

## **Nanofiltration membrane fouling by aluminum species transformed with different pH in presence of Ca ion**

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### **ABSTRACT**

Coagulation treatment using polyaluminum chloride (PACl) might be employed as pretreatment of salt rejecting membrane such as nanofiltration membrane (NF). However, undesirable effect could be occurred by residual aluminum resulting from improperly controlled coagulation treatment such as poorly dosed PACl in nanofiltration membrane. Aluminum (Al) is transformed to variable species form such as polymeric Al, aluminum hydroxide, and aluminate ion with low, neutral, and high pH conditions respectively. Influence of Al species on nanofiltration membrane fouling could not understand clearly due to unpredictable pH conditions on the nanofiltration membrane surface. Individual Al species fouling on nanofiltration membrane through pH adjustment i.e., pH 4.52, 7.54 and 9.54 at feed water is investigated with 4.0 mM Al and also influence of Ca ion selectively rejected by nanofiltration on Al species fouling is studied. Membrane fouling for polymeric Al and aluminate ion is more pronounced than aluminum hydroxide. The impact of Ca ion with 5.0 mM was observed in case of aluminum hydroxide and aluminate ion fouling. The flux decline rate was slightly increased and especially, ion rejection was deteriorated

### **1. INTRODUCTION**

The coagulation as pretreatment of salt rejecting membrane such as nanofiltration (NF) and reverse osmosis (RO) to be more vulnerable in colloid and natural organic matter fouling have been suggested to enhance membrane performances by removing particulate, colloidal matter, and particularly, natural organic matter (NOM) (Bérubé et.al., 2002, Lee et.al., 2006). Listiarini et al. (2009) also argued that compared to larger pore membranes i.e., microfiltration (MF) and ultrafiltration (UF), NF membranes suffer little or no pore blocking and thus there are feasibilities of employing hybrid coagulation-nanofiltration technology in removing organic matter. However, some researchers have been reported that the use of coagulation pretreatment causes an undesirable effect of Al presence on NF/RO membrane performance (Gabelich et. al., 2006).

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It is generally known that alum solubility can be adequately described by the four monomeric Al species:  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ , and  $\text{Al}(\text{OH})_4^{1-}$ , as well as by the possible polymeric Al species: a dimer ( $\text{Al}_2(\text{OH})_2^{4+}$ ), a trimer ( $\text{Al}_3(\text{OH})_4^{5+}$ ) and the tridecamer ( $\text{Al}_{13}(\text{OH})_{24}^{7+}$ ) in equilibrium with an amorphous  $\text{Al}(\text{OH})_{3(\text{am})}$  solid phase (Bertsh et al., 1989, Duan et al., 2003). In other words, aluminum in feed waters, at the membrane surface and/or pores can be obviously transformed to other Al species to be acted on foulants. Waite (2005) mentioned that polymeric Al species with high molecular weight would accumulate at the membrane surface and lead, eventually, to precipitation of an aluminum hydroxide solid. However, it does not easily predict which species is occurred near the membrane surface with considerable transportation of ions.

NF membrane was shown to be excellent in remove hardness such as Ca and Mg and thus have been widely used to water softening (Bodzek et al., 2006). Yet, the ions rejected on the membrane did negative effect on the membrane fouling such as combined fouling. The influence of Ca on the membrane fouling by either colloid or NOM has been investigated by some researchers (Schäfer et al., 1998).

To date, however, there have been little studies on the Al species fouling and the impact of Ca presence on individual Al species fouling as well as combined fouling on the NF membrane fouling. Therefore, the objective of this paper is to investigate the individual Al species fouling on the NF membrane performance and the influence of Ca on membrane fouling attributed to the individual Al species.

## 2. Experimental Methods

### 2.1 Interaction between Al species and Ca ion

17% PACl (Yun Hap Chemical Ind. Co., Ltd., Commercial grade, Korea) hydrolysis over a pH range of 4 to 10 was observed by adding known amounts of NaOH (Showa, Japan) to a 4.0 mM Al solutions in presence or absence of 3.5 mM Ca. 0.87 g of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (Showa, Japan) was dissolved in 1.0 L of water After 2 minutes of rapid mixing at 250 rpm, NaOH was added and pH was measured. When the pH was stabilized, samples were taken (without settling), filtered through a 0.45  $\mu\text{m}$  polypropylene (PP) membrane filter (Whatman, USA) and analyzed for the dissolved Al concentrations by atomic absorption spectrometer (AA6501F, Shimadzu, Japan).

