distances between GO sheets and the thickness of sheets as well. However, the distances equal to 1.5 nm (which were determined for highest water fluxes, i.e. 16,640 L/bar·h·m^2) allow for poor NaCl retention equal to 50%. It has also been found that transport of particles through GO sheet (in multilayer GO) takes place between edges of contiguous sheets and through pores localized within a sheet plane (Wei et al., 2014; Huang et al., 2013).
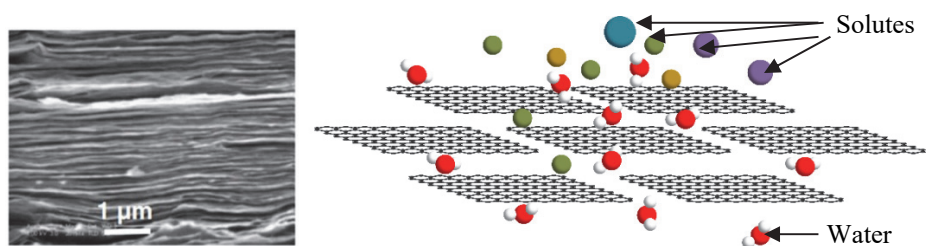

Fig. 2. The image of GO nanosheets pile and mechanism of water transport

It also has to be noted that GO based materials reveal excellent antibacterial properties. Liu et al. (2011) have compared four carbon derivatives, i.e. GO, reduced GO (rGO), graphite (Gt) and graphite oxide (GtO) in regard to their antibacterial properties using *Escherichia coli*. They have observed, that at the same concentration, incubation time and process conditions, GO reveals the best antibacterial features and if followed by rGO, Gt and GtO, what allows for the use of membranes based on GO to biofouling control. Moreover, hydrophilic GO character enables antifouling modifications of membranes' properties, as GO

possesses the ability to stop bacteria cells growth during the direct contact (Liu et al. 2011, Akhavan & Ghaderi 2010, Hu et al. 2010). These antibacterial features are durable and GO remains unwashed at the surface and inside membrane pores during a long time operation).

3. Preparation of membranes from graphene and graphene oxide

Novel, composite membranes for desalination and water and wastewater treatment, which contain NPG and GO can be divided into two groups (Manawi et al. 2016):
1. Membranes made of only GO or NPG named as freestanding,
2. Polymeric/ceramic membranes modified by GO or NPG.

The former group uses directly GO/NPG as a membrane, while the latter applies nanomaterials as membrane surface modifiers or introduces GO/NPG to a polymeric/ceramic matrix (Hegab & Zou 2015). The most commonly used methods to production of membranes based on GO/NPG are filtration, self-assembly layer by layer (LBL), dip or spin coating, GO/NPG sheets casting, interface polymerization or phase inversion techniques (Songa et al. 2018, Kim et al. 2013, Hu & Mi, 2013, Sun et al. 2012, Wang et al. 2012b, Hu & Mi, 2014).

3.1. Freestanding GO/NPG membranes

Freestanding membrane may be defined as a set of GO/NPG nanosheets, which create a series of layers packed and placed one on one with properly kept distances between particular layers (Hegab & Zou 2015). GO monolayer characterizes with a thickness of 0.5 nm, while the lateral thickness may vary from hundreds of nanometers up to dozens of micrometers (Hu & Mi 2013). Nair et al. (2012) have minimized distances of GO/NPG sheets to 1 nm using dip or spin coating with stabile solutions of dispersed GO. Additionally, for preparation of GO/NPG membranes of proper distances between particular nanosheets a range of vacuum filtration techniques can be used (Xu et al. 2013). Freestanding GO/NPG membranes are flexible and mechanically stable (Eda & Chhowalla 2010) and even though they are completely impermeable for gases, vapors and liquids, including helium, they allow water to permeate unlimitedly. Additionally, the rate of water permeation for such membranes is ca. 10^6 time higher than of helium (Nair et al. 2012), due to almost frictionless flow of water monolayer through 2-D capillaries formed between shortly-distanced graphene sheets (Goh et al. 2016). It has also been shown, that hydroxyl and epoxide functional groups present in GO/NPG nanosheets are responsible for keeping proper distances between sheets (Wang et al. 2012b).

Freestanding GO/NPG membranes can be prepared by filtration methods, which relies on introduction of GO/NPG on a porous membrane (usually micro- or ultrafiltration one) (Wang et al. 2015) at vacuum conditions (Chen et al. 2015), and next it involves filtration and drying applied for porous layer formation. This method can be used to preparation of GO/NPG containing membranes, of the thickness of their layer from several nanometers up to several microns, however, bindings between particular layers are relevantly weak, thus the stability of a membrane is rather poor. The self-assembly layer by layer method of films preparation relies on staggered laying of a charged substance on a surface charged of opposite charge (Xu et al. 2017). Sequential adsorption of charges polymers and/or nanoparticles is a valuable technique of multilayer preparation.

