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Coagulation of humic acid: The performance of preformed and non-preformed Al species

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Abstract

Inorganic polymeric Al coagulants have been being widely used in water treatment due to their advantages of applicability within broad pH and temperature ranges, high capacity of charge neutralization as well as less alkalinity consumption. However, the removal of dissolved organic matter (DOM) by such kind of coagulants has not been well understood because of the complexity of natural organic matter and the diversity of such polymeric Al coagulants. In this paper, coagulants with different Al speciation characteristics were prepared to conduct coagulation of humic acid (HA). The humic acid used was peat origin and was characterized physicochemically. The results showed that coagulants with preformed Al species were less effective than conventional Al salt in removing humic acid with large molecular and hydrophobic properties. The flocs formed by preformed Al species were smaller than those formed by conventional Al salt. Decreasing pH could improve the coagulation performance of all coagulants. Coagulation of humic acid might not follow the same charge neutralization rules associated with coagulation of mineral colloids. In the presence of humic acid, Al_{13} could be decomposed during coagulation process.

Keywords: Coagulation; Humic acid; Polyaluminum chloride; Al_{13}

1. Introduction

Coagulation is one of the critical operation units for removing colloidal particles and dissolved organic matter (DOM) in surface water treatment. However, the mechanisms involved in colloidal particle and DOM removal could be significantly different. Charge neutralization and sweep flocculation (the incorporation of impurities in amorphous hydroxide precipitate) are considered to be the two most distinct mechanisms in removing mineral colloidal particles [1]. But much less has been understood on the mechanisms of DOM removal by coagulation. It was proposed that formation of insoluble complexes between DOM and coagulant species as well as the adsorption of DOM onto freshly formed hydroxide precipitate could be the determining mechanisms [2]. Due to the differences between coagulation of mineral colloids and DOM, the present designs and operating procedures that are effective for removing turbidity may not be the most effective for removing DOM [3].

The commonly used conventional coagulants in water treatment include alum, sodium aluminate, ferric chloride, ferric sulfate, etc. Preformed polymeric metal coagulants have been shown to improve some of the coagulation performance compared to conventional coagulants [4–6]. Polymeric forms of metal coagulants in water treatment have become increasingly used due to their wider availability and reduction in cost [7]. Polyaluminum chloride (PACl) is one of the most important prehydrolyzed coagulants. PACl is less sensitive to changes in pH and temperature [8–10]. In addition, the high positive charge of some polycations, such as Al_{13} [$AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$], is highly effective in neutralizing the negative charges of colloidal particles [11].

However, contradictory results have been reported concerning the effectiveness of PACl in DOM removal. Some researchers found that PACl was able to directly precipitate fulvic acids (FA) over a broad pH range and could be a better coagulant than alum at more acidic and basic pH values [3,12]. While some investigators observed that PACl did not reduce DOM as effectively as alum [13,14].

The discrepancies related to the coagulation of DOM by PACl are mainly due to the complexity of DOM and the vari-

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ety of PACl products. DOM consists of a large number of organic compounds including natural and synthetic matters. Humic substances are ubiquitous in surface water and are the major organic constituent of unpolluted water. The molecular weight and hydrophobic/hydrophilic properties of humic substances are important factors associated with their treatment efficiencies [15]. Typically, humic substances are operationally divided into the more soluble fulvic acids and the less soluble humic acids (HA). On the other hand, most of PACl coagulants used in past studies were commercial products, and little is known about their exact chemical composition. The content of Al_{13} in commercial products is usually very low. In addition, PACl products from different manufacturers may contain different additives, such as sulfate and organic polymers.

The objective of this work was to get more understanding on the coagulation mechanisms of PACl in removal of humic substances by using well-characterized materials. Since more in-depth studies had been reported on the coagulation of fulvic acids, the emphasis of this paper was placed on the effect of Al species on the coagulation of humic acid. $AlCl_3$, laboratory prepared PACl and purified Al_{13} were selected as coagulants with different speciation characteristics; a kind of peat humic acid was chosen to conduct the coagulation experiments and the humic acid was characterized by ultrafiltration and resin fractionation. To avoid the interference of some cations and anions in natural water (e.g. calcium, magnesium, sulfate, phosphate), synthetic test water was prepared to conduct the investigation.

