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Microfiltration of humic-rich water coagulated with cationic polymer: The effects of particle characteristics on the membrane performance

Hyun-Chul Kim *,[1]

Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

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 natural organic matter (NOM) were characterized and the impact of Ca^{2+} on these characteristics and on the performance of the MF membrane was determined. The multi-cycle MF experiments with hydraulic wash between cycles were conducted for raw and coagulated humic-rich water, and the performance was evaluated by measuring the permeate water quality, resistance to filtration, and permeability recovery with cleaning. Coagulant (polydiallyldimethyl-ammonium chloride) additions from 50% to 100% 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-NOM and resulted in the highest permeability recovery. The median diameter and the two-dimensional 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.

1. Introduction

Many studies have 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 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. 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 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; thus, very few attempts have been made to evaluate the use of polyamine-based cationic polymers for the removal of NOM, especially ahead of the membrane filtration process. 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) also remain unanswered. Furthermore, a $>9000\ \mathrm{L\,m^{-2}\,h^{-1}}$ (LMH) permeate flux was employed in the previous study, which was more extreme than the range of operating fluxes typically encountered in low-pressure membrane filtration.

Experimental studies focusing on the impact of divalent metal ions on the humic acid fouling of MF membranes are relatively more limited. Divalent cations interact specifically with humic carboxyl functional groups; thus, substantially reduce humic charge and the electrostatic repulsion between humic molecules [9]. Especially, calcium ions greatly enhance complexation and subsequent formation of intermolecular bridges among organic

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* Tel.: +82 10 7373 1517; fax: +82 2 3408 4332.
E-mail address: animaplus@hanmail.net

[1] Present address: Water Resources Research Institute, Sejong University, 98 Gunja-Dong, Gwangjin-Gu, Seoul 143-747, Republic of Korea.

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foulant molecules [10]. Although fouling governed by electrostatic adsorption of organic components might be expected to be minimal on large pore size MF membranes, Yuan and Zydney [11,12] 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. 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 [13–16]. 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 [15,16]. They attributed this phenomenon to the development of a cake with relatively high permeability on the membrane surface as a result of larger humic acid aggregates formed with added calcium.

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. [17], 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 polyvinylidine 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 [18]. 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 feasibility of using a quaternary amine polymer as a primary coagulant for the pretreatment of humic-rich water prior to the MF process, without removal of the flocs produced via the coagulation pretreatment. We have determined that coagulation pretreatment using quaternary polymers such as pDADMAC is very effective at improving the performance of the 0.22 μm PVDF membrane that has been previously employed for recycling laundry wastewater. This motivated us to use pDADMAC to remove NOM mainly consisting of anionic humic-like substances that have been implicated as the most important foulants in natural water and thus to improve the performance of the downstream membrane process. This study characterized the physicochemical and morphological properties of flocs produced with coagulation of the humic-rich water. The impact of Ca^{2+} on these characteristics and on the performance of the MF membrane was also investigated. The size distribution and two-dimensional (2-D) fractal dimension of flocs formed through different coagulation conditions were determined using direct magnified photographic image analysis which offers statistical accuracy to flow microscopy. 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.

2. Materials and methods

2.1. Preparation of NOM solution using commercial humic acids

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, filtered by glass-fiber filters with a nominal pore size of 1.2 μm, 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 L min^{-1} m^{-2} to remove colloids from the bulk solution [19]. The column effluent was prepared as a NOM stock solution in which 74% 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).

NOM solutions were prepared in 2.4 L glass beakers, with sequential additions of 1.8 L deionized water, NOM stock solution to achieve 8.2 ± 0.2 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 added at a concentration of 1 mM to investigate the effect of Ca^{2+} on the performance of the membrane. The conductivity and total dissolved solids were measured using a conductivity meter (Orion 115A$^+$), and pH was measured using a pH meter (Orion 290A).

2.2. Coagulation of NOM with pDADMAC

pDADMAC (Cat-floc 8108 plus, Nalco Company, USA), among the most commonly used cationic polymers in water treatment, was employed for coagulation of humic-rich water prior to MF operation based on the findings reported in the previous study [20]. In this previous study conducted using the seven quaternary amine polymers, Cat-floc 8108 plus provided the steepest rise in zeta potential (ZP) as a function of added cationic charge and effectively decreased clogging of PVDF MF membranes by a factor of 10 even at pH 11. The physicochemical properties of Cat-floc 8108 plus have been reported in detail elsewhere [20]. ZEN3600 Zetasizer was used to determine the volume-based size distribution of the polymer at pH 4, 7, and 10. pDADMAC was diluted with deionized water to 1% (v/v) and pH adjusted before the analysis. Each distribution was obtained by averaging six measurements.

The polymer dose required for charge neutralization (ZP between ± 10 mV) of NOM was determined by direct titration using pDADMAC. Two liters of Ca-free NOM solution were placed in a 2.4 L glass beaker and adjusted to a pH of 7. A given volume of the polymer was then added to the beaker while being vigorously agitated using a mechanical stirrer. The polymer dose was stepped until ZP showed a positive value. The variation in solution pH was also monitored during the titration tests.

Separate batch experiments were conducted to determine the minimum mixing time required for either the lowest concentration or the highest median diameter of flocs formed by coagulation of NOM using pDADMAC. Each polymer dose that was quantified to achieve a ZP of ± 10 mV was added to the 2 L Ca-free NOM solution using an overhead stirrer (RW 20 digital, IKA) with a conventional blade (2.5×7.6 cm^2) and a 2.4 L rectangular beaker. The contents were mixed at a velocity gradient of 400 s^{-1} for 30 min. During the mixing, a 5 mL mixture was collected from the beaker at intervals to determine particle concentration and ZP.

Jar tests were performed to characterize and select the different coagulation conditions. Tests were conducted using a Phipps & Bird stirrer with conventional blades (Model 7790-400) and cylindrical 600 mL beakers. pDADMAC was added to the beakers at seven different doses ranging from 0 to 70 ppm (μL L^{-1}), which corresponded to 0.089 meq-cationic charge L^{-1}. Rapid mix was conducted at a velocity gradient of 200 s^{-1} for 20 min and the mixture was then allowed to settle for 3 h. ZP was measured at the end of the rapid mix using the ZEN3600 Zetasizer. The supernatant was collected from each beaker after settling for 1 h and was then filtered manually with 0.22 μm hydrophilic polyethersulfone (PES)