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# Coagulation and sludge recovery using titanium tetrachloride as coagulant for real water treatment: A comparison against traditional aluminum and iron salts

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ABSTRACT

Coagulation/flocculation performance of titanium tetrachloride ($TiCl_4$), ferric chloride ($FeCl_3$) and aluminum sulfate ($Al_2(SO_4)_3$) was comparatively investigated for real water treatment. Comparisons were made under different coagulant dose and initial solution pH conditions and their performances measured in terms of $UV_{254}$ (absorbance at 254 nm) and DOC (dissolved organic carbon) removal and residual turbidity. Characteristics of aggregated flocs during the coagulation/flocculation process by the three coagulants were studied using a laser diffraction particle sizing device. The performances of the three coagulants were also assessed in terms of the membrane fouling potential of the ultrafiltration (UF) membrane or during coagulation–ultrafiltration (C–UF) process using a stirred and dead-end batch UF unit. Additionally, the $TiCl_4$ flocculated sludge was recovered to produce titanium dioxide ($TiO_2$) under thermal treatment. The results indicate that the $TiCl_4$ showed superior coagulation performance compared to that of $FeCl_3$ and $Al_2(SO_4)_3$, with the optimum removal of $UV_{254}$ and DOC of 54.9% and 55.1%, respectively. The aggregated flocs formed by $TiCl_4$ showed the highest growth rate with the largest size compared to those by $FeCl_3$ and $Al_2(SO_4)_3$, but with the weakest floc strength and the worst re-growth ability. The $TiCl_4$ and $FeCl_3$ yielded the flocs with comparable degree of compaction, higher than that by $Al_2(SO_4)_3$. Additionally, the investigation of membrane fouling demonstrated that the severity of flux decline followed the order of $Al_2(SO_4)_3 < FeCl_3 < TiCl_4$. $TiCl_4$ coagulated sludge was also characterized by X-ray diffraction, Thermal analysis and scanning electron microscope.



## 1. Introduction

Coagulation–flocculation is one of the most common and important water treatment processes for particle and natural organic matter (NOM) removal [1]. Using conventional Al and Fe salts as coagulants suffers from two major issues or challenges: toxicity of the residual coagulant and sludge production [2,3]. The significant advantage of using titanium tetrachloride ($TiCl_4$) as a coagulant is that, its flocculated sludge can be recovered to produce a valuable by-product, namely titanium dioxide ($TiO_2$) by thermal treatment, which is not possible with the conventional coagulants [3,4]. $TiO_2$ is the most widely used metal oxide, whose applications include photocatalysts, cosmetics, paints, electronic paper, and solar cells [5,6]. The toxicity of the supernatant after $TiCl_4$ coagulation is very low, and the residual Ti salt concentration in the treated water meets the World Health Organization's (WHO) guidelines (0.5–15 μg/L) for drinking water standards [7]. Therefore, $TiCl_4$ is expected to be a promising alternative coagulant to the conventional Al and Fe salts.

The size and strength of flocs formed during the coagulation/flocculation process are considered fundamental to the separation and purification process [8]. Regions of high shear force, such as areas around the impeller zone of flocculating tanks and transfer over weirs and ledges, are prevalent in units at water treatment works [9]. The resultant broken flocs with reduced sizes result in lower sedimentation rate and may not only contaminate the filter (depending on the pore size and filter thickness), which may result

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in lower filtration performance, but also may pass through the filter resulting in the incomplete separation [10]. In addition, newly exposed surface of the aggregates may alter the surface charge of the floc aggregates, leading to partial re-stabilization [9]. Moreover, the floc shapes (often described in terms of fractal geometry concept or the fractal dimension) affected particle behavior, particularly with regard to collision efficiency and settling rates [11,12]. Therefore, floc size, strength, recoverability and structure are considered as important parameters to provide valuable information in understanding coagulation performance and coagulation mechanisms of a new coagulant, while few researches have focused on those by $TiCl_4$. Since $TiCl_4$ is only studied recently as a novel coagulant, only few of these parameters are accurately assessed and compared with the conventional coagulants.

Recently, ultrafiltration (UF) technology has been widely used for removal of suspended solids, colloidal material, NOM and disinfection byproducts precursors [13,14]. Due to serious membrane fouling and poor NOM removal, coagulation pretreatment prior to membrane filtration has been suggested both for improving NOM removal and for reducing membrane fouling [15–17]. The practical effects of precoagulation using conventional Al and Fe salts on membrane fouling have been widely investigated [18–20]. The coagulant type and floc characteristics are believed to play significant roles in membrane fouling [21–23]. However, none of the previous studies have addressed the effect of $TiCl_4$ precoagulation on the performance of membrane process particularly in the fouling potential of UF membrane in the coagulation–ultrafiltration (C–UF) hybrid process.