Nicolai's et al. (2014) have found that freestanding GO membranes allow for complete retention of salts at doubled permeation of water, in refer to commercial RO membranes permeation, due the very low membrane thickness. Sun et al. (2012) have prepared freestanding GO nanofiltration membranes using drop casting with distances between particular layer equal to ca. 0.82 nm. The membranes have next be used to efficient separation of sodium salt from organic impurities and copper. Cohen and Grossman (2012) have stated that graphene layer with nanopores of diameter below 0.55 nm may be applied to water desalination, and the retention of salt is higher than in case of commercial RO membranes, while water permeability is several orders higher. Han et al. (2013) have obtained GO nanofiltration membranes of capacity 21.8 $L/m^2 \cdot h$ and 40% retention of salts. This poor retention has been explained by the presence of cracks formed during membrane preparation. Hu and Mi (2013) have also observed poor salt retention ranging from 6-46% while performing desalination tests with graphene oxide membrane, even though the water flux has been equal to 80 and 276 $L/m^2 \cdot h \cdot MPa$ in dependence of a number of GO nanosheets. At presence of NaCl or Na_2SO_4 the distance between GO sheets decreases with solution ionic strength (~1-2 nm at 100 mM), due to hydration and impact of charge, which compresses double electrical layer and favors transportation of K^+ and Na^+ ions, what disables water desalination (Joshi et al., 2014).

The possible method of the prevention of enlargement of distances between GO nanosheets is the partial decrease of a film thickness. In case of water desalination, distances between GO layers should be below 0.7 nm in order to retain hydrated Na^+ ions (Hu and Mi 2013). Mi (2014) and Yuan et al. (2017) have stated that these distances may also be decreased by GO reduction or by covalent binding of small particles with GO sheets, what may overcome hydration forces. For example, membrane after GO carboxylation (GO-COOH) with glycine has revealed higher salt retention and permeability, as negatively charged

GO-COOH surface favors electrostatic repulsion, improves surface hydrophilicity and multiplies number of channels for water transport (Yuan et al., 2017). Nano-sheet distances may be also increased by immersion of a membrane in a polar solution of e.g. sodium hydroxide. Xu et al. (2017) have stated that water permeability and GO membrane selectivity depend on a membrane interlayer nanostructure. This interlayer structure, in turn, depends on a rate of layers' embedding during membrane preparation, so, it may be adjusted by controlling the amount of sprayed GO. The retention of salts and water flux observed for membranes prepared by slow laying of GO (interlayer distances of 0.82 nm) is approximately 4 times higher than in case of GO membranes prepared with fast laying (0.84 nm).

Xu et al. (2013) have used a vacuum filtration technique to prepare GO/TiO$_2$ membrane by introducing TiO$_2$ nanoparticles between GO nanosheets. Freestanding membranes have been made by preparation of stable GO-TiO$_2$ dispersion followed by vacuum filtration. The average pores' diameter of the prepared membrane have been equal to 3.5 nm. It has been stated, that TiO$_2$ nanoparticles react with GO nanosheets, what finally results in the increase of distances between nanosheets and enlarges channels for water transport through the membrane. Nanofiltration GO-TiO$_2$ membranes have revealed complete retention of orange methylene and rhodamine B, what confirms their usability to the removal of dyes from wastewater.

In Table 1, selected data of freestanding GO/NPG membranes is presented.

Table 1. Exemplary characteristics and efficiencies of freestanding GO/NPG membranes

Preparation method	Membrane type	Process/ conditions	Permeability/Flux	Retention	Reference
LBL	GO/PAA/PAN	NF/5 bar	0.84 L/m^{2}hbar	43.2% Na$^+$, 92.6% Mg^{2+}	Wang et al. 2012b
LBL	GO/PSF	NF/3.4 bar	27.6 L/m^{2}hbar	46% Na$_2$SO$_4$ 93-95% rhodamine	Hu & Mi 2013
LBL	GO/PAH/PAN	NF/FO NF – 3.45 bar	6 L/m^{2}hbar	FO: 99% sucrose	Hu & Mi 2014
Vacuum filtration	GO/TiO$_2$/PC	NF/100 kPa	7 L/m^{2}hbar	100% methyl orange	Cohen-Tanugi & Grossman 2015
Vacuum filtration	GO- PAN nanofibres	NF/1-3 bar	2 L/m^{2}hbar	56.7% Na$_2$SO$_4$ 100% Kongo red	Wang et al. 2016a
Vacuum filtration	GO/PDA/Al$_2$O$_3$	PV/90ºC	48.4 L/m^{2}h	99.7%- 3.5% NaCl	Xu et al.,2016a; b
Vacuum filtration	Epoxy	FO	0.5 L/m^{2}h	97% NaCl	Abraham et al. 2017

Table 1. cont.

