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# Inhibition of disinfection by-product formation in silver nanoparticle-humic acid water treatment

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ABSTRACT

Health risk of disinfection by-products (DBPs) makes the removal of trihalomethanes (THMs) precursors a great concern in water treatment. This study investigated the THMs precursors removal by coagulation with four coagulants, namely $TiCl_4$, polymerized titanium chloride (PTC), $Al_2(SO_4)_3$, polymerized aluminum chloride (PAC), in silver nanoparticle-humic acid (AgNPs-HA) water treatment. Flocs formed during coagulation process were characterized using a laser diffraction particle-sizing device, and the residual dissolved organic matter (DOM) in coagulated water was characterized using three-dimensional Excitation and emission matrix (3DEEM) fluorescence spectroscopy. Results showed the reduction of THMs by a large margin through coagulation by the four coagulants, and $CHCl_3$ and $CHBrCl_2$ were observed as main species. Compared with conventional $Al_2(SO_4)_3$ and PAC, $TiC_4$ and PTC achieved efficient AgNPs removal and were superior in terms of DOM removal with improved floc characteristics in terms of floc growth rate and floc size. Analysis of 3DEEM results suggested the fluorescent substance removal ability of $TiCl_4$ > PTC > $Al_2(SO_4)_3$ > PAC, and the predominant fulvic acid-like DOM was removed to the largest extent through coagulation. Besides, anatase structured $TiO_2$ with efficient photocatalytic performance was finally recovered from $TiCl_4$ and PTC coagulated sludge. The atomic percentage of Ag-doped $TiO_2$ was $TiO_{1.82}Cl_{0.25}Na_{0.29}Ag_{0.14}$.



## 1. Introduction

Chlorine is widely and increasingly utilized in water and wastewater disinfection process due to its strong sterilization ability, low cost and potential of residual chlorine to prevent bacteria regrowth [1]. However, the disinfection process is generally accompanied by potential reaction between residual chlorine and dissolved organic matter (DOM) to produce disinfection by-products (DBPs) with genotoxicity and cytotoxicity, such as trihalomethanes (THMs) and haloaceticacides (HAAs) [2]. Balance the control of pathogen and formation of DBPs is, consequently, of great importance to guarantee the ecological and healthy safety of water supply.

Elimination of DBPs precursors before disinfection process was reported as efficient method to inhibit DBPs production [3]. Coagulation was designated as the most feasible technology for DOM (THMs precursor) removal to limit THMs formation by US-EPA [4]. The DOM removal methodology, reaction of chlorine with DOM and the subsequent DBPs generation have drawn extensive research [5,6]. Conventional Al-based and Fe-based coagulants, such as aluminum sulfate ($Al_2(SO_4)_3$, polyaluminum chloride (PAC), ferric chloride ($FeCl_3$) and polyferric sulfate (PFS), are commonly and widely used for DOM removal in drinking water and wastewater treatment to restrict THMs production in the following disinfection process [7]. Iriarte-Velasco et al. [8] reported 48% reduction in THMs formation by enhanced coagulation with $Al_2(SO_4)_3$ and PAC in surface water treatment. Polyferric chloride (PFC) and PAC achieved efficient DOM removal in reservoir water treatment, followed by limited DBPs formation potential as proved by a chlorine decay model [6]. Han et al. [3] demonstrated strong ability of $FeCl_3$ coagulation for hydrophobic acids (HoA) precursor removal to reduce THMs concentration in bio-treated wastewater treatment. The titanium (Ti) based coagulants, such as titanium tetrachloride ($TiCl_4$) [9], titanium sulfate ($Ti(SO_4)_2$) [10] and polytitanium chloride (PTC) [11], were recently developed as new emerging coagulants, and could achieve higher, at least comparable, DOM removal compared to conventional coagulants.

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The Ti-based coagulants are, therefore, expected to obtain efficient THMs precursor removal. However, few investigation of the THMs formation was conducted during disinfection process of Ti-based coagulated water. Additionally, a significant advantage of Ti-based coagulation was valuable $TiO_2$ recovery from coagulated sludge [11,12]. Sludge handling is a challenging environmental problem with its disposal accounting for at least half of the total water treatment cost. Thus, employing Ti-based coagulants in water/wastewater treatment is expected to be not only beneficial in DOM (THMs) removal but also economical in sludge recycle.

Nowadays, the engineered inorganic nanoparticles (EINP) are increasingly used in industrial and agriculture, leading to the unintended nanoparticles (NPs) release in water environment. As one of the widespread used EINP, silver nanoparticles (AgNPs) have long been reported to be antimicrobial [13], and toxic to cells, bacteria and algae [14], posing risk to animals and humans alike associated with their exposure. Removing AgNPs from water environment is essential to control environmental and health risks and becomes increasingly important. Coagulation has long been reported as the most cost-effective methodology for AgNPs removal [15], with its high performance having been proved by $Al_2(SO_4)_3$, $FeCl_3$, PAC and PFS [16,17]. As aforementioned, the Ti-based coagulation could achieve good water/wastewater purification and offer economical sludge disposal idea by recovering functional $TiO_2$ from coagulated sludge. However, the AgNPs removal by Ti-based coagulants was barely reported. Release of AgNPs into water environment will be inevitably accompanied by AgNPs-particle and AgNPs-DOM composite contaminates formation through adsorption of AgNPs on particle and DOM surface. Surface charges of both DOM and AgNPs will be modified and characteristics of AgNPs-DOM suspension will be changed, making the simultaneous removal of AgNPs-DOM a different story. Thus, although the Ti-based coagulants have already been demonstrated efficient for DOM removal, their ability for AgNPs-DOM removal still requires investigation.

