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Fate of hydrolyzed Al species in humic acid coagulation

Jr-Lin Lin [a], Chihpin Huang [a,*], Brian Dempsey [b], Jing-Yi Hu [a]

[a] Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan
[b] Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

The hydrolysis of Al-based coagulants in acidic conditions is necessary for the removal of organic matter by the coagulation/sedimentation process. However, interactions between hydrolyzed Al species and organic matter are complicated and this makes it difficult to optimize coagulant dosing for organics removal. The goal of this study was to investigate the reactions of hydrolyzed Al species in the coagulation of organic matter. Two polyaluminum chloride (PACl) coagulants, a commercial product with sulfate (PACl-C) and lab-prepared material (PACl-Al_{13}) containing 7% and 96% of total Al as Al_{13}, respectively, have been applied to investigate the coagulation of humic acid (HA). At pH 6, a lower dosage of PACl-Al_{13} than of PACl-C was required for optimized HA removal through coagulation/sedimentation due to the strong complexation and charge neutralization by Al_{13}. Observation of the coagulation process using wet scanning electron microscopy showed that PACl-C produced both clustered flocs and linear precipitates in the presence of sulfate while PACl-Al_{13} produced curled precipitates due to the formation of intermolecular complex, when both coagulants were added at the optimum doses. Investigation of Al–HA floc by ^{27}Al-NMR and Al 2p XPS suggested that monomeric Al (Al_m) was hydrolyzed into $Al(OH)_3$ with tetrahedron for PACl-C coagulation while a half of Al_{13} slowly decomposed into octahedral Al–HA precipitates for PACl-Al_{13} coagulation. Meanwhile, C ls XPS indicated that aromatic C=C of HA was preferentially removed from solution to Al–HA flocs for both PACl-C and PACl-Al_{13} coagulation. It was concluded that Al–HA complexation strongly affects the reