



Research article

Humic acid removal using cellulose acetate membranes grafted with poly (methyl methacrylate) and aminated using tetraethylenepentamine

Kibrom Alebel Gebru ^b, Chandan Das ^{a,*}^a Department of Chemical Engineering, Indian Institute of Technology Guwahati, 781039, Assam, India^b Department of Chemical Engineering, College of Engineering and Technology, Adigrat University, Tigray, Ethiopia

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ABSTRACT

Graft copolymerization of cellulose acetate (CA) and poly (methyl methacrylate) (PMMA) was synthesized through free radical polymerization in the presence of cerium sulfate (CS) as initiator under nitrogen atmosphere in an aqueous solution. During the grafting reactions, the effects of polymerization time and temperature on the grafting were investigated. Furthermore, functionalization of the synthesized product was done using amine group (tetraethylenepentamine, TEPA). The results from Nuclear Magnetic Resonance (¹H NMR) spectra confirmed a successful grafting of PMMA on the CA membrane surfaces. Zeta potential (ζ), field emission scanning electron microscopy (FESEM), and atomic absorption spectrophotometer (AAS) characterization studies were done. The maximum removal efficiencies for un-grafted CA (un-g-CA), CA-g-PMMA, and CA-g-PMMA-TEPA membranes at pH of 7.0 were 34.5%, 83.3%, and 99.1%, respectively. The removal percentage results were detected to increase with increasing in the regeneration cycles. At the end of the fourth cycle, the HA removal percentages were 41.6%, 87.4%, and 99.9% for un-g-CA, CA-g-PMMA and CA-g-PMMA-TEPA membranes, respectively.

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1. Introduction

Humic acid (HA) is considered as the main component of dissolved organic matter (DOM) which can be found in both surface and ground water. It is also known that HA contaminated water shows undesirable color and has been associated in bacterial development in wastewater (Kumar et al., 2016). On the other hand, the need for elimination of HA has currently become more important due to having haloacetic acids (HAA) and trihalo-methane (THM) as by-products. Carcinogenic organic compounds which are risky to human health are developed when water contaminated with HA is treated with disinfection processes such as chlorination (Lowe and Hossain, 2008; Shao et al., 2013). Furthermore, HA has the ability to bind pesticides, heavy metals, and herbicides exist in wastewater and complexed materials with high concentrations can be developed (Ma et al., 2015; Shao et al., 2011). Therefore, the removal of HA is an important issue in water treatment. Currently membrane based HA removal process has

been getting more attention due to their operational simplicity, low energy consumption, and environmental friendly nature. Nano filtration and reverse osmosis techniques are able to remove HA effectively from contaminated water, but they require higher energy consumption when compared with ultrafiltration (UF) and microfiltration (MF) membrane processes. However, the conventional UF and MF membrane separation processes wouldn't remove the HA easily due to their larger pore sizes. Moreover, HA has been known as one of the main membrane fouling components during treatment of wastewater by means of membrane separation process. Therefore, modification of the conventional UF/MF membranes is required to achieve selective removal of HA from aqueous solutions (Bessbousse et al., 2008; Kumar et al., 2016; Shao et al., 2011). Therefore, appropriate charge modification on the neutral UF membranes could be an effective method for the removal of natural organic matter (NOM) and reduction of the membrane fouling. Moreover, electrostatic interactions are also significant to achieve higher humic acid removal and less membrane fouling (Shao et al., 2011). Zeta potential (ζ) analysis is one of the most important methods used to obtain information on the surface charge properties (Kato et al., 2003). Therefore, the ζ or electrical charge properties of the powder or film polymers impact their

* Corresponding author.

E-mail address: cdas@iitg.ac.in (C. Das).

