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Shielding membrane surface carboxyl groups by covalent-binding graphene oxide to improve anti-fouling property and the simultaneous promotion of flux

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ABSTRACT

Graphene oxide (GO) is an excellent material for membrane surface modification. However, little is known about how and to what extent surface functional groups change after GO modification influence membrane anti-fouling properties. Carboxyl is an inherent functional group on polyamide or other similar membranes. Multivalent cations in wastewater secondary effluent can bridge with carboxyls on membrane surfaces and organic foulants, resulting in serious membrane fouling. In this study, carboxyls of a polydopamine (pDA)/1,3,5-benzenetricarbonyl trichloride (TMC) active layer are shielded by covalently-bound GO. The process is mediated by *N*-(3-dimethylaminopropyl)-N'-ethylcarbodiimide (EDC)/N-hydroxysuccinimide (NHS). For GO containing low quantities of carboxyls, X-ray photoelectron spectroscopy (XPS) and zeta potential analyzer test results reveal that the carboxyl density decreased by 52.3% compare to the pDA/TMC membrane after GO modification. Fouling experiments shows that the flux only slightly declines in the GO functionalized membrane (19.0%), compared with the pDA/TMC membrane (36.0%) after fouling. In addition, during GO modification process the pDA/TMC active layer also become harder and thinner with the aid of EDC/NHS. So the pure water permeability increases from 56.3 ± 18.2 to 103.7 ± 12.0 LMH/MPa. Our results provide new insights for membrane modification work in water treatment and other related fields.

1. Introduction

Membrane fouling limits the more widespread applications of nanofiltration (NF) or precise ultrafiltration (UF) membranes in water or wastewater treatment (Zhao and Yu, 2014). The membrane fouling caused by organic foulants in wastewater secondary effluent and some natural water is a difficult problem (Hong and Elimelech, 1997). For membranes surface with much carboxyls, the fouling process can be greatly enhanced by low concentrations of Ca^{2+} or other multivalent cations, because these cations can effectively coordinate with the carboxyls on the membrane surface and organic foulants (Mo et al. 2011, 2012). As Ca^{2+} or other multivalent cations widely coexist with organic foulants in actual wastewater (Lu et al., 2013), reducing the carboxyls density on membrane surface can be a feasible choice to control this type of membrane fouling.

Carboxyl is an inherent group on polyamide (PA) membranes or other similar membranes, which can originate from the hydrolysis of unreacted acyl chloride groups during active layer preparation (Mo et al., 2012). Carboxyls can be the source of fixed charges in the membrane active layer after partial hydrolysis (Childress and Elimelech, 2000, 1996), and fixed charges have an important influence on the rejection efficiency of nanofiltration (NF) or similar precise ultrafiltration (UF) membranes (Szymczyk and Fievet, 2005). Above all, during the active layer formation, the excess numbers of acyl chloride groups may be favorable to the formation of three-dimensional active layer structures. The experiment

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described in previous work revealed the density of carboxyl groups could be decreased by selecting monomers with fewer acyl chloride groups to form the polyamide layer (Mo et al., 2012). But this method may also have an influence on the membrane divalent ion separation efficiency and flux (Mo et al., 2012). In addition, surface carboxyl groups can also be used for surface modification (Jie et al., 2015; Li et al., 2016; Yu et al., 2016).

Membrane active layer modification can improve membrane anti-fouling properties. The existing modification methods mainly include surface coating, surface grafting, incorporation of hydrophilic monomers/inorganic particles and zwitterionic modification (Zhao and Yu, 2014). However, in some cases, membrane flux, rejection efficiency, robustness and anti-fouling properties are mutually exclusive. Therefore, membrane modification methods may influence the water permeability (Lu et al., 2013; Van Wagner et al., 2011; Liu et al., 2015), surface roughness (Van Wagner et al., 2011), or rejection efficiency (An et al., 2011; Ye et al., 2015). Materials possessing better characteristics may help to handle these problems better.

