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Comparative study of the effects of experimental variables on growth rates of aluminum and iron hydroxide flocs during coagulation and their structural characteristics

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ABSTRACT

In this study, the dimensions of over six thousand flocs were analyzed to quantitatively and comparatively investigate the effects of several experimental variables on the growth rate of aluminum (Al) and ferric (Fe) hydroxide flocs. Results show that Fe hydroxide flocs have faster growth rate than Al hydroxide flocs; and the average size of the former is larger than that of the latter. Increasing the concentration of the bivalent sulfate ion (SO_4^{2-}), initial turbidity, or slow mixing rate, was able to increase the growth rate of both kinds of flocs. On the other hand, steady floc sizes were found to decrease with the increase in SO_4^{2-} concentration, initial turbidity, or shear rate. Fe hydroxide flocs are more prone to be influenced by the changes in the variables than Al hydroxide flocs. While the steady floc sizes became smaller when initial turbidity or slow mixing speed increased, the roundness and smoothness of flocs were found to increase, indicating that higher initial turbidity or larger slow mixing rate produces flocs with more regular and round shape. Furthermore, at a fixed shear rate, Fe hydroxide flocs are stronger than Al hydroxide flocs. However, Fe hydroxide floc sizes are much easier to decrease with the increase in slow mixing intensity.

1. Introduction

A coagulation process using hydrolyzable metal salts (HMS), e.g., Al(III) or Fe(III) salts, is commonly applied in the field of water treatment. Coagulation mechanisms are believed to be adsorption–destabilization coagulation and enmeshment (or sweep coagulation). Hydrolyzed Al or Fe species are usually positively charged. They destabilize the negatively charged particles via charge neutralization or double-layer depression, leading to adsorption–destabilization coagulation. On the other hand, enmeshment refers to the process by which an amorphous Al or Fe hydroxide floc snares particles. As pointed out by Letterman et al. [1], the rate of adsorption–destabilization coagulation is much lower than that of enmeshment through voluminous flocs [2]. A fast floc growth rate indicates a fast coagulation process, which in turn requires a small coagulation tank. Furthermore, a large floc usually has a fast settling velocity [3], which in turn means a small sedimentation tank. Therefore, engineers and operators in a water-treatment plant attach a great importance to floc size. However, previous studies on floc sizes tend to employ a particle size analyzer. Unlike solid particles, such as kaolinite particles, the snowflake-like floc formed during coagulation has an irregular and open structure and a large content of water (over 90% [4]). Reed and Mery [5] found that the particle size analyzer they used monitored only the solid parts of flocs and thus underestimated floc size. The authors in the present study adopt microscopy to investigate floc size. Among the methods for determining floc structural characteristics, microscopy is a relatively inexpensive approach, and allows individual flocs to be analyzed at high magnification. The disadvantage of microscopy is that it requires the painstaking individual analysis of hundreds of flocs. Our experience shows that evaluating the floc growth rate in a 20-min flocculation process requires at least 400 flocs to be captured. In this study, over six thousand flocs were analyzed.

Several factors exert influences on floc growth rate. For example, using a photometric dispersion analyzer (PDA), Wang et al. [6] found that coagulation rate was greatly affected by the concentration of SO_4^-. However, the PDA can only monitor the flocs smaller than 0.2 μm [7]; and there is no direct relationship between the output of PDA and floc size. Therefore, people still do not know the exact effects of $[SO_4^-]$ on floc size and floc growth rate.

Another significant factor influencing coagulation performance is the initial turbidity or particle number concentration. High initial turbidity can occur in the case of heavy rain when surface runoff brings mud and particles to the surface waters. Quantitative study about the effects of initial turbidity on floc growth rate may be able to

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provide information for a water-treatment plant encountering heavy rain. However, a clear understanding about the effects of initial turbidity on floc growth rate has not yet been well established.

Alum ($Al_2(SO_4)_3 \cdot 18H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) are two kinds of commonly applied coagulants among environmental communities. A quantitative comparison between the growth rates of Fe hydroxide flocs and Al hydroxide floc, however, is lacking in literature. Furthermore, researchers still do not know whether or not the variables mentioned above exert parallel influences on these two kinds of flocs.

Ching et al. found that slow mixing considerably affected coagulation rate [8]. However, engineers in a water-treatment plant demand quantitative data showing the effects of slow mixing speed on the floc size variation during coagulation to design the coagulation and sedimentation tanks, since mixing intensity is connected with the electronic charge. Furthermore, the variation of floc sizes as a function of slow mixing intensity can provide the information about floc strength [9]. However, a comparison of the strength of Fe hydroxide flocs and that of Al hydroxide flocs is lacking in the literature.

The shape factor is the term commonly applied to quantify the deviation of a floc shape from a sphere. For instance, the roundness is a measure reflecting the curvature variations along the grain surface. Smaller distortions of the surface can increase the drag coefficient and thus decrease the settling velocity [10]. As such, a floc with a low smoothness factor has a relatively jagged shape. Variables, such as initial turbidity and share rate, may affect the shape factors of hydroxide flocs. A comparison of the shape factors of Fe hydroxide and Al hydroxide flocs with the changes in variables needs to be conducted.

