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Polymerized titanium salts for municipal wastewater preliminary treatment followed by further purification via crossflow filtration for water reuse

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ABSTRACT

Research concerning polymerized titanium salts for preliminary treatment of municipal wastewater remains limited. We proposed the pre-coagulation of municipal wastewater with polymerized titanium based coagulants, followed by direct crossflow ultrafiltration for water reuse by avoiding biological treatment. Compared with polymerized aluminum chloride (PAC), polymerized ferric sulfate (PFS) and polymerized titanium sulfate (PTS), the polymerized titanium chloride (PTC) achieved higher coagulation efficiency, with chemical oxygen demand (COD) and total phosphorus (TP) removal reached 80.5% and 99.1%, respectively. Besides, PTC produced larger flocs (median equivalent diameter of 1408.1 μm) with better settling ability (flocs sedimentation in 1 min), higher shear resistance (strength factor reached 95.87%) and stronger re-aggregation capability (recover factor of 225.13%). The subsequent direct crossflow ultrafiltration of primary settled municipal wastewater could achieve complete suspended solids and P removal, being accompanied by additional 10–15% of organics removal. Specifically, ultrafiltration of PTC effluent obtained larger permeate flux up to 499.5 $\mathrm{L\,m^{-2}\,h^{-1}}$ and the reused water having higher quality (COD removal of 90.4%). Current study demonstrated the feasibility and superiority of utilizing polymerized titanium salts (especially PTC) for preliminary treatment of municipal wastewater. The resultant high-quality effluent through direct ultrafiltration provides alternative schemes for the demanding reclaimed wastewater reuse.

1. Introduction

Coagulation is recognized as the most cost-effective technology for water and wastewater pretreatment [1–3]. Polymerized Al- and Fe-based metal salts have been increasingly applied as coagulants and their development has received great attention, such as polyaluminum chloride (PAC), polyferric sulfate (PFS), and polyferric chloride (PFC) [4–7]. Disputes existed about the adverse effect of Al on human health and the effluent after Fe-based coagulation has color problem [8–10]. Moreover, nothing valuable could be recovered from the Al- and Fe-based coagulated sludge, which requires further disposal either at landfills or ocean dumping.

Recently, the Ti-based coagulants were developed [11–13], with the most significant advantage of the recycling of coagulated sludge to produce valuable by-products, TiO_2 [14–16]. The Ti-based coagulants showed at least comparable coagulation efficiency as conventional Al- and Fe-based coagulants. The Ti-salts produced larger flocs with faster floc growth rate, and the resultant flocs had higher settling speed [13,17]. Additionally, titanium and its compounds have low toxicity and are rarely included in water quality guidelines [18,19]. Polymerized titanium salts were recently synthesized and investigated for surface water treatment [20,21], with both polytitanium tetrachloride (PTC) and polytitanium sulfate (PTS) showed improved coagulation performance and floc properties compared with non-polymerized Ti-salts. Existing literatures reported and demonstrated high performance of polymerized titanium salts for surface water [22,23], micro-polluted water [24,25] and coal mining wastewater treatment [26]. Strong coagulation ability of the polymerized titanium salts indicates their great potential for municipal wastewater pretreatment, which is barely reported.

Municipal wastewater contains significant amounts of organics and phosphorus (P). Coagulation was highly efficient to extract organics and P from municipal wastewater and concentrated them into primary sludge [27,28], which could be utilized for energy and resources

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recovery other than being wasted to landfill [29,30]. Regarding the primary settled municipal wastewater after coagulation, the follow-on direct membrane filtration provides alternative options for water reuse in specific applications [28,31]. The effluent from direct crossflow membrane ultrafiltration of municipal wastewater reached the quality criteria for agriculture irrigation [28]. The micro-filtered effluent from resort complex could be applied for toilet flushing [32]. The increasing water resource scarcity makes the wastewater reuse for specific applications a big necessary.

The coagulation-direct membrane filtration technology is a high effective technology to separate sewage into two parts [33–35]: the concentrated part with rich organics and nutrient and the filtrate part with low pollutants remained. Pre-coagulation could not only dissolve organics out from sewage, but also reduce the membrane fouling during the follow-on membrane filtration procedure [36]. Based on their reported strong coagulation ability [21,24], the polymerized titanium salts are expected to achieve efficient extraction of organics and nutrients from sewage. And, the direct filtration of coagulated supernatant is expected to produce effluent with high quality for secondary application directly without biological treatment. Few studies have focused on optimizing of coagulants to enhance organics and nutrients extraction from sewage. It is not clear whether polymerized titanium salts are superior to conventional coagulants for dissolving organics out from sewage. Moreover, the subsequent membrane filtration performance needs investigation to see the feasibility of pre-coagulation with polymerized titanium salts for the subsequent direct filtration of municipal wastewater.