Graphene oxide (GO) is an excellent material for membrane modification (Hegab and Zou, 2015). Water can nearly unimpeded permeated though graphene two-dimensional nanocapillaries (Nair et al., 2012). GO has other unique qualities, including ultrahigh strength (Lee et al., 2008), atomic-scale thickness (Novoselov et al., 2004), high antibacterial property and low cytotoxicity (Hu et al., 2010; Tu et al., 2013), and the possibility of producing ultraflat surface (Lui et al., 2009). It also possesses good chemical stability (Dreyer et al., 2010) and hydrophilic properties (Nair et al., 2012; Dreyer et al., 2010), and can be prepared from inexpensive graphite (Hu et al., 2010; Hummers and Offeman, 1958). Furthermore, there are abundant oxygen-containing functional groups on GO available for membrane modification. Several membrane surface modification reports have been published that use GO to improve flux (Chae et al., 2015; Berean et al., 2015), increase antibiofouling properties (Hegab et al., 2015; Perreault et al., 2014; Zou et al., 2016) and enhance chlorine resistance properties (Choi et al., 2013). Previous studies also found that after surface modification by GO, the membrane anti-fouling properties to the protein, alginate or humic acid foulants were obviously improved (Hegab et al., 2015; Choi et al., 2013; Hu et al., 2016; Han et al., 2015). And the improvement of fouling resistance was attributed to hydrophilicity increase and surface roughness reducing (Hegab et al., 2015; Choi et al., 2013; Hu et al., 2016; Han et al., 2015). Even though GO have demonstrated effective adsorption performance (Perreault et al., 2015), it was explained that the organic foulants were adsorbed mainly on the basal plane of GO nanosheets while water enters in the GO modified membrane surface primarily around the oxidized edges of GO nanosheets (Hu et al., 2016). However, to the best of the authors' knowledge, there is little report on whether membrane surface functional groups change after GO surface modification influence membrane anti-fouling properties or not. A better understanding of these processes will help to the development of GO surface modification applications. Carboxyl group are present in low quantities at the periphery of moderately oxidized GO (Nair et al., 2012; Dreyer et al., 2010; Perreault et al., 2014). Here, we hypothesize that by covering carboxyls on the membrane active layer surface with GO nanosheets, Ca^{2+} bridged fouling could be significantly mitigated, whereas the rejection efficiency would not be affected because the volume charge density is maintained by protecting the carboxyls in the active layer using GO.

Novel polydopamine (pDA)/1,3,5-benzenetricarbonyl trichloride (TMC) composite membranes have the enormous potential for application in wastewater treatment and other fields (Zhao et al., 2014) because of their excellent structural and chemical stability (especially their chlorine resistance properties (Zhao et al., 2014)). Dopamine can be easily self-deposited on nearly all types of inorganic and organic substrates with controllable thickness (Hu and Mi, 2013), and pDA has excellent durability (Liu et al., 2014). The amino and hydroxyl groups on the polydopamine can react with acyl chloride groups of TMC and other similar compounds to form amide bonds and ester bonds, constituting the active layer (Zhao et al., 2014; Hu and Mi, 2013; Liu et al., 2014). Thus, the pDA/TMC composite membrane is a good candidate membrane to investigate the relationship of how the surface carboxyl groups change affect the anti-fouling properties after surface modification by GO. As the pDA/TMC active layer could be low in roughness, high in hydrophilic properties (Zhao et al., 2014) the influence of these two aspects can be excluded easier. In addition, the controllable auto-polymerized membrane avoids uncontrolled errors during manually scraping membrane (Mo et al., 2012).

N-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide (EDC)/N-hydroxysuccinimide (NHS) can be used to convert the native carboxyl groups of the polyamide surface into intermediate amine-reactive esters to covalently-bind GO or carbon nanotubes to membrane surface (Perreault et al., 2014; Tiraferri et al., 2011). EDC/NHS is also widely used to catalyze amide-crosslinks between carboxyl groups and amino groups (Wissink et al., 2001; Peng et al., 2013; Staros et al., 1986). The decline of membrane flux during the early stage of filtration is significantly affected by membrane compaction (Petersen, 1993). Thin-film composite (TFC) membrane compaction can occur in both the supporting layer and active layer. As the flux of the TFC membranes is controlled by the active layer (Petersen, 1993), Hussain et al. stated that the surface pore collapse may be the key mechanism for membrane compaction (Hussain et al., 2013). If EDC/NHS can enhance the amide-crosslinks between carboxyl groups and amino groups of pDA/TMC active layer, and suppress the surface pore collapse, the membrane flux can be promoted.

In this study, we use an environmentally friendly method to covalently-bind GO to the surface of pDA/TMC active layer, by EDC/NHS mediated interfacial polymerization to shield, but not remove, the carboxyls in the membrane active layer. We aim to simultaneously promote the anti-fouling property and flux, and maintain the membrane rejection efficiency.

2. Material and methods

2.1. GO preparation

GO was prepared from flaky graphite using the Hummers' method (Hummers and Offeman, 1958; Marcano et al., 2010). The high-temperature oxidation process at 98 °C was shortened to obtain moderately oxidized graphite oxide. The graphite oxide was washed using ultrapure water (Milli-Q) until the pH of the supernatant stabilized. Ultrasonic exfoliation (40 kHz, 100 W, Kun Shan Ultrasonic Instruments, China) of the GO nanosheets was performed in an ice bath for 1 h. The prepared GO solution was stored at 4 °C. Prior to use, the stock solution of GO was indirectly ultrasonicated for 10 min and diluted to the required concentration. The details of GO characterization methods and results (Figs. S1–S7) are listed in the Supplementary Information section.

2.2. Brief description of membrane fabrication

A new method was developed to prepare the GO functionalized pDA/TMC TFC membranes (Fig. 1). The main reactions and detailed description of the TFC membrane fabrication are provided in the Supplementary Information section. Briefly, a poly(vinylidene fluoride) (PVDF) microfiltration membrane (Shanghai SINAP Membrane Tech, Shanghai, China) with an average surface pore diameter of 80 nm was used as supporting membrane. The pDA/