Preparation method	Membrane type	Process/ conditions	Permeability/Flux	Retention	Reference
Casting	fGO-280 nm	FO/0.25M NaCl and KCl- water	0.36 L/m^{2}h	-	Chen et al. 2017b
Self-assembly	GO-COOH	NF/1.5 MPa	-	48.2% NaCl 91.3% Na$_2$SO$_4$	Yuan et al. 2017
Vacuum filtration	Graphene Various supports	NF/5 bar	21.8 L/m^{2}hbar	>99% dyes ~20-60% salts	Sun et al. 2012
Vacuum filtration	GO/ Cationic Porphyrin	NF	9.3 L/m^{2}h	87.7% Na$_2$SO$_4$	Xia & Ni 2015
Oxygen plasma etching	NPG single layer	RO/17 kPa	106 g/m^{2}s	~100% monovalent ions	Ali et al. 2016

GO – graphene oxide; PAA – polyallylamine; PAN – polyacrylonitrile; PSF – polisulphone; PEI – poliethylenimine; PVP – polyvinylpyrrolidone; PVDF – polyvinylidene fluoride; PDA – polydiacetylene; PC – polycarbonate; fGO – functionalized grapheme oxide; PC – polycarbonate; PAH – polyaromatic hydrocarbons; NPG – nanoporous graphene; RO – reverse osmosis; NF – nanofiltration; FO – forward osmosis; PV – pervaporation; LBL – layer by layer

3.2. Modification of polymeric/ceramic membranes with GO/NPG

A modification of polymeric membranes may be made by introduction of a nanomaterial either to a membrane's surface or to casting solution followed by membrane formation from the mixture of a polymer and a nanomaterial (Yang et al. 2018, Hegab & Zou 2015, Songa et al. 2018, Manawi et al. 2016, Anand et al. 2018).

3.2.1. Modification of a polymeric membranes' surface

Modification of membranes' surface may be done by direct nanomaterial coating with „layer by layer" method, vacuum filtration (Wang et al., 2016a; Hu and Mi, 2014) or interfacial polymerization with TFC membrane finalized with TFN membrane formation (Yang et al. 2018). The introduction of a nanomaterial on a membrane's surface may also be made by covalent (Perreault et al. 2014), electrostatic (Choi et al. 2013) or coordination (Gao et al. 2014) bonding. Modification with graphene and its derivatives may improve a number of properties, including antifouling and antibacterial character and resistance to chlorine (Liu et al. 2011; Tu et al. 2013). Modification of membrane surface additionally requires relatively low nanomaterial amount, what is the economic benefit and, moreover, the production of nanomaterial is environmentally acceptable.

Wang et al. (2016a) have prepared GO containing membranes using polyacrylonitrile fibers by means of vacuum GO suspension filtration. The obtained membranes have revealed high retention of dyes (ca. 100% for Congo red) and moderate retention of bivalent ions (ca. 56.7% observed for Na_2SO_4), while water permeability has been established at ca. 2 $L/m^2 \cdot h \cdot bar$. Similarly, Xu et al. (2016b) have made membranes using vacuum filtration of GO suspension at aluminum oxide surface coated with polydopamine, which next have been introduced to semi-product burning. After thermal processing, GO nanosheets have been strongly bonded with the support surface, thus stability of the obtained membrane has been sufficient. In desalination of seawater, of NaCl concentration equal to 3.5%, membranes have revealed high water flux reaching 48.4 $L/m^2 \cdot h$ at NaCl retention 99.7% at 90°C. Hu and Mi (2013) have used cross-linking of GO nanosheets on polysulphone (PSF) support coated with polydopamine using 1,3,5-benzenetricarbonyl chloride (TMC), what has resulted in covalent bonds formation. The obtained GO membrane have revealed water permeability from 8 to 27.6 $L/m^2 \cdot h \cdot bar$ at relatively low retention of mono- and bivalent ions (6-46%) and high retention of dyes (93-95%).

Except for vacuum filtration, modified membranes with GO enriched with carboxylic, hydroxyl, epoxide or amine groups may be obtained using LBL method. Kim et al. (2013) have modified RO membranes with polyether-sulphone (PES) support by coating membrane surface with negatively charged GO

nanoparticles, on the layer of which they have next laid positively charged with amine groups GO layer. The modified membrane has revealed high water flux equal to 28 L/m^2·h and 98% salt retention. Choi et al. (2013) have also used LBL technique to modify polyamide (PA) membrane surface using GO nanosheets and GO nanosheets containing amine groups (NH_3^+) (Fig. 3). The modified membrane has revealed sufficient resistance to chlorine degradation due to the presence of GO protective layer on PA surface As a result, the fouling resistance of the modified membrane has been significantly improved and the water flux has increased by 10%, while NaCl retention (measured using water NaCl solution of salt concentration 2,000 mg/L) has decreased only by 0.7%.
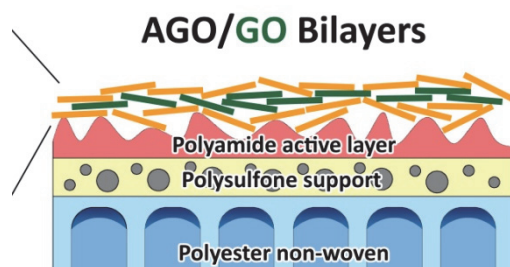

Fig. 3. The scheme of layer by layer coating of TFC polyamide membrane using electrostatic interaction with GO and positively charged amine GO (AGO)

Hung et al. (2014) have prepared flexible, GO containing PAN membranes using LBL technique. The composite membrane have revealed high capacity during pervaporative separation of a mixture composed of 70% wt. isopropanol (IPA) and water. At 30°C, 99.5% of water has passed to permeate, whereas the permeability has reached 2.047 g/m^2·h, while at temperature 70°C the concentration of water in permeate has been kept, while the permeability has increased to 4.137 g/m^2·h. The high selectivity results from dense GO film composed of a highly ordered and packed layers, what allows for water transport and rejection of IPA particles. GO possesses amphiphilic character, i.e. water particles are firstly adsorbed at hydrophilic ends of a layer (containing OH$^-$ groups) and next they quickly diffuse through hydrophobic cores of GO layers (mainly composed of carbon), forming channels used in further water transport, what improves the capacity.

GO may be used to covalent modification of surface of membranes used to desalination. Covalent bond may be obtained using amide binding of carboxyl groups present in nanosheets with other carboxyl groups present in polyamide skin layer of TFC membranes (Perreault et al. 2014) (Fig. 4). The functionization of PA surface in TFC membranes allows GO nanosheets to be uniformly placed

on a membrane surface, what has strong and positive influence on antibacterial features and hydrophilic character of modified membranes. It has been found, however, that hydrophilicity increase does not improve water flux in such membranes, as it is mostly regulated by solution-diffusion mechanism in PA skin layer of TFC membrane, regardless of surface modification (Elimelech & Phillip 2011). Despite covalent binding, GO can be attached to membrane surface by electrostatic interactions using LBL method, as it is shown in Fig. 5.
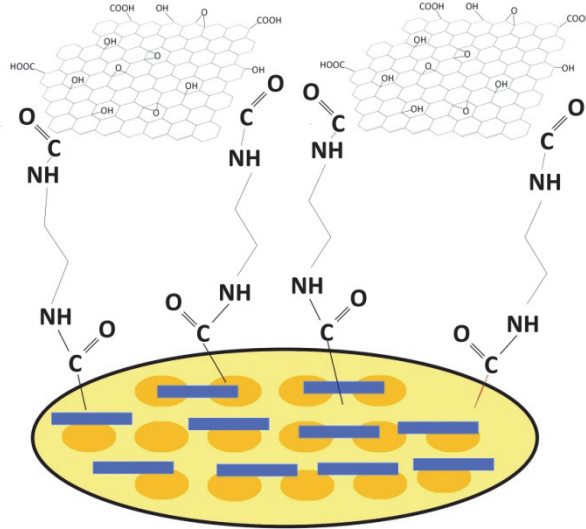

Fig. 4. The scheme of modification of membrane surface by covalent bonging

The main issue of membranes exploitation in water treatment is their affinity to fouling. The intensity of fouling depends on many factors, among which membrane material, chemical character of surface and porosity are of the highest importance (Kochkodan et al. 2014). Membranes containing NPG or GO show improved antifouling character, as they inactivate bacteria during direct contact with their cells (Lee et al. 2008), while their surface is more hydrophilic and smoother after modification. Perreault et al. (2014) have investigated the influence of modification of PA TFC membranes with GO on antibacterial properties. GO nanosheets have been binded to membrane surface by amide and carboxylic bonds. It has been shown that 65% of *E.Coli* cells become inactivated during direct contact with modified membrane within 1 hour. It has turned out, that GO inactivates bacteria due to initiation of physical damage of cells' membrane followed by eventual extraction of lipids from cells' interior (Tu et al. 2013). SEM images show, that cells, which are in contact with GO membrane are flattened

and squeezed in comparison with cells, which contact reference, non-modified membrane. Additionally, antibacterial effect of GO modified membranes does not affect their transport properties. Sun et al. (2015) have presented studies on preparation of composite membranes of antibiofouling properties made of cellulose acetate (CA) modified with graphene and containing silver nanoparticles (GO-AgNP). Composite GO-AgNP membrane effectively prevent bacteria growth, thus also the formation of biofilm on the membrane surface, causing *E.Coli* inactivation by 86% after 2 hour of their contact with the membranes. Ma et al. (2017) have introduced in-situ copper nanoparticle (CuNP) to polyamide RO membrane in order to decrease its biofouling. The use of cystamine (Cys) and GO has increased the amount of binded CuNP, decreased their size, caused more uniform distribution of CuNP on membrane surface and improved membrane antibacterial properties, due to formation of covalent bond between CuNP and membrane surface. Zhang et al. (2013) have connected GO with oxidized carbon nanotubes (CNT) in order to modify PVFD membrane surface. Modified GO-CNT membrane has shown significant hydrophilicity increase and antifouling improvement in refer to membranes modified separately with CNT or GO.
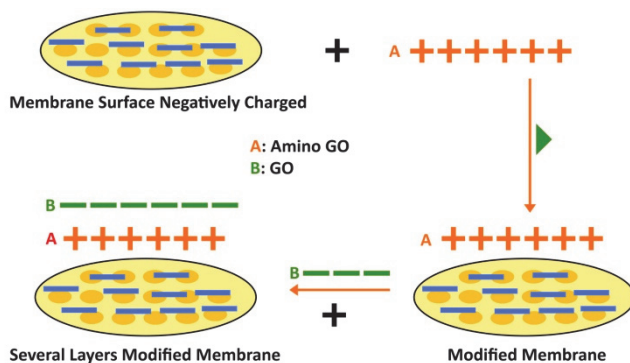

Fig. 5. The scheme of modification of membrane surface by electrostatic interactions using LBL method

In Table 2, the list of selected surface modified membranes with GO/NPG is given together with their characteristics.

Table 2. Selected results of studies on surface modification of polymeric membranes using GO/NPG

Preparation method	Base polymer	Membrane process/ Pressure	Permeability/ Flux	Retention	Ref.
IP	GO-PA	RO -15.5 bar	Ab. 1.06 L/m^{2}hbar	99% NaCl	Chae et al. 2015
IP	GO-PA	RO - 20.5 bar	Ab. 2.9 L/m^{2}hbar	94-96 % NaCl	Yin et al. 2016
IP	GO/PA	RO - 15 bar	29.6 L/m^{2}h	>97% NaCl	Ali et al. 2016
LBL	GO-PA	RO - 15.5 bar	Ab.0.9 L/m^{2}hbar	96.4% NaCl	Choi et al. 2016
Coordinate bond	fGO-PA	RO - 27.6 bar	Ab.1.45 L/m^{2}hbar	97.8% NaCl	Perreault et al. 2014
Coating LBL	aGO/GO/aPES	RO - 5500kPa	28 L/m^{2}h	98%NaCl	Perreault et al.2014
IP	rGO/TiO$_2$ (0,2%wt.)/PA	RO -15 bar	3.42 l/m^{2}hbar	99.45% NaCl	Sefarpour et al. 2015
IP	GO/PAN	NF	22 L/m^{2}h	>88% NaCl >97%MgSO$_4$	Bano et al. 2015
IP	GO/PA	NF - 8 bar	353.5 L/m^{2}hbar	59.5% NaCl 95.2% Na$_2$SO$_4$ 91.1% MgSO$_4$ 62.1% MgCl$_2$	Lai et al. 2016
IP	GO/polypiperazine amide	NF - 0.6 MPa	87.6 L/m^2 h	56.8% NaCl 98.2% Na$_2$SO$_4$ 96.5% MgSO$_4$ 50.5% MgCl$_2$	Wang et al. 2016b

Table 2. cont.

Preparation method	Base polymer	Membrane process/Pressure	Permeability/Flux	Retention	Ref.
Coating	PSF-GO (0,3%wt.)	NF - 0.6 MPa	2.45 L/m^{2}hbar	59.5 NaCl 95.2 Na$_2$SO$_4$	Lai et al. 2016
IP	rGO/TiO$_2$/PSF	NF - 10 bar	60.6 L/m^{2}h	36.6 NaCl 93.6 Na$_2$SO$_4$	Sefarpour et al. 2015
Vacuum filtration	GO/PAN	NF - 1.0 bar	8.2 L/m^{2}hbar	9.8% NaCl 56.7% Na$_2$SO$_4$	Wang et al. 2016a
Vacuum filtration	rGO-CNT-AAO	NF	31.5 L/m^{2}hbar	42% NaCl 84% Na$_2$SO$_4$	Chen et al.2016
Self-assembly LBL	GO-chitosan/PSF	NF	1.78 L/m^{2}hbar	62% NaCl 92.7% Na$_2$SO$_4$	Wang et al. 2015
Coating	GO-PSF	NF -10 bar	5.47 L/m^{2}hbar	33% NaCl 89.8% Na$_2$SO$_4$	Sefarpour et al. 2015
Pressure coating drop by drop	GO/PAN	PV - 5 kg/cm^2	4137 g/m^{2}h	IPA/water 70%-99.5%	Hung et al. 2014
Self-assembling LBL	GE/GO/PAN	PV - vacuum 0.3 kPa	2,275 g/m^{2}h	Ethanol/water 98.7% wt.	Zhao et al. 2015

Table 2. cont.