This study aims to investigate the performance of polymerized titanium salts for municipal wastewater pre-treatment. On-line measurement of coagulation process was carried out to investigate the floc properties in terms of floc size, strength and recoverability. After coagulation process, the supernatant was subjected to direct membrane ultrafiltration in crossflow mode to characterize their filterability. Specifically, the influence of coagulant dosage, transmembrane pressure, and crossflow velocity on permeate flux was studied. Membrane fouling mechanisms of crossflow filtration for coagulated effluent was explored according to both standard law of filtration and classical cake filtration model. The conventional PAC and PFS cases were studied for comparison.

2. Experimental

2.1. Test water and coagulants

Test water was raw wastewater from Stanley Sewage Treatment Works (Stanley STW), Hong Kong. The sewage was collected regularly after preliminary treatment, mainly bar racks and screening. Four polymerized metal salts were utilized in this study, namely polymerized titanium chloride (PTC), polymerized aluminum chloride (PAC), polymerized ferric sulfate (PFS), and polymerized titanium sulfate (PTS). Concentration of titanium-based, iron-based and aluminum-based coagulants was calculated as mg Ti/L, mg Fe/L and mg Al/L, respectively. Detailed information about the sewage and coagulants are presented in the Supporting information (SI S1).

2.2. Jar-test

A programmable jar tester (PB-700, Phipps & Bird) was utilized to perform standard jar tests. Domestic sewage was first subjected to 30 s of rapid mixing (200 rpm) through mixing, followed by immediate coagulant addition. Rapid mixing (200 rpm) was continued for another 1 min, followed by slow mixing at 40 rpm to allow floc growth. Then, the mixing was stopped to allow aggregates settle down for 15 min. The supernatant was carefully drawn out for quality measurement. Detailed methods for turbidity, UV_{254}, COD, TP, PO_4-P, zeta potential and pH can be found in SI, S2.

2.3. Floc characterization

On-line measurement of floc properties was achieved by a laser diffraction particle size analyzer (Mastersizer 3000, Malvern). Schematic diagram of on-line monitoring system can be found in Fig. S1. Briefly, municipal wastewater went to coagulation tank for pre-treatment by dosing coagulants. The resultant suspended flocs were monitored every 20 s through optical unit of Mastersizer 3000 as coagulation process proceeded. The corresponding data were recorded by computer automatically. The lab scale setup is shown in Fig. S2. To investigate the floc strength and recovery ability, the aggregated flocs after coagulation process were exposed to high shear force (200 rpm) for 5 min, followed by 15 min of slow mixing (40 rpm) to allow broken flocs regrowth. Floc strength and recovery ability were expressed using floc strength factor (S_f) and floc recovery factor (R_f), respectively, with the equations being shown below [37,38]:

$$S_f = \frac{d_2}{d_1} \times 100 \tag{1}$$

$$R_f = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \tag{2}$$

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

2.4. Crossflow membrane filtration

Fig. S3 shows the schematic diagram of crossflow filtration procedure. After coagulation procedure, jar-tests allowed the aggregates settle down for 15 min. The supernatant was then collected and pumped to membrane filtration unit (CF042, Sterlitech, Kent, WA). Herein, a high pressure pump was used to circulate and pressurize the water solution. A pressure gauge was mounted between membrane filtration unit and high-pressure pump for continuous pressure measurement. The crossflow tube system was equipped with a needle valve and a pressure relief valve to allow pressure setting. Flux was measured by electronic balance (Adventurer Pro AV8101, OHAUS), which was connected to computer for data recording. Membrane was provided by Mosu Shanghai, and general characteristics of membrane are shown in Table 1.

2.5. Membrane fouling mechanisms

The membrane fouling mechanisms are generally expressed as internal membrane pores clogging and the external surface cake-layer build-up [39]. Previous studies reported that the dynamic membrane formation initially obeyed the standard law of filtration in few minutes' of filtration, followed by further evolution of dynamic membrane according to classical cake filtration model [39,40]. Visvanathan and Ben Aim [41] and other investigators [42,43] reported the following standard law of filtration (see Eq. (3)) and the classical cake filtration model (see Eqs. (4) and (5)).

$$\frac{t}{V} = \frac{1}{Q_0} + \frac{k_1 t}{2} \tag{3}$$

Table 1
Characteristics of the membrane.

Configuration	Flat-sheet
Material	PVDF
Total surface area	33.15 cm^2
Cross-sectional area	0.819 cm^2
Wall thickness	0.19 mm
Hydraulic resistance	4.895×10^8 (m^{-1})
pH resistance range	2–14
Molecular weight cut-off (MWCO)	100 kDa