# Organic fouling of nanofiltration membranes: Evaluating the effects of humic acid, calcium, alum coagulant and their combinations on the specific cake resistance

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## ARTICLE INFO

## ABSTRACT

Fouling of nanofiltration (NF) membranes by pre-treated Aldrich humic acid (PAHA), alum coagulant, calcium, and their combinations was systematically investigated in a dead-end filtration system in conjunction with analysis of the specific cake resistance. The severity of flux decline was greatly decreased when alum coagulant was added regardless the presence of calcium. Cake compressibility and fouling mechanism were found to be different in each system: non-compressible for system with only PAHA, compressible for system with PAHA and calcium, and in the presence of alum more than one fouling mechanisms co-existed. Specific cake resistances of these systems were determined using the membrane fouling index (MFI) curve, and the values were compared with the empirical ones. A correlation between foulant attachment and specific cake resistance was observed. Finally, a new attachment coefficient in the fouling index was proposed. With this new coefficient, the foulant attachment is accounted for in the determination of specific cake resistance using the MFI curve.

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## 1. Introduction

Nanofiltration (NF) has been gaining attention as the polishing step in water treatment technology. Having characteristics half-way between ultrafiltration (UF) and reverse osmosis (RO), NF offers higher permeate flux compared to that of RO [1] and allows rejection of smaller and charged molecules compared to that of UF. Compared to larger pore membranes such as UF and microfiltration (MF), NF membranes suffer little or no pore blocking [2,3] and hence the resistance due to pore blocking which contributes to the total cake resistance is minimal. Some researchers investigated the rejection abilities of NF towards trace organic and inorganic contaminants [4–6]. These advantages have accelerated the use of NF technologies in drinking water treatment and wastewater effluents reclamation as an alternative for RO and UF. One major challenge in NF technology is membrane fouling. At constant applied pressure, fouling causes a decline in permeate flux over time. Although periodic membrane cleaning will restore the permeate flux, membrane replacement will eventually be inevitable resulting in higher operational and maintenance costs.

Foulants can be categorized into several groups such as sparingly soluble (inorganic) salts, organic substances, colloidal and particulate matter and biological growth. Natural organic matter (NOM) such as humic acid is considered to be one of the major causes of membrane fouling. Numerous studies have reported the physical and chemical aspects of fouling of NF by humic acid [7–13]. Tang et al. [14] reported that humic acid fouling of NF and RO membranes was a function of initial flux and feed water composition, and that the flux decline was likely more dependent on the foulant-deposited foulant interaction rather than on the virgin membrane properties.

In drinking water treatment train, NOM is commonly removed via coagulation/flocculation using coagulating agents such as aluminum. When coagulation is performed together with membrane filtration ("hybrid coagulation-filtration"), the organic matter can be removed effectively while high flux recovery is maintained [15,16]. Although hybrid coagulation-microfiltration and -ultrafiltration have been proposed by some researchers [17–20], it was shown that flocs and uncoagulated humics with sizes smaller or similar to membrane pores may cause irreversible fouling [19]. In addition to this, hybrid coagulation-filtration for these membranes only marginally improves permeate flux in some cases and results in considerable amount of coagulant in permeate due to low rejection [18,20]. These results give insights to the possibilities of employing hybrid coagulation-nanofiltration technology in removing organic matter since pore blocking in NF membranes is negligible, and NF membranes give higher rejection compared to MF and UF membranes.

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In addition, divalent ions such as calcium and magnesium that are naturally present in raw waters may complicate the system even further. These ions which have a strong potential to form complexes with NOM are capable of forming bridges between membrane surface and NOM [14,21,22]. A number of studies have been conducted to investigate the effect of divalent ions on NOM fouling of various membranes [11,14,22–26], and found that more severe flux declines occurred in these systems. While these studies give insights on the foulant–foulant and foulant–membrane interactions when calcium ions are present in the system, these interactions might behave differently when coagulant pre-treatment is conducted.

The objectives of this study are to systematically investigate the flux decline trends in systems containing humic acid, calcium ions, aluminum-based coagulant and their combinations, and subsequently evaluate the cake compressibility and fouling mechanism of these systems based on the findings. In this study, a dead-end bench-scale nanofiltration membrane system was used and resistance calculation was performed to assess the foulant–foulant and foulant–membrane attachments. Permeate quality in each system was analyzed to determine humic acid and divalent ions removals. Other characterization methods such as jar tests and laser diffraction techniques were performed.

