An investigation of low biofouling copper-charged membranes for desalination

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HIGHLIGHTS

- Modification of cellulose acetate membrane surfaces by charging with copper ions
- Chemical and morphological characterization of copper-charged membranes
- Copper-charged membranes displayed low biofouling tendencies.

ARTICLE INFO

ABSTRACT

The goal of this project was to develop low-biofouling membranes through the functionalization of cellulose acetate (CA) membranes with metal chelating ligands charged with biocidal metal ions, i.e. copper ions. To this end, glycidyl methacrylate (GMA),[1] an epoxy, was used to attach a chelating agent, iminodiacetic acid (IDA),[2] to facilitate the charging of copper to the membrane surface. CA and copper charged membranes were characterized chemically and structurally. The permeation experiments were conducted with DI water and then subjected to protein rejection measurements. The permeation of the copper-charged membranes was initially lower than the cellulose acetate membrane during the filtration of DI water. The membranes were then subjected to bovine serum albumin (BSA) and lipase filtration. The copper charged membrane showed higher permeation values of both proteins as compared to CA membranes. This resulted from an increased resistance from the IDA and copper on the surface during DI water filtration, and later, from reduced fouling from both proteins. The rejection of BSA and lipase was the same for both the copper charged and CA membranes. Therefore, the modified membranes have a potential to be used as low-biofouling membranes in the future.

1. Introduction

In an era of raising water scarcity, water purification through membrane separations has gained significant attention, but the performance of these membranes is severely degraded due to fouling. During the purification of source waters such as brackish water, sea water and waste water, materials that are rejected by the membrane may accumulate on the surface of the membrane as layers of cake to foul it [1]. Fouling is detrimental to the membrane performance by increasing the pressure drop leading to membrane flux decline, increasing cleaning frequency, and reducing membrane life span; thus, increasing the cost of operation [38]. In order to regain the original flux of the membranes, the cake layer can be partly removed by backwashing, by rinsing the membranes, or by pretreating the feed water with chemicals [29]. Fouling can be categorized into organic matter, colloidal and microbial depending on the nature of foulants. The former two can be controlled via pretreatment; however, the accumulation of microorganisms is more problematic to membranes. Biofouling is the accumulation and growth of microorganisms on the surface of membranes and on feed spacers [19]. After attachment, microorganisms excrete extracellular polymeric substances (EPS), which form a matrix around the organism's outer surface as biofilm [21]. These biofilms keep growing at the expense of nutrients available in the feed water and form microbial aggregates [30]. Subsequently, these microbial aggregates and individual microorganisms adhere to the membrane surface [14]. This microbial adhesion is often reversible initially but becomes irreversible in time through excretion extra-cellular polymeric substances (EPS), which adsorb to the membrane surface causing biofouling [5]. As a result of biofouling, greater pressure is required to produce the same amount of water.

Biofouling is difficult to control by physical means of pretreatment, such as coagulation, flocculation, sand filtration, ultrafiltration and cartridge filtration [4], because even if 99.9% of the microorganisms are removed, the remaining that enters into the system may keep growing at
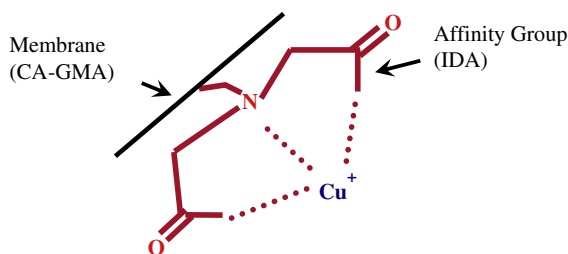
Fig. 1. Chelated copper ions by metal–ligand IDA onto the blended GMA.

Table 1
Neutral solutes used for pore size distribution analysis.

Solute	Mw (g/mol)	Stokes radii (nm)
Glycerol	92.09	0.26
Glucose	180.16	0.37
Sucrose	342.3	0.47
Raffinose	504.42	0.58
PEG 600	600	0.61
PEG 1000	1000	0.80
PEG 2000	2000	1.14
PEG 4600	4600	1.75
PEG 8000	8000	2.31
Dextran 10	10,000	2.30
Dextran 40	40,000	4.50
Dextran 70	70,000	6.00

the expense of the nutrients available in the feed water [30]. Chemical pretreatment of nanofiltration (NF) and/or reverse osmosis (RO) membrane units are also shown to be unsuccessful in completely removing and/or completely destroying the complex multicellular structures [12]. Chlorine-containing substances are notorious for chemical corrosion of RO membranes and can also form toxic disinfectant byproducts [24]. Therefore, chemicals required to control fouling increase system complexity and cost, and reduce system reliability; thus, making NF/RO simply useless and unreliable especially for small systems. Therefore, antimicrobial membranes have the potential to be easier and more reliable.

