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Mechanism of natural organic matter removal by polyaluminum chloride: Effect of coagulant particle size and hydrolysis kinetics

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ABSTRACT

The mechanism of natural organic matter (NOM) removal by AlCl_3 and polyaluminum chloride (PACl) was investigated through bench-scale tests. The fraction distributions of NOM and residual Al after coagulation in solution, colloid and sediment were analyzed as changes of coagulant dosage and pH. The influence of NOM, coagulant dose and pH on coagulation kinetics of AlCl_3 was investigated using photometric dispersion analyzer compared with PACl. Monomeric Al species (Al_a) shows high ability to satisfy some unsaturated coordinate bonds of NOM to facilitate particle and NOM removal, while most of the flocs formed by Al_a are small and difficult to settle. Medium polymerized Al species (Al_b) can destabilize particle and NOM efficiently, while some flocs formed by Al_b are not large and not easy to precipitate as compared to those formed by colloidal or solid Al species (Al_c). Thus, Al_c could adsorb and remove NOM efficiently. The removal of contaminant by species of Al_a , Al_b and Al_c follows mechanisms of complexation, neutralization and adsorption, respectively. Unlike preformed Al_b in PACl, in-situ-formed Al_b can remove NOM and particle more efficiently via the mechanism of further hydrolysis and transfer into Al_c during coagulation. While the presence of NOM would reduce Al_b formed in-situ due to the complexation of NOM and Al_a .

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1. Introduction

After the discovery of potentially toxic halogenated organics as by-products produced in drinking waters after chlorination (Rook, 1974), research on coagulation in drinking water shifted from the removal of particle toward the removal of natural organic matter (NOM) and disinfection by-products

precursors (Semmens and Field, 1980). According to the classical theory of coagulation for colloid removal, destabilization could be achieved by *compressing double electric layers*, *neutralizing*, *adsorption* and *bridging or sweep flocculation* (Duan and Gregory, 2003). The presence of NOM would complicate the process of coagulation because of its complex structure such as high negative charge and wide molecular weight

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range. Part of the NOM is dissolved and is unlikely to provide nuclei for precipitate formation as particle. Two mechanisms of NOM removal most commonly referred to are charge neutralization and adsorption (Hundt and O'Melia, 1988; Randtke, 1988; Van Benschoten and Edzwald, 1990b; Gregor et al., 1997; Edzwald and Tobaison, 1999). Charge neutralization is the mechanism used to explain the precipitation of NOM in operational regions where aluminum hydroxide precipitation is minimal. Cationic aluminum interacts electrostatically with anionic NOM to form insoluble charge-neutral products. This mechanism applies mainly to the removal of colloidal and higher molecular weight NOM, which can act as nuclei for precipitate formation. In the operational regions where insoluble aluminum hydroxide forms, NOM can be removed by surface adsorption. The concentration of coagulant has to be high enough to cause rapid precipitation of $\text{Al}(\text{OH})_3$. A third mechanism, complexation is also occasionally alluded, is the chemical interaction of soluble NOM with soluble coagulant metal ions such as aluminum (Van Benschoten and Edzwald, 1990b; Gregor et al., 1997). The complex of metal cation and NOM remains in solution until either the binding capacity of the NOM has been saturated or the solubility of the metal–NOM complex is exceeded. The operational conditions for charge neutralization, adsorption and complexation are not the same, and mechanisms involved under different operational conditions are still not clear. It would be determined not only by NOM characteristics but also by hydrolysis chemistry of coagulant.

When alum is added to water, Al^{3+} rapidly undergoes hydrolysis reactions to form other dissolved Al species or Al-hydroxide precipitates, including monomeric Al species $\text{Al}(\text{OH})_2^{2+}$, $\text{Al}(\text{OH})_3^+$ and $\text{Al}(\text{OH})_4^-$, dimer $(\text{Al}_2(\text{OH})_4^{4+})$, trimer $(\text{Al}_3(\text{OH})_4^{5+})$, tridecamer $(\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+})$ and amorphous precipitate $\text{Al}(\text{OH})_{3(\text{am})}$ (Van Benschoten and Edzwald, 1990a). A large number of investigations and practical applications show that the $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}^{7+}$ (simplified as Al_{13}) is the most efficient species for contaminant removal because of its high stability and positive electric charge (Van Benschoten and Edzwald, 1990a; Duan and Gregory, 2003). Polyaluminum chloride (PACl), the intermediate products during the hydrolysis–polymerization–precipitation process of Al^{3+} ions under specifically controlled conditions was developed to enhance the content of Al_{13} .

