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Evaluation of Al_{30} polynuclear species in polyaluminum solutions as coagulant for water treatment

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Abstract

Polyaluminum coagulant with a content of 76.8% of Al_{30} (PAC_{Al30}) was prepared. Its coagulation behaviors were compared with high Al_{13} content polyaluminum coagulant (PAC_{Al13}) and $AlCl_3$. The species stability was studied using Al-Ferron method and ^{27}Al NMR. The coagulation performances were investigated by studying the rate of flocs development, the turbidity removal efficiency and charge neutralization capacity under fixed pH conditions and uncontrolled pH conditions. The effect of pH on coagulation was also studied. The results show that PAC_{Al30} are stable for using as coagulant. PAC_{Al30} causes less pH depression than PAC_{Al13}. The charge neutralization capacity of PAC_{Al30} is slightly lower than that of PAC_{Al13} at pH $\geqslant 6.8$ and higher at pH $\leqslant 6.5$. PAC_{Al30} achieves the most effective turbidity removal in these three coagulants. And it acts effectively within a much broader dosage range and a wider pH range when compared with PAC_{Al13}. PAC_{Al30} achieves the highest turbidity removal due to its strong flocs formation capacity. The results verify that Al_{30} is another highly active coagulation/flocculation species for turbidity removal.

Keywords: Al_{13} species; Al_{30} species; Charge neutralization; Coagulation; Polyaluminum chloride; Turbidity removal

1. Introduction

Coagulation/flocculation is a common process in water and wastewater treatment, which destabilizes the suspended and dissolved materials, followed by aggregation into large flocs that are easily separated from the water by subsequent sedimentation/flotation and filtration processes. Coagulant plays a key role during the process of coagulation. The pre-hydrolyzed polyaluminum coagulants are the most widely used coagulants and receive extensive research (Duan and Gregory, 2003). Compared with the conventional Al salts such as $AlCl_3$ and alum, polyaluminum coagulants have the advantage of being more effective within a broader pH range and more rapid aggregation velocity (Gao et al., 2002). Additionally, the high charge neutralization capacity of polyaluminum species often results in a decrease in dosage and the associated waste sediment production. Polyaluminum coagulants can achieve higher turbidity removal efficiency than traditional Al salts because the hydrolysis degree of polyaluminum can be controlled during manufacturing, and the hydrolytic Al species in polyaluminum coagulant can be tailor made. The polynuclear Al species in polyaluminum coagulant remains relatively stable for a long-term after dosing. However, the traditional Al salts hydrolyze and precipitate rapidly after dosing into water (Luan, 1997). The formation of Al species during this process is uncontrollable, and varies with the change of raw water nature.

Various meta-stable or transient state species such as monomers, oligomers, Al_{13} ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) polymer, other high polymers and Al sols coexist in

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polyaluminum coagulant (Tang, 1998). It is generally believed that Al_{13} species is the optimal species for coagulation in polyaluminum coagulant due to its high charge neutralization capability, strong structure stability and nanometer molecular diameter (1.0 nm). Thus, the high content of Al_{13} is one of the goals in the production of polyaluminum coagulants. However, the commercial polyaluminum coagulant only contains small amount of Al_{13} due to the aggregation of Al_{13} (Wang and Hsu, 1994), which is an insurmountable problem in the production of polyaluminum coagulant.

Al_{30} ($[Al_{30}O_8(OH)_{56}(H_2O)_{24}]^{18+}$) polymer is another polycation with Keggin structure in hydrolytic polyaluminum solutions, which was characterized by ^{27}Al nuclear magnetic resonance (NMR) and single-crystal X-ray diffraction. Al_{30} species is composed of two δ-Al_{13} connected by four Al monomers. The two tetrahedral coordinated Al in Al_{30} species produce a broad ^{27}Al NMR signal at $\delta = 70$ ppm (Allouche et al., 2000; Rowsell and Nazar, 2000). Al_{30} is more temperature resistant and less sensitive to pH variations than ε-Al_{13} (Allouche et al., 2000). Al_{30} possesses eighteen positive charges and unique nanometer molecule dimension (2.0 nm in length) (Allouche et al., 2000). It may be another promising active species in polyaluminum coagulant responsible for coagulation/flocculation besides Al_{13} species. But there is still no report on the coagulation/flocculation performance of Al_{30} species.

