



# Insights into the roles of recently developed coagulants as pretreatment to remove effluent organic matter for membrane fouling mitigation



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## ABSTRACT

Membrane fouling by dissolved organic matter (EfOM) in secondary treated effluent is a problematic and inevitable issue during wastewater reclamation using low pressure membrane filtration. This study evaluates the performance of coagulation/flocculation (C/F) using two recently developed coagulants (namely  $\text{TiCl}_4$  and  $\text{ZrCl}_4$ ) in comparison to conventional alum (i.e.  $\text{Al}_2(\text{SO}_4)_3$ ) as pretreatment to remove EfOM for subsequent ultrafiltration (UF) membrane fouling mitigation. At the optimal dosage,  $\text{TiCl}_4$ -based C/F pretreatment showed the greatest performance in membrane fouling mitigation, followed by  $\text{ZrCl}_4$  and then alum. The underlying mechanisms were well explained by classical fouling models and the extended Derjaguin-Landau-Verwey-Overbeek (xDLVO) theory, highlighting a dominant role of standard blocking in the fouling potential of the C/F treated EfOM. The interfacial free energy of cohesion and adhesion showed that C/F pretreatment using  $\text{TiCl}_4$  and  $\text{ZrCl}_4$  as coagulant can lower the binding affinity between EfOM molecules and between EfOM molecules and membrane surface, ultimately reduce membrane fouling. The results of size exclusion chromatography (SEC) and fluorescence excitation emission matrix-parallel factor analysis (EEM-PARAFAC) also supported the classical fouling mechanisms, providing additional insights into the potential roles of chemical interactions in the preferential removal of certain organic substances by C/F pretreatment and the chemical composition of subsequent membrane foulants. Protein-like components were highly associated with reversible fouling after the C/F, while the reversibility of humic-like substances was enhanced upon C/F pretreatment. After C/F pretreatment, small sized EfOM molecules became the dominant fraction responsible for UF membrane fouling.

## 1. Introduction

Water reclamation is a pragmatic and cost-effective practice to address water shortage in highly populated areas [1]. In this context, ultrafiltration (UF) has emerged as a preferred treatment option due to its capability to remove a broad range of contaminants, including colloids, bacteria, pathogens, and other organic pollutants, as well as low energy consumption compared to high pressure membrane processes (e.g., nanofiltration and reverse osmosis) [2,3]. However, membrane fouling is a major technical challenge to cost-effective implementation of UF for water reclamation [2]. Fouling of UF membrane is typically governed by the composition of effluent dissolved organic matter (EfOM), which is mostly produced during biological wastewater treatment [4,5]. EfOM contains various organic materials consisting of polysaccharides, proteins, humic substances (HS), amino sugars, and nucleic acids, which originate primarily from soluble microbial products (SMP) and uncharacterized refractory dissolved organic matter

(DOM) [6,7]. High molecular weight (MW) biopolymers and HS are major contributors to UF membrane fouling [5,8]. There is also evidence that other organic constituents can be involved in the fouling process. For example, a previous report has shown a connection between neutral and low MW organics and membrane fouling potential [9].

Several treatment options prior to UF filtration have been proposed to address membrane fouling mitigation. In particular, coagulation/flocculation (C/F) is probably the most widely used and cost-effective method to reduce membrane fouling and enhance the subsequent filtration performance [10–12]. C/F can remove particulate matter and a large fraction of DOM, thus improving the membrane filterability in subsequent processes [3,11]. The effectiveness of C/F processes towards the fouling mitigation depends upon the types of coagulants, the C/F conditions, and the characteristics of the wastewater to be treated [13]. Recently, Ti- and Zr-based coagulants have received much scientific attention due to their enhanced DOM removal [14–16] and hence

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### Nomenclature

LW	Lifshitz – Van der Waals interactions
AB	short-range acid-base interactions
EL	electrostatic double layer interactions
$\delta^+$	electron-accepting component (mJ/m <sup>2</sup> )
$\delta^-$	electron-donating component (mJ/m <sup>2</sup> )
$\delta^{LW}$	Lifshitz – Van der Waals component of surface free energy (mJ/m <sup>2</sup> )
$\delta^{AB}$	acid-base component of surface free energy (mJ/m <sup>2</sup> )
$\delta^{EL}$	electrostatic double layer component of surface free

	energy (mJ/m <sup>2</sup> )
L	probe liquid(s) (i.e. DDW, Diiodomethane, Glycerin)
m	virgin membrane surface
i:	solid surface i.e. virgin or foulants
$\theta$	contact angle (degree)
$\Delta G_{ili}^{LW}$	LW component of cohesion free energy (mJ/m <sup>2</sup> )
$\Delta G_{ili}^{AB}$	AB component of cohesion free energy (mJ/m <sup>2</sup> )
$\Delta G_{ili}^{TOT}$	total interfacial free energy of cohesion (mJ/m <sup>2</sup> )
$\Delta G_{ilm}^{LW}$	LW component of adhesion free energy (mJ/m <sup>2</sup> )
$\Delta G_{ilm}^{AB}$	AB component of adhesion free energy (mJ/m <sup>2</sup> )
$\Delta G_{ilm}^{TOT}$	total interfacial free energy of adhesion (mJ/m <sup>2</sup> )

