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Cross-linking to prepare composite graphene oxide-framework membranes with high-flux for dyes and heavy metal ions removal

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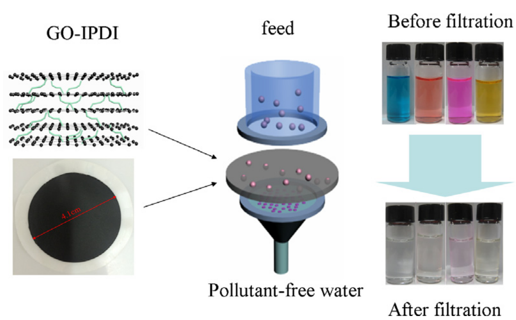
HIGHLIGHTS

- GO-IPDI membranes with high flux and excellent rejection for dyes were prepared.
- The retention performance was excellent for organic dyes, and moderate for heavy metal ions.
- Physical sieving nano-channel was mainly contributed to the rejection of dyes.
- The decreased interaction force was the main reason for the retention of heavy metal ions.

GRAPHICAL ABSTRACT



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ABSTRACT

Although graphene oxide framework-based membranes separation represent an effective and potential process in water purification and desalination, instability and low flux of the membrane make them still challenging in industrial application. Herein, isophorone diisocyanate (IPDI) was selected as cross-linking for covalent modification of graphene oxide nanosheets to design the newly graphene oxide-framework membranes (GOF) by a facile vacuum-assisted filtration method. The cross-linked GO-IPDI membrane can be used to effectively remove dyes and heavy metals via filtration. Results of filtration experiments and microstructure characterization confirmed that IPDI cross-linking GO not only enhanced structural stability but also enlarged the nano-channels among GO sheets for higher water permeability. The GO-IPDI membrane exhibited a high flux of 80–100 L m^{-2} h^{-1} bar^{-1} under an extremely low external pressure (1.0 bar). It exhibited a high rejection rate (above 96%) for dyes including methylene blue, methylene orange and rhodamine-B and congo red. While the retention was moderate for Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+} ranging from 40% to 70%. These results demonstrated the potential application of GO-IPDI in wastewater and provided a novelty way of design and fabrication of high water permeability and excellent separation performance of graphene-based membranes product.

1. Introduction

Nowadays, the lack of clean water has emerged as a serious challenge because of the fast population growth and environmental pollution caused by industry acceleration, infrastructure construction and ecology climate changes [1–4]. All kinds of pollutants in water can cause various threats to plants, animals and humans. Generally, the various wastewater treatments, such as chemical precipitation [5,6], microbial decomposition[7,8], and physical adsorption [9–12], can dispose the pollutant in wastewater at a certain extent. However, the above treatments have many

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disadvantages. For instance, it is easy to cause the generation of high amount of toxic sludge and liquid waste, time consumption and poor efficiency. Owing to their excellent adsorption capacity, fast kinetics and high efficiency, nano-materials were widely studied for removal contaminants in wastewater. It is inescapable that leaching of nanoparticles and their post treatment are not yet studied well. Although magnetic separation technology as an efficient and fast method for separating magnetic micro/nano-materials may be a promising approach for removal the organic pollutions and metal ions in aqueous solution [13–15], required the introduction of magnetic field, undoubtedly, it will be complicated for practical application.

The pressure-driven ultrafiltration technology plays a key role in separation applications and has been recognized as an alternative for water purification and treatment, recently some researches claimed that the graphene oxide (GO) membrane showed a potential in the separation of monovalent and divalent ions [16–18]. Compared to the technologies of biological and physical adsorption, its advantages include high efficiency, simple operation and energy consumption, and limited chemical requirement. At the same time, the novel film materials with low price and good removal efficiency have become the focus of the researchers [19]. Because of their high porosity, well-defined nanoscale pore size, thermal stability, rich functionalities and outstanding mechanical strength, more studies about the graphene oxide-framework have been undertaken in applications such as gas storage and separation, catalysis [20], the preparation of membranes or films [21,22], and sensing [23,24]. Nevertheless, the application of graphene oxide-framework for wastewater treatment is scarce. The membranes based on graphene oxide-framework as a novel inorganic material can have great potential for specific removal of pollutant from aqueous solution.

