



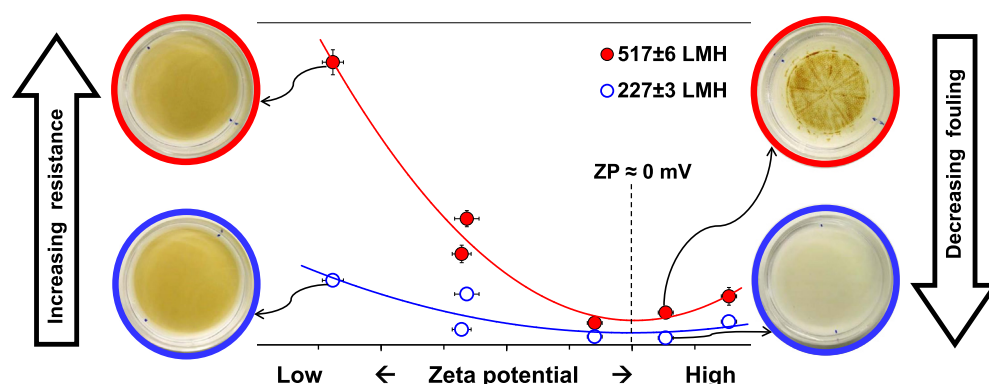
In-line coagulation with quaternary amine polymer prior to microfiltration of humic-rich water



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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 1 July 2015
Revised 10 August 2015
Accepted 10 August 2015
Available online 11 August 2015

Keywords:

Natural organic matter
Quaternary amine polymer
In-line coagulation
Particle characteristics
Membrane fouling

ABSTRACT

This work was designed to investigate the feasibility of using a low molecular-weight epichlorohydrin/dimethylamine (epi/DMA) polymer as a primary coagulant for the pretreatment of terrestrial humic-rich water prior to the microfiltration (MF) process, without removal of the flocs produced via the coagulation pretreatment. The main issue explored was the effects of different coagulation conditions on the particle characteristics that would also significantly affect the performance of membranes when filtering coagulated humic-rich water. The size distribution and morphological properties of flocs formed through the coagulation of humic-rich water were characterized and the impact of Ca^{2+} on these characteristics that were associated with the performance of the MF membrane was also determined. Epi/DMA additions from 50% to 150% of the charge neutralization dose substantially decreased fouling compared to when filtering raw humic-rich water. Short-term fouling was increased when 1 mM Ca^{2+} was added, but the charge neutralization coagulation removed almost all of the fouling tendency that had occurred when filtering Ca-humic solution. The median diameter and the fractal dimension of flocs produced were increased as the zeta potential reached close to zero, which resulted in the formation of a cake layer that was easily removed from the surface of the membrane.

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1. Introduction

While the performance of organic polymers satisfies the increasing demand for natural organic matter (NOM) removal, the high potential that could severely foul the negatively-charged

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membrane limits the extensive application of cationic polymers in the treatment of potable and waste water. The electrostatic attraction between negatively-charged membrane materials and oppositely charged polyelectrolytes would lead to a strong particle attachment and/or organic flocculation on the pore walls of the membrane. Due to its adverse impact (despite not yet being fully verified), the use of cationic polymers as the primary coagulant has been controversial and even banned. Many studies have thus focused on polymer use in conjunction with a metal salt in an attempt to improve the treatability of surface and waste water (especially, the settleability of flocs) prior to conventional rapid-filtration [1–4]. However, fewer studies have been carried out on using cationic polymers as a primary coagulant ahead of membrane filtration processes. Yu et al. [5] reported that the most effective removal of humic acids prior to reverse osmosis treatment was achieved by a combination of metallic coagulants (e.g., ferric chloride and aluminum sulfate) and a cationic polymer such as polydiallyldimethyl-ammonium chloride (pDADMAC). More recently Wang et al. [6,7] examined three different polymer coagulants for the subsequent flocculation immediately after coagulation of surface water with polyaluminum chloride, in which fouling of hollow-fiber microfilters significantly increased with addition of all polymers regardless of their molecular charge. Even though the latest study [8] reveals surface pore blockage by cationic molecules smaller than the pore size of microfilters, the interactions between anionic humic molecules, divalent cationic ions, positively-charged organic polymer, and negatively-charged membrane materials have not been systemically studied so far and the impacts on the performance of microfiltration (MF) membrane also remain unanswered.

