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Surface initiated polydopamine grafted poly([2-(methacryoyloxy) ethyl]trimethylammonium chloride) coatings to produce reverse osmosis desalination membranes with anti-biofouling properties

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ABSTRACT

Commercial polyamide (PA) reverse osmosis (RO) membranes were surface modified in a sequential two-step polymerization process to impart anti-biofouling properties to the membrane surface. In the first step, a 2-bromoisobutyryl bromide initiator-polydopamine (BiBBr-initiator-PDA) layer was deposited onto the membrane surface from a Tris(hydroxymethyl)aminomethane buffered solution of dopamine hydrochloride and 2-bromoisobutyryl bromide at ambient conditions. In the second step, polymer chains of [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MTAC) were grafted-from the BiBBr-initiator-PDA surface using activators regeneration by electron transfer-atom transfer radical polymerization for between 1 and 24 h. The modified surfaces were characterized using attenuated reflectance-Fourier transform infrared spectroscopy and water contact angle and their pure water flux, saline water flux and ability to reject salt were determined. Results showed that the water flux and salt rejection properties of the PDA-g-PMTAC modified membranes were similar to the unmodified PA RO membranes. Chlorine resistance tests showed the coating had enhanced stability in regards to salt rejection properties. Significantly, after six days of incubation in nutrient solution there was 93.2% less bacteria on the PDA-g-MTAC modified PA RO membranes, compared to the unmodified membranes.

1. Introduction

One of the major challenges affecting the desalination of seawater for the production of drinking water is biofouling of reverse osmosis (RO) membranes [1–5]. Many strategies exist to reduce biofouling and often revolve around surface modification of the membrane to introduce anti-bacterial and anti-fouling properties [6]. Surface modification can be achieved in a variety of ways and on a variety of water treatment membranes including RO, microfiltration (MF), nanofiltration (NF) and ultrafiltration (UF) [7]. These modifications include coating a membrane [8,9], blending components to make a membrane [10–12], making a composite membrane [13,14], chemical modification of a membrane [15,16], grafting onto a membrane (chemical initiation [17,18], photo-initiation [19–21], plasma initiation [22–24] and enzymatic initiation [25]) or a combination of any of these methods [26–28].

One of the more common surface modification methods for reducing biofouling involves the introduction of polymeric coatings in order to increase the anti-microbial and anti-adhesion properties of the surface [29]. The initial adhesion of bacteria to a surface has been identified as one of the crucial stages in the formation of the biofilm, as once attached they modify the surface chemistry of the membrane, effectively ensuring that their attachment is unable to be reversed [5]. Matin et al. [5] have copolymerized hydroxethyl methacrylate (HEMA) and perfluorodecyl acrylae (PFDA) onto thin film composite high-rejection (TFC-HR) commercial RO membranes using a chemical vapour deposition technique. A surface coating of approximately 40% PFDA was shown to decrease *Escherichia coli* adhesion by greater than 95% on the membrane surface [5].

The incorporation of silver nanoparticles with anti-fouling polymer brushes has also been shown to reduce biofouling [30]. Rahaman et al. [30] coated commercial TFC RO membranes with alternating layers of poly(acrylic acid) (PAA) and poly(ethyleneimide) (PEI) coated silver (Ag) nanoparticles, followed by grafting with poly(sulfobetaine) or poly(dimethylsiloxane). Membranes coated with PAA/Ag-PEI showed a significant increase in anti-bacterial effect, with up to 95% of bacteria killed after contact with the modified membrane after 1 h [30]. Salt rejection properties were shown to increase, along with a slight increase in water permeance [30].

A potentially interesting way of modifying membranes is the use of polydopamine (PDA) [29,31–34]. Lee et al. were the first to report a method to dip coat objects in solutions of dopamine and

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tris(hydroxymethyl)aminomethane (tris) buffer. This resulted in the formation of thin films of PDA on surfaces including noble metals, metals with native oxide, oxides, semiconductors, ceramics and many types of synthetic polymers [35]. Atomic force microscopy (AFM) measurements showed that the film thickness could be controlled by the dipping period, with a thickness of 50 nm obtained after 24 h [35].

At present the mechanism of PDA polymerization is not well understood and this is also true of its attachment mechanism to surfaces. It has been suggested that polymerization involves the oxidation of the dihydroxybenzene (catechol) group of dopamine to quinone groups, followed by polymerization in a process similar to the formation of melanin [35]. In contrast, Dreyer et al. [36] have suggested that instead of considering PDA as a covalent polymer, it should rather be considered as a supramolecular aggregate of monomers (consisting of 5,6-dihydroxy indoline and its dione derivatives) which are comprised of intra- and inter-chain non-covalent interactions linked together via a mixture of charge transfer, π-stacking and hydrogen bonding interactions. They further suggested that it was these interactions which led to the high stability and insolubility of the formed PDA coating. More recently, Della Vecchia et al. [37] have proposed that PDA was a mixture of uncyclized catecholamine/quinine groups, cyclized 5,6-dihydroxyindole groups and previously unreported pyroolecarboxylic acid groups where the monomer units are linked through various binding mechanisms.

