

Graphene Oxide (GO) Membrane in Removing Heavy Metals from Wastewater: a Review

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Excessive heavy-metal (HM) ions in water system cause both environmental and human health problems. Therefore, the discharged wastewater has to be remediated from these HM contaminants. Membrane is the most promising water treatment technology that combines high separation efficiency, modest operation, concise of space, low footprints, and low operating cost. However, the current membrane technology has limitations in permeability and solute rejection which are highly influenced by membrane material and operating conditions. Incorporation of graphene oxide (GO) on membrane promotes the permeation and metal ions rejection rates. Factors that affect GO membrane performances in the removal of HM ions from wastewater (e.g., pH, temperature, pressure, initial feed concentration, metal ions solubility in solution, interaction between solution and GO membrane, complexing agent), as well as several proposed rejection-mechanisms (e.g., size exclusion, adsorption, and electrostatic interaction) have been reviewed and discussed in a comprehensive way. Perspectives and future development of GO membrane technologies for metal ions removal are given as complement.

1. Introduction

Rapid industrialization, especially in batteries, electroplating, mining, circuit board manufacturing, refinery, fertilizer, textile, pulp and paper industries, produces a huge amount of heavy-metals-contaminated wastewater that leads to environmental problems. Despite the fact that living organisms need metal ions to biochemically and physiologically function, the excess dose of these ions is harmful (Singh, 2011; Makertihartha, 2017; Zunita, 2018). Therefore, the government has strictly instituted environmental regulations towards the effluent standard for HM ions; and consequently, the removal of HM ions from wastewater before its discharge to the environment is mandatory. Research on metal-ions removal technologies has been pursued to achieve cheaper yet more efficient process to meet the challenges of lower consent levels. Membrane technology has been considered as the most promising one that combines excellent product quality, simplicity in process, low footprints, and minimal space requirements (Makertihartha, 2017). However, the membrane technology is still having some drawbacks, such as biofouling, that limit its performance in water treatment application. Improvements have been attempted by means to enhance the permeability and selectivity of the membrane, and membrane material is one of the most intensively studied. Graphene oxide (GO) is a two-dimensional nanomaterial which structure resembles a honeycomb bound to a variety of oxygen-functionalized groups (Makertihartha, 2017; Zunita, 2018). The presence of these oxygen-functionalities facilitates the interaction between GO sheets with metal ions to form metal complexes and therefore, effectively removes the metal ions from the treated wastewater (Sun, 2013). GO has been considered as an energy-saving material for membrane due to its ultrathin structure (monolayer GO nanosheet is about 0.7–1.2 nm thickness). Moreover, the intercalation of GO into a membrane can improve antifouling and antibacterial properties (Zinadini, 2014). This review remarks on the latest performances of GO membrane in HM ions removal, including some key concepts to achieve a high heavy-metal-ions-rejection.

