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# Polyacrylamide as coagulant aid with polytitanium sulfate in humic acid-kaolin water treatment: Effect of dosage and dose method

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ABSTRACT

This study focused on the application of polyacrylamide (PAM) as a coagulant aid of polytitanium sulfate (PTS) in humic acid-kaolin water treatment. Coagulation performance and floc properties were all measured in terms of dose amount and dose sequence of PAM and PTS which is meaningful for the practical application. Results showed that PTS-PAM (PTS dosed firstly) attained better natural organic matter (NOM) removal and PAM-PTS (PAM dosed firstly) attained better turbidity removal. Floc size was significantly enhanced by the PTS-PAM, while floc size of PAM-PTS attained similar size as that of PTS alone. Floc strength and recovery ability were also significantly improved by PTS-PAM. Moreover, PTS-PAM floc had a looser structure than that of PTS, while PAM-PTS floc and PTS floc had similar and more compact structure. The effect of PAM on the sludge reuse process was also studied. Results showed that the addition of PAM had a positive effect on the photocatalytic activity of sludge prepared $TiO_2$.



## 1. Introduction

Coagulation-flocculation is one of the most commonly used water treatment processes to remove colloid particles and natural organic matter (NOM) in water during the past decades. Generally, coagulation performance mostly depends on the coagulants and flocculants. Aluminum salts and iron salts such as $Al_2(SO_4)_3$, polyaluminum chloride (PAC) and $FeCl_3$ are commonly used metal coagulants for their low cost and high coagulation performance [1]. However, there are still some problems caused by the application of these metal coagulants. For example, some studies have proved that there seem to be a link between residual aluminum and neuropsychic diseases, such as Alzheimer's disease [1,2]. Besides, the effluent of iron-based flocculation system is usually has high chroma and high corrosivity which is unfavorable to the following process [3]. In addition, a common problem caused by aluminum salts and iron salts is that a large amount of sludge is produced [4]. Therefore, the development of new coagulants is still highly meaningful. Recently, titanium salts which have been used as a new coagulant gradually attract more and more attention for its sludge reuse possibility [5,6].

Titanium salts have first been used in water treatment for color and turbidity removal in 1960s by Upoton and Buswel [7]. Then for few decades, titanium salts was not been widely used for its relatively high price. With the economic development, the price of titanium salts is dropping for these years and the titanium salts are resumed the application in water treatment [8]. Shon et al. first found that the sludge reuse possibility of titanium tetrachloride [5]. The flocculation sludge of titanium salts can be used to produce widely used photocatalytic material-$TiO_2$ which was proved to have better photocatalytic activity than commercial P-25 $TiO_2$ [5]. Shon et al. and Zhao et al. also suggested that titanium tetrachloride could achieve good flocculation activity as iron salts and aluminum salts [5,9]. Afterward, Wu et al. also found that titanium sulfate was more favorable under acid condition compared to tradition coagulants and also proved the sludge reuse possibility for titanium sulfate flocculation sludge [8]. Additionally, Zhao et al. synthesized polytitanium salts to attained better coagulation behavior and wider application range of pH [10]. Previous studies also suggested that the effluent pH of titanium salt too low for the subsequent process and flocs were difficult to recover after breakage [11]. Therefore, an organic polymer can be used as coagulant aid for titanium salts to improve coagulant performance and floc properties.

Polyacrylamide (PAM) is usually a widely used polymer flocculant due to its high molecular weight, water solubility and low cost [12,13]. Aguilar et al. suggested that coagulation efficiency and floc settling rate of ferric sulpfate, aluminum sulfate and PAC can be improved by anionic polyacrylamide (APAM) and the required amount of coagulants could also be reduced by the addition of APAM [14]. Ahmad et al. have also proved that addition of PAM improved coagulation performance of PAC in pulp and paper mill wastewater treatment [15]. In addition, Zhao et al. studied the

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combination of $TiCl_4$ and PAM in which have proved that the addition of PAM enhanced the NOM removal and floc recovery ability [11]. Yu et al. also studied the effect of PAM on the membrane fouling process and found that the membrane fouling process was significantly affected by the addition amount of PAM [16]. However, there is little study focused on using PAM as coagulant aid for polytitanium salts.

This study mainly studied the coagulation performance and floc properties when PAM was used as coagulant aid with polytitanium salts. The effect of dosing sequence and dosage was considered in this study. Additional coagulation performance was evaluated in terms of residual turbidity, $UV_{254}$ and DOC removal. Floc properties was evaluated in terms of floc size, floc breakage and recovery factor and fractal dimension. Zeta potential was measured for further analysis. Flocculation sludge was also used to calcinied to prepare $TiO_2$ and the photocatalytic activity of sludge prepared $TiO_2$ was evaluated by degradation of dye wastewater.

## 2. Materials and methods

### 2.1. Coagulants

Polytitanium sulfate (PTS) (10 g/L as Ti) was prepared by slow base injection of a certain amount NaOH solution into titanium sulfate solution under rapid mixing.

Cationic polyacrylamide Cationic PAM (K6641) (molecular weight 8000,000 Da), was obtained from Kolon Co., Korea and dissolved to 1 g/L for use.

