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Dependence of floc properties on coagulant type, dosing mode and nature of particles

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ABSTRACT

Kaolin suspensions were coagulated with $AlCl_3$ and a high-basicity PACl at pH 7, at dosages that gave zeta potentials close to zero. The actions of the two coagulants were completely different. With $AlCl_3$, the formation of an amorphous hydroxide precipitate played a dominant role. When the coagulant was added to the suspension, flocs grew rapidly and incorporated most of the kaolin particles within the hydroxide precipitate. When the suspension was added some time after the coagulant, the clay particles were found to be mainly on the outer floc surfaces, although the floc size was about the same. The light scattering properties of the flocs were very dependent on the number and location of particles in the precipitate. With PACl, delaying the addition of kaolin had no influence on the final floc properties.

In further tests, different suspensions over a range of concentrations were coagulated with alum at pH 7. Monitoring by a 'turbidity fluctuation' technique showed an apparent increase in floc size with increasing particle concentration. However, floc sizes determined from microscope images were very nearly constant, independent of particle nature and concentration. With different particle types, the monitoring results were greatly dependent on the light scattering properties of the particles.

Particles incorporated within hydroxide flocs appeared to have no influence on floc properties, such as size and strength.

1. Introduction

Coagulation is a widely-used process for conventional water treatment, and Al(III) is a very common coagulant in treating drinking water. Pre-hydrolyzed coagulants such as polyaluminum chloride (PACl) have been known for many years (e.g. Bottero et al., 1980) and their use in water treatment has been investigated in many previous studies (Dempsey et al., 1984; Gray et al., 1995; Matsui et al., 1998; Xiao et al., 2008; Hussain et al., 2013).

Al(III) and PACl have different coagulation mechanisms and efficiencies. PACl has often been found to be more efficient in the removal of natural organic matter (NOM) from high alkalinity and high pH water than traditional coagulants based on Al(III) and Fe(III) (Yan et al., 2008a) or in neutral pH

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water through charge neutralization and bridging (Yan et al., 2008b), especially at low dosage (Zouboulis et al., 2008). PACl proved to be a more efficient coagulant than alum and produced treated water with low turbidity and residual aluminum content without requiring acid addition for pH adjustment and subsequent base addition for re-stabilizing the water (Zouboulis et al., 2008; Zarchi et al., 2013). PACls with higher basicity (OH/Al) are more efficient for turbidity and NOM removal (Yan et al., 2008b,c). PACls with a high content of the Al tridecamer (Al_{13}) can give larger flocs, higher floc growth rate and shorter floc settling times than other Al-based coagulants (Hussain et al., 2013). However, some researchers have come to different conclusions. Trinh and Kang (2011) found that PACl was more effective in removing particles from water, but less effective in removal of NOM compared with alum. Shi et al. (2007) also found that coagulants with preformed Al species were less effective than conventional Al coagulant in removing humic acid with high molecular weight and hydrophobic character, giving smaller flocs.

The coagulation mechanisms of alum and PACl are different. Under most practical conditions, precipitate formation and sweep flocculation occur with alum, whereas charge neutralization by the Al_{13} polycation, electrostatic patch and bridging interactions are more important for PACl (Wu et al., 2009). After dosing into water, Al(III) undergoes a series of hydrolysis, polymerization, precipitation and aggregation processes. Amorphous $Al(OH)_3$ has a low solubility around neutral pH and can remove impurities by a combination of adsorption and precipitate enmeshment. PACl also forms precipitates at sufficiently high pH, but the polymeric structure of PACl is retained upon precipitation yielding a solid phase with different light scattering characteristics, electrophoretic mobility and solubility than amorphous $Al(OH)_3$ (Van Benschoten and Edzwald, 1990). Klute (1990) found that the preformed species in PACls are more stable than those formed in situ after alum addition; Matsui et al. (1998) assumed that those preformed species could destabilize particles faster. The preformed polymeric species contained in PACl are fairly stable and highly positively charged and these species can be adsorbed on surfaces of clay and other particles and undergo surface aggregation and rearrangement to form "electrostatic patches" (Ye et al., 2007). The Al_{13} polycation ($[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$) has a tetrahedral $Al(O)_4$ center surrounded by 12 octahedrally coordinated Al atoms (Johansson, 1960). Further hydrolysis or rearrangement of Al_{13} subunits can occur (Bottero et al., 1987; Bertsch, 1987). Both $Al(OH)_3$-rich and Al_{13}-aggregate flocs do not possess long-range crystalline structure, but Al_{13}-like crystals have been found in the flocs formed by PACl and the chemical compositions of the $Al(OH)_3$ precipitates and Al_{13} aggregates are markedly different (Lin et al., 2009).

In recent years, some researchers have focused on the floc breakage and re-growth process to better understand floc characteristics and coagulation mechanisms. It has been found that only limited re-growth of broken flocs occurred for alum and PACl, indicating a significant irreversibility of the floc break-up process (Yukselen and Gregory, 2004). It is likely that there are some changes on the surface of broken flocs. According to our previous research (Yu et al., 2011b), if sweep coagulation dominates the coagulation mechanism, a small additional dosage of alum added at the time of floc breakage, can greatly improve the re-growth ability of broken flocs. However a similar small addition of high-basicity PACl has no effect on floc re-growth, indicating that floc surfaces are quite different in the two cases.

In this work, coagulation of clay suspensions with Al(III) coagulants and a high-basicity PACl has been carried out with different dosing conditions and with different suspensions. The main aims of the work were:

- To compare the effects of Al(III) and PACl coagulants on the structure of flocs, by optical microscopy
- To gain further insight into the mechanism of floc formation by adding particles at different times after coagulant addition
- To investigate the effect of the nature and number of particles included within hydroxide flocs on the apparent floc size determined by an optical technique

2. Materials and methods

2.1. Materials

Kaolin clay (Imerys, St Austell, Cornwall, UK) was used as a model suspension. 200 g 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 pH of the suspension to about 7.5, which was achieved by adding 5 mL of 0.1 mM NaOH. After blending at 4000 rpm for 10 min the clay suspension was diluted to 1 L with deionized water and allowed to stand overnight (12 h) in a measuring cylinder. The top 800 mL was decanted and its solids content was determined gravimetrically and found to be 133 g/L.

Spherical silica particles (Geltech Inc) were dispersed in dilute NaOH solution to give a concentration of 10 g/L. These particles were porous, with a density of 2 g/cm^3 and a mean diameter of 1.5 μm, with a narrow size distribution.

Polystyrene latex was prepared by emulsifier-free polymerization of styrene, with potassium persulfate as initiator. The particles were highly uniform with a mean diameter of 1.6 μm, determined by an Elzone particle counter. The sample had been purified by repeated sedimentation, decantation and redispersion in deionized water and the final concentration was 40 g/L.

$AlCl_3$ and $PACl_{25}$ (OH/Al ratio = 2.5) were used as coagulants. $AlCl_3$ was purchased from Aldrich. The $PACl_{25}$ was prepared using a laboratory base titration method at room temperature (Wang et al., 2004) as described in detail in our previous paper (Yu et al., 2011a). The final concentration of both coagulants is 0.1 M (as Al). The samples, after being left to age one week, were analyzed using the ferron method as described by Wang et al. (2004). $AlCl_3$ was found to contain 97.1% Al_a (mainly monomer Al) and $PACl_{25}$ 93.6% Al_b (mainly Al_{13}).

Aluminum sulfate, $Al_2(SO_4)_3$, $NaHCO_3$ and HCl were of analytical reagent grade and prepared as a 0.1 M solutions in deionized water.