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Floc characteristics of titanium tetrachloride ($TiCl_4$) compared with aluminum and iron salts in humic acid–kaolin synthetic water treatment

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ABSTRACT

The floc strength and regrowth properties of $TiCl_4$, $FeCl_3$, and $Al_2(SO_4)_3$ were comparatively evaluated using humic acid–kaolin synthetic water sample. At the given optimum dosage (20 mg/L as Ti, 8 mg/L as Fe, and 2 mg/L as Al, respectively), the floc growth, breakage and regrowth of $TiCl_4$, $FeCl_3$, and $Al_2(SO_4)_3$ were investigated by use of a laser diffraction particle sizing device. Jar tests were conducted to investigate the impact of shear force and breakage period on floc breakage and re-aggregation potential. Results indicated that the responses of flocs to increasing shear force and breakage period depend on the coagulant used. The ability of floc to resist breakage decreased with the increase of shear force. Floc strength properties were also measured in response to increasing shear force, with the results suggesting that the order of floc strength was $TiCl_4 > FeCl_3 > Al_2(SO_4)_3$. Floc regrowth of these three coagulants after exposure to high shear was limited, and flocs formed by $TiCl_4$ displayed the weakest recoverability. Similar results were obtained when breakage period was different.

1. Introduction

Coagulation/flocculation is the most common process used for the removal of turbidity particles and natural organic matter (NOM) at water treatment works (WTW) [1]. Due to the effectiveness in treating a wide range of waters at a relatively low cost, Al-salts become the most commonly used coagulant in water treatment. However, Al-salts are considered to cause harmful effects to human and living organisms [2]. This has led to the increasing use of Fe-salts which give higher dissolved organic carbon (DOC) removal compared with Al-salts [3,4]. Nonetheless, the flocculation processes using Al- and Fe-salt coagulant produce a large amount of sludge. Most of the sludge is solid waste from which nothing can be recovered or reused, and thus further treatment such as incineration, landfill, etc. are required, which makes the process to be inefficient for the waste water treatment.

To resolve the sludge disposal problem, a chemical coagulant that can reduce the amount of sludge or produce reusable material is required to make the process efficient by offering environmental and economical benefits associated with sludge handling. Shon et al. [5] used titanium tetrachloride ($TiCl_4$) as a coagulant for the treatment of wastewater, and the most significant advantage is recovering sludge and producing valuable by-product namely titania (TiO_2) [6]. TiO_2 is the most widely used metal oxide for environmental applications as photocatalyst, cosmetics, paints, electronic paper, and solar cells [7,8]. Therefore, the demand of TiO_2 would greatly be increased. They also reported that up to about 40 mg-TiO_2 nanoparticles/L-wastewater was produced from wastewater sludge. This quantity is quite significant given the huge demand for TiO_2 in the market. In addition, better photocatalytic activity of recycled TiO_2 was observed than the commercially available TiO_2 (P-25). Therefore, recycling of Ti-flocculated sludge not only produces TiO_2 with wide range of environmental applications but also solves the problem of sludge disposal from water and wastewater treatment plants.

The possibility of using titanium compounds as coagulant in water treatment was first investigated by Upton and Buswell [9]. They found that titanium sulfate ($Ti(SO_4)_2$) was more effective in removing fluoride due to a quadrivalent cation instead of the trivalent aluminum or iron ions. The effectiveness of Ti-salts has been performed in terms of removal of organic matter, turbidity, nutrients and floc properties by Shon et al. [5]. They found that removal of organic matter of different molecular weight by Ti-salt flocculation was similar to that of Fe- and Al-salt flocculation. Aquatic toxicity of the $TiCl_4$ flocculation processes was investigated to assess the environmental safety [10]. The result clearly indicated that TiO_2 nanoparticles produced from artificial wastewater, biologically treated sewage effluent and seawater show low acute toxicity under aqueous condition.

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However, few researchers have focused on the breakage and regrowth nature of floc coagulated by $TiCl_4$. High shear regions, such as areas around the impeller zone of flocculating tanks and transfer over weirs and ledges, are often prevalent in unit processes at WTW [11]. If small increases in shear during water works unit processes give rise to floc breakage, downstream systems will be challenged by smaller particles [12]. Flocs with reduced sizes result in lower sedimentation rate and may not only contaminate the filter (depending on the pore size and filter thickness), which may result in lower filtration performance, but also may pass through the filter resulting in the incomplete separation [13,14]. In addition, newly exposed surface of the aggregates may alter the surface charge of the floc aggregates, leading to partial re-stabilization [11]. Consequently, floc strength and recoverability should also be considered as an important parameter for overall process optimization. Previous research has shown that aggregates formed at a low velocity gradient in salt solutions that are then broken into smaller aggregates on exposure to an increased shear field will re-form to their initial size if the original velocity gradient is subsequently reapplied [15]. That is also observed during cyclical breakage and regrowth of activated sludge flocs [16] and is known as reversible breakage. However, in most instances, irreversible breakage is seen, such that the initial floc size is never subsequently achieved after breakage period [17,18]. Monodisperse polystyrene beads coagulated with aluminum sulfate have been shown to have variable regrowth depending on the intensity of the breakage shear [15]. Yukselen and Gregory [19] reported that, for the coagulation of kaolin particles, flocs formed by alum and polyaluminumchloride have been shown to have the poorest regrowth, reaching only a third of their previous size after shear while poly(diallyldimethylammonium) chloride (polyDADMAC) showed near complete regrowth and a copolymer of acrylamide and cationic monomer showed total regrowth. The studies mentioned above indicate that the coagulant used and therefore the coagulation mechanism involved has a considerable impact on floc regrowth potential. And floc aggregation depends on not only characteristics of source water and coagulant, but also various other parameters, such as applied shear force, shear exposure time, etc. [1,20].

