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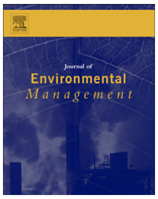

Comparison of a novel polytitanium chloride coagulant with polyaluminium chloride: Coagulation performance and floc characteristics

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ABSTRACT

Polymerized inorganic coagulants are increasingly being used in the water supply and wastewater treatment process, yet there is limited research on the development of polytitanium coagulants. The aim of this study is to synthesize polytitanium chloride (PTC) coagulants and investigate their coagulation behavior and floc characteristics for humic acid removal in comparison to polyaluminum chloride (PAC). The PTC samples with different B (molar ratios of OH/Ti) values were prepared using an instantaneous base-feeding method, employing sodium carbonate as the basification agent. The coagulation efficiency was significantly influenced by different B values. The results suggest that the humic acid removal increased with the increasing B value for PAC, while the inverse trend was observed for PTC. The optimum B value was chosen at 1.0 and 2.0 for PTC and PAC, respectively. Under the optimum coagulant dose and initial solution pH conditions, the PTC coagulant performed better than the PAC coagulant and the floc properties were significantly improved in terms of floc growth rate and floc size. However, the PAC coagulants produced flocs with better floc recoverability than the PTC coagulants.

1. Introduction

Humic acid (HA) is the major component of natural organic matter (NOM) and has been recognized as a significant generator of carcinogenic disinfection-byproducts (DBPs) (Kazpard et al., 2006). Additionally, its high affinity for various pollutants causes water contamination and creates a yellowish or brown color. Thus, the removal of HA found in water has become increasingly important.

Coagulation-flocculation is one of the most important and common chemical treatment methods adopted for NOM removal. Utilization of aluminum (Al)-salts as coagulants for NOM removal dates back centuries, however, there have been disputes regarding the potential adverse effects of Al on humans and organisms (Cheng and Chi, 2002). This has led to the increasing use of iron (Fe)-salts (Bell-Ajy et al., 2000; Edzwald and Tobiason, 1999). Nonetheless, one problem is the generation of large quantities of sludge, from which nothing can be recovered or reused and which then requires further disposal either at landfills and/or by ocean dumping.

To overcome the sludge disposal problem, Shon and his co-workers proposed Ti-salts as coagulants for water purification. The most significant advantage of this coagulant is that the final coagulated sludge can be recovered to produce a valuable titanium dioxide (TiO_2) as byproduct (Okour et al., 2009; Shon et al., 2007; Yousef, 2009; Zhao et al., 2011a, 2011b, 2011c). The effectiveness of Ti-salts used as coagulants for water purification has since been well studied (Wu et al., 2011; Zhao et al., 2011a, 2011b). Ti-salts achieve higher removal efficiency of suspended particles and NOM than conventional Al- and Fe- salts. The settled flocs have better decantability, which indicates a shorter retention time and the need for a more compact sedimentation tank for Ti-salts coagulation. Moreover, titanium and its compounds are reported to have little toxicity (Lee et al., 2009) and they are rarely included

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in water quality guidelines. It is therefore concluded that Ti-salts have high potential for water purification and can be used as alternative coagulants to conventional Al- and Fe-salts.

Prehydrolyzed inorganic coagulants based on Al or Fe salts have received considerable attention during the last 20 years (Cao et al., 2011; Cheng, 2002; Gao et al., 2005; Jiang and Graham, 1998; Moussas and Zouboulis, 2009; Zouboulis et al., 2008). They are highly efficient in removing numerous pollutants, are less sensitive to low temperature, and reduce the need for pH adjustment through prehydrolysis. Although there has been renewed interest in Ti-salts as coagulants for water purification, few studies have addressed the need to develop prehydrolyzed Ti coagulants. In the case of Ti coagulants, large amounts of H^+ are released during the Ti hydrolysis process, leading to low effluent pH values of 3.5–5.0 where optimum coagulation efficiency occurs (Hu et al., 2005; Shon et al., 2007). According to earlier studies with inorganic polymeric Al and Fe coagulants, the low effluent pH during the titanium coagulation process is expected to be solved by developing polytitanium salts that can minimize H^+ release through prehydrolyzed titanium coagulants. Polytitanium salts are also expected to be less pH dependent and may achieve higher particle and NOM removal than Ti coagulants without polymerization. Polyaluminum chloride (PAC) is a commonly-used prehydrolyzed conventional coagulant (Edzwald, 1993; Sinha et al., 2004). It is generally prepared by slow base-feeding using NaOH or Na_2CO_3 as the basification reagent (Bottero et al., 1980; Tang et al., 2004; Thompson et al., 1987; Yang et al., 2011). In the same manner, we have recently developed a polytitanium tetrachloride (PTC) coagulant using NaOH as the basification reagent, and the results have proved PTC to be an efficient coagulant for water purification (Zhao et al., 2013). However, a number of previous studies with PAC have reported difficulty in producing stable high-concentration coagulants using NaOH as the basification reagent, since NaOH releases OH^- ions rapidly. Thus, using Na_2CO_3 as the basification reagent is expected to produce more stable PTC coagulants with high concentration.