2. Methodology of producing graphene oxide membrane

2.1 Structure and preparation of graphene oxide nanosheets

Generally, GO is prepared via two successive routes: (1) oxidation of graphite and (2) exfoliation of graphite oxide (GrO). The exfoliation of GrO could be done through chemical, physical or mechanical methods. GrO was firstly discovered by Brodie et al. (Brodie, 1859) from mixing potassium chlorate (KClO_3) into graphite slurry in fuming nitric acid (HNO_3) media. Oxidation took place several times until the stable yellowish product was achieved. The product was washed to remove the salt produced during the reaction, before dried and stored. Staudenmaier et al. (Staudenmaier, 1898) performed Brodie's work in a single reaction vessel with the addition of concentrated sulphuric acid (H_2SO_4) and potassium chlorate (KClO_3). Graphite oxide produced by Staudenmaier has a similar composition to Brodie's; nevertheless, Staudenmaier's method is more hazardous and consumes more time. Hummers and Offeman (Hummers, 1958) further modified Brodie's work through mixing the concentrated H_2SO_4 , sodium nitric (NaNO_3), and potassium permanganate (KMnO_4) which is maintained under a temperature of 45°C ; after two hours, the final product of higher oxidation degree was obtained. The Hummers method is indeed more efficient and less hazardous than the previous work, yet it still produces toxic gasses like nitrogen-oxide (NO_2) and -tetroxide (N_2O_4). Leaving a room for Marcano et al. (Marcano, 2010) to improve the method by substituting NaNO_3 with phosphoric acid (H_3PO_4) while increasing the amount of KMnO_4 that resulted in the efficiency enhancement of oxidation process and the elimination of toxic gasses. This modified Hummers method has been the most commonly used preparation method for GO. As a product of strong oxidation processes, GO nanosheet is contented with hydroxyl, carboxyl, epoxy, and carbonyl. Hydroxyl and epoxy are mainly distributed at the basal plane while carboxylic, carbonyl, and phenol lie at the edges of the sheet. The edges are hydrophilic due to the domination of carboxyl ions; while the basal plane has both hydrophilic and hydrophobic regions, constituting the amphiphilic nature of GO lamellar sheet (Raidongia., 2014). The amphiphilic nature of GO allows both organic and inorganic molecules to be bonded/adsorbed on its surfaces (Li, 2017). Despite its high metal ions adsorption efficiency (Peng, 2017), there are some challenges in incorporating GO to a membrane. Besides the high fabrication cost, leaching of GO nanoparticles from the membrane is possibly happened due to their high affinity towards water. Therefore, considerations should be taken while selecting the proper method for GO membrane fabrication.

2.2 Fabrication of graphene-oxide membrane

GO membrane could be fabricated through casting/coating, filtration, layer-by-layer construction, or other methods. Coating/casting methods, including spin-coating/casting, cloth-coating, spray-coating, dip-coating, and drop-casting, are highly scalable even for continuous production; the modest operation adds its advantages (Song, 2018; Zunita, 2018). Although there are some drawbacks from the method (i.e., non-uniform deposition and poor control over thickness), yet the free-standing GO membrane prepared by drop-casting has selective penetration and water purification properties from its nanocapillary network (Sun, 2013). It has been found that a simple drop-casting method yields remarkable properties and excellent mechanical strength.

Filtration methods, such as vacuum and pressure-assisted methods, provide good control over the membrane thickness and highly scalable (Ma, 2017). A highly-ordered GO laminate structure could be obtained via a pressure-assisted method, while vacuum filtration yielded a random loose structure (Tsou, 2015). The vacuum-assisted technique is commonly applied to prepare a composite ceramic hollow fiber or a self-assembled GO membrane. Yang et al. (Yang, 2018) prepared a nanofiltration GO-ceramic membrane by immersing ceramic tube in the ZIF-8@GO/PEI while connecting the one side with a vacuum pump and found that the permeability of the prepared membrane was improved because of the formation of favorable water channels.

Layer-by-layer (LbL) construction method was introduced to stabilize the negatively charged groups (carboxyl, hydroxyl) of GO nanofilm via electrostatic forces and covalent bonding (Mi, 2014). This method offers control over the GO layer number, packing, and thickness. A study of Zhao et al. (Zhao, 2016) in fabricating a GO composite membrane via LbL-assembly of poly(ethylenimine) and a mixture of GO and poly(acrylic acid) (PAA) on a poly(acrylonitrile) (PAN) support membrane successfully enhances the selectivity of monovalent cations and hydrophilicity of the polyelectrolyte composite membrane.

GO membranes could be constructed as a free-standing membrane, a modified/support membrane, a thin-film composite membrane, or a mixed-matrix membrane. The free-standing GO membrane produced via spin/spray-coating (Nair, 2012) results in an ultrafast permeation of water vapor; yet the inclusion of water molecules between GO nanosheets causes a swelling effect that reduces the separation performance as well as the mechanical properties of the membrane.