PTS dosage was 2, 10, 18, 26, 32 and 38 mg/L. PTS was added firstly at the start of rapid mixing, followed by various amount (0.5, 1.0 and 2.0 mL) of PAM addition after 0.5 min, and this dual-coagulant was denoted as PTS-0.5PAM, PTS-1PAM and PTS-2PAM, respectively. When the other addition sequence of PTS and (0.5, 1.0 and 2.0 mL) PAM was reversed, it was denoted as 0.5PAM-PTS, 1PAM-PTS and 2PAM-PTS, respectively. The dosage of PTS was calculated according to concentration of Ti in mg/L, while that of PAM was calculated according to concentration of flocculant in mg/L.

### 2.2. Test water

Test water was prepared by humic acid (HA) and kaolin. More details can be found in reference [17]. The properties of the test water were as follows: $UV_{254} = 0.300 \pm 0.010$, $DOC = 4.70 \pm 0.05$ mg/L, pH $8.30 \pm 0.05$.

### 2.3. Jar tests

A series of jar tests was conducted to evaluate the coagulation performance of dual-coagulants. The coagulation experiment was performed with an electronic program-controlled mixing mechanism in six 1.5 L beakers (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China). Each beaker was filled with 1 L test water for coagulation. Immediately after the end of coagulation process, about 200 mL water samples were collected from each beaker. Residual turbidity and zeta potential of the unfiltered water samples were measured by a 2100P turbidimeter (Hach, USA) and a Zetasizer 3000HSa (Malvern Instruments, UK), respectively. The water sample was then filtered through a 0.45 μm glass filter for measurement of ultraviolet absorbance at 254 nm ($UV_{254}$) (Precision Scientific Instrument Co. Ltd., Shanghai, China) and dissolved organic carbon (DOC) (TOC-VCPH, Shimadzu, Japan).

### 2.4. On-line monitoring of floc properties

Dynamic flocs size during the whole flocs formation, breakage and re-growth process was measured using Mastersizer2000 (Malvern, UK). Floc size is expressed as an equivalent volumetric diameter and *d*50 (refers to the 50% floc size).

Floc breakage and recovery factors have previously been used to compare the relative breakage and re-growth of flocs [18,19].

They were calculated as follows:

$$\text{Breakagefactor}(\%) = \frac{d2}{d1} \times 100 \quad (1)$$

$$\text{Recoveryfactor}\,(\%) = \frac{d3 - d2}{d1 - d2} \times 100 \quad (2)$$

where $d_1$, $d_2$ and $d_3$ are the sizes of flocs in the steady phase before breakage, after the breakage period and after the re-growth to another steady phase, respectively.

Floc fractal dimension ($D_f$) can be measured by Small Angle Laser Light Scattering (SALLS). The total scattered light intensity $I$ is a function of the scattering vector $Q$, where $Q$ is the difference between the incident and scattered wave vectors of the radiation beam in the medium, which is given by (3), and more details can be found in ref. [18].

$$Q = \frac{4\pi n \sin(\theta/2)}{\lambda} \quad (3)$$

where $n$ is the refractive index of the suspending medium, $\theta$ is the scattering angle, and $\lambda$ is the wavelength of the radiation in a vacuum. For independently scattering aggregates, $I$ is related to $Q$ and the fractal dimension ($D_f$) in Eq. (4):

$$I \propto Q^{-D_f} \quad (4)$$

where $D_f$ is the mass fractal dimension which can be determined by the slope of a plot of $I$ as a function of $Q$ on a log–log scale.

### 2.5. Sludge reuse

Coagulation sludge was first dried at 105 °C and then calcined at 700 °C for 12 h to prepare $TiO_2$. After that, the sludge prepared $TiO_2$ was washed by deionized water for 3 times. Finally, the $TiO_2$ was dried and grinded for use. XRD analysis was performed by a Rigaku (Japan) D/MAX-rA diffractometer (Cu K$\alpha$ radiation). The evaluation of photocatalytic activity of the sludge produced $TiO_2$ was conducted by using photodecomposition of a dye (Reactive Red X-B) wastewater and more details can be found in ref. [20].

## 3. Results and discussion

### 3.1. Effect of PAM on coagulation performance: residual turbidity, removal of $UV_{254}$ and DOC and zeta potential

Coagulation performance of PTS and dual-coagulants is shown in Fig. 1 which is evaluated in terms of residual turbidity, removal of $UV_{254}$ and DOC and zeta potential. Residual turbidity dramatically decreased as Ti dosage increased, and decreased more sharply when Ti dosage ranged from 2 to 18 mg/L. Additionally, Fig. 1(a) suggested that for PTS+2PAM and 2PAM+PTS, residual turbidity dropped from about 6.5 NTU to 3.5 NTU and 2 NTU, respectively. For other coagulants, residual turbidity decreased from around 5 NTU to 2 NTU. It can be noted that the turbidity of PTS-PAM was higher than that of PAM-PTS. In addition, Fig. 1(a) suggested that more addition of PAM did not mean lower residual turbidity. Residual turbidity of PTS-2PAM was the highest among these coagulants, meanwhile 1PAM-PTS attained lowest residual turbidity. When PTS was dosed after PAM, residual turbidity of PAM sharply decreased below 2 NTU when Ti dosage was higher than 18 mg/L. However, when PTS was dosed firstly, residual turbidity was all above 2 NTU. As for $UV_{254}$ and DOC, the removal efficiencies were all gradually increased as Ti dosage. It was obvious that the addition of PAM