Journal of Water Process Engineering 11 (2016) 32–38

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

# Mechanism of clarification of colloidal suspension using composite dry powdered flocculant

Hiroto Kadooka[a], Mohammed Saedi Jami[b], Takanori Tanaka[a,*], Masashi Iwata[a]

[a] Department of Chemical Engineering, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka, Japan
[b] Department of Biotechnology Engineering, Faculty of Engineering, International Islamic University Malaysia, Kuala Lumpur, Malaysia

ARTICLE INFO

*Article history:*
Received 3 November 2015
Received in revised form 16 February 2016
Accepted 9 March 2016
Available online 24 March 2016

*Keywords:*
Flocculation
Coagulation
Composite flocculant
Powdered flocculant
Water/wastewater treatment

ABSTRACT

Flocculation is a widely used process for particle removal in water/wastewater treatment. Clarification method by using composite flocculants in powder form has been proposed in the literature. Such composite flocculants are conveniently used in the flocculation process of small volume suspensions. In this study, fundamental aspects of the clarification mechanism of the composite dry powdered flocculant are investigated. 1.00 mg/mL suspension of polymethyl methacrylate particle (PMMA, 0.15 μm in diameter) is used as a colloidal material. A model composite flocculant comprising an inorganic flocculant (aluminum sulfate), anionic polymer flocculant (copolymer of acrylic acid and acrylic amide), and a flocculation aid (calcium carbonate) is studied. The effects of each component on turbidity removal are examined. It is clarified that the order of addition, the state of polymer flocculant (powdered form or liquid form), and combination of components (polymer flocculant with/without aid particles) are critical for turbidity removal with combined use of flocculation aid, inorganic flocculant and polymer flocculant. When the composite dry powdered flocculant is added to a colloidal suspension, the inorganic flocculant dissolves immediately. The polymer flocculant particles disperse well in the suspension with the help of flocculation aid particles and dissolve moderately. The ions from inorganic flocculant result in formation of microflocs composed of both PMMA and flocculation aid particles. Flocculation aid particles play an important role; *i.e.* they accelerate flocculation of PMMA particles and attenuate the ability of the polymer flocculant particles to produce undissolved lumps.



## 1. Introduction

Flocculation is a process in which individual stable particles dispersed evenly in a suspension are made to aggregate to form flocs capable of settling resulting in clarification. Materials that cause or promote the flocculation of particles are classified into three categories: *i.e.* inorganic flocculant, polymer flocculant, and flocculation aid. General features of these materials are as follows. When inorganic flocculant is added to water, it reacts with the water and results in charged ions. It is well known that these ions compress the electric double layer of the particle and lead to the formation of micro flocs [1]. There are a variety of inorganic flocculants which can be used in the clarification process of suspensions. One of the earliest flocculant, and still the most extensively used, is aluminum sulfate (alum). The polymer flocculant is a water-soluble material which has adsorbable sites onto suspended particles. Flocculation occurs by a process of adsorption of polymers on the particles, followed by a process of bridging of polymer chains between particles and/or charge neutralization of the particles [2–6]. Since dissolved polymer flocculant molecules repel each other in water, particles perfectly covered by flocculant molecules do not form flocs. Thus, a flocculation process depends strongly on the amount and morphology of adsorbing polymer molecule [5,6]. It is also a well known fact that the manner of addition of a polymer flocculant solution to a colloidal suspension affects the resulting floc property [7,8]. Fleer and Lyklema reported that the flocculation by polymer flocculant is most effective when equal amounts of nearly completely covered particles and uncovered particles are mixed [3], while Sakohara et al. reported the effectiveness of stepwise addition of polymer flocculant solution into the colloidal suspension [9]. To promote the settling of particles, a flocculation aid is introduced to the flocculant as it adds density to the slow-settling flocs as well as a strong bonding enabling the flocs not to break during the mixing and settling processes. Calcium carbonate as flocculation aid is used to increase the alkalinity of the water, resulting in an increase in ions in the water; these ions help colloidal particles form flocs. Since

* Corresponding author.
*E-mail address:* tanaka@chemeng.osakafu-u.ac.jp (T. Tanaka).

http://dx.doi.org/10.1016/j.jwpe.2016.03.004
2214-7144/

flocculation aid particles are generally bigger than colloidal particles, the aid particles act as targets for heterocoagulation among all suspended particles [10].

The composite use of the above materials is also employed in the modern system of wastewater treatment. Clarification methods by adding composite flocculants in powder form were disclosed in some patents [11–15]. The composite powdered flocculant contains an inorganic flocculant, a polymer flocculant, and a flocculation aid all in powder form. These dry powders are mixed thoroughly. The composite dry powdered flocculants do not require a dissolving tank; they are added directly to a suspension. Thus, such composite powdered flocculants are conveniently used in the flocculation process of small volume suspensions: *e.g.* batch operation of wastewater discharged from a small-scale plant such as the printing industry, on-site wastewater treatment in regions where the infrastructure is poorly developed, and flocculation treatment of dredged sludge for an environmental improvement. However, very limited work has been reported on the flocculation behavior using composite flocculants in powder form. In this study, we will discuss fundamental aspects of the clarification process of a suspension by adding a composite dry powdered flocculant; the role of each component (inorganic flocculant, polymer flocculant and flocculation aid) and their interactions will be clarified.