## 2. Theory

Specific cake resistance, $\alpha$, is defined as the cake resistance, $R_c$, normalized by the accumulated cake mass per unit of membrane area [16]:

$$\alpha = \frac{R_c}{(M/A)} = \frac{R_c A}{V C_b} \tag{1}$$

where $M$ is the mass of the cake deposited on membrane surface, $A$ is the effective area of membrane, and $C_b$ is the bulk concentration of particles. According to the Carman–Kozeny equation, $\alpha$ is inversely proportional to cake porosity to the power of three, or:

$$\alpha = \frac{180(1-\varepsilon)^2}{\rho d^2 \varepsilon^3} \tag{2}$$

where $\rho$ is the particle density and $d$ is the mean diameter of particles. Schippers and Verdouw [27] developed a theory of cake filtration, where particles are retained on membrane by a mechanism of surface deposition. By assuming that there is no compression of the cake, the following equation is proposed:

$$\frac{t}{V} = \frac{\eta I}{2 \Delta P A^2} V + \frac{\eta R_m}{\Delta P A} \tag{3}$$

where $\Delta P$ is the applied trans-membrane pressure (TMP), $\eta$ is the dynamic viscosity of water, and $I$ is the fouling index. A plot of $t/V$ versus $V$ is then constructed as shown in Fig. 1. Schippers and Verdouw [27] then divided this plot into three regions: (I) pore blocking region, (II) cake formation without compression, and (III) cake formation with compression to differentiate the fouling mechanisms over filtration period. Membrane fouling index (MFI) is then defined as the gradient of the plot of $t/V$ versus $V$ of region II, and the fouling index can be determined using the following equation:

$$I = \alpha C_b \tag{4}$$

## 3. Experimental

### 3.1. Materials

#### 3.1.1. Chemicals
Unless stated otherwise, all chemicals were analytical grade. Chemical and feed solutions were prepared with deionized (DI) water (Elga LabWater, UK) with a resistivity of $18.2\,M\Omega\,cm$.
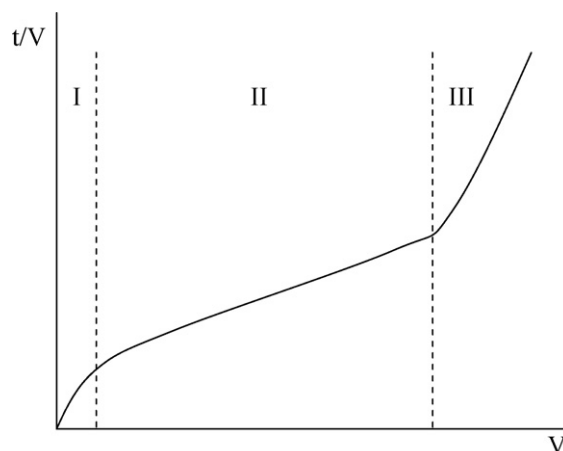


**Fig. 1.** Sketch of $t/V$ (ratio of filtration time and filtrate volume) as a function of total filtrate volume, taken from [27]. I: pore blocking region, II: cake formation without compression region, III: cake formation with compression region.

Sodium hydroxide (1 and 0.01 N), hydrochloric acid (0.1 N) and sodium chloride (1 N) were purchased from Fisher Scientific (Pittsburg, PA). Sodium hydroxide and hydrochloric acid were diluted from 1 N volumetric standard; 6 N hydrochloric acid was diluted from concentrated hydrochloric acid (34–37% HCl, trace metal grade, Fischer Scientific, Pittsburg, PA). Reagent grade alum salts $(Al_2(SO_4)_3 \cdot 14–18H_2O)$ and calcium chloride (Fisher Scientific, Pittsburg, PA) were used as the model coagulant and calcium ions, respectively.

#### 3.1.2. Purified Aldrich humic acid (PAHA)
Aldrich humic acid (AHA) (Sigma–Aldrich, H16752, technical grade, St. Louis, MO) was pre-treated following the method described in [13] in order to remove fulvic, metal and ash contents. In summary, the pre-treatment includes acidifying AHA to pH 1 using hydrochloric acid, adjusting the pH to 13 using sodium hydroxide, filtering the solution through 0.2 μm filter, dialyzing the solution with 3500 Dalton membranes (Membrane Filtration Products Inc., TX), and freeze-drying. Stock solutions of 3 g/L were prepared from the freeze-dried PAHA, stored in the dark at 4 °C, and discarded after 3 months. Feed solutions for fouling experiments were prepared from the stock solution.

#### 3.1.3. NF membranes
All experiments were performed with NF270 membrane (Dow/FilmTec, Minneapolis, MN). This polyamide thin-film composite membrane is considered as smooth membrane with a reported average roughness of $9.0 \pm 4.2\,nm$ [14]. The average hydraulic resistance of the membrane was determined to be $2.46 (\pm 0.2) \times 10^{13}\,m^{-1}$ (measured with DI water at $25 \pm 1.0\,°C$). The range of pH for this membrane for continuous operation as specified by manufacturers is 3–10. Other properties of this membrane are 43% NaCl transmission [4] determined at 80 psi (550 kPa), 40–60% $CaCl_2$ and <3% $MgSO_4$ transmissions (given by manufacturers).

### 3.2. Bench-scale dead-end nanofiltration setup

Fouling experiments were conducted in a bench-scale dead-end nanofiltration system which comprised of a reservoir tank (Millipore Corporation, Bedford, MA) with a volume of 800 mL, connected to a stainless steel cell (Millipore Corporation, Bedford, MA) with a volume of 50 mL and housed a 47 mm diameter membrane sample. The effective membrane area was 13.4 cm². Pressure was provided by a compressed nitrogen gas tank which was applied to the reservoir tank. Permeate flux was collected and the mass