capacity to reduce membrane fouling [17] compared to conventional coagulants (e.g. alum or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>). Their superior performance is thought to be related to many factors including floc growth rate, the size, and the structures, as well as a variety of hydrolyzed species produced and the involved complex interactions (e.g., charge neutralization, adsorption, and sweep coagulation) [13,15,18,19]. For instance, highly charged hydrolysis products of the novel coagulants, such as (Zr(OH)<sub>2</sub>·4H<sub>2</sub>O)<sub>4</sub><sup>8+</sup>, Zr<sub>3</sub>(OH)<sub>3</sub><sup>9+</sup>, Zr(OH)(H<sub>2</sub>O)<sub>7</sub><sup>3+</sup>, have been proposed to play a crucial role in enhancing the destabilization of suspension and removing different fractions of DOM compared to those of the traditional Fe- or Al-based coagulants [15,16]. Despite recent successful demonstration of these novel coagulants, however, most studies to date have focused only on the drinking water treatment [15–17,20]. There are only a few studies available to compare the performance of the novel versus the conventional coagulants on the removal of DOM from wastewater [21,22]. In these studies, the removal efficiencies of different coagulants were compared based on the bulk EfOM parameters such as chemical oxygen demand [22] and dissolved organic carbon (DOC) [21]. These bulk parameters provide little information on EfOM composition [7]. To date, there has been no effort in the literature to explore the pretreatment performance of these novel coagulants on the removal of EfOM through the post-treatment of membrane filtration and the subsequent membrane fouling mitigation.

Recently available advanced organic fraction characterization techniques can provide new insights to the performance of C/F pretreatment to mitigate membrane fouling. In particular, fluorescence excitation mission matrix coupled with parallel factor analysis (EEM-PARAFAC) can decompose bulk DOM into several fluorescent components with specific characteristics and structures to produce detailed information on the distributions of different fluorophores in DOM [23]. EEM-PARAFAC has recently become a popular and useful tool to probe the dynamic changes in EfOM for natural and engineering systems [4,24–26]. Although EEM-PARAFAC is not able to reflect non light-absorbing constituents (e.g., (poly)saccharides) [27], this limitation can be overcome by complementary application of size exclusion chromatography (SEC) equipped with organic carbon detector (SEC-OCD) [28]. The combined use of SEC-OCD and EEM-PARAFAC has proven to be useful to track the fate of different EfOM constituents upon many treatment processes [4,24,29]. Nevertheless, there has not yet been any studies to utilize such advanced DOM analyses for the evaluation of the novel coagulants as the pretreatment for membrane filtration.

The extended Derjaguin, Landau, Verwey and Overbeek (xDLVO) theory can describe the fouling potential of biologically-derived organics on membrane surface via three different interactions including van der Waals (LW), electrostatic (EL) and acid-base interactions [30,31]. Despite its ability to unravel the underlying mechanisms associated with the interactions between DOM and membrane, only a few studies have adopted the theory to explain the pretreatment effects on membrane fouling such as chlorination [32] or ozonation [33]. It remains unclear whether this approach can also be practical to the C/F as a pretreatment to membrane filtration.

This study aims to (1) to comprehensively compare the performance

of three coagulants, including TiCl<sub>4</sub>, ZrCl<sub>4</sub>, and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (alum), as the pretreatment option to UF for wastewater reclamation by utilizing the complementary combination of EEM-PARAFAC and SEC-OCD, and (2) explore the underlying mechanisms of UF membrane fouling mitigation by the xDLVO theory and advanced DOM analyses.

## 2. Materials and methods

### 2.1. Coagulation/flocculation (C/F) experiments

Biologically treated wastewater was collected after gravity clarification from a municipal wastewater treatment plant in Seoul, South Korea. The collected sample was filtered through 0.45 μm (cellulose acetate, Advantec) and was denoted as EfOM. DOC concentration and UV absorption coefficient at 280 nm (UV<sub>280</sub>) of this wastewater sample were 5.7 ± 0.3 mgC/L and 0.12 ± 0.03 1/cm, respectively. This biologically treated wastewater has a pH of 6.8.

Aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O), zirconium chloride (ZrCl<sub>4</sub>), and titanium chloride (TiCl<sub>4</sub>) were purchased from Sigma Aldrich and were used as coagulants. Stock solutions were prepared in 2000 mg-metal/L by adding the corresponding amounts of the metal coagulants into Milli-Q® water (Rephile, US). The C/F experiments were conducted using a jar test apparatus (C-JT, Chang Shin Science). Each C/F experiment consisted of 2 min rapid mixing at 200 rpm, followed by flocculation for 20 min at 30 rpm. After 30 min settling, the supernatant was carefully taken at 3 cm below the solution surface for the measurements of zeta potential values using a Zetasizer (model 380 ZLS, PSS NICOMP). All C/F experiments were conducted in duplicate. The supernatant was adjusted to pH 3 prior to fluorescence measurements to prevent potential quenching effect of multi-valent cations on the fluorescence spectra [34]. C/F treated samples were filtered through 0.45 μm membrane filter (Advantec, Japan) to remove particulate matter, re-adjusted to pH 7.0, and used for subsequent UF experiments.

### 2.2. UF membrane filtration and the estimation of membrane fouling potential

A flat-sheet polyethersulfone (PES) membrane with a molecular weight cutoff (MWCO) of 30 kDa was purchased from Pall Corp. (USA). The membrane surface contact angle was 51.4 ± 2.4°. The zeta potential of this membrane was previously reported to be –14 mV at pH 7.0 in 10 mM KCl solution [35]. The membrane was submerged in distilled deionized water (DDW) for 48 h before use.

UF experiment was conducted using a 400 mL dead-end stirred cell (Amicon 8400, Millipore Corp., USA) with an effective filtration area of 41.8 cm<sup>2</sup>. A pressurized nitrogen cylinder was connected to the UF unit to maintain a constant pressure of 0.03 MPa. Water flux of the clean membrane was 99.2 ± 1.0 L/m<sup>2</sup>/h. Detailed descriptions of the UF operation and the extraction method for foulants are available elsewhere [36,37]. Briefly, the UF filtration was operated in three cycles using 330 mL-feed solution at a neutral condition. Each cycle was terminated when 300 mL of permeate solution was obtained. DDW

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