### 2.2 Nanofiltration (NF) experiments

Polypiperazine amide thin-film composite NF membrane (Dow-Filmtec, Edina, MN, USA) which contains carboxylic and amine functional group (Schaep et al., 2001, Her et al., 2000), was used throughout the study. A plate-and-frame membrane module (Sepa-CF cell, Osmonics, Minnetonka, MN, USA) was used with a width of 0.095 m, channel length of 0.146 m and the effective membrane surface area of 0.014  $\text{m}^2$ . A plastic sieve type feed spacer (Low foulant, Osmonics, Minnetonka, MN, USA) stayed inside the cavity on the feeding side of the membrane. Dead-end mode membrane test was performed using batch cells (180-mL capacity, Millipore, Billerica, MA, USA). Each cell was pressurized with nitrogen gas at  $40 \pm 0.05$  psi using a pressure controller (CZ-68026-58, Cole-Parmer International, USA). An electronic balance (AND, Cole-Parmer International, IL, USA) was employed to measure permeate mass, which was converted to permeate volume based on feed water density.

### 3. Interaction of Al species with Ca

Variations in Ca concentration were observed in different Al species by adjusting pH conditions for mixed solutions with 3.5 mM Al and 4.0 mM Ca as presented in Fig. 1. The Ca concentration was decreased adjusting pH 4.81 by dosing a 3.5 mM Al solution where polymeric Al species were possibly dominant. The dissolved Ca concentration at pH 7.26 adjusted by NaOH was increased during transformation of polymeric Al to Al hydroxides. The increases were probably due to release of Ca from binding sites at polymeric Al. The Ca concentration was 3.4 mM at pH 10.11 where Al hydroxides were transformed to aluminate ion. Interaction characteristics between Al species and Ca could be one of the major factors relevant to salt rejecting membrane fouling such as NF and RO. It is possible when adjusting pH for the Al solution in presence of Ca, combined foulants lead to more deteriorated membrane performance compared to Al species alone.

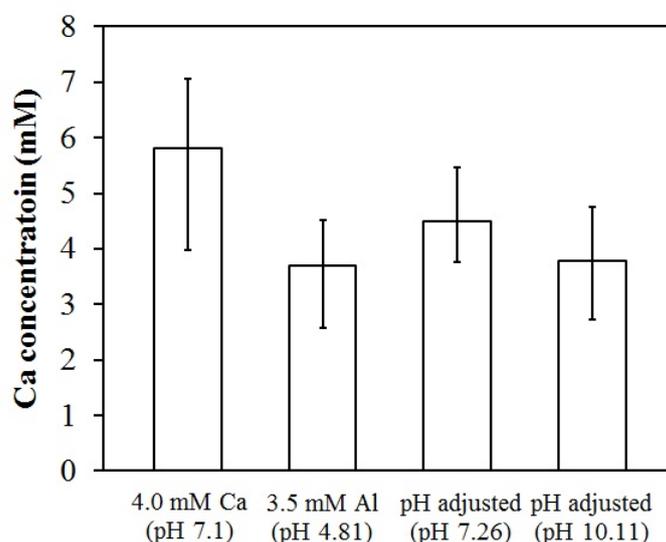


Fig. 1 Variation in dissolved Ca concentration with pH adjustment.

### 4. Influence of Ca on Al species fouling

#### 4.1. Flux decline

NF fouling experiments were performed in presence or absence of Ca to investigate effect of Ca on Al species fouling. For each set of experiments, the flux decline was appeared in two different forms, namely specific flux (Fig. 2a-2c) and the corresponding normalized flux (Fig. 2d-2f). A different initial flux is attributed to intrinsic membrane resistance as shown to Fig. 2a-2c. For Al species fouling alone, a greater rate of flux decline was observed for adjusting pH 4.29 and pH 9.68 with dominant polymeric Al and aluminate ion respectively.