performances towards specific applications. Recently, polysaccharides characterized by cellulose and its derivatives have fascinated a great consideration of researchers as environmental friendly materials. Cellulose acetate (CA) among the hydrophilic polymers is considered as the most important organic ester of cellulose due to its most abundance and broad applicability for the synthesis of different products because of having tough, biocompatible, hydrophilicity characteristics, and moderately less expensive (Algarra et al., 2014; Konwarh et al., 2013; Abedini et al., 2011). The drawback of cellulose acetate membranes is that it is susceptible to thermal and chemical stabilities depending on the environments and conditions of application (Arthanareeswaran et al., 2004). Therefore, modification of cellulose acetate using graft copolymerization process gives a substantial way to modify its chemical and physical properties (Shen and Huang, 2004). Recently, the modifying of polymers has received great attention and grafting is one of the promising approaches. Grafting co-polymerization is an attractive technique to introduce different functional groups to the backbone of a polymer (Bhattacharya, 2004). A hydrophilic cellulose acetate-graft-(glycidylmethacrylate-g-polyethylene glycol) (CA-g-(GMA-g-PEG)) was synthesized and incorporated into acetylated methyl cellulose (AMC) to prepare antifouling ultrafiltration membranes for the effective rejection of humic acid (HA) (Jayalakshmi et al., 2015). The fouling tendency of the modified AMC membranes decreased when compared to the unmodified AMC membranes because of the higher hydrophilicity and smoother surfaces of the AMC blend membranes. Moreover, grafting is one of the chemical modification methods advanced to date and has appeared as a simple and versatile method to develop surface properties of polymers for various applications. For the graft copolymerization to be occurring, groups which can generate radicals should be introduced onto the backbone of the polymer first in order to activate the polymer surface. Most of the polymers having chemically inert properties can be activated via UV irradiation (Khayet et al., 2010), plasma treatment (Kim et al., 2010), ion and electron beam (Lingawati et al., 2009, 2012; Mukherjee et al., 2005; Wanichapichart et al., 2014), benzoic per oxide oxidization (Pulat and Babayigit, 2001; Pulat and Isakoca, 2006; Sanli and Ünal, 2002), and Ce⁴⁺ oxidization (Joshi and Sinha, 2007). In most of the grafting processes, the free radicals are initiated on the backbone of polymer by numerous irradiations and free radical polymerizations of vinyl monomers or chemical initiators. Generally, cellulose and its derivatives are considered as an excellent polymers for surface modification purpose because of having hydroxyl groups (Habibi et al., 2010; Yu et al., 2013). In this study, free radical polymerization was used for the synthesis of the graft copolymer of CA with PMMA using cerium sulfate (CS) as initiator. The grafting copolymer of the CA with the second polymer containing functional groups, such as PMMA, could radically increase the interaction of CA polymer with a wide range of materials. Thus, the grafting copolymerization of vinyl monomer onto the cellulose acetate using electron transfer method, a variant of living radical polymerization to achieve a controlled graft polymerization, was considered as a new approach to potentially produce copolymers with well-defined structures. Furthermore, functionalization of the synthesized product was done using TEPA amine to improve the membrane selectivity. The main assumption of this study was that the surface charges of the modified membranes were altered after the grafting and amination process of the CA polymer. The main objective of this study was to prepare modified CA membranes using PMMA and amine group with improved selectivity for HA molecule removal. An effort was made to investigate the influence of polymerization time and temperature during the graft copolymerization process. Flat sheet membranes were prepared from the modified CA using phase inversion process. As far as our knowledge

is concerned, this work is the first report on the modification of CA polymer using graft copolymerization and amination/functionalization techniques for HA molecules removal.

2. Materials and methods

2.1. Material

Cellulose acetate polymer (acetyl: 29–45% content, MW = 50,000 g/mol); humic acid (60–70%, dry basis) and were purchased from M/s. Loba Chemie, India. Methyl methacrylate (MMA, 99% purity and MW = 86.09) was purchased from M/s. Chemika Biochemika Reagents, Mumbai, India. Ceric (IV) sulfate (CS), hydroquinone (MW = 110.11 g/mol with 99.5% purity), deuterated dimethyl sulfoxide (DMSO-d₆, deuteration degree min. 99.8% for NMR spectroscopy) and sulfuric acid (98% purity) was obtained from M/s. Merck, Germany. Tetraethylenepentamine (TEPA, MW = 189.3 g/mol and with purity of 99%) was purchased from M/s. Sigma-Aldrich Co., USA. Methanol (with 99.8% purity HPLC grade) was purchased from M/s. SRL, India. Polyethylene glycol (MW = 4000) was obtained from M/s. Merck Specialties Private Limited, Mumbai, India; TiO₂ nanoparticle with purity of 99.5% was obtained from M/s. Sigma-Aldrich Co., USA. Deionized water (DI) was used throughout this experiment which was purified using Millipore system. Ceric (IV) sulfate and sulfuric acid were analytical reagent grade and used without further purification.

2.2. Materials and methods

2.2.1. Graft polymerization

During synthesis of CA-g-PMMA and CA-g-PMMA_TEPA, cellulose acetate powder was washed using methanol and deionized water, respectively, for three times and then was vacuum dried at 60 °C for 12 h before use. As seen in the schematic of the graft copolymerization process (Fig. S1), the graft copolymerization of MMA onto CA was took place using a three necked round bottom reactor vessel with magnetic stirrer inside the aqueous solution. For graft copolymerization, 8.0 g of CA was added into the reactor vessel comprising 100 mL of an aqueous solution of 0.006 mol/L of CS in 0.4 M sulfuric acid. After that, the reaction mixture was purged using N₂ gas approximately for 30 min prior to addition a 25 mL of 0.08 mol/L MMA monomer to start graft copolymerization. Consequently, the aqueous solution was stirred continuously at a constant rate (250 rpm) to avoid the influence of stirring on the degree of grafting copolymerization. A condenser was connected to ensure that any solvent or aqueous solution vapor cools, and drips back down into the chamber containing the solid sample. Finally, the polymerization reaction was stopped with addition a 5.0 wt % hydroquinone solution at a fixed time of reaction and the mixture was discharged into a mixture of water and methanol (1:1) and the grafted CA powder was separated.

The polymerization reaction was conducted at temperature of 60 °C in an oil-bath using heating magnetic stirrer. The pH of the polymerization reaction was adjusted at 2.0 before the reaction was started. On the other hand, the duration of the copolymerization was kept for 8 h. The contents in the reactor were stirred continuously throughout the reaction period to avoid the homopolymer precipitation on the substrate surfaces. The grafted samples were quickly taken out after the desired polymerization time from the reactor vessel and washed repetitively using methanol and deionized water. To remove all the unreacted MMA monomer, its low MW PMMA homopolymer, and the impurities precipitated along with grafted CA powder, the PMMA grafted cellulose acetate (CA-g-PMMA) samples were Soxhlet extracted using methanol/acetone (1:1) for 24 h and repeatedly washed using deionized water.

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