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The effect of additional coagulant on the re-growth of alum–kaolin flocs

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ABSTRACT

The process of floc formation, breakage and re-growth by aluminum sulfate (alum) with kaolin suspension was investigated by continuous optical monitoring. This paper focuses on the re-growth ability of broken flocs after an additional low dosage of alum, added during floc breakage.

When coagulated by charge neutralization at pH 5, the broken flocs could re-grow almost fully without additional coagulant dosage. In this case an additional low dosage of alum during floc breakage lowered re-growth ability of broken flocs, because of charge reversal and restabilization of the clay particles. However, without additional coagulant dosage, broken flocs showed incomplete re-growth ability at pH 7, where an amorphous hydroxide precipitate was formed. In this case, additional dosage of coagulant led to re-grown flocs that were larger than those before breakage. It is likely that, under these conditions, new precipitate coats the surface of the broken flocs so that stronger bonds are formed between floc fragments. It seems that surface characteristics of flocs and not just their zeta potential are important in influencing the re-growth of flocs.

1. Introduction

The size and structure of flocs greatly influence the efficiency of solid/liquid separation processes. Furthermore, type and concentration of coagulants, applied shear and variables such as concentration and size of particles will influence floc growth. Characteristics such as floc strength and the re-growth ability of broken flocs, are of great practical and fundamental interest. In water and wastewater treatment, hydrolyzing metal salts are commonly used as coagulants, but the mechanisms involved in the formation, breakage and re-growth of flocs formed with these coagulants, are still not well understood [1,2].

Flocs tend to break when they are subjected to an increased shear rate and several recent investigations have dealt with the reversibility of floc breakage. Yukselen and Gregory [2,3] found that only limited re-growth of broken flocs occurred with aluminum sulfate (“alum”) and polyaluminum chloride (PACl) as coagulants, indicating a significant irreversibility of the floc breakage process. Solomentseva et al. [4] showed that the formation, breakage and re-growth of flocs could be repeated several times, but the re-grown flocs would be smaller after each breakage. Some results have shown that broken flocs following breakage at high shear were difficult to re-grow when alum and polyacrylamide were used as coagulants [5,6]. Also natural organic matter (NOM) flocs formed with hydrolyzing salts were difficult to re-grow. Following addition of alum, ferric sulfate and polyDADMAC, the re-growth of broken NOM flocs after exposure to high shear was limited in all cases [1,7,8].

Nearly all of the results show that there is a distinct irreversibility of floc breakage, but there is no adequate model to explain these findings [9]. In order to provide a better understanding of the re-growth of broken flocs, the effect of an additional low dosage of coagulant, added during floc breakage, was investigated.

2. Materials and methods

2.1. Suspension and coagulant

Kaolin clay (Imerys, St. Austell, Cornwall, UK) was used as a model suspension. Two hundred grams of kaolin was dispersed in 500 mL of deionized water in a high-speed blender. To obtain full dispersion it was necessary to raise the suspension pH to about 7.5 by adding 5 mL of 0.1 mM NaOH. After mixing at 4000 rpm for 10 min the clay suspension was diluted to 1 L with deionized (DI) water and allowed to stand overnight in a measuring cylinder. The top 800 mL was decanted and its solids content was determined gravimetrically and found to be 133 g/L.

Aluminum sulfate hydrate ($Al_2(SO_4)_3{\cdot}16H_2O$; Fisons, >96%) ‘alum’ was used to prepare stock solutions at concentration of 0.2 M (as Al).

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2.2. Jar test and continuous monitoring

The test solutions were prepared using DI water with the addition of 5 mM $NaHCO_3$. All reagents used were of analytical grade. For the flocculation tests, the stock suspension was diluted in the water to give a clay concentration of 50 mg/L. The final suspension pH (after coagulant addition) was controlled at 5 or 7 by prior addition of a pre-determined amount of 0.1 M HCl. The temperature was maintained at 25 ± 1 °C.

A known amount of alum was added into the test suspension (800 mL) and at the same time the stirrer was started at 200 rpm. This rapid mixing speed was maintained for 1 min and then the stirrer speed was reduced to 50 rpm, to allow growth of flocs. After 10 min of slow stirring, the stirrer speed was increased to 200 rpm for 1 min to break the flocs. Finally, the speed was reduced to 50 rpm for 10 min, so that re-growth of broken flocs could occur. In some cases an additional dosage of alum was added into suspension during floc breakage, mostly at about half way through the 1 min period of high-speed stirring. The jar tests were carried out using a Flocculator 2000 (Kemira Kemi, Helsingborg, Sweden), which allows stirring speeds and times to be pre-set.

