Application of graphene oxide in water treatment

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Abstract. Graphene oxide has good hydrophilicity and has been tried to use it into thin films for water treatment in recent years. In this paper, the preparation methods of graphene oxide membrane are reviewed, including vacuum suction filtration, spray coating, spin coating, dip coating and the layer by layer method. Secondly, the mechanism of mass transfer of graphene membrane is introduced in detail. The application of the graphene oxide membrane, modified graphene oxide membrane and graphene hybrid membranes were discussed in RO, vaporization, nanofiltration and other aspects. Finally, the development and application of graphene membrane in water treatment were discussed.

1. Introduction
Graphene is a carbon material, a two-dimensional honeycomb lattice structure, with a single layer of atomic thickness [1]. In 1940, graphene was considered a constituent element of graphite [2]. In 1962, Boehm et al. separated the carbon flakes by heating and chemically reducing the oxidized graphite (GO). However, until the 2004, Geim used special tape repeatedly peeled high directional pyrolytic graphite, obtaining monolayer graphene, its thermodynamic stability in the atmosphere was firstly recognized [3]. The special structure of graphene has excellent mechanical properties (Young's modulus and breaking strength is 1100 GPa and 125 GPa, respectively), high electrical properties (electron mobility is 200 000 cm²/(V·s)) [4], excellent thermodynamic properties (5300 W/(m·k) and large specific surface area (2600 m²/g) [4]. This revolutionary discovery has rapidly attracted all scholars from physical, chemical, biological fields.

There is a strong van der Waals force between the graphene sheets, which leads to the difficult application of graphene materials directly. Graphene oxide is the most common derivative of graphene. The surface of the graphene oxide obtained by the chemical oxidation-stripping method is distributed with a large number of polar oxygen-containing functional groups, including the in-plane distributed hydroxyl groups, the epoxy groups and the carboxyl groups at the edges [5], due to the presence of these oxygen-containing functional groups, Graphene has good hydrophilicity. When the graphene is dispersed in water, the carboxyl group is hydrolyzed to negatively charged acid and hydrogen ions to form a stable oxidized graphene dispersion. Researchers enabled the new properties of graphene through different modification methods [5]. The modified graphene can not only prevent the agglomeration of the lamellae in the solution, but also can be prepared by vacuum suction filtration, spray coating, spin coating, dip coating and the layer by layer method. In this paper, the preparation method of graphene oxide membrane is reviewed, and the research progress of graphene membrane in water treatment is reviewed, and its future prospect is reported.

2. Preparation of Graphene Oxide Membrane
The graphene oxide is added into deionized water, and it can obtain a stable oxidized graphene
dispersion through the ultrasonic and stirring, which provides a great convenience for the preparation of graphene oxide membrane. The main methods of preparation are vacuum suction filtration, spray coating, spin coating, dip coating and the layer by layer method, these methods are low energy consumption, simple operation, what’s more, the oxide graphene membrane thickness is uniform, its flexibility is well, it is easy to transfer it to other substrates.

2.1 Vacuum Filtration Method
Vacuum filtration is the most commonly used method for the preparation of graphene oxide membrane. The graphene solution was adjusted to a suitable concentration before the fumed graphene dispersion was filtered, and then the graphene oxide was deposited onto a membrane (microporous membrane / alumina film) for vacuum filtration. During the filtration process, the graphene oxide will cover the entire membrane evenly due to the flowability of water. The obtained graphene oxide membrane has a uniform dispersibility, and the control of the dispersion concentration can change the thickness of the graphene membrane. Huang et al. used filtration method prepared graphene oxide membrane by controlling the pressure, salt concentration and pH, which can be used to regulate the size of graphene oxide channel [6].

The surface of the graphene oxide membrane prepared by the vacuum filtration method is relatively flat. Due to the limitation of the equipment, the size of the graphene membrane prepared by the vacuum suction method is small and it is difficult to realize the large area preparation. At the same time, the thickness of the graphene oxide membrane is less than 100 nm, and it is difficult to use it without the support material.

2.2 Spray Coating Method
Spraying coating method is using spray coating equipment to spray the solution into the substrate evenly, and then the solvent is evaporated to get the desired membrane. The role of the gun is making liquid atomization, forming the small droplets, the substrate will generally be preheated to accelerate the role of volatile solvents. The advantage of the spray method is that the production efficiency is relatively high, a large area can be prepared, the process is simple, and can be sprayed on any substrate. However, the uniformity of the membrane prepared by this method is relatively poor. Pham et al. prepared a chemically modified graphene membrane by spray coating. The preparation method is simple, low cost and fast filming [7].