Although fouling governed by electrostatic adsorption of organic components might be expected to be minimal on large pore size MF membranes, experimental studies focusing on the impact of divalent metal ions on the humic acid fouling of MF membranes are relatively more limited. Yuan and Zydney [9,10] found a rapid decline in flux during humic acid filtration through a 0.16 μm polyethersulfone (PES) membrane at a constant feed pressure of 69 kPa (10 psi). The rate of flux decline increased sharply with increasing calcium concentration from 0.5 to 10 mM (Ca/TOC ratios between 20 and 400 mg mg^{-1}), which was inconsistent with observations in other studies using less porous ultrafiltration (UF) membranes. Many studies have attempted to investigate the effects of calcium concentration on the flux decline and removal of humic acid through UF membranes with molecular cutoff sizes ranging from 30 to 150 kDa [11–14]. They reported that calcium addition (Ca/TOC ratios between 16 and 25 mg mg^{-1}) resulted in a significant increase in the rate of flux decline, but generally decreased the humic acid rejection. Some of these studies also showed that the trend in which the flux decline was accelerated as calcium concentration was increased, was reversed at high concentrations of calcium [13,14]. For filtration with large pore size MF membranes, little attention has been given to the role of NOM aggregates (which are formed by calcium addition and subsequently flocculated on the membrane surface), in the reversibility of fouling after cleaning. According to Yang et al. [15], a calcium addition resulted in a significant decrease of the specific resistance to filtration of calcium-humic aggregates accumulated on the surface of 0.22 μm polyvinylidene fluoride (PVDF) membranes compared to the filtration of humic acids in the absence of calcium. A similar trend regarding the reduction in both specific cake resistance and cake compressibility was also shown in a previous study [16]. These previous observations are very suggestive, because calcium addition might make it possible to produce a cake favorable to large pore size microfilters, which would also be easily removed from the microfilters by simply using a hydraulic wash.

The main objective of this research was to investigate the applicability of quaternary amine polymer as a substitute for traditional metallic coagulants in the coagulation of terrestrial organic-rich water prior to the MF process. We have determined that coagulation pretreatment using quaternary polymers such as epichlorohydrin/dimethylamine (epi/DMA) is very effective at improving the performance of the 0.22 μm PVDF membrane that has been previously employed for recycling laundry wastewater [17]. Especially, we noticed that a dramatic reduction of specific cake resistance can be achieved with epi/DMA even at an under-dosing condition relative to the charge neutralization condition (i.e., zeta potential of ± 10 mV). This motivated us to use epi/DMA to remove NOM mainly consisting of anionic humic-like substances that have been implicated as the most important foulants and thus to improve the performance of the downstream membrane process. In this study, the membrane performance was quantified by the removal of organic matter, by hydraulic resistance to filtration, and by the permeability recovery of the fouled membrane after sequential hydraulic and chemical cleanings.

This work differs from other recent work in the following ways.

(1) Commercial humic acid was used as the source of terrestrial-origin NOM after 99% removal of particles > 30 nm that can dominate the fouling of large pore size MF membranes. (2) In multi-cycle membrane filtration experiments, both sub- and super-critical constant flux conditions were used for the humic-rich water, rather than immediately applying extreme super-critical conditions as is often necessary with laboratory constant pressure conditions. (3) Almost all of the fouling was removed using an in-line coagulation strategy with an epi/DMA cationic polymer. (4) This study characterized the physicochemical and morphological properties of flocs produced with the coagulation of humic-rich water. The impact of Ca^{2+} on these characteristics that were associated with the performance of the MF membrane was also investigated. (5) The size distribution and fractal dimension of flocs formed through the different coagulation conditions were determined using direct magnified photographic image analysis which offers statistical accuracy to flow microscopy.

2. Materials and methods

2.1. NOM solution

Powdered humic acids (Aldrich Chemical, Milwaukee, WI) were completely dissolved in 6 L deionized water at 1 g L^{-1} at pH 10.5. The humic solution pH was adjusted to 7 using 5 M HCl, filtered by glass-fiber filters with a nominal pore size of 1.2 μm (Whatman Grade GF/C) using vacuum pressure, and subsequently passed through a column of diethylaminoethyl cellulose that was fully pre-saturated with an identical humic solution at a surface loading rate of 0.5 $\text{L min}^{-1} \text{m}^{-2}$ to remove colloids from the bulk solution [18]. These separation strategies were employed to minimize the colloidal interference which can interrupt the direct adsorption of organic molecules onto the membrane materials. The column effluent was prepared as a NOM stock solution in which 76% of total organic carbon (TOC) remained. The NOM molecular size was determined by dynamic light scattering using a ZEN3600 Zetasizer (Malvern Instruments Ltd., Malvern, UK), and showed that NOM < 30 nm accounted for 99% of the total particles (Supplementary Information, SI-1).

NOM solutions were prepared in 2.4 L glass beakers, with sequential additions of 1.8 L deionized water, NOM stock solution to achieve 8.1 ± 0.1 mg L^{-1} TOC, diluted NaHCO_3 solution to obtain 1 mM, 5 M NaCl to reach 1.5 mS cm^{-1} conductivity, pH adjustment to 7.2 ± 0.1 , and additional deionized water to obtain 2 L of NOM solution for each experiment. In some experiments, CaCl_2 was

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