2. Materials and methods

2.1. Jar test and test solution

Experiments were performed using deionized (D.I.) water containing 1×10^{-3} mol/L HCO_3^-, 2×10^{-3} mol/L Cl^-, 2×10^{-3} mol/L Na^+, and 1×10^{-3} mol/L K^+ as the test solution. Different initial turbidities were realized by dispersing different amounts of kaolinite particles in the solution. The particles in the suspension had a mean diameter of 0.5 µm with a narrow size distribution [2]. Turbidity was measured by a portable turbidimeter (2100P Portable Turbidimeter, HACH Company, USA). All reagents used were of analytical grade, and the solution pH was ~8.0. The test solution was stored in a closed glass container for 12 h to allow the equilibration of all the components. The experiments were conducted at a temperature of 25 ± 0.3 °C. Different sulfate-ion concentrations were achieved by adding 0.25 mol/L Na_2SO_4 stock solution.

A jar test was used to simulate the coagulation process. Ref. [2] shows the dimension of the jar test beaker. Alum ($Al_2(SO_4)_3 \cdot 18H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$, FC) were applied as the coagulants in this study. After a known amount of alum or ferric chloride was added to the test solution, the solution was allowed to rapidly mix for 1 min at 150 rpm followed by 20 min of slow mixing at 45 rpm to promote floc growth. For investigating the effects of mixing intensity on floc properties, slow mixing speed was adjusted to 60, 80, or 100 rpm. After coagulation, the motor was switched off and the coagulated suspensions were allowed to settle for 30 min. The alum and ferric chloride dosages were 18.0 mg/L and 14.6 mg/L, respectively, to let the molar concentration of Al equal to that of Fe, 5.4×10^{-5} mol/L.

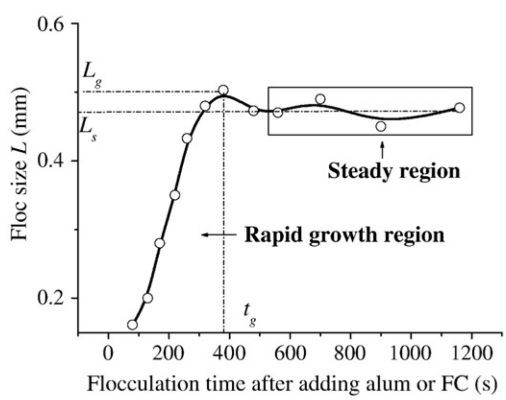

Fig. 1. A typical floc growth curve.

2.2. Floc image analysis

The steps for capturing a floc image have described previously [2]. The floc dimension was obtained by processing the floc image using Scion Image software showing the area and perimeter of a selected area. The software also calculated a best-fit ellipse with the same projected area as the floc. The major axis of the ellipse is viewed as the floc size *L*. The averaged value of the sizes of the captured flocs (around fifty) in an experimental setting is taken as the average floc size in this setting. As shown in Fig. 1, during a coagulation process, the floc size rapidly increases, and reaches a maximum. Given sufficient time, floc sizes reach steady state that reflects the balance between aggregation and breakup. The floc growth rate *F* in this study is calculated by the slope of the rapid growth region,

$$F = {}^{L_g}\!\big/_{t_g}, \tag{1}$$

where L_g and t_g are, respectively, the average floc size and flocculation time at the end of the rapid growth region (see Fig. 1b). The floc growth rate *F* is a measure of coagulation rate. The average size of flocs captured during the steady region was termed as the steady floc size L_s.

2.3. Floc shape

Floc shape was described by two shape factors, roundness, *R*, and smoothness, *S*.

$$R = \frac{4A}{\pi L^2}, \tag{2}$$

$$S = \frac{P}{P_e}, \tag{3}$$

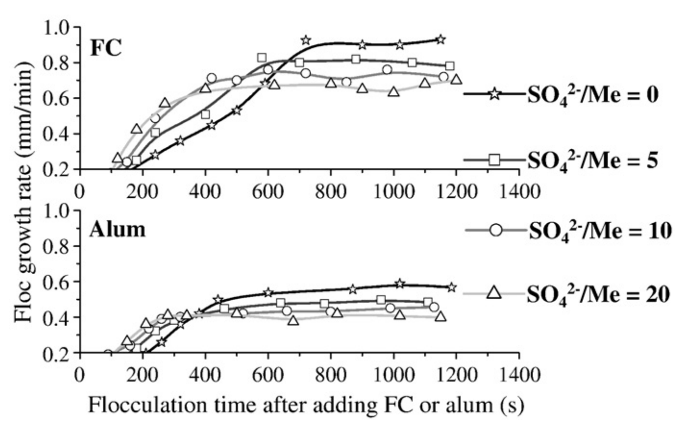

Fig. 2. Effects of SO_4^{2-}/Me on floc sizes during FC and alum coagulation processes (pH 8.0. FC and SO_4^{2-}/Me, respectively, refer to ferric chloride, $FeCl_3 \cdot 6H_2O$, and the molar ratio of sulfate ion to aluminum or ferric from coagulants; the practices are remained in following discussion. [Al] = [Fe] = 5.4×10^{-5} mol/L).