Unlike polymeric Al fouling, behavior of aluminate ion fouling was shown that permeate flux was rapidly decreased at the early stages of filtration. This result means that membrane fouling became higher in a short time possibly due to colloid and/or fine particulate matter occurred during transformation Al hydroxide to aluminate ion.

Contrary to polymeric Al and aluminate ion fouling, no significant effect of Al hydroxide was shown on membrane fouling as presented to Fig. 2b. It seems that although considerable turbid matters were produced due to precipitation formation,

membrane fouling was not likely occurred. Such precipitates might create positive effects on the membrane fouling possibly due to formation of porous and low resistant fouling layer without inner and/or external pore fouling at the membrane surface.

Fig. 2d shows that addition of 3.5 mM Ca did not affect flux decline behavior in presence of polymeric Al. The interaction between polymeric Al and Ca observed at Fig. 1 was not demonstrated as polymeric Al fouling. However, the slight increase for Al hydroxide and aluminate ion fouling rate in presence of Ca (Fig. 2e and 2f) was, to some extent, attributed to mutual interaction between Al species and Ca. As discussed through the results of interaction between Al species and Ca, some portion of polymeric Al species could not be completely transformed to Al hydroxide and produced foulants having greater flux decline. A combined foulant might have also occurred at pH 10.11 where the Ca was favorably interacted with aluminate ion (Fig. 1). The relatively severe membrane fouling was probably caused by such as fine particulate and/or colloid matter.

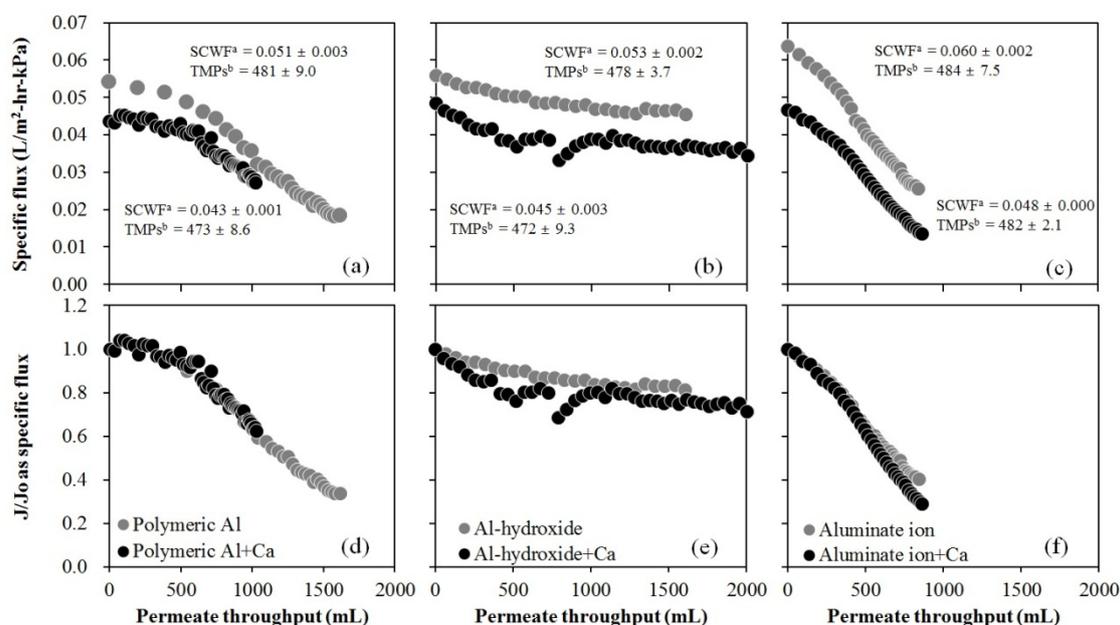


Fig. 2 Effect of Al species on NF membrane specific flux decline (a-c) and normalized flux decline (d-f) in presence and absence of Ca.