2. Materials and methods

2.1. Coagulants preparation and characterization

All the reagents used to prepare each coagulant were of analytical grade and deionized water was used to make all solutions. The procedures of preparing each coagulant can be described as follows: (1) conventional Al salt ($AlCl_3$): directly dissolving $AlCl_3{\cdot}6H_2O$ into deionized water; (2) PACl: adding pre-determined amount of Na_2CO_3 slowly into $AlCl_3$ solution under intense agitation. The temperature was kept at 70 °C by using recycling water bath. The target basicity (OH/Al molar ratio) of the PACl was 2.20; (3) Al_{13}: it was separated and purified from PACl using sulfate precipitation and nitrate metathesis reactions. The detailed procedures can be found in [16]. The total Al concentrations for all the coagulants were all adjusted to $0.1\ \mathrm{mol\,l^{-1}}$. All the coagulants were stored in refrigerator after preparation for later use. No obvious turbidity appeared in the coagulant solutions during the study.

The speciation distributions of the three coagulants were characterized using both liquid-state ^{27}Al nuclear magnetic resonance (NMR) spectroscopy (Avance 500, Bruker, USA) and ferron colorimetric assay [8]. The ^{27}Al NMR patterns of the three coagulants are demonstrated in Fig. 1. The signal at 0 ppm corresponds to monomeric species and the signal at 62.5 ppm corresponds to Al_{13} species (only the central Al atom in Al_{13} structure can produce resonance signal), the signal at 80 ppm is ascribed to the inner standard of $NaAl(OD)_4$. Other Al species, such as colloidal species cannot be observed by ^{27}Al NMR. No Al_{13} was detected from $AlCl_3$ solution, and the predominant species in $AlCl_3$ was monomers. Both Al_{13} and monomeric Al species existed in PACl while the content of monomers was relatively low. As to the purified Al_{13}, the signal of monomeric species was almost negligible.

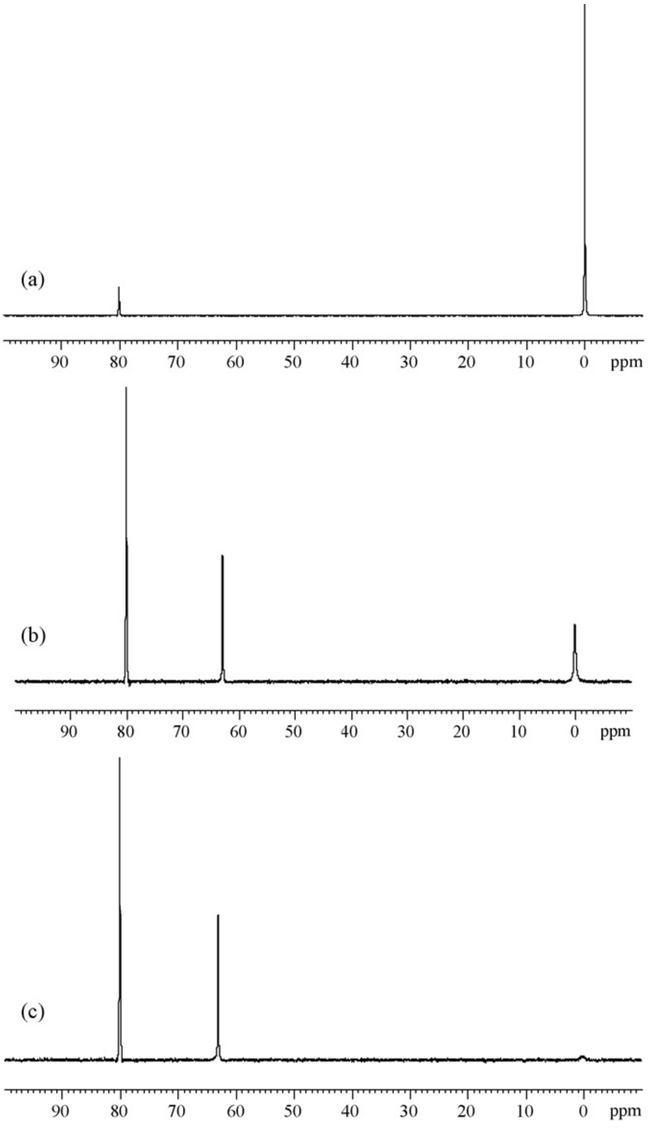

Fig. 1. ^{27}Al NMR patterns of three coagulants ((a) $AlCl_3$; (b) PACl; (c) Al_{13}).

Ferron assay can differentiate Al species into three categories: Al_a, monomeric (possibly some oligomeric) species; Al_b, polymeric species which could be rationally regarded as Al_{13} in this study; Al_c, colloidal species. The speciation characteristics of three coagulants are listed in Table 1. As evidenced by ^{27}Al

Table 1
Species distribution of three different coagulants

	pH	Al_a (%)	Al_b (%)	Al_c (%)
$AlCl_3$	3.28	91.7	8.3	0.0
PACl	4.02	6.2	29.5	64.3
Al_{13}	4.24	2.0	95.8	2.2