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Advanced treatment of effluent from municipal WWTP with different metal salt coagulants: Contaminants treatability and floc properties

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ABSTRACT

Chemical coagulation with three representative inorganic coagulants was used for the advanced treatment of secondary effluent from WWTP to enhance total phosphorus (TP) and organic removal. The effect of chemical coagulation on organic contaminants was investigated with combined fluorescence excitation–emission matrix (EEM) spectroscopy and High-performance size-exclusion chromatography (HPSEC). The results showed that different coagulation features and benefits were exhibited by $FeCl_3$, $Al_2(SO_4)_3$ and polyaluminum chloride (PACl). PACl had better performance in chemical oxygen demand (COD) removal, while $FeCl_3$ and $Al_2(SO_4)_3$ were more efficient in removing TP. The optimal coagulant in this study was $FeCl_3$. The floc obtained from $FeCl_3$ coagulation was larger, easier to settle and break than that of $Al_2(SO_4)_3$ and PACl. Coagulation mainly removed orthophosphate and the major phosphorus fraction of coagulated effluent was organic phosphorus. The macromolecule organics (molecular weight (MW) >10 kDa) were completely removed regardless of their chemical nature, while inorganic coagulants showed different effects on removal efficiency of organic matters with a MW less than 10 kDa. Besides, 71.24% of the total dissolved organic carbon (DOC) was tryptophan-like proteins and soluble microbial byproduct-like materials which could easily be removed by coagulation.

1. Introduction

With the rapid growth of population and development of industry in China, there has been an increasing pressure of water pollution, especially the eutrophication of lakes and streams. In order to cope with this problem, the water quality of discharge standard in China becomes more and more stringent [1]. For domestic wastewater treatment, the traditional activated sludge process is the prevailing method all over the world because of low operating costs and easy maintenance [1,2]. However, the quality of effluent from wastewater treatment plant (WWTP), as is called the secondary effluent, fails to achieve the required more stringent discharge standards (ammonium, total phosphorus and chemical oxygen demand). Therefore, advanced treatment technologies of wastewater are in urgent need [3]. These technologies include chemical coagulation, membrane filtration, advanced oxidation, activated carbon adsorption and so on [4–6]. Chemical coagulation has been applied widely due to its advantages of low equipment cost, high efficiency and low operating costs, easy maintenance and other characteristics [2]. Chemical coagulation of several types of wastewaters, resulting in considerable nutrient elimination, has been reported by some researchers [7–10]. But organic components analysis in chemical coagulation process has rarely been reported so far.

Effluent from WWTPs mainly contains refractory compounds and soluble microbial products (SMP) [11]. Fluorescence excitation–emission matrix (EEM) spectroscopy is a powerful and widely used technique for characterizing the heterogeneous composition of fluorescent organic matter normally found in aquatic environments. Fluorescence regional integration (FRI) divides EEMs into five regions which each represents a dissolved organic matter (DOM) fraction, according to the location of EEM peaks of many typical organic matters [12,13]. High-performance size-exclusion chromatography (HPSEC) is also an effective means of determining polymer molecular weights (MW) and molecular weight distributions (MWD), and therefore can be used to predict and estimate the efficiency of coagulation by analyzing the organic composition in effluent [14,15].

The objective of this work was to investigate the coagulation behavior of three commonly used inorganic coagulants in effluent from WWTPs. Three metal salt coagulants were comprehensively compared from organics and total phosphorus (TP) removal efficiency and floc properties. In addition, particular emphasis

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was paid to understanding the coagulation treatability of contaminants with phosphorus species, EEM and HPSCE analysis. Furthermore, this work provided a comprehensive insight into the mechanism of coagulation for the treatment of domestic sewage.

2. Materials and analytical methods

2.1. Raw water

Secondary effluent was collected from the WWTP located in Nantong, Jiangsu province, China. Samples were kept in polypropylene containers and protected in 4 °C refrigerator during the sampling periods. The water quality of the secondary effluent is given in Table 1.

2.2. Coagulants

Ferric chloride ($FeCl_3 \cdot 6H_2O$), aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) and a commercial poly-aluminum chloride (PACl, Beijing Wanshui Co. Ltd., China) were used. They were typical ferric salt, aluminum salt and polymer coagulant, respectively. The PACl used in this study contains 31.3% Al_a, 16.1% Al_b and 52.6% Al_c.

2.3. Test methods

2.3.1. Jar tests

During each experiment, 250 mL of well-mixed raw (secondary treated) wastewater was poured into a 500 mL glass beaker and placed to the jar test apparatus. The coagulation process consisted of a rapid agitation stage at 250 rpm for 0.5 min, and a rapid agitation stage at 200 rpm for 1.5 min, followed by a slow agitation stage at 40 rpm for 10 min and then a step of sedimentation for 30 min. A certain dosage of coagulant was added at the end of the first agitation step. Each run was conducted in triplicate and the supernatant of treated wastewater from the three beakers was withdrawn for further analysis.

