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## Assessing the interaction effects of coagulation pretreatment and membrane material on UF fouling control using HPSEC combined with peak-fitting



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#### ABSTRACT

In this paper, the effects of alum coagulation pretreatment on the removal of natural organic matter (NOM) from surface water, and on fouling control of the subsequent ultrafiltration (UF) membrane filtration, were studied. Two kinds of UF membrane, made from polyvinyl chloride (PVC) and cellulose acetate (CA), respectively, were tested. The dissolved organics were characterized by high performance size exclusion chromatography (HPSEC) with ultraviolet/visible (UV/vis) and dissolved organic carbon (DOC) detectors, in addition to the conventional organic parameters, such as nonpurgeable dissolved organic carbon (NPDOC) and UV<sub>254</sub>. The results show that coagulation pretreatment could reduce the flux decline of UF membrane filtration by removing some of the NOM. Alum coagulation was found to have higher removal for large molecular weight organics, such as biopolymers and humic substances, than for low molecular weight acids. The results from HPSEC revealed that the PVC membrane removed some of the more hydrophilic low molecular weight acids. As alum coagulation preferably removed biopolymers over low molecular weight acids, pre-coagulation had less effect on CA membrane flux decline control than on PVC membrane flux decline control.

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#### 1. Introduction

Due to the more stringent water quality regulations that have been introduced over the past few decades, UF membranes are becoming an increasingly popular alternative to granular media filtration [1]. UF membranes can be used to remove particulate/ colloidal matter, turbidity, and disinfection by-product (DBP) precursors from source water. They are especially effective for the control of pathogenic protozoa, such as Giardia and Cryptosporidia, from surface water [2], and also have the advantages of a small footprint and being easy to adapt for use with automatic control methods. However, fouling is one of the major factors which prevent the wider application of UF membranes. Fouling results in a gradual reduction in flux (or increase in transmembrane pressure), as a consequence of the adsorption or deposition of foulants, either within the pores or on the surface of the membrane. This thus reduces the productivity and increases the total costs of a UF membrane system. Such fouling can be caused by particulate/ colloidal, organic, and/or biological growth [3].

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Fouling caused by natural organic matter (NOM) is a major issue when treating surface water with UF membranes. NOM is ubiquitous and has a broad range of characteristics. It may be carried into the water body by runoff from the catchment, and thus include humic substances. It may also be produced by the biological activity that occurs inside the water body itself, as seen in the production of extracellular polymeric substance (EPS), which may include polysaccharides, proteins, and so on [4]. Much research has been done in order to explain the role of NOM in membrane fouling, but the results are either not conclusive or sometimes even contradictory. Some researchers have suggested that humic substances are the major NOM foulants [5–7]. However, some studies have concluded that non-humic, hydrophilic NOM, namely polysaccharides and proteins, might be more significant foulants for UF membranes [8–10]. Further, Jermann et al.[11] used a bench-scale flat sheet UF membrane test unit, with humic and alginate as model NOM, to reveal the importance of mutual influences among various foulants with regard to UF fouling.

Coagulation is currently the most common pretreatment for low pressure membranes, i.e. UF and MF. Coagulation can mitigate fouling by removing inorganic colloids and/or NOM from the feed water [12]. However, the effectiveness of fouling control by pre-coagulation is affected by many factors, such as the type of coagulants and dosage, the NOM contents and characteristics of the feed water, and the pore size and the hydrophobicity of the membranes. Kabsch-Korbutowicz [13] used three types of coagulants in a constant pressure UF membrane filtration system with coagulation and sedimentation pretreatment, and found that alum and polyaluminum chloride (PACI) had better NOM removal and flux decline control than sodium aluminates.

Carroll et al. [14] studied the causes of fouling when filtering precoagulated surface water through a polypropylene hollow fiber MF membrane, and reported that NOM was the major foulant. especially the fraction comprising small, neutral, hydrophilic compounds. Tran et al. [15] compared the effects of precoagulation with aluminum-based or polysilicato-iron coagulants on MF membrane fouling control. Two types of membrane, namely polyvinylidene fluoride (PVDF) and polypropylene (PP), were used to treat high DOC surface water. The type of residual organic fraction in the feed water was noted to have a greater impact on membrane performance than the DOC concentration. They also reported that the use of a high aluminum-based coagulants dosage for effective DOC removal caused a severe flux decline for the PP membrane, but had no adverse effect on the PVDF membrane, indicating that the membrane material has an impact on the fouling control effect of pre-coagulation.

A number of characterization techniques have been employed to obtain a better understanding of the types of NOM present in the source water, and their removal or transformation through the water treatment process train [16]. High performance size exclusion chromatography (HPSEC) has proved to be a useful analytical tool for organic characterization studies in the water field [17–19]. First, it was mainly used to generate qualitative information based on comparisons between raw water from different sources waters and from different stages of the treatment process. Later, peak-fitting was also applied to resolve the chromatographic peaks of HPSEC and provide quantitative information on DOC removal by coagulation, and to identify the removable and nonremovable components of DOC [20–22].

In this research precoagulated surface water under various coagulant dosages was filtered through two hollow-fiber UF membranes made of polyvinyl chloride (PVC) and cellulose acetate (CA), respectively. Our emphasis is on the NOM removal under various coagulant dosages, and the interaction between residual NOM constituents and the two types of membrane materials. The latter was examined based on the flux decline under constant transmembrane pressure. For NOM characterization, in addition to bulk parameter analysis, such as DOC and UV<sub>254</sub>, the NOM was also characterized by size exclusion chromatography with UV/vis and on-line DOC detectors combined with peak-fitting.

#### 2. Materials and methods

#### 2.1. UF membrane filtration

Membrane filtration was conducted with a bench-scale deadend membrane testing system (Fig. 1) under room temperature  $(23 \pm 2 \degree C)$ . The central element of the system was the single hollow fiber UF membrane with a length of 12 cm, which was put inside a Teflon tube (I.D. 4 mm). Two T-type connectors (polypropylene material) were plugged into both ends of the Teflon tube, and epoxy resin was used to seal and fix the hollow fiber inside the Teflon tube, as shown in Fig. 2.

First, the feed water was put into a reservoir (RC-800 minireservoir, Amicon, U.S.A.), and was mixed with a magnetic stirrer at 25 rpm. It was then pushed into the hollow fiber membrane in an inside-out flow pattern. Constant-pressure filtration (0.7 bar) was maintained by gas pressure regulated from a nitrogen cylinder, and monitored by a digital pressure gauge (Model P-100 PSIG-D, Alicat Scientific, U.S.A.). Membrane permeate flow was determined by weighting the permeate on a top-loading balance at timed intervals with computerized data acquisition. The permeate flux was obtained by dividing the permeate flow by the membrane



Fig. 2. Schematic diagram of the single hollow fiber UF membrane.

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