Desalination 385 (2016) 126–137

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Effective in-situ chemical surface modification of forward osmosis membranes with polydopamine-induced graphene oxide for biofouling mitigation

Hanaa M. Hegab [a,b], Ahmed ElMekawy [c,d], Thomas G. Barclay [e], Andrew Michelmore [e], Linda Zou [a,f], Christopher P. Saint [a], Milena Ginic-Markovic [e,*]

[a] Natural & Built Environments Research Centre, University of South Australia, Adelaide, SA 5095, Australia
[b] Institute of Advanced Technology and New Materials, City of Scientific Research and Technological Applications, Borg Elarab, Alexandria, Egypt
[c] Genetic Engineering and Biotechnology Research Institute, University of Sadat City (USC), Sadat City, Egypt
[d] School of Chemical Engineering, University of Adelaide, Adelaide, Australia
[e] Future Industries Institute, University of South Australia, Adelaide, SA 5095, Australia
[f] Department of Chemical and Environmental Engineering, Masdar Institute of Science and Technology, Abu Dhabi, United Arab Emirates

HIGHLIGHTS

- The performance of in-situ surface modified forward osmosis membrane was optimized.
- Polydopamine induced graphene oxide (GO-pDA) was utilized as a modifier coating.
- GO-pDA modified membrane enhanced water flux and selectivity compared to pristine.
- The superior modified membrane showed remarkable bactericidal properties.

ARTICLE INFO

Article history:
Received 12 October 2015
Received in revised form 10 February 2016
Accepted 12 February 2016
Available online 20 February 2016

Keywords:
Graphene oxide
Forward osmosis
Membrane surface modification
Biofouling
Taguchi method

ABSTRACT

The superior biocidal properties of graphene oxide (GO) nanosheets have enabled their recent application in novel antifouling coatings for membrane filtration. Nevertheless, a practical method for attaching the GO nanosheets to the membrane surface remains a big challenge. This work presents a new methodology for achieving an optimized process for incorporating GO nanosheets onto the surface of thin-film composite (TFC) FO membranes using the bioadhesive polydopamine (pDA). The pDA deposition occurs through self-assembly and oxidative polymerization, both reducing the GO nanosheets and immobilizing them onto the membrane surface. Taguchi's statistical experimental design was used to optimize the process conditions to satisfy the simultaneous enhancement of water flux, reverse solute flux selectivity and antibiofouling performance. Compared to an unmodified membrane the optimum membrane modification both improved pure water flux (21.5%) and reverse solute flux selectivity (80%) and greatly extended the onset of biofouling due to remarkable bactericidal properties. The superior performance of GO-pDA modified membrane in all aspects illustrates its strong potential for application to industrial FO membranes.

1. Introduction

Forward osmosis membrane-based water separation technologies have extraordinary potential to sustainably secure drinking and agricultural water resources with low energy consumption [1–4]. Polyamide thin-film composite (PA TFC) membranes are favoured in FO technology [1,5] due to having superior performance compared to cellulose acetate membranes [5,6]. Nevertheless, the inherent physicochemical surface properties of the PA TFC membranes make biofouling a significant issue [7,8] and FO PA TFC performance in terms of water flux (Jw) and reverse solute flux (Js) still needs optimization when compared to the performance of PA TFC membranes used in reverse osmosis [9].

An innovative approach in the efforts to improve membrane performance is the use of nanomaterials [10–12]. Graphene oxide (GO)-based nanomaterials are decorated with epoxide, hydroxyl and carboxyl functional groups and so provide outstanding potential to make functionalized-nanocomposite materials. Further, the characteristics of GO nanosheets can be used both to increase membrane surface hydrophilicity and provide antibiofouling properties. Consequently GO

* Corresponding author.
E-mail address: milena.ginic-markovic@unisa.edu.au (M. Ginic-Markovic).

http://dx.doi.org/10.1016/j.desal.2016.02.021
0011-9164/

nanosheets have recently featured in many researchers' efforts to tailor membrane surface properties without hindering their vital transport parameters [13–16].

Despite some successes in the use of GO nanosheets to improve the properties of filtration membranes, a practical method for attaching the GO nanosheets to the membrane surface remains a challenge. GO nanosheets have been attached to the membrane surface through three different approaches. The first one is to chemically modify the PA (TFC) membrane such that a covalent bond to the GO nanosheets can be made [17]. In the second approach, GO nanosheets are non-covalently attached to the membrane surface through a layer-by-layer self-assembly (LbL-SA) technique [18]. The third method is to apply GO nanosheets with an adhesive polymer in a one pot reaction [16,19]. The covalent attachment and LbL-SA both suffer from the complexity of multiple steps, making these processes industrially unfavourable compared to a single pot technique.