In this paper, PTC samples were synthesized using Na_2CO_3 as the basification reagent and their coagulation performance was evaluated for artificial water treatment (using HA as the model NOM) compared to traditional PAC. The evolution of floc size with coagulation time was measured on-line using a laser diffraction instrument and the aggregates were characterized in terms of floc growth rate, size, strength, recoverability and fractal dimension. Additionally, the coagulation mechanisms were investigated based on coagulation performance, floc properties and floc zeta potential measurement.

2. Experimental

2.1. Coagulant preparation

The PAC samples were synthesized by a slow base titration at room temperature (Gao et al., 2005; Gong et al., 2008; Urabe et al., 2008). The pre-determined amount of Na_2CO_3 solution, varied with the target OH/Al molar ratio (B value), was slowly added to $AlCl_3$ solution under intensive agitation. The B values chosen in this research were 0.3, 0.5, 1.0, 1.5 and 2.0, and the resultant PAC samples were denoted as PAC_{03}, PAC_{05}, PAC_{10}, PAC_{15} and PAC_{20}, respectively. Further increase of the B value deteriorated the stability of the PAC solution and resulted in precipitates.

Similarly, the PTC samples were also synthesized using a slow alkaline titration method. First, a predetermined volume of concentrated $TiCl_4$ solution (purity $\geq$ 99%) was slowly added to cubes of frozen distilled water drop by drop under continuous stirring to obtain 20% $TiCl_4$ solution (density (ρ) = 1.26 g/mL). Cubes of frozen distilled water were used since the dilution process released exothermal heat. The predetermined amount of Na_2CO_3 solution was then added to the $TiCl_4$ (20%) solution under intensive agitation. The B (molar ration of OH/Ti) values chosen were 0.3, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 until irreversible precipitation occurred at the final stage of titration, and the resultant samples were thereafter denoted as PTC_{03}, PTC_{05}, PTC_{10}, PTC_{15}, PTC_{20}, PTC_{25} and PTC_{30}. The experiments in this study were conducted immediately after coagulant preparation to avoid the aging effect.

2.2. Test water and jar-test

Coagulation experiments were performed using artificial water containing humic acid (HA) as model NOM. Standard jar tests were conducted using a programmable jar-tester. Details about the experimental procedures and characteristics of the water samples are described in S1 of the Supporting Information (SI).

2.3. Dynamic determination of 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 online monitoring system for the dynamic floc sizes can be referred to elsewhere (Zhao et al., 2011b). The flocs are characterized in terms of floc size, growth rate, strength, recoverability and fractal dimension (Cao et al., 2011; Jarvis et al., 2005; Zhao et al., 2011b). Detailed information can be referred to S1.3.

3. Results and discussion

3.1. The effect of different B values on coagulation efficiency

The impact of different B values on coagulation performance with PTC and PAC was comparatively investigated for HA artificial water treatment and assessed in terms of residual turbidity, UV_{254} (absorbance at 254 nm) and DOC removal, floc zeta potential and effluent pH (Fig. 1). As shown in Fig. 1(a), the residual turbidity for PTC decreased from around 7.0 NTU at B = 0 to the lowest value of 1.2 NTU at the B value of 1.0, beyond which a slight increase in residual turbidity was observed as B values increased further. The residual turbidity for PAC was approximately 10.5 NTU at the B value range of 0.0–1.0, but decreased to 3.9 NTU and 0.3 NTU at the B value of 1.5 and 2.0, respectively. This shows that the increase in the B value enhanced turbidity removal for both the PTC and PAC samples. However, the responses of UV_{254} and DOC removal as a function of the B value varied significantly for PTC and PAC (Fig. 1(b)). A gradual decrease in both UV_{254} and DOC removal with increasing B value was observed for PTC, while in contrast, the increase in B value was accompanied by a significant increase in both UV_{254} and DOC removal for PAC. With the increase of the B values, for PTC, the hydrolysis of the $TiCl_4$ coagulant is a process of polymerization toward decomposition (Zhao et al., 2013), while for PAC, the dominant species often transform into high polymers with higher charges and fewer categories (Feng et al., 2011). The hydrolyzed species of the chemical coagulants are often used to explain the difference of their coagulation performance for water treatment. Results indicate that, under high B values conditions, the hydrolyzed high polymers of PAC favored UV_{254} and DOC removal, while the decrease in UV_{254} and DOC removal by PTC may due to the decomposition of hydrolyzed Ti species.

Fig. 1(c) shows the variation of floc zeta potential and effluent pH with B values after coagulation with PTC and PAC. Zeta potential of the flocs formed by PTC decreased gradually from +2.1 mV to −1.3 mV as the B value increased from 0.0 to 2.0, followed by a significant drop to −10.3 mV and −19.9 mV respectively at the B