To promote its mechanical properties, the structure of GO layer membrane could be modified by a chemical crosslinker, such as isocyanate, chitosan, or polyallylamine that bonds well enough with GO-functionalities

(Gao, 2015). The objective of this effort is to adjust the interlayer spacing so the mechanical integrity and stability of the GO-based membrane could be maintained. Another way to improve the properties is by incorporating GO into a polymer solution before it is cast to form a mixed-matrix that consolidate the advantages of both materials. Illustrations of the configuration of each GO membrane are shown in Figure 1.

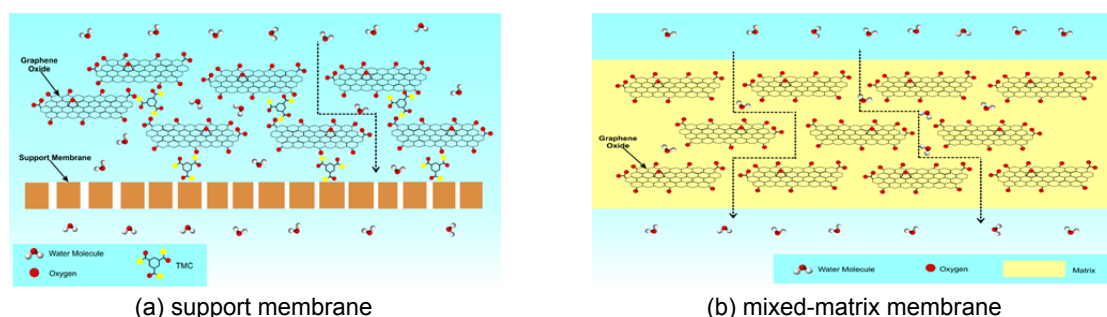


Figure 1: Various configurations of graphene-oxide membrane

Mixed matrix membrane (MMM) was obtained by combining polymeric and inorganic material in the construction of membrane. It is done to consolidate the advantages of those materials. The phase inversion method is generally applied for GO-assisted mixed matrix membrane preparation. The first step is by dispersing a certain amount of GO in the solvent, then the polymer substrate added into the solution. Casting solution (dopant), cast and cut using a casting knife. The produced membrane is then immersed in a coagulating bath of a non-solvent (e.g., deionized water) until the solvent entirely reduced (Akhair, 2017). The dense skin layer on the top and porous support could be obtained through the addition of GO to polymer substrate. The pores production is due to the exchange rate of solvent and non-solvent in the coagulation bath during the phase inversion process. The finger-like pores found in membrane because of the faster exchange rate of solvent and non-solvent behavior. The faster exchange rate by means the rapid mass transfer is generated as the addition of GO into dope solution. The above statements respect the permeability and rejection rate improvement.

3. Result and discussions of graphene-oxide membrane performances in the heavy metal remediation

The rejection of HM ions by the GO membrane has been associated with several mechanisms (i.e., size exclusion, adsorption, and electrostatic interaction) shown in Figure 2. Size exclusion is based on the radii of subjected ions; if they are larger than the interlayer spacing of GO nanosheets then these ions would get rejected. The affinity between HM ions and GO membrane results in an electrostatic interaction. This interaction will be depended on the properties of the subjected ions and charged properties of GO membrane. Originally, GO membrane is negatively charged as the result of deprotonation of carboxyl and hydroxyl groups which are found in the GO nanosheets, leading to higher rejection of HM ions. GO also has a remarkable potential in the removal of HM ions due to its high adsorption capacity. Due to its large specific surface area, surface hydrophobic π - π interaction, hydrophilicity, high negative charge density as well as abundant resources, GO is regarded as the most promising adsorbent for HM ions (Peng, 2017). Incorporation of GO on membrane promotes both permeation and metal ions rejection rates of the membrane.