Preparation method	Base polymer	Membrane process/ Pressure	Permeability/ Flux	Retention	Ref.
UV–LBL	GO-TiO$_2$/PSF	Photo-catalyse 69 kPa	45 L/m^{2}h	90% methylene blue	Gao et al. 2014
Covalent bonding	GO/PAN	UF - 1 bar	987 L/m^{2}hbar	85% BSA	Prince et al. 2016
Self-assembling LBL	GO/Ag-PAA GO/TiO$_2$-PAA	UF -1 bar	396 L/m^{2}hbar 453 L/m^{2}hbar	83-91% BSA 26-38% MO	Jiang et al. 2015

IP – interfacial polymerization; LBL- „layer by layer"; CNT – carbon nanotube; PA – polyamide; fGO – functionalized GO; PES – polyethersulphone; aPES – aminated polyethersulphone PSF – polysulphone; PAA – polyallylamine; PVDF – polyvinyli-dene fluoride; PAN – polyacrylonitrile; PEI – poliethylenimine; AAO – anodized aluminum oxide; GE – gelatine; BSA – bovine serum albumin; MO –methyl orange

3.2.2. Modification by introducing nanoparticles to polymeric matrix

Polymeric membranes, made of aromatic and aliphatic polyamide, cellulose acetate, polyvinylidene fluoride, polysulphone, polyethersulphone and other polymers, as well as non-polymeric materials (ceramics, metals) and their composites, are widely used to membrane preparation for filtration of various solutions (Basile et al. 2015). Currently, carbon material are added to polymeric matrices in order to obtain membrane of nanomaterial/polymer for RO, NF, UF and other membrane processes. The introduction of carbon nanomaterials to a polymeric membrane matrix influences on its structure and antibacterial properties, hydrophilicity, capacity, retention and mechanical stability (Zhao et al. 2013a, Aba et al. 2015, Chung et al. 2017, Lee et al. 2013, Zhao et al. 2014b, Xu et al. 2014, Zhao et al. 2013b, Wang et al. 2012c, Zhang et al. 2013). In comparison with conventional membranes, the surface of modified membranes reaches beneficial density and pores' structure, which result from precipitation of nanomaterial in phase inversion process. The significant increase of a membrane's hydrophilicity leads to the increase of permeability of a modified membrane (Teli et al. 2012). The introduction of carbon nanomaterials also enables their exploitation in dry state with no permeability affection, what is important in regard to a membrane resistance to bacteria and transport enhancement. The introduction of small amounts of functionalized GO to a membrane material results in porosity and membrane pores' size increase, but only to a certain boundary dose (Xu et al. 2014, Zhao et al. 2013b), but if GO amount exceeds 0.05%, membranes porosity significantly decreases (Zhao et al. 2014a, b). This trend also influence on membranes permeability, which increases with nanomaterial dose increase up to the critical point, after exceedance of which it decreases. This decrease is assigned to pores' blocking and narrowing caused by overamount of GO nanosheets in a membrane matrix. Lee et al. (2013) have explained GO role in a membrane casting process by means of phase inversion. At the absence of GO, polymer solidifies quickly at boundary phase between polymer and non-solvent during phase separation, what is caused by concentration gradient and fast interaction between all mixture components. In instable places on a surface of solid polymer phase, some breakages appear due to the pressure caused by continuous desolvatation shrinking. The introduction of hydrophilic substances (GO) to a membrane casting solution improves the overall hydrophilicity of the solution and influences on a mass exchange rate between solvent and non-solvent during phase separation, what leads to the formation of more porous membrane structure. As a results, the appearance of fractures and micro-breaks is minimized.

Xia & Ni (2015) have prepared PVDF membranes of different GO content using phase inversion method, what has significantly improved water transport rate and antifouling properties. The permeate obtained during NOM-

containing solution filtration has been analyzed toward dissolved organic carbon content (DOC), specific UV absorbance (SUVA) and molecular mass distribution. It has been found, that GO, due to the presence of acidic groups, may enable the appearance of a negative charge of a membrane surface within the whole pH range (Dimiev et al. 2013), what favors separation of positive ions due to electrostatic repulsion of negative ions by negatively charged membrane surface. The research carried out by Lai et al. (2016) has shown that higher water flux and salt retention can be obtained by introduction of non-functionalized GO to PSF support coated with polyamide layer. Membranes produced from solution containing 0.3wt.% GO have retained Na_2SO_4, $MgSO_4$, $MgCl_2$ and NaCl in 95.2%, 91.1%, 62.1% and 59.5%, respectively. Zinadini et al. (2014) have prepared NF GO/PES membranes of various GO content and produced modified UF membranes of GO/PVDF type. These membranes have also revealed improved antifouling features caused by higher hydrophilicity and proper surface morphology. Fryczkowska (2018) obtained UF composite membranes of GO-PAN type containing 0.8wt.%, 4.0wt.% and 7.7wt.% of GO in PAN matrix, for the dyes removal from industrial wastewater. Cationic (Indigo – IS; methylene blue – MB) and anionic (thymolic blue – TB; Congo red – CR) dyes have been selected for the research.

GO introduced to membrane casting solutions based on different polymers can be modified with the use of various substances, among which the most often used are: hyperbranched polyethylenimine (HPEI) (Wang et al. 2012c), triethoxy-3-aminopropylsilane (APTS) (Xu et al. 2014) and isocyanate (Zhao et al. 2013b). For example, GO functionalized by HPEI has been mixed with PES (Yu et al. 2013) and PVDF (Xu et al. 2014) solutions, and membranes produced by phase inversion method have revealed polyvinyl alcohol (PVA – 30-70 kDa) and polyethylene glycol (PEG – 20 kDa) retention equal to 90% and 85%, respectively. Also, modified membranes, type isocyanate-GO/PS (Zhao et al. 2013b) and APTS-GO/PVDF (Xu et al. 2014) retain BSA in 95% and 57%, respectively. TEM images of *E.Coli* cells have shown the loose of integrity and cytoplasm efflux during contact with modified HPEI-GO membrane (Yu et al. 2013).