## 2. Experimental

### 2.1. Materials and method

0.15 μm polymethyl methacrylate (PMMA: MP1451, Soken Chemical & Eng. Co.) particles were used as a colloidal material. Aluminum sulfate hydrate (alum, $Al_2(SO_4)_3 \cdot 16H_2O$) was used as an inorganic flocculant. The critical coagulation concentration (c.c.c), defined as the minimum concentration of ions necessary to cause rapid coagulation of colloids, of a PMMA suspension/alum system was determined from the measurement of the time rate of optical density change d(OD)/d$t$ of the PMMA suspension just after the addition of alum aqueous solution [16,17]. The logarithmic value of d$t$/d(OD) at time $t = 0$ decreases linearly with the logarithmic value of alum concentration in slow coagulation region and shows a constant value in rapid coagulation region; the c.c.c. value can be determined from the intersection of these linear relations. As a polymer flocculant, acrylamide-acryl acid copolymer (SENKAFLOCK S2015A, charge density: 1.15 meq/g, viscosity: 300 mPa·s at 0.5 wt% aqueous solution (25 °C)) was used. The particle size of the polymer flocculant powder was ranging from 75 to 106 μm. Calcium carbonate powder of median diameter of 10 μm was used as a flocculation aid. The composite flocculant used in the experiments was prepared by mixing thoroughly the above three components, all in powder form, with a spatula on the chartula for more than one minute.

20 mL of 1.00 mg/mL PMMA suspension was introduced into a 25 mL test tube. This suspension was mixed with a composite flocculant in powder form by turning upside down by hand, ten times in twenty seconds. Then, a 3.5 mL aliquot of the upper liquid (obtained at a position 2.5 cm below the liquid surface) was taken in a 10 mm cuvette to measure the optical density (OD) of the liquid at 660 nm. The light at this wavelength is scattered by colloidal particles without absorption by chemicals in the system. A time course of optical density of the aliquot is measured by using the spectrophotometer (Hitachi, U-2000A). The effect of flocculant composition on the turbidity removal was examined by comparing the optical density. The dissolution process of polymer flocculant was monitored by using the Tuning Fork Vibro Viscometers (A&D, SV-10A). The dissolution process of inorganic flocculant was monitored by using a conductance meter (Horiba, DS-14).

### 2.2. Experiment to elucidate the effects of dosages of each component on turbidity removal

To elucidate the optimum composition of composite flocculant for a 20 mL of 1.00 mg/mL PMMA suspension, the dosage of inorganic flocculant was varied as 0, 0.25, 0.50, 1.00, 2.50, 5.00, and 10.00 mg/mL in the final suspension, while the dosage of polymer flocculant was varied as 0, 0.05, 0.10, 0.25, 0.50, and 1.00 mg/mL in the final suspension, and that of flocculation aid was varied as 0, 2.50, 5.00, 10.00, 25.00, and 50.00 mg/mL in the final suspension.

### 2.3. Experiment to elucidate the effect of particle size of polymer flocculant on turbidity removal

In the Sections 3.1, 3.2 and 3.3 shown below, the optimum dosage of each component in the composite flocculant is determined to be "1.00 mg/mL of inorganic flocculant, 0.25 mg/mL of polymer flocculant, and 10.00 mg/mL of flocculation aid". In this optimum composition of composite flocculant, the effect of particle size of polymer flocculant on turbidity removal was examined. This was done using four different samples of polymer flocculant with sieve sizes between 45–75 μm, 75–106 μm, 106–150 μm, and 150–212 μm. These different composite flocculants were applied separately to clarify samples containing 20 mL of 1.00 mg/mL PMMA suspension.

### 2.4. Experiment to elucidate the effect of manner of addition of each component on turbidity removal

In the optimum composition of the composite flocculant, each component of the composite flocculant was dosed to a 10 mL of 2.00 mg/mL PMMA suspension separately in various combinations in two steps in series as shown in Table 1. The concentration of PMMA in the final suspension was 1.00 mg/mL; this is the same as in the above experiments. The OD value of supernatant 20 min after the addition of flocculant to the suspension was measured. The performance of composite dry powdered flocculant (case I in the table) was compared with that of a conventional method (case II), in which the dry mixture of inorganic flocculant and flocculation aid were added first, and then 10 mL of polymer flocculant aqueous solution was added to the PMMA suspension. To clarify the reason for the difference in performance (shown later) of the two methods, three more experiments were conducted; 10 mL of alum aqueous solution was added first and then the dry mixture of polymer flocculant and flocculation aid was added to the suspension (case III); alum powder was added first and then the mixture of flocculation aid and 10 mL of polymer flocculant aqueous solution was added to the suspension (case IV); and the dry mixture of polymer flocculant and flocculation aid was added first and then 10 mL of alum aqueous solution was added to the suspension (case V). Comparing the results of cases III and IV, the effect of the addition manner (*i.e.* liquid or powdered) on the turbidity removal was investigated; comparing the results of cases III and V, the effect of the order of addition of each component on the turbidity removal was observed.

## 3. Results and discussion

### 3.1. Effect of dosage of flocculation aid on turbidity removal

As shown later, flocculation aid particles play an important role in turbidity removal when the composite powdered flocculant was used. A suitable dosage of flocculation aid was determined first. Fig. 1 shows the effect of flocculation aid dosage on the clarification process of 1.00 mg/mL PMMA suspension, where the dosages of both inorganic and polymer flocculants were fixed at 1.00 mg/mL and 0.25 mg/mL, respectively. In the figure, the solid