The aggregation of dopamine (DA) under gentle, aqueous conditions results in the spontaneous deposition of durable, flexible, nanoscale, hydrophilic coatings on almost any surface, which is readily further chemically modified [20–24]. As such, polydopamine (pDA) can be used as a versatile adhesive agent to bind functional substances to materials that may not be easy to modify through other methods using a single pot approach. The deposition of DA commences with the oxidation of the catechol group to quinone under mildly alkaline conditions followed by a range of possible cyclisation, rearrangement and further oxidation reactions before incorporation of adjacent quinone and catechol groups to two semiquinone radical groups. The free radicals can combine, resulting in covalent coupling reactions between adjacent aromatic nuclei [25,26]. The covalent coupling combined with self-assembly through hydrogen bonding and π–π stacking results in a chemically heterogeneous coating that has yet to be fully structurally resolved, but has clear similarities to natural melanin [27]. The result is that the macromolecular structure of pDA stabilizes otherwise unstable redox forms of the monomer catechol groups (semiquinone and quinone) [26]. This allows pDA to not only securely attach GO nanosheets to the surface, but also to act as a reductant of the GO surface chemistry. Further, several studies have revealed a positive impact of pDA coatings applied to water treatment membranes, improving both water flux and fouling resistance [20,28–31].

A number of factors influence the optimization of the membrane coating for improved filtration performance. Coating variables such as the GO nanosheet content and DA deposition time are key, as is the draw solution concentration in the filtration experiment. Within the context of statistical design of experiments, numerous experiments are required to optimize surface modification conditions using factorial designs, which can be discouraging for many researchers. Unlike factorial designs, the Taguchi experimental design is a practical method that reduces the number of required experiments for detecting the influence of potential combinations of all factors [32].

In this study we demonstrate the utilization of oxygenated, aqueous deposition of DA to immobilize the GO nanosheets onto the membrane surface. The coating conditions and draw solution concentration were optimized based on Taguchi's statistical experimental design and the resultant membranes were analysed for surface chemistry, roughness, morphology, surface charge, hydrophilicity and antibacterial properties.

2. Experimental

2.1. Materials

Nitric acid (70%), sulphuric acid (98%), hydrochloric acid (30%), acetic acid (99.7%), $KMnO_4$ powder, H_2O_2 (30%), DA-HCl, Tris–HCl, sodium hydroxide and potassium chloride were purchased from Sigma-Aldrich™. Graphite powder SP-1, size <20 μm was purchased from Bay Carbon™ (USA). Flat sheets TFC FO membrane (HTI, OsMem™ TFC Membrane, USA-first generation) were used throughout this study. Analytical grade sodium chloride was obtained from Ajax Finechem Pty Ltd. (Australia). Sodium acetate, sodium nitrate, sodium dihydrogen phosphate were procured from Merck (Australia), Ajax Chemical Ltd. (Australia) and May and Baker Ltd. (England), respectively. MilliQ water (18.2 MΩ) from ultrapure water purification system (Millipore, Synergy®) was used throughout this study.

2.2. Experimental design and statistical analysis

In this study an experimental matrix following Taguchi design was generated, including three main factors (GO nanosheets content, DA deposition time and draw solution concentration) with three different levels [33]. The L_9 orthogonal array was employed to examine the effects of the three independent factors on membrane performance properties, including water flux and reverse solute flux as dependent variables. The results were analysed by calculating the signal-to-noise ratio (S/N), where S refers to the standard deviation of the parameters' response per experiment and N is the entire number of experiments within the orthogonal array. Also, analysis of variance (ANOVA) was applied to highlight the significance of selected factors and determine the optimum level of each. Minitab software v.17 was used for optimizing and analysing the obtained results. The different experimental values of the selected levels for the independent factors, along with their different experimental combinations, are provided in Table 1. By using this experimental design the number of experiments was reduced to 9 sets instead of 27 ($3 \times 3 \times 3$ for full factorial design). The nine experiments were repeated in triplicate under similar experimental conditions. In order to obtain the optimum performance of the modified membranes, the quality characteristic of "smaller the better" (S/N_S) and "larger the better" (S/N_L) in S/N ratio analysis was chosen for the optimization of reverse solute flux (Js) and water flux (Jw), respectively, as defined according to Eqs. (1) and (2) [34,35].

$$S/Ns = -10\log\left(\frac{\sum_{i=1}^{n}(y_i^2)}{n}\right) \quad (1)$$

$$S/N_L = -10\log\left(\frac{\sum_{i}^{n}\left(\frac{1}{y_i^2}\right)}{n}\right) \quad (2)$$

where n is the number of experiments and y_i is the response of each experiment.

2.3. GO synthesis and in-situ chemical surface modification of membranes

In this study, GO nanosheets were prepared using modified Hummers chemical exfoliation method of graphite. The details of this preparation method were mentioned in our previous study [19] and the basic modification steps are schematically captured in Fig. 1. To modify the FO membrane surface, the membranes were soaked in deionized water for at least

Table 1
Taguchi L_9 orthogonal array.

Run	Operating parameters (independent factors)		
	GO conc (μg/mL)	DA deposition time (min)	Draw solution conc (M)
1	40	15	1
2	40	30	1.5
3	40	45	2
4	80	15	1.5
5	80	30	2
6	80	45	1
7	120	15	2
8	120	30	1
9	120	45	1.5