Several authors have modified membranes with GO and Ag in order to improve antibiofouling character of membranes by introducing GO-Ag composite to membrane casting solution and prepared membranes using phase inversion method. For example, Wu et al. (2017) modified PVDF membrane and Mahmoudi et al. (2015) PSF membrane. Chung et al. (2017) have functionalized PSF membranes using graphene oxide nanosheets doped with ZnO. Zinc oxide nanoparticles are known as very good antifouling and antibacterial material, thus they can be used in exploitation of membrane based desalination processes.

In table 3, the comparison of selected GO/NPG containing membranes obtained with the use of wet phase inversion method, including their characteristics, is shown.

Table 3. The selected research on composite membranes obtained with the use of phase inversion method from a mixture of a polymer and GO/NPG

Polymer	Process/ Conditions	Permeability/Flux	Retention	Reference
GO/ /PSF	NF/400kPa	50 L/m^{2}h	72% Na$_2$SO$_4$	Ganesh et al. 2013
GO/ /PES	NF/400kPa	53 kg/m^2 h	90.5% Protein	Yuan et al. 2017
GO/PVDF	UF/1 bar	26.5 L/m^{2}hbar	79% BSA	Wang et al. 2012c
GO/Isocya-nine/PSF	UF/1 bar	135 L/m^{2}hbar	95%BSA	Zhao et al. 2013b
GO/HPEI/PSF	UF/1 bar	153.5 L/m^{2}hbar	85% PEG(20,000) 90% PVA	Yu et al. 2013
CNT/PVDF	UF/1 bar	410 L/m^{2}hbar	98.3% BSA	Zhang et al. 2013
GO/PES	UF/4 bar	6 L/m^{2}hbar	96% dye (Direct Red 16)	Zinadini et al. 2014
GO/APTS/PVDF	UF/1 bar	401 L/m^{2}hbar	57% BSA	Xu et al. 2014
rGO/Ag-PES (0,2%wt.)	UF/	107.5 L/m^{2}hbar		Vatanpour et al. 2015
Co$_3$O$_4$-GO/PES (1,5%wt.)	UF/	347.9 L/m^{2}hbar	89.8% *Escherichia coli*	Ouyang et al. 2015
GO-Ly/PES	UF/0.2 MPa	318 L/m^{2}hbar		Duan et al. 2015

Table 3. cont.

rGO-Ly/PES	UF/0.2 MPa	372 L/m²hbar		Duan et al. 2015
GO/PVDF	MF/0.25 bar	1298 L/m²hbar	80% mushrooms	Zhao et al. 2013ab
GO/C$_3$N$_4$/ PES/PA[*]	FO/2M NaCl-Demi	41.4 g/m²h	-	Wang et al. 2012b
GO/PSF/PA[*]	FO/0.5M NaCl-Demi	19.8 g/m²h	-	Park et al. 2015

[*] – phase inversion method and interphase polymerization; GO – graphene oxide; rGO – reduced graphene oxide; PSF – polysulphone; PVDF – polyvinylidene fluoride; HPEI: hyper-branched polyethylenimine; CNT – carbon nanotube; PES – polyethersulphone; PVA – polyvinyl acid; Ly – lysozyme; APTS – 3-aminopropyltriethoxysilane; NF – nanofiltration; FO – forward osmosis; UF – ultrafiltration; MF – microfiltration; BSA – bovine serum albumin

4. Summary and development prospective

Graphene is a novel material, which possesses many advantageous features, that allow for preparation of next generation membranes of high efficiency to desalination and water and wastewater treatment. It excellent mechanical properties, single-atom layer structure, large specific surface area and wide modification possibilities make it highly useable for membranes formation.

Novel composite membrane containing NPG and GO can be divided into freestanding membranes, and polymeric/ceramic membrane modified with the use of graphene-based nanomaterials. Modification of polymeric membranes can be achieved either by introduction of a nanomaterial onto a membrane surface or to a membrane casting solution followed by membrane formation from a polymer and a nanomaterial mixture.

GO/NPG membranes as well as polymeric or ceramic ones containing graphene, when used in pressure driven membrane processes, often characterize with high water/permeate flux and reveal unique antifouling and antibacterial features as well as high mechanical and thermal stability. The capacity of membranes containing NPG/GO is higher than in case of conventional RO or NF membranes, whereas retention of low molecular weight compounds is comparable. The efficiency of membranes is beneficial for dyes removal, separation of mono- from bivalent ions and dewatering of water-solvent mixtures. Additionally, graphene-based separation membranes have been successfully used in pervaporation, forward osmosis,

capacitive deionization, electrodialysis, or in formation of photocatalytic membranes, due to their stability and high effectiveness.