2.3 Spin Coating Method
The spin coating method is to apply the graphene solution to the substrate, rotate the substrate and adjust the rotation speed of the substrate. In this way, the solution is uniformly dispersed on the surface of the substrate, and the substrate is dried to obtain an oxidized graphite film. During the filming process, we can control the concentration of graphene solution and the speed to adjust the film thickness. Hector et al. prepared an oxidized graphite film by spin coating. The substrate was first rotated at a speed of 600 r/min to allow the solution to be sufficiently dispersed on the substrate, and then the speed was raised to 800 r/min. The film thickness was reduced and the rotational speed was increased to 1600 r/min to obtain the desired film [8].

2.4 Dip Coating Method
Dip coating method is to soak the substrate in the solution of graphene oxide, after immersion, using a machine to remove the substrate and then recovering the excess solution. This method can control the thickness of the film by controlling the temperature, concentration and pulling speed of the solution, and can use mechanical batch processing. Vollmer et al. used a dip coating to treat a quartz substrate to prepare an oxide graphene film.

2.5 Layer by Layer Method (LBL)
LBL is the method that the multilayer film of polyelectrolyte is prepared by alternately depositing the
charged substrate in the opposite charge. The surface of the graphene oxide has a large amount of oxygen-containing groups, which can be used to covalently modify the surface of the graphene oxide with the negative charge of the oxygen-containing group or the polymer. Mi et al. used trimesic acid chloride as a cross-linking agent, graphene layer of self-loaded, to prepare a new separation membrane [9].

3. Mass Transfer of Graphene Oxide membrane

The mass transfer phenomenon of graphene oxide layered film gas, water molecules and ions in the solution is widely studied. Nair et al. [10] firstly studied the GO film mass transfer phenomenon, as shown in Figure 1. The spin coating method is exhibited (A) to (c), a series of experimental results show that GO film is completely impermeable to liquid, vapor and gas (including helium), as shown in Fig. 1 (d) And (e), but the film allows water molecules to pass through without obstruction (Fig. 2 (f)).

![Figure 1](image_url)

Figure 1 (a) Photograph of a 1 μm thick GO film peeled off from a Cu foil; (b) electron micrograph of the film’s cross section; (c) schematic view for possible permeation through the laminates; (d) examples of He-leak measurements for a freestanding submicron-thick GO membrane and a reference PET film (1 mbar = 100 Pa); (e) weight loss for a container sealed with a GO film; (f) permeability of GO paper with respect to water and various small molecules [10].

Sun et al. [11] prepared a non-existent GO film with a micron-thickness thickness using a drop coating method to study the permeation behavior of the different ions in the solution, as shown in Figures 2 (a) and (b). The mechanism of salt ion penetration is shown in Fig. 2 (c) and (d).
4. Research Progress of Graphene Oxide membrane in Water Treatment

4.1 Graphene Oxide Membrane

There is a strong hydrogen bond in the graphene layer, and the dried graphene film can be stably present in the aqueous solution. Therefore, the graphene film is considered to be a new type of carbon-based film [13], which has been widely used in water purification, ion screening and other fields.

Tanugi et al. used molecular simulation results to show that the appropriate pore size of the oxidized graphene tablets can allow water molecules pass, while the effective retention of Na⁺ and Cl⁻. Due to the strong hydrophilicity of graphene oxide, the graphene film is used for desalination, and the water flux can be increased by several orders of magnitude compared with conventional reverse osmosis membranes [14]. Nair et al. demonstrated there is the low resistance flow of the monolayer of water molecules between the graphene sheets. These works opened the door of the separation of graphene oxide membrane.