Various polymeric membranes are commercially available for water separation processes and are made of several polymers ranging from hydrophilic cellulose acetate (CA) to highly hydrophobic polymers, such as polyethylene (PE) and polypropylene (PP) [15]. Asymmetric CA membranes were first developed by Loeb and Sourirajan [41] for the desalination of water. Since CA membranes are hydrophilic and have an isoelectric point of 3.5, causing a slightly negative surface charge, they foul less [27]. CA membranes have high affinity to water [22], low protein adsorption [31], good mechanical strength and low cost. On the other hand, the higher hydrophilicity of CA membranes, caused by hydroxyl groups that can form hydrogen bonds in presence of water to make the membrane prone to hydrolysis, limits the operating pH range (low pH 3 to 5 and high pH 6 to 8, depending on the manufacturers [16]. At higher temperatures, CA membranes are susceptible to hydrolysis and have very low rejections for lower molecular weight contaminants. Because of this property change on heating, CA membranes are limited to operating temperatures below 35 °C [3]. Cellulose triacetate membranes were developed

with improved temperature resistance, salt rejections and microbial resistance [8]. However, they have lower permeability than cellulose acetate membranes due to the replacement of hydrophilic hydroxyl groups with acetyl groups [16]. Cellulose acetate and cellulose triacetate blends benefit from the characteristics of both these membranes. CA membranes have very low resistance to chlorine causing biodegradation and shortening of the membrane life span [8].

Surface modification of polymeric membranes has gained significant attention to develop new polymeric membranes with enhanced flux, salt rejections and reduced fouling by natural organic matter and biofouling by microorganisms [45]. The key techniques for polymer modifications are blending, grafting, crosslinking and composite formation. Blending of polymers provides a means of producing new materials to modify pore structure and binding sites [42]. Membranes developed by blending of graft homopolymerized glycidyl methacrylate (GMA) with hydrophilic polymers like CA which enhances the performance of the membranes; wherein the epoxide-containing GMA on CA improves the flexibility of the ligands as well as their ability to form novel materials [34]. Furthermore, GMA is a commercial material and less expensive when compared to other vinyl monomers containing epoxy rings.

This project focused on the development of a low biofouling CA–GMA membrane blend functionalized using specific metal chelating ligands for binding of copper; that is, immobilized metal affinity chromatograph (IMAC) for binding of copper ions. The IMAC system was chosen because of ease of functionalization and ability to control the
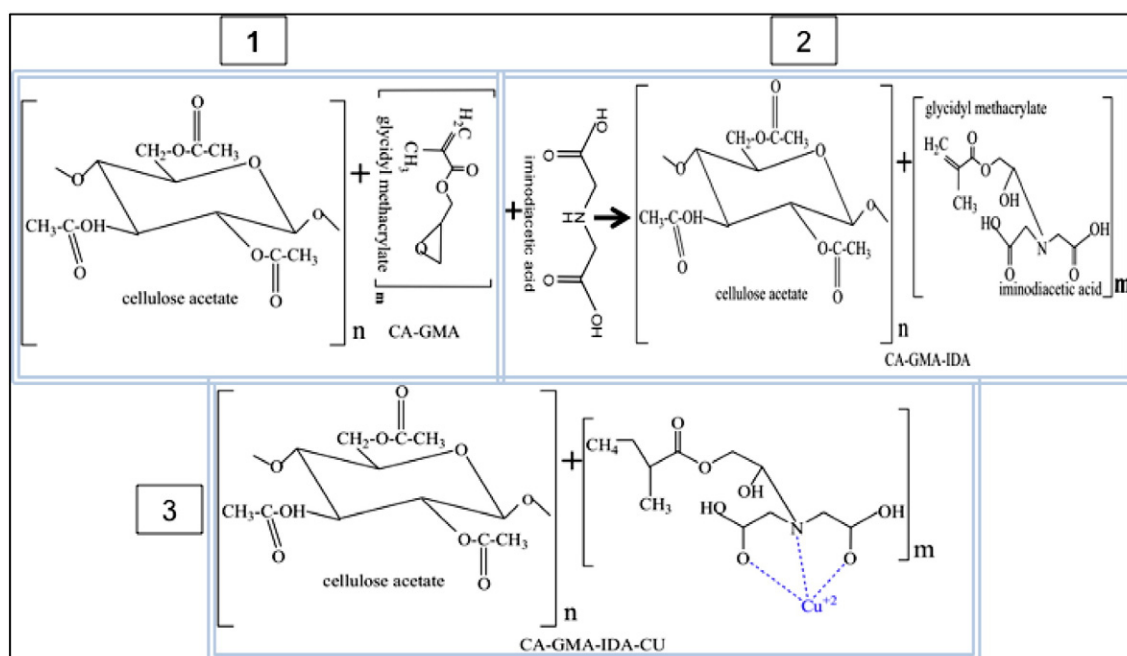

Fig. 2. Reaction scheme of the Cu(+2)–CA–GMA–IDA membranes [2].