The future development of NPG/GO containing membranes should focus on the improvement of their separation features by using various formation techniques. A lot of effort has to be given to understand and properly explain both, role and interaction mechanisms of graphene-based nanomaterial with a membrane, especially in case of freestanding GO membranes. Additionally, the scaling up required for commercial production of ultra-thin membranes of high permeability, based on graphene-oxide, is one of the greatest challenge for scientists and engineers. Moreover, the release of nanomaterial from such membranes and their potential toxicity has to be investigated in detail for their further practical use in desalination processes.

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Abstract

In recent decades, novel and promising materials (e.g. carbon nanotubes, nanoporous graphene and graphene oxide) suitable to be used in preparation of high-capacity membranes for water desalination and water and wastewater treatment have been developed. Membranes made of NPG and GO materials enable to obtain significantly higher water/permeate fluxes than currently used thin film composite membranes for RO and other separation processes as pervaporation, forward osmosis, capacitive deionization, electrodialysis, or in formation of photocatalytic membranes. Novel composite membrane containing NPG and GO can be divided into freestanding membranes (prepared only from NPF/GO), and polymeric/ceramic membranes modified with the use of graphene-based nanomaterials. Modification of polymeric membranes can be achieved either by introduction of a nanomaterial onto a membrane surface or to a membrane casting solution followed by membrane formation from a polymer and a nanomaterial mixture.

The future development of NPG/GO containing membranes should focus on the improvement of their separation features. A lot of effort has to be given to understand and properly explain both, role and interaction mechanisms of graphene-based nanomaterial with a membrane, especially in case of freestanding graphene oxide membranes. GO nanosheets are very promising material for manufacturing of desalination membranes, however more attention has to be dedicated to potential disadvantages such as mechanical instability, nanosheets formation, non-uniform distribution of layers and surface damage.

Additionally, the scaling up required for commercial production of ultra-thin membranes of high permeability, based on graphene-oxide, is one of the greatest challenge for scientists and engineers. The success reached in this area will lead to the decrease in energy consumption in RO installation and in other membrane processes. Moreover, the release of nanomaterial from such membranes and their potential toxicity has to be investigated in detail for their further practical use in desalination processes.

Keywords:
graphene, graphene oxide, separation membranes preparation, desalination, water treatment, wastewater treatment

Grafen – nanomateriał do wytwarzania nowej generacji membran półprzepuszczalnych

Streszczenie

W ostatnich dziesięcioleciach opracowano nowe i obiecujące materiały (np. nanorurki węglowe, nanoporowaty grafen i tlenek grafenu) odpowiednie do wytwarzania membran o wysokiej efektywności odsalania i uzdatniania wody i oczyszczania ścieków. Membrany wykonane z NPG i GO pozwalają na osiągnięcie znacznie wyższej wydajności wody/permeatu, niż obecnie stosowane membrany kompozytowe cienkowarstwowe do RO i innych procesów separacji, jak np. perwaporacji, osmozy prostej, dejonizacji pojemnościowej, elektrodializy, lub membran fotokatalitycznych. Nowe membrany kompozytowe zawierające NPG i GO można podzielić na membrany „wolnostojące" (wykonane tylko NPF/GO) i membrany polimerowe/ceramiczne modyfikowane za pomocą nanomateriałów z grafenu. Modyfikację membran polimerowych można osiągnąć albo przez wprowadzenie nanomateriałów na powierzchnię membrany lub do roztworu błonotwórczego, z którego wytwarza się membrany metodą inwersji fazowej.

Rozwój membran zawierających NPG/GO powinien koncentrować się na poprawieniu ich własności separacyjnych. Należy uwagę skierować na zrozumienie i prawidłowe wyjaśnienie zarówno roli i mechanizmów interakcji nanomateriału na bazie grafenu z membraną, zwłaszcza w przypadku membran „wolnostojących". Nano-arkusze GO są bardzo obiecującym materiałem do wytwarzania membran do odsalania wody, należy jednak więcej uwagi zwrócić na potencjalne wady takie jak niestabilność mechaniczna, tworzenie nano-arkuszy, nierównomierny rozkład warstw i uszkodzenia powierzchni. Ponadto, należy rozwiązać powiększanie skali wytwarzania membran, co jest wymagane dla komercjalizacji produkcji membran opartych na grafenie i tlenku grafenu oraz stanowi jedno z największych wyzwań dla naukowców i inżynierów. Sukces osiągnięty w tej dziedzinie doprowadzi do zmniejszenia zużycia energii w instalacji RO i innych procesach membranowych. Należy również szczegółowo zbadać proces uwolnienia nanomateriału z membran i jego potencjalną toksyczność, z uwagi na bezpieczeństwo stosowania membran zawierających nanomateriały.

Słowa kluczowe:
grafen, tlenek grafenu, wytwarzanie membran separacyjnych, odsalanie, uzdatnianie wody, oczyszczanie ścieków