Aims of this study are to (i) investigate coagulation ability of $TiCl_4$ and PTC in terms of AgNPs removal, DOM removal and coagulation mechanisms in silver nanoparticles-humic acid (AgNPs-HA) water treatment; (ii) characterize specific component of DOM in coagulated water using three-dimensional excitation and emission matrix (3DEEM) fluorescence spectroscopy to explore fluorescence substances removal by $TiCl_4$ and PTC; (iii) study THMs production, THMs species associated with their distribution during the chlorine disinfection procedures of Ti-based coagulated water; (iv) analyze properties of Ti-based flocs in terms of floc growth rate, size, strength, recoverability and structure; and (v) recover the Ti-based coagulated sludge by incineration to produce functional by-product $TiO_2$. Research on conventional $Al_2(SO_4)_3$ and PAC served as reference in this study.

## 2. Experimental

### 2.1. Coagulants and test water

Four coagulants were utilized in this study, named $TiCl_4$, PTC, $Al_2(SO_4)_3$, PAC. The 20% $TiCl_4$ stock solution (density = 1.25 g/mL) was diluted from the concentrated $TiCl_4$ solution (purity ≥99%, Fulka) through slowly adding cubes of frozen distilled water drop by drop under continuous stirring. The PTC coagulant with varied basicity value (B, molar ration of OH/Ti) of 0.5, 1.0 and 1.5 was synthesized using slow base titration method according to previous publication [11]. The $Al_2(SO_4)_3$ (2.0 mg/L) coagulant was prepared by dissolving the predetermined $Al_2(SO_4)_3{\cdot}18H_2O$ (analytical pure grade) into deionized water directly. Preparation of PAC stock solution can be referred to Zhao et al. [9]. The PAC solution (1.0 g/L) with B value of 2.0 was selected for this study. Concentration of $TiCl_4$ and PTC was expressed as mg Ti/L, while that of $Al_2(SO_4)_3$ and PAC was calculated as mg Al/L.

The AgNPs-HA simulated water was used as test water and the preparation method was as follows: First, the synthetic HA solution was prepared using biochemical reagent HA (Aladdin Industrial Corporation) as model organic matter, with the detailed procedure in Zhao et al. [9]. Second, the homogeneous silver nanoparticle (Aladdin Industrial Corporation) suspension was prepared by ultra-sonication in an ultrasonic bath (KQ-250B) twice for a cycle of 30 min. The AgNPs-HA simulated water was prepared by thoroughly mixing the predetermined AgNPs with HA simulated solution. Properties of the water sample were: HA concentration = 10.0 mg/L, AgNPs concentration = 5.0 mg/L, $UV_{254}$ = 0.259 ± 0.051 mg/L, DOC = 4.179 ± 0.559 mg/L, conductivity = $2.30 * 10^{-2}$ - S/m, alkalinity = 280 mg $CaCO_3$/L, pH = 8.44 ± 0.30. The particle zeta potential decreased from −11.0 ± 0.90 mV to −15.9 ± 0.40 mV due to AgNPs inclusion, which might be ascribed to the mutual repulsion between HA and AgNPs [18].

### 2.2. Jar test

A programmable jar tester (ZR4-6, ZhongrunWater Industry Technology Development Co. Ltd., China) was used to conduct coagulation process, including a three-stage process: 1.5 min rapid mixing at 200 rpm, 15 min slow mixing at 40 rpm, and a 15 min settling period. The supernatant samples were then collected for the measurements of turbidity, $UV_{254}$ absorbance, dissolved organic carbon (DOC), zeta potential, and effluent pH, with the analytical methods shown in Zhao et al. [9]. The residual AgNPs concentration was measured by atomic absorption spectrophotometer TAS-990 (Beijing Purkinje General Instrument Co. Ltd., China).

### 2.3. Excitation and emission matrix (EEM) fluorescence spectroscopy analysis

A luminescence spectrometry (F-4500 FL spectrophotometer, Hitachi, Japan) was used to measure the EEM spectra, which was collected with scanning emission spectra from 250 nm to 550 nm at 5 nm increments by varying the excitation wavelength from 200 nm to 400 nm at 5 nm sampling intervals. The EEM spectra of raw water and the treated effluents are plotted as contours. The fluorescence regional integration (FRI) was conducted to quantitatively analyze the fluorescence spectra according to the following equations [19]:

$$\Phi_{i,n} = MF_i \int_{ex} \int_{em} I(\lambda_{ex}\lambda_{em}) d\lambda_{ex} d\lambda_{em} \quad (1)$$

$$P_{i,n} = \Phi_{i,n}/\Phi_{T,n} \times 100\% \quad (2)$$

$$\Phi_{T,n} = \sum_{i=1}^{i=V} \Phi_{i,n} \quad (3)$$

where $\Phi_{i,n}$ refers to the normalized EEM volume of region i; $I(\lambda_{ex}\lambda_{em})$ is the intensity of fluorescence at each wavelength pair of excitation and emission; $MF_i$ equals to the inverse of fractional projected excitation–emission area, and is a multiplication factor accounting for the secondary or tertiary responses at longer wavelengths; and $P_{i,n}$ means the percentage of fluorescence response of region i.

### 2.4. Chlorine disinfection

To prevent the influence of light transmission and algae appearance, chlorine disinfection for raw water and treated water