Our previous research investigated the formation conditions of Al_{30} species, and the results show that Al_{30} species can become the dominant species in polyaluminum solution when the freshly prepared polyaluminum solution is heated for 12 h at 95 °C. And the formation of Al_{30} is accelerated by the increase of total Al concentration (Chen et al., 2005). The formation conditions of Al_{30} coincide with the production conditions of commercial polyaluminum coagulant, in which polyaluminum coagulant has a high total Al concentration and is prepared at high temperature for a long time.

In the present research, polyaluminum coagulant with 76.8% Al_{30} content (PAC_{Al30}) was prepared. Its stability, flocs formation rate and coagulation performance were evaluated by comparison with Al_{13} species and $AlCl_3$.

2. Materials and methods

2.1. Materials

The reagents used in the current research are all of analytical grade. All solutions were prepared by deionised water. The coagulant that contains high content of Al_{13} (abr. PAC_{Al13}) was prepared by slowly neutralizing 1.0 M $AlCl_3$ aqueous solution with 0.6 M NaOH solution at 80 °C under vigorous stirring until the Al hydrolysis ratio ($B = [OH]/[Al]$) reached 2.4. The final Al concentration (Al_T) was 0.2 M. The coagulant that contains high content of Al_{30} (abr. PAC_{Al30}) was prepared by heating PAC_{Al13} at 95 °C for 12 h under stirring and refluxing. Both samples were rested at room temperature for 5 d before analysis, characterization and coagulation experiments. Al_T was measured by inductively coupled plasma-atomic emission spectroscopy (Vista-MPX ICP-AES, Varian). *B* value was measured by chemical analysis according to the Chinese standard method (GB 15892-1995). The pH values were measured on a pH meter (Orion 710A).

The Al species distribution in these two coagulants as well as 0.2 M $AlCl_3$ aqueous solution (abr. $AlCl_3$) were measured by the time-developed Al-Ferron complex colorimetry on UV–Vis spectrophotometer (DR/4000U, Hach) and by high-field ^{27}Al NMR method on Fast Fourier Transformation spectrometer (JNM-ECA600, JOEL). Based on the difference of the dissociation and complex reaction kinetic rate between Ferron and hydrolyzed Al species, Al species in coagulants were divided into three types: monomeric species (Al_a) (reacting with Ferron within 1 min), planar oligomeric and medium polymeric species (Al_b) (reacting with Ferron from one to 120 min), and three-dimensional species or sol–gels (Al_c) (reacting with Ferron after 120 min and non-reacting with Ferron). Al_c was obtained by Al_T minus Al_a and Al_b (Parker and Bertsch, 1992). In ^{27}Al NMR analysis, the aluminum at 0 ppm was assigned to Al monomer (Al_m). The concentration for 62.5 ppm and 70 ppm signals were multiplied by 13 and 15, respectively, to obtain the concentration of Al_{13} and Al_{30}, respectively. The concentration of Al species that cannot be clearly measured (Al_u) was calculated by Al_T minus Al_m, Al_{13} and Al_{30} (Chen et al., 2006). The detailed specifications of these coagulants are listed in Table 1. All coagulants were used directly, without prior dilution to avoid the change of Al species arose from dilution.

A stock suspension of kaolin clay was prepared by dispersing a measured amount of reagent-grade kaolin in deionised water by high shear mixing. The suspension was settled overnight, and the upper half of solution was collected and diluted to a concentration of $20\ g\ l^{-1}$. The particle size distribution of the kaolin suspension was measured on laser particle size analyzer (Mastersizer 2000, Malvern). The mean particulate size was 1.5 μm, and with 87.4% of particle size was below 2.0 μm. The working solution was prepared by diluting a calculated amount of stock suspension with deionised water. The concentration of alkalinity and electrolyte of working solutions were adjusted using 0.5 M $NaHCO_3$ and 0.5 M $NaNO_3$, respectively.

2.2. Methods

The development of flocs size during coagulation period was measured on a modified Laser Particle Size Analyzer (Mastersizer 2000, Malvern). The input and output tubes of the particle size analyzer were connected to a jar test flocculator with a single-paddle stirrer. The suspension in the beaker of flocculator was sucked into the particle size analyzer by a peristaltic pump continuously for online measurement of particle size during coagulation. The