Therefore the main objectives of this study are to (i) evaluate the coagulation performance of $TiCl_4$ in real water treatment and compare to traditional $Al_2(SO_4)_3$ and $FeCl_3$ coagulants, (ii) characterize the floc properties using a laser diffraction instrument, and (iii) investigate the mechanisms involved in the coagulation–flocculation process based on coagulation performance, floc properties and zeta potential measurement, (iv) comparatively investigate the membrane performance with different coagulants in C–UF hybrid process, and (v) produce $TiO_2$ from the $TiCl_4$ flocculated sludge and study its characteristics by X-ray diffraction (XRD) analysis, Thermal analysis and scanning electron microscope (SEM).

## 2. Experimental

### 2.1. Coagulants and test water

$TiCl_4$ solution (20%, density = 1.150 g/mL) was obtained from Photo & Environment Technology Co. Ltd. (South Korea), and was used directly without any pretreatment. Stock solutions of $Al_2(SO_4)_3$ and $FeCl_3$ were prepared at a concentration of 1 g/L by Al and 2 g/L by Fe, respectively. Deionized water was used for all the reagent preparation.

The water source used in this study was withdrawn from Xiaoqing River, which is the main drainage channel in central region of Shandong Province, China and also plays an important role for farmland irrigation. The water was collected in spring season, and the water temperature was at 10–15 °C. The turbidity, $UV_{254}$ absorbance, DOC, zeta potential and pH of the simulated water were 6.20–9.44 NTU, 0.067–0.073 $cm^{-1}$, 3.90–4.55 mg/L, −11.0 ± 1.0 mV and 7.95–8.46, respectively.

### 2.2. Jar-test

Standard jar tests were conducted using a programmable jar-tester. Detailed experimental procedures are described in S1 of the Supplementary data (SD).

Coagulation–flocculation experiments under different solution pH values were conducted after the optimal coagulant dosages were determined. The target coagulation pH values were achieved by adding appropriate quantities of HCl and NaOH solutions with the concentration of 0.1 mol/L.

### 2.3. Determination of dynamic floc properties

A laser diffraction instrument (Mastersizer 2000, Malvern, UK) was used to measure dynamic floc size as the coagulation and flocculation process proceeded. The schematic diagram of the on-line monitoring system for dynamic floc size can be found in Zhao et al. [24].

Following the floc growth phase, the aggregated flocs were exposed to a shear force at 200 rpm for 1 min, followed by a slow mixing at 40 rpm for 15 min to allow floc regrowth. The median equivalent diameter, $d_{50}$, was selected as the representative floc size, although the same trends were observed for $d_{10}$ and $d_{90}$ floc sizes.

The floc growth rate was calculated by the slope of the rapid growth region [25]:

$$\text{Growth rate} = \frac{\Delta size}{\Delta time} \tag{1}$$

Floc strength factor ($S_f$) and recovery factor ($R_f$) are used to compare the floc breakage and recoverability [24,26–28]:

$$S_f = \frac{d_2}{d_1} \times 100 \tag{2}$$

$$R_f = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \tag{3}$$

where $d_1$ is the average floc size of the plateau before breakage, $d_2$ is the floc size after the floc breakage period, and $d_3$ is the floc size after regrowth to the new plateau.

Previous researches have reported the determination of aggregate mass fractal dimension ($D_f$) by using Mastersizer 2000 [27,29,30]. The total scattered light intensity $I$, the scattering vector $Q$, and $D_f$ followed a power law [31]:

$$I \propto Q^{-Df} \tag{4}$$

The scattering vector $Q$ is the difference between the incident and scattered wave vectors of the radiation beam in the medium [29]:

$$Q = \frac{4n\pi \sin(\theta/2)}{\lambda} \tag{5}$$

where $n$, $\lambda$ and $\theta$ are the refractive index of the medium, the laser light wavelength in vacuum, and the scattering angle, respectively.

Densely packed aggregate has a higher $D_f$ value, while lower $D_f$ value results from a large, high branched and loose bound structure.

### 2.4. Coagulation–ultrafiltration (C–UF)

UF membrane with a molecular weight cut-off (MWCO) of 100 kDa was provided by Mosu Shanghai. All the UF experiments were carried out using a magnetically stirred cell (MSC050, Mosu, China), with a total holding capacity of 300 mL and an effective membrane area of 50.2 $cm^2$. The cell was pressurized with nitrogen gas at 0.15 ± 0.05 MPa without shaking. An electronic balance (MSU5201S-000-D0, SARTORIUS AG GERMANY) connected to PC was employed to measure mass of the UF permeate. The mass data was recorded every 10 s and the flux decline with time was calculated to assess the membrane fouling. Schematic diagrams of the experiment of C–UF hybrid process can be found in the reference [18].