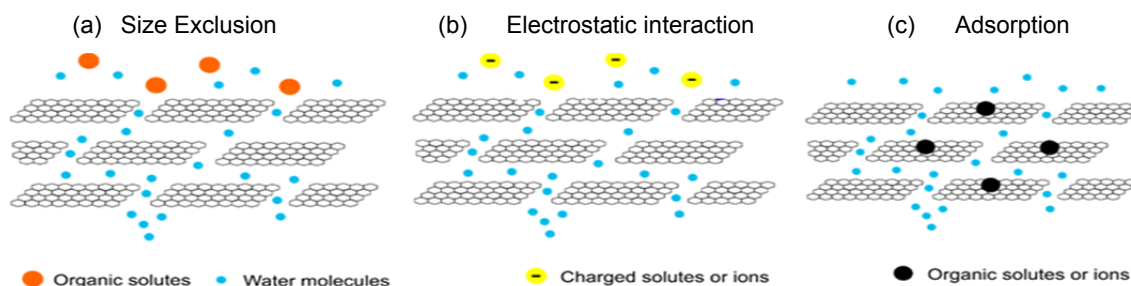


Figure 2: Schematic diagram of the separation mechanisms in graphene oxide membrane, adapted from Zhang et al. (Zhang, 2017)

The adsorption of HM ions on GO membrane is affected by many factors. Initial pH governs the species of the HM ions in the solution and affects the surface potential of GO; the electrostatic interaction between HM ions and negatively charged GO sheets becomes stronger with the increase of pH. Increasing temperature and pressure accelerate the adsorption capacity and rate. Selective penetration properties of GO membrane are influenced by feed concentration and variation of HM involved as well as number of oxygen-functionalities and morphology of the membrane. Sun et al. (Sun, 2013) have reported that different interaction strengths (i.e., electrostatic attractions and chemical interactions) between hydrated metal-ions and GO functional groups are responsible for their different penetration abilities ($\text{Na}^+ > \text{Mn}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$). The permeation of metallic ions through a freestanding GO membrane is limited by the coordination between the HM ions with the oxygen-functionalized groups on the membrane. The more oxygen-functionalized groups on GO membrane, the more metal ions get adsorbed through coordination. Increasing the feed concentration and pressure slightly decreased the removal performance (Shukla 2018).

The shape of the membrane is also important. Zhang et al. (Zhang, 2016) have produced the LbL GO-modified Torlon hollow fiber membrane to separate the HMs ion and achieve excellent rejection. The mechanical strength and thermal resistance properties of a hollow-fiber membrane are more excellent than those of layer membrane counterpart. Zhang's membrane can be used for 10 cycles and keeps showing good performance. Thicknesses of GO layer and its produced nano-sieving channels are tuneable and play an important role in membrane separation performance; for wastewater treatment, water channels can be adjusted by inserting rigid chemical groups or soft polymer chains as the spacer (Mi, 2014).

Instability of GO membrane impedes its industrial application, therefore, the role of complexing agent is necessary to improve the structural stability of the membrane. Zhang et al. (Zhang, 2017) have successfully prepared an isophorone diisocyanate (IPDI)/GO framework membrane that not only is stable in structure, effective in removing dyes and HM ions but also possesses high-water permeability. The crosslinking between GO and IPDO indeed reduces the surface charge of the membrane, hence lowers the rejection of HM ions, yet rejection of HMs could be improved by increasing the pH of the feed solution.