2.3.2. Floc properties test

Floc size, fractal dimension (D_f), breakage factor (B_f), recovery factor (R_f) and strength factor (S_f) were studied to compare the properties of different systems. A higher D_f normally corresponds to a more compact interior floc structure [16]. An increased value of B_f indicates flocs that are more likely to be broken, while an increase of R_f implies better regrowth after high shear and high S_f shows better strength [17].

Floc breakage and regrowth experiments were carried out and repeated three times as follows: a regular coagulation process (without sedimentation) followed by a breakage phase at 400 rpm for 1 min and a regrowth phase at 40 rpm for 10 min. A small-angle light scattering instrument (Malvern Mastersizer 2000, Malvern, UK) was used to measure dynamic floc size and fractal dimension (D_f) as the coagulation process proceeded. Flocs were monitored by drawing the suspension through the optical unit of the Mastersizer and back into the jar by a peristaltic pump at a flow rate of 1.5 L/h. The detailed methods for measuring D_f can be found in previous studies [18]. The B_f, R_f and S_f may be calculated as follows [17]:

$$B_f = \frac{d_a - d_b}{d_a} \times 100\% \quad (1)$$

$$R_f = \frac{d_c - d_b}{d_a - d_b} \times 100\% \quad (2)$$

$$S_f = \frac{d_b}{d_a} \times 100\% \quad (3)$$

where d_a is the average floc size of the plateau before breakage, d_b is the floc size after the floc breakage period, and d_c is the floc size after regrowth to the new plateau.

2.4. Analytical methods

Chemical oxygen demand (COD) was measured by a HACH DRB200 COD analyzer. Zeta potential was measured using a Malvern Zetasizer 2000. Dissolved organic carbon (DOC) was determined with *Phoenix* 8000 TOC analyzer (Tekmar Dohrmann). A UV–Vis spectrophotometer (U-2910, Hitachi) was used for the determination of UV absorbance at 254 nm wavelength (UV254), while the floc size and D_f were measured by a small angle light scattering instrument (Malvern Mastersizer 2000, Malvern). Fluorescence EEM measurements were conducted using a Hitachi F-7000 fluorescence spectrometer. Determination of HPSEC was carried out by Waters 1525 high performance liquid chromatograph [19]. The water samples were diluted 10 times for EEM measurement and 50 times for HPSEC. TP, soluble orthophosphate (SOTP), soluble organic phosphorus (SOGP) and particle phosphorus (PP) were analyzed in accordance with the Standard Methods [20].

Table 1
Water quality of the secondary effluent.

Parameters	Secondary effluent
COD (mg/L)	62.0
TOC (mg/L)	25.50
Total phosphorus (mg/L)	3.48
Dissolved orthophosphate (mg/L)	2.69
Dissolved organic phosphorus (mg/L)	0.28
Particulate phosphorus (mg/L)	0.51
UV_{254} (cm^{-1})	0.293
SUVA	1.15
pH (20 °C)	7.2

3. Results and discussion

3.1. Coagulation treatment of secondary effluents

Fig. 1 shows the finished water quality as a function of coagulation dose, using $FeCl_3$, $Al_2(SO_4)_3$ and PACl. At low dosages, the zeta potential remained negative and kept growing, and the COD levels decreased with the increase of coagulant dosages before reaching the optimal dosages. Whereafter, at the higher dosages, COD levels turned around and began to rise because the formation of positively charged small flocs may restabilize particles [21]. It's worth noting that zeta potentials were close to the isoelectric point at the optimal dosages. The change in DOC was similar to that of COD under coagulation.

As illustrated in Fig. 1(a), PACl managed to decrease COD from 62.0 mg/L in raw effluent to 19.8 mg/L, corresponding to a removal efficiency of 68%, which was much higher than the 49% removal exhibited by $FeCl_3$. Overall, PACl was the most efficient coagulant for organic removal, followed by $Al_2(SO_4)_3$ and $FeCl_3$. The reason for this observation was that PACl exhibited the high level of positively charged polymeric hydrolysis products [21]. Furthermore, it can be seen that aluminum salts presented a better performance than ferric salts in removing organic contaminants.

Fig. 1(b) shows that the change in TP concentration under chemical coagulation with different coagulants followed the same trend. $FeCl_3$ was the optimal coagulant for TP removal. At the dosage of 0.6 mmol/L $FeCl_3$, TP decreased from 3.48 mg/L to