Despite the poorly understood mechanism of PDA formation studies have shown that deposition of PDA onto membrane surfaces used in water treatment can improve water flux and increase fouling resistance of the membranes [29,31–34]. Liu et al. [34] modified polyester filter cloth surfaces with PDA and found a maximum anti-fouling performance with a dopamine concentration of 1.5 g/L and a coating time of 24 h [34]. Using a yeast suspension, water flux through the modified membrane was shown to be 142.7% better than unmodified membranes [34]. Comprehensive work by Freeman et al. [31–33] deposited PDA onto RO, NF, UF and MF membranes and observed retention of the water flux and an increase in anti-fouling using an oil/water emulsion [31]. They were also able to modify membrane modules rather than just flat sheet membranes, showing that the coating could be successfully scaled up and still reduce fouling [31]. Further studies led to the grafting of poly(ethylene glycol) (PEG) onto PDA modified flat sheet membrane and to graft Jeffamine® M-1000 polyetheramine onto the PDA modified membrane from the modules, further improving the fouling resistance of the MF membranes [31]. PDA deposition onto RO membranes (XLE, Dow Water and Process Solutions) showed that water flux and adhesion of bovine serum albumin (BSA) decreased with increasing deposition times [32,33]. Furthermore, the water flux continued to substantially decrease after the PDA coated surface was modified with PEG [33]. More recently, Karkhanechi et al. [29] deposited PDA (1.5–24 h) onto ES20 Nitto Denko (Osaka, Japan) commercial RO membranes. Deposition was confirmed by a colour change on the membrane surface and by X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy and field emission-scanning electron microscopy (FE-SEM) [29]. Little change in surface hydrophillicity was observed (air contact angle), while salt rejection was found to be maintained and there was a small decrease in pure water flux [29]. Using a bacterial suspension (*Pseudomonas putida*) as the feed solution they showed an increase in the flux for the modified membranes (retained 80% of initial flux after 1200 min filtration) in comparison to the unmodified membranes (retained 61% of initial flux after 1200 min filtration) [29]. FE-SEM imaging of both modified and unmodified membrane surfaces clearly showed no bacteria present on the PDA modified membrane but the formation of a biofilm on the unmodified membranes [29].

For further post-polymerization of PDA, Zhu and Edmondson [38] have synthesized a surface which was amenable to surface initiated polymerization (SIP). They reacted dopamine hydrochloride with 2-bromoisobutyryl bromide (BiBBr) (a polymerization initiator) onto a variety of surfaces [38]. Interestingly, this new monomer was shown to polymerize at a rate equivalent to that of unmodified dopamine (45 nm layer of BiBBr-initiator-PDA in 24 h) [38]. They then used activators regenerated by electron transfer – atom transfer radical polymerization (ARGET-ATRP) (first reported by Matyjaszewski et al. [39]) to grow chains of poly(methyl methacrylate) PMMA and poly(2-hydroxyethyl methacrylate) PHEMA from the BiBBr-initiator modified PDA surface [38]. ARGET-ATRP offers several advantages over traditional ATRP, particularly when used in an industrial setting. ARGET-ATRP uses smaller amounts of copper catalyst (reducing cost to industry) which is constantly reformed in the presence of excess reducing agent, allowing the reaction to take place in the presence of oxygen, and thus be more industrially friendly.

In this work we modify RO membrane surfaces with a BiBBr-initiator-PDA layer then polymerize an anti-microbial agent [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MTAC), using ARGET-ATRP from the surface. The anti-microbial properties of MTAC have been known for quite some time [40] and have been exploited by many researchers in order to introduce anti-fouling and anti-biofouling characteristics to materials [6,41–45]. It is thought that the improvement in anti-fouling properties comes largely from the positively charged groups which will be imparted on the membrane surface [44]. The positive charge is thought to act as a contact killer [44]. Zhou et al. [41,42] employed photo-induced grafting of PMTAC onto poly(ethersulfone) (PES) membranes. They were able to reduce the presence of natural organic matter on the membranes significantly, although exposure to BSA resulted in significant fouling to the surface [41]. Fouling resistance was also shown towards immunoglobulin G [42]. Hilal et al. [46] modified PES membranes using a photoinduced (benzophenone initiated) grafting technique with either poly-(2-acrylamido-2-methyl-1-propsanesulfonic acid) (PAMPSA) or PMTAC. AFM using a colloid probe microscope showed that the force of adhesion was much lower on a membrane modified with PMTAC (510 μg/cm^3), suggesting surfaces modified with this polymer will be useful as a non-biofouling membrane [46]. Hilal et al. [47] were also able to produce a PMTAC coating on PVDF membranes, again showing excellent anti-biofouling properties towards *E. coli*. The anti-microbial action towards *E. coli* was proposed to be due to the penetration of the polymeric polycationic chain into the bacteria cell wall [47]. Kochkodan et al. [6] also used photochemical modification to modify poly(vinylidene fluoride) (PVDF) and polysulfone membranes with PMTAC as well as PAMPSA and PHEMA. Looking in particular at *E. coli*, it was observed that approximately 240 *E. coli* colonies formed on an unmodified membrane, compared to only 32 on a membrane grafted with 220 μg/cm^2 PMTAC [6]. Only single colonies were found on membranes grafted with 530 μg/cm^2 and 720 μg/cm^2 PMTAC [6]. Anti-microbial properties towards *E. coli* were not observed for PHEMA or PAMPSA modified membranes [6].

In this paper we present for the first time a method to modify the surface of commercially available TFC PA RO membranes with PMTAC in order to reduce biofouling. Initially the commercial membrane was modified to introduce an adhesive BiBBr-initiator-PDA layer onto the surface. This was then followed by surface initiated ARGET-ATRP of the anti-microbial monomer MTAC onto the BiBBr-initiator-PDA modified membrane surface. Results showed that the PMTAC modified TFC PA RO membranes had an increased resistance to biofouling compared to unmodified membranes, whilst still retaining water permeance and salt rejection properties.