4.2 Modified Graphene Oxide Membrane

Modified graphene oxide membrane can effectively change the surface properties of graphene oxide, introduce the new functional groups and change the distance between graphene sheets. The modified graphene film is used in the fields of water purification, pervaporation and desalination. Lou et al. used dip coating method with ceramic as the support base film, the preparation of silane modified graphene film. Silane modification improves the adhesion between the graphene and the ceramic base film, and the hydrophilicity of the membrane is improved. Gao et al. prepared an ultra-thin modified graphene oxide membrane by filtration. Sodium membrane flux is very large, and for the dye has a good retention effect, for the salt ion, the retention rate is 20% to 60% [15].
4.3 Hybrid Graphene Oxide Membrane

Hybrid Graphene Oxide Membrane not only has the advantages of organic film and nanoparticles, to make up for their own defects, but also can develop the original film material which does not have the comprehensive performance to meet specific needs. In this hybrid film, graphene oxide is a good filler, which can improve the permeability of the membrane permeability and has been in the organic separation, pervaporation and other fields. Huang et al. have prepared a graphene/polyvinyl alcohol hybrid film, which has a good interception effect due to the hydrogen bonding between grained graphene nanoparticles and polyvinyl alcohol. Compared with the PVA film, the permeability coefficient of water is decreased by 68%, and the experimental results provided an effective idea for the preparation of polymer nanocomposite films with high retention performance. Wang et al. investigated the separation performance of the graphene/polyvinyl alcohol nanocomposite film on the toluene/n-heptane mixture. The hybrid membrane improved the affinity of the aromatic compound and changed the permeability of the toluene/n-heptane mixture.

5. Conclusion

The graphene oxide membrane, the modified graphene oxide membrane and the oxidized graphene hybrid membrane have the advantages of simple preparation process and good separation performance, it has great potential in the field of water treatment. In the view of the ion transport principle in graphene membrane is not yet clear, and it needs a deep understand of the mechanism when being applied to desalination, sodium filtration, pervaporation and other fields. At the same time, for the new separation membrane of enriched graphene group, how to improve the strength of the separation membrane and put it into practical application, is an urgent problem to be solved.

Reference

[1] GH Wu, P Li, SG Wang. Study on treatment of pharmaceutical wastewater by coagulation [J]. Water Treatment Technology, 2000, 26(1): 53-55.
[2] ZQ Pan. Chemical flotation treatment of oxytetracycline and midecamycin wastewater [J]. Industrial Water Treatment, 1991, 11(1): 24-26.
[3] ZQ Chen. Study on treatment of high concentration Chinese herbal medicine wastewater by low pressure distillation [J]. Journal of Harbin University of Civil Engineering, 1999, 32(6): 16-18.
[4] TT Li, XJ Wang, TS Liu. Experimental study on treatment of traditional Chinese medicine wastewater by integrated membrane bovine reactor [J]. Journal of Harbin University of Commerce, 2009, 25(4): 419-423.
[5] M Wang, Y Lei. Treatment of traditional Chinese medicine wastewater by integrated membrane bioreactor [J]. Chemical Environmental Protection, 2004, S1: 237—239.
[6] XL Liu, NQ Ren, Y Zhang. Experimental study on treatment of traditional Chinese medicine wastewater by electronically controlled recoil [J]. Journal of Harbin Institute of Technology, 2006, 6:881-883.
[7] M Wang, MG Ding. Design of high concentration Chinese herbal medicine wastewater treatment project [J]. Water Treatment, 2006, 7:79-81.
[8] W Rauch. general model for single sludge wastewater treatment systems [J]. Water Research, 2006, 40(17): 3149.
[9] M Henze, CPL Grady, W Gujer, GR Marais. Activated sludge model N°1 [R] London: IAW-PRC Task Group on Mathematical Modeling for Design and Operation of Biological Wastewater Treatment, 1987.
[10] RR Nair, AK Geim. Unimpeded permeation of water through helium-leak-tight graphene-based membranes [J]. Science, 2012, 335(6067): 442-444.
[11] P Sun, M Zhu, K Wang, M Zhong, J Wei. Selective ion penetration of graphene oxide membranes [J]. ACS Nano, 2013, 7(1): 428.
[12] P Sun, H Liu, K Wang, M Zhong, D Wu. Ultrafast liquid water transport through graphene-based nanochannels measured by isotope labelling [J]. Chemical Communications, 2015, 51(15): 3251-
[13] AG Livingston, LMFD Santos, P Pavasant, EN Pistikopoulos, LF Strachan. Detoxification of industrial wastewaters in an extractive membrane bioreactor [J]. Water Science & Technology, 1996, 33(3):1-8.

[14] JA Scott, KL Smith. A bioreactor coupled to a membrane to provide aeration and filtration in ice-cream factory wastewater remediation [J]. Water Research, 1997, 31(1): 69-74.

[15] Y Wang. Discussion on wastewater treatment technology of traditional Chinese medicine [J]. Guangdong Chemical Engineering, 2009, 4: 138-140.