<sup>a</sup>: specific clean water flux (L/m<sup>2</sup> · hr · kPa)

<sup>b</sup>: trans-membrane pressures (kPa)

#### 4.2. Rejection characteristics

The NF membrane rejection of conductivity, Al, and Ca was observed for different Al species fouling in presence of Ca. Fig. 3 demonstrates that contrary to polymeric Al fouling, Al hydroxide and aluminate ion fouling resulted in a tremendous deterioration of ion rejection for Ca and conductivity. When Al hydroxide and aluminate ion fouling was happened, Ca removal was 32.8% and 1.19% and conductivity removal was 24.9% and 39.1% respectively. The rejection at pH 4.52 showed that surface charge of membrane appeared at strongly positive due to rejection of almost polymeric Al species with positive charge and thus Ca was rejected by electrostatic repulsion. In case of

predominant Al hydroxide at pH 7.54, the charge of membrane surface accumulated by the neutral Al hydroxides must be electrostatically neutralized and resulted in increased transport of Ca through the NF membrane. Rejected aluminate ion and pH condition i.e., pH 9.54 was considered to show negative charge at the membrane surface. A rise of Ca as CaCl removal rate was expected. As shown in Fig. 3 however, it did not increase Ca removal. Negatively charged aluminate ion was neutralized in presence of Ca and thus ion transport was increased through the membrane without electrostatic repulsion i.e., Donnan (charge) exclusion.

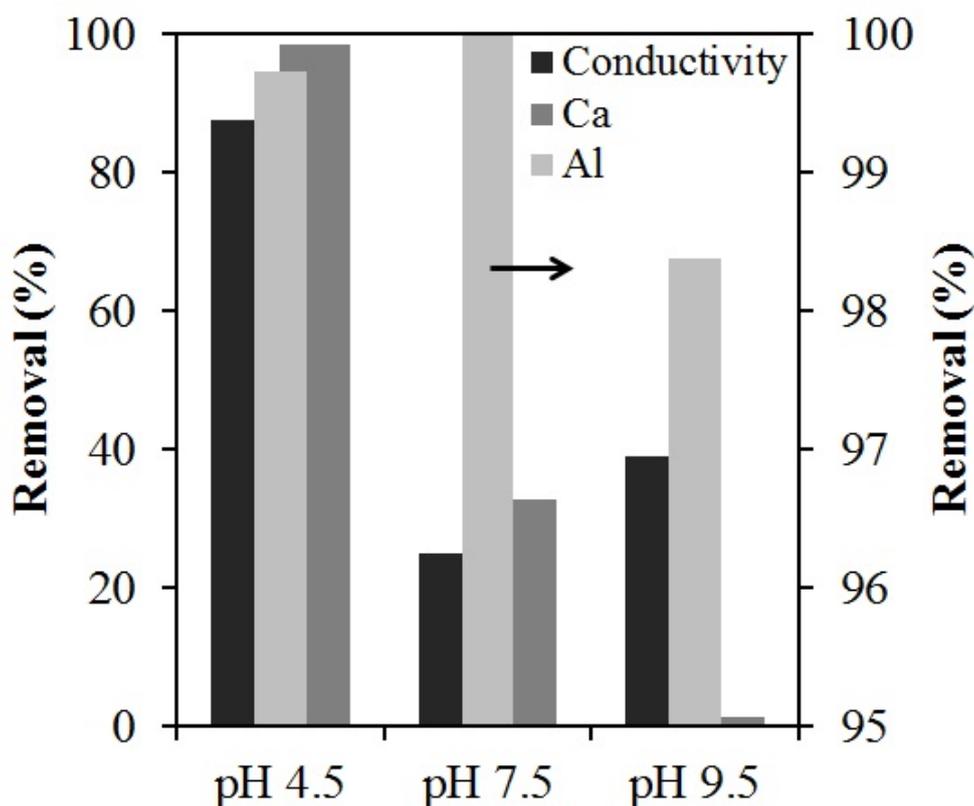


Fig. 3 Effect of Al species fouling on rejection characteristics in presence of Ca

#### 4.3. Fouled membrane analysis: Surface charge properties

The properties of charged NF membrane surface can substantially influence the rejection of ions. It has been generally known that because there is an electrostatic repulsion i.e., Donnan (charge) effect between the charged membrane surface and ions in a chemical solutions (Childress, et.al., 1996, Choi, et.al., 2001). Surface charge of fouled membrane was analyzed to discuss the impact of Ca on flux decline and rejection characteristics by Al solution with different pH. Fig. 4 indicated that in presence of Ca, fouled membrane surface showed relatively low value, mostly near zero zetapotential, compared without Ca. This result was one of the major reason of substantial decreased the removal of conductivity and Ca as shown in Fig. 3 where ions were not repulsed by the membrane surface.