Table 1: Separation performances of GO-assisted membranes

Membrane	Rejected metal-ions	Testing condition	Rejection	PWP* (LMH/bar)	Ref.
Torlon hollow fiber modifies LbL GO framework membrane	Pb^{2+}	1000 ppm, 3 bar	95.88	4.7	Hu et al. (Hu, 2014)
	Ni^{2+}		99.74		
	Zn^{2+}		98.07		
HPEI modified GO&EDA framework membrane	Pb^{2+}	1000 ppm, 1 bar	95.7	5.01	Zhang et al. (Zhang, 2015)
	Ni^{2+}		96		
	Zn^{2+}		97.4		
	Cd^{2+}		90.5		
PSF+GO+DMF mixed matrix membrane	As^{3+}	300 ppm, 4 bar, pH 3-11	~83	50	Rezaee et al. (Rezaee, 2015)
PSF+GO+DMF mixed matrix membrane	Cr^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+}	500 ppm, 4 bar, pH 3.5-10	~90	~10	Mukherjee et al. (Mukherjee, 2016)
PSF@PDA@IRMOF-3/GO-1 GO-IPDI membrane	Cu^{2+}	200 ppm, 7 bar, pH 5	~90	31	Rao et al. (Rao, 2017)
	Congo red	20 mL, 1 bar, pH 7	99.3	80-100	Zhang et al. (Zhang, 2017)
	Rhodamine		96.1		
	Methyl orange		97.7		
	Methylene blue		98.5		
	Cu^{2+}		46.2		
	Pb^{2+}		66.4		
	Cr^{3+}		71.1		
	Cd^{2+}		52.8		

*PWP = pure water permeability

Rejection of HM ions by GO membrane has been proven superior compared to the bare membrane. The rejection of HM ions through GO incorporated polysulfone (PSF)/polydopamine (PDA) membrane is higher compared to the pristine PSF/PDA membrane (Rao, 2017). The rejection rate of Cr^{6+} is increased significantly by 148 % (from 40 % to 99 %) when polyester⁵/polyacrylonitrile⁴ membrane is incorporated with GO (Koushkbaghi, 2016). GO impregnated Polysulfone (PSf) mixed matrix membrane (MMM) displays a high adsorption capacity of HMs due to the interplay of adsorption, diffusion, and convection (Mukherjee, 2016). Carboxylated-GO incorporated polyphenylsulfone (PPSU) nanofiltration-membrane is found enhanced in properties and performances (Shukla, 2018). Zhang et al. (Zhang, 2015) have successfully constructed a stable and highly charged GO framework membrane with 70 nm GO selective layer thickness for effective heavy metal removal through cross-linking and framework construction by ethylenediamine (EDA) then amine-enrichment modification by hyperbranched polyethylenimine (HPEI). The EDA cross-linking not only enhanced structural stability but also enlarged the nanochannels among the laminated GO nanosheets resulting higher water permeability. HPEI was found increasing the surface charge and decreasing the transport resistance in GO framework membranes. These GO assisted membranes, therefore, become more and more potential to be applied in industry. Separation performances of the discussed GO membranes are summarized in Table 1.

4. Perspectives and future development

Technological innovations in HM ions removal from industrial wastewater are essential to mitigate the water scarcity. In this case, membrane technology presents as an advanced technology with great advantages including high efficiency, modest operation, and space retrenchment. The hydroxyl and carboxyl groups of GO are undoubtedly able to adsorb the soluble HM ions from the treated water. The hydrophilic nature of GO can also increase the water flux permeation. Moreover, GO membrane possesses high surface area, good mechanical strength, light weight, flexibility, and chemical stability. Relatively, the runtime of GO for HM removal is concise and the process costs lower than nanofiltration, which requires high-pressure. The commercial feasibility of the GO membrane for HM removal is highly recommended due to their selectivity and high hydrophilic nature for water permeation and resistance to fouling and poisoning on the membrane surfaces.

The rejection of HM ions by the GO membrane is associated with several mechanisms; the latest comprehension refers to size exclusion, adsorption, and electrostatic interaction. While the performances of the GO-assisted membrane to remove HM ions depend on pH, temperature, pressure, initial feed concentration, the miscibility of metal ions in solution, interaction between solution and GO membrane, as well as the role of complexing agents. Each HM species has its own optimum condition in the separation process. Future development has to be directed to stabilize the GO in membrane structure; thus it could resist the harsh environment of industrial wastewater that particularly contains HM ions.

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