Various chemical and physical methods have been applied in monitoring the Al(III) hydrolysis/polymerization processes and the species in PACl stock solution (Wang and Tang, 2001). However, the performance of coagulant is determined by the species present during the coagulation process. The Ferron reaction is the only one which can be used to determine the speciation of Al under water treatment conditions (generally at concentrations in the sub-millimolar range, 10^{-4} – 10^{-5} M). Based on the kinetic difference of reactions between Ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonic acid) with different hydrolyzed species, hydrolyzed Al species can be divided into three types: monomeric Al species (Al_a), medium-polymerized Al species (Al_b) and colloidal or solid Al species (Al_c). It is found that dilution has little effect on the species distribution of PACls after dosing in the range of dilution factors of 200–2000 times if the solution alkalinity is not too high, while pH has significant effect on further species

transformation of PACl. The Al_a fraction in the primary coagulants is the most unstable species. After dosing, these species would transform into Al_b , and finally Al_c within minutes depending on the reaction conditions. The polymeric and colloidal species, once preformed, are quite stable. There is a great difference between the stability of the preformed Al_b species and that formed in-situ after dosing. The higher the B (OH/Al molar ratio) value of PACls, the less the Al_a species, and the more stable the Al speciation after dosing (Wang et al., 2004; Yan et al., 2008b).

However, the presence of strongly complexing anions such as citrate, tartrate or oxalate results in the formation of complexes with Al that do not readily react with Ferron (Jardine and Zelazny, 1987a,b). The Ferron method cannot provide enough information in the study of natural water sources directly.

The removal of NOM is also affected by the kinetics of coagulant hydrolysis and of reaction between coagulant and contaminants. Precipitates of $\text{Al}(\text{OH})_{3(\text{s})}$ induced by turbidity formation can be formed in 1 s under certain conditions (Letterman et al., 1973). Since both precipitation and polymerization have dimerization as an intermediate step, dimerization must happen at the same speed as precipitation or polymerization. Some researchers estimated the dimerization rate constant of 10^2 – $10^3 \text{ M}^{-1} \text{ s}^{-1}$ in water at 25 °C when Al^{3+} is the predominant monomeric species (Holmes et al., 1968; Owens and Eyring, 1970). This result suggests that dimerization of aluminum may be partially completed in about 1 s (at 10^{-3} M Al_T). Langford and Khan (1975) provided indirect evidence that complexation between NOM and monomers of aluminum appeared to be several orders of magnitude slower than conversion among monomeric forms of aluminum, as well as adsorption–destabilization reactions between Al and particle (Hahn and Stumm, 1968), and the process of the destabilized NOM and particle to aggregate to form larger floc in the settling process is relatively slower, and depends on the collision frequency and efficiency of the particle (Hahn and Stumm, 1968). Whether the dimerized and monomeric Al species would further hydrolyze to form larger polymer and precipitate in minutes depends upon pH condition (Wang et al., 2004; Yan et al., 2008b).

In general, although the interactions between coagulants and NOM are well understood via the broad reaction principles, there are still some uncertainties regarding the nature of the aqueous chemistry of metal coagulant, the polymer type (preformed and in-situ formed), and the effectiveness of particle size of hydrolyzed species, beyond the charge density parameters, for their application. A clear picture of the coagulation process has been limited by the complexity and diversity of both NOM and aqueous Al species. In this paper, the mechanism of NOM removal with typical PACls is investigated.

2. Materials and methods

2.1. Materials

All the reagents used were of analytical grade, except for those being specified. Three aluminum chloride-based coa-

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