Recently, a number of theoretical studies have predicted that graphene with sub-nanometer pores could act as a highly selective and permeable filtration membrane with greater efficiency, for their superior thermal stability, mechanical strength and chemical resistance. Han et al. reported that ultrathin (≈22–53 nm thick) graphene nanofiltration membranes (uGNMs) on microporous substrates were presented for efficient water purification, which showed high retention for organic dyes and moderate retention for ion salts. However, the pure water flux of uGNMs would be less than 5.0 $L\,m^{-2}\,h^{-1}\,bar^{-1}$, when the base-refluxing reduced graphene oxide (brGO) loading more than 21.2 mg/m^2, and it was still a limited factor [25]. Hu et al. synthesized a new type of water separation membrane with high flux using graphene oxide (GO) nanosheets via a simple via layer-by-layer deposition of GO nanosheets. The Rejection showed the low rejection (6–46%) of monovalent and divalent salts and a moderate rejection (46–66%) of methylene blue was tested [26]. Jang et al. reported ambivalent rejection behavior of a graphene oxide membrane (GOM) having a reduced interlayer spacing [27]. They found that different methods to prepare GO membranes may lead to the reduction of the rejection rate. Moreover, graphene oxide membrane infiltrated humid conditions for a long time, the hydration effect will destroy the hydrogen bond and its layer spacing would become larger. Therefore, the separation performance would be unstable. In summary, it was urgently necessary to find a solution to enhance the flux of graphene membrane without sacrificed the rejection rate.

In the present paper, we studied that the chemical cross-linked modification of graphene oxide membrane to form hybrid structures and further increase the water flux and the performance of the removal for dyes and heavy metal ions from wastewater. Four hydrophilic dyes, namely, congo red (CR), rhodamine B (RB), methyl orange (MO), and methylene blue (MB), and four heavy metal ions, Cu^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, were chosen to study the separate behavior of graphene oxide-framework membranes in water. We found that the cross-linked GOMs with IPDI showed good stability, high water permeability, and the rejection rate of it had not been greatly sacrificed. The useful way on design and fabrication of graphene oxide membrane may be provided.

2. Experimental

2.1. Materials

All reagents were used as received without further purification: graphite powder was purchased from Qingdao Risheng Graphite Co., Ltd., (Qingdao, China). Sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2) and sulfuric acid (H_2SO_4) were purchased from Sinopharm chemical reagent Co., (Shanghai, China). N-methyl pyrrolidone (NMP) and *N, N*-Dimethylformamide (DMF) were obtained from Shanghai Xingrong Chemical Co. Ltd., (Shanghai, China). Analytical reagent grade isophorone diisocyanate (IPDI) were obtained from Aladdin Industrial Inc., (Shanghai, China). Polyvinylidene fluoride (PVDF) ultrafiltration (UF) membranes with a pore size of 0.22um were provided by the shanghai xingya Filter CO., Ltd. Methylene blue (AR, 95%), congo red (AR, 99%), methyl orange (AR, 99%) and rhodamine B (AR, 99%) were obtained from Jining Baiyi Chemical Co. Ltd., (Shandong, China). Cupric nitrate ($Cu(NO_3)_2$), lead nitrate ($Pb(NO_3)_2$), chromium nitrate ($Cr(NO_3)_3$) and cadmium nitrate ($Cd(NO_3)_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Deionized water was used by in all experiments.

2.2. Fabrication of GO-IPDI membrane

Graphene oxide (GO) was prepared by modified method as described in previous papers [28]. Then, the obtained graphene oxide powder was obtained by freeze drying for 24 h at −50 °C. Typically, 10 mg the GO powder was dispersed in 50 ml of DMF under ultrasonic condition for 20 min. IPDI with 1 mmol was slowly added into the GO suspension with vigorous stirring for 24 h at 80 °C to prepare GO-IPDI suspension. The composite graphene oxide-framework membranes were prepared through PVDF microfilter membrane (48 mm in diameter, 0.22 μm pore size) by vacuum filtration method. After an hour vacuum filtration in the GO-IPDI suspension, crosslinked graphene oxide (GO) sheets were deposited onto the surface of microfiltration membrane to form a uniform coating. The continuous GO-IPDI membrane was obtained, but the membranes still remained wet. A certain amount of NMP was used to continue filtration to removal of non-reactive IPDI with subsequent GO-IPDI membrane being dried at room temperature for 48 h. The thickness of the membranes was adjusted by tuning the volume of GO-IPDI suspension to be filtrated. Preparation process and digital photo were shown in Fig. 1. Before and after filtration, the GO and GO-IPDI membranes were shaken in water for 48 h to investigate the membranes stability.

2.3. Evaluation of separation performance

The evaluation of membrane separation performance was carried out by a self-designed dead-end filtration cell at 25 °C (Fig. S1, Supporting Information). The effective area of a membrane sample was 12.56 cm^2. The trans-membrane pressure (P) was set by nitrogen pressurization of the cell (in the range of 1–6 bar). The water flux J ($L\,m^{-2}\,h^{-1}\,bar^{-1}$) was measured by collecting the permeate water (V) through the membrane using an electronic balance and calculated using the following equation:

$$J = \frac{V}{A \times t \times P}$$