Experiments on the kinetics of formation, breakage and subsequent re-growth of flocs were performed with a custom-made monitor based on the 'turbidity fluctuation' principle. This is essentially the same technique as the Photometric Dispersion Analyzer (PDA 2000, Rank Brothers, UK), which has frequently been used in similar studies. The methodology used was similar to that of Yukselen and Gregory [2]. In this method the average transmitted light intensity (dc value) through the flowing sample and the root mean square (rms) value of the fluctuating component are measured. The ratio between the rms and the average transmitted light intensity (rms/dc) provides a sensitive measure of particle aggregation and it is termed Flocculation Index (FI) [10]. (In this work, the reported FI values are the absolute rms/dc ratios, taking into account the gain applied to the fluctuating signal.) The FI value is strongly correlated with floc size and always increases as flocs grow, providing a sensitive measure of particle aggregation [11]. It also decreases when aggregates are broken and so gives a useful indication of floc strength. In this work, after the FI value reached an initial steady value with the staring suspension, coagulant was added and rms and dc values recorded through USB data acquisition system (Pico ADC 11) and saved to a PC hard disk at 1 s intervals.

2.3. Electrophoretic mobility

Electrophoretic mobility (EM) was measured on the kaolin suspension, after coagulant addition and 1 min of rapid mixing, by a Particle Electrophoresis Apparatus Mk 2 (Rank Brothers Ltd., Cambridge, UK). In addition, the EM of flocs after 1 min of breakage by high stirring speed was measured. The delay time of the measurement was about 40 s. The average EM value for a sample was determined from 20 measurements.

3. Results and discussion

3.1. EM of flocs before and after breakage

The effect of the solution pH and alum concentration on the EM of flocs before and after breakage is shown in Fig. 1. Prior to alum dosage, the EM values of kaolin particles at pH 7 and 5 were −3.6 and −2.2 ($\mu m\,s^{-1}\,V^{-1}\,cm^{-1}$), respectively. For all alum dosages, the EM values were higher (less negative) at pH 5 than that at pH 7. This is due partly to the more positive EM value of kaolin, but also to the more positive nature of Al hydrolysis products at the lower pH. Low dosages of alum added at pH 5 caused a very steep increase of EM which then became positive and relatively constant with alum dosage. At pH 7 there was also a sharp increase of EM with increasing Al, but a significantly higher dosage was needed to give charge neutralization.

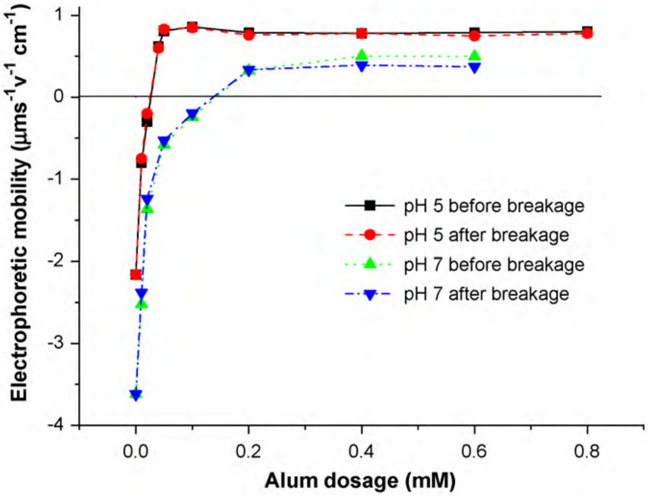

Fig. 1. Variation of electrophoretic mobility with alum dosage (mM Al) for flocs before and after breakage.

The EM obtained 1 min after alum addition was found to be nearly the same as that obtained after 1 min of floc breakage for both pH values (Fig. 1). This indicates that most particles were neutralized by hydrolyzed Al species during the initial 1 min after alum dosage and the average EM of particles (flocs) did not change when the flocs were broken. Although the average EM did not change as a result of floc breakage, the newly exposed surface of aggregates may have a negative, positive or neutral charge [12]. This may influence the re-growth of broken flocs.

3.2. The re-growth ability of broken flocs formed by two different coagulation mechanisms

According to Amirtharajah and Mills [13], there are two primary coagulation mechanisms—charge neutralization and sweep coagulation. These are dependent on alum dosage and solution pH. In order to cause coagulation by these two mechanisms, different dosages of alum were added and two pH values were fixed. Charge neutralization dominated the coagulation mechanism when 0.01 or 0.02 mol/L of alum was added and suspension pH was fixed at 5 (Fig. 1). For pH 7, the EM value becomes zero at around 0.15 mM Al. Under these conditions significant precipitation of amorphous hydroxide occurs and it is likely that charge neutralization occurs by adsorbed precipitate [14]. In this case coagulation is more influenced by the precipitate (sweep coagulation) and charge effects may be less important. The variation of FI with time during formation, breakage and re-growth of flocs coagulated at pH 5 and 7 is shown in Fig. 2. These all show the FI reaching a certain limiting, or plateau value after a certain time. This represents the steady state floc size, which depends on the floc strength and the effective shear rate in the stirred vessel. When the stirring speed is increased, there is a rapid reduction in FI, because of floc breakage, and a (partial) recovery when the slow stirring speed is restored.

Results for pH 5 and very low alum dosages (0.01 and 0.02 mM) are shown in Fig. 2a. At these dosages, the EM value is close to zero (Fig. 1) and it is very likely that charge neutralization is the reason for particle destabilization and coagulation. FI values for flocs formed with 0.02 mM alum began to rise earlier and the plateau FI value is rather higher than for 0.01 mM. These results indicate that destabilization is not complete at the lower dosage, leading