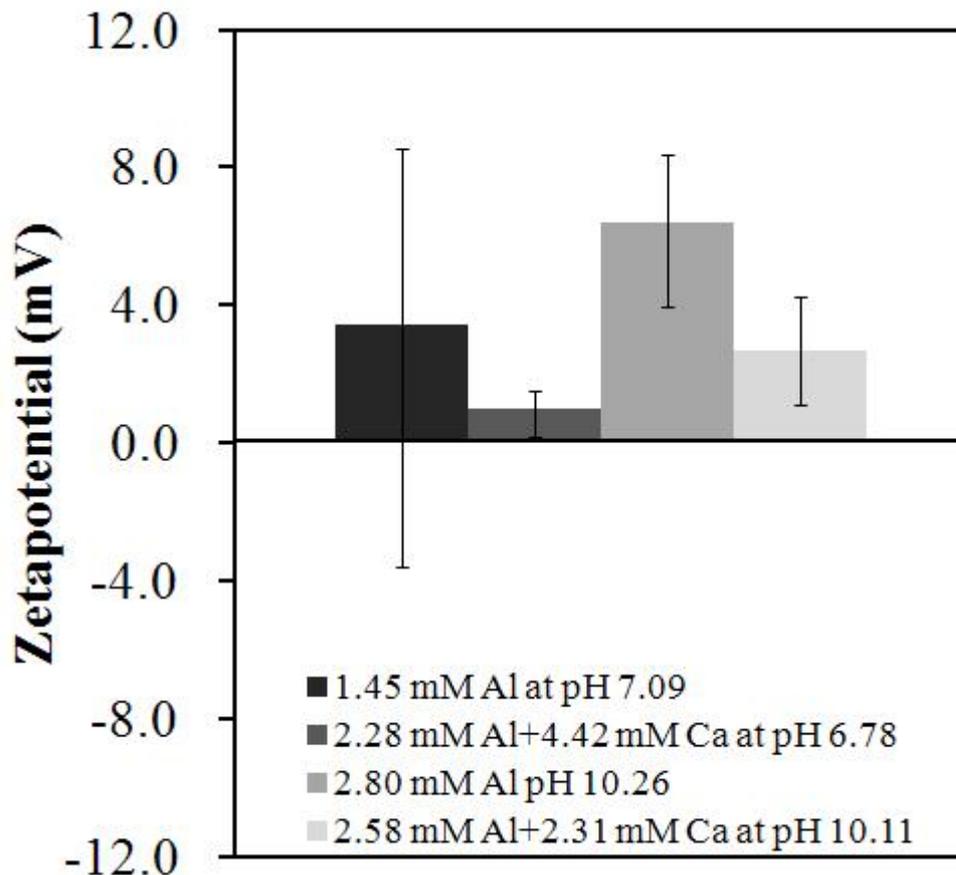


Fig. 4 Zetapotential of fouled membrane with Al species foulants in presence and absence of Ca.

## CONCLUSION

The effect of aluminum species hydrolyzed from polyaluminum chloride coagulant on the nanofiltration membrane fouling in presence of Ca is discussed in this study. Polymeric Al and aluminate ion transformed at pH 4.0 and pH 10.0 respectively are shown to be more significant membrane fouling phenomenon i.e., flux decline than aluminum hydroxide transformed at pH 7.0 with a little flux decline. This result indicates when aluminum hydroxide is predominant in feed waters with neutral pH conditions significant flux decline will be avoided. However, aluminum hydroxide and aluminate ion fouling was slightly increased in presence of Ca ion resulting in a tremendous deterioration in observed Ca ion and conductivity rejection. In case of Ca presence, surface charge of membrane was analyzed as mostly near zero zetapotential.

## ACKNOWLEDGEMENT

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