In this study, $TiCl_4$, $Al_2(SO_4)_3$, and $FeCl_3$ were comparatively investigated in terms of strength and regrowth properties in the coagulation of humic acid–kaolin synthetic water. Floc strength and regrowth property were measured in response to increasing shear force through breakage and subsequent regrowth potential. This work also investigated the effect of breakage period on the strength and recoverability of floc. The relationship between floc strength and coagulation mechanism was also discussed.

2. Experimental

2.1. Water used in this study

The commercial humic acid (HA) (biochemical reagent) was used in the preparation of HA–kaolin synthetic water, and was purchased from the Jufeng Chemical Technology Co. Ltd., Shanghai, China. The HA stock solution was prepared as follows: 1.00 g HA was dissolved in 1000 ml of 0.4 mol/L NaOH solution with continuous stirring for 30 min. The HA–kaolin synthetic water was prepared by adding a certain amount of HA stock solution and kaolin into deionized water and tap water, with the volume ratio of the deionized water and tap water was 1:1 [21]. The UV_{254} absorbance, DOC, turbidity and pH of the test water were 0.450 ± 0.02 cm^{-1}, 3.900 ± 0.5 mg/L, 15.0 ± 0.3 NTU, and 8.23–8.47, respectively.

2.2. Coagulants

$TiCl_4$ stock solution (20%, density = 1.148 g/ml) was obtained from Photo & Environment Technology Co. Ltd (South Korea), and was used as received without any further purification. Stock solutions of $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3 \cdot 6H_2O$ were prepared at a concentration of 1 g/L by Al and 2 g/L by Fe, respectively. Deionized water was used for the reagents preparation.

2.3. Jar tests

Jar tests for HA–kaolin synthetic water treatment were conducted with a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) at 26 ± 1 °C of room temperature. Test water of 1000 ml was transferred to a 1.4 L beaker; under rapid stirring of 200 rpm ($G = 106.6$ s^{-1}), predetermined amount of coagulant was dosed. After 1.5 min, the stirring speed was reduced to 40 rpm ($G = 12.2$ s^{-1}) with a duration of 15 min, and then settled (0 rpm) for 15 min. At the end of jar test, the supernatant sample was withdrawn by syringe from about 2 cm below the water surface for analysis. The samples were prefiltered through a 0.45 μm fiber membrane before testing for UV_{254} (absorbance at 254 nm using a UV-754 UV/VIS spectrophotometer) and DOC (measured by a Shimadzu TOC-VCPH analyzer), while the turbidity was measured without filtration using a 2100P turbidimeter (Hach, USA) and zeta potential was analyzed with a Zetasizer 3000HSa (Malvern Instruments, UK).

2.4. Floc breakage and regrowth

After the slow stir phase of flocculation, the effect of increased shear force on floc breakage and regrowth was investigated by increasing the rpm on a jar tester for a further 5 min. Each experiment was repeated twice at rpm of: 75, 100, 150, 200, 300, followed by another slow mixing at 40 rpm for 15 min for floc to reform. The dynamic floc size was measured using laser diffraction Mastersizer 2000 (Malvern, UK) as coagulation proceeded. The suspension was monitored by drawing water through optical unit of Mastersizer and back into the jar by a peristaltic pump (LEAD-1, Longer Precision Pump, China) on a return tube with a 5 mm internal diameter peristaltic pump tubing. Floc size was measured every 0.5 min for the duration of jar test and the results were automatically recorded.

In addition, a series of jar tests were conducted to investigate the effect of breakage period on floc strength and recoverability. After the slow stir phase was completed, flocs were exposed to a shear force at 200 rpm. Two separate breakage periods were investigated: (i) a long breakage period of 15 min and (ii) a short breakage period of 30 s. After the breakage phase, the slow stir at 40 rpm was reintroduced for a further 15 min. Floc size was monitored as before.

2.5. Floc strength

The rate at which a floc size decays on exposure to shear is indicative of the floc strength. The empirical relationship between the applied shear force and broken floc size has been used by many researchers [22–24]:

$$\log d = \log C - \gamma \log G$$

where d is the floc diameter (μm); C is the floc strength constant that strongly depend on the method used for particle size measurement; G is the average velocity gradient (s^{-1}) and γ is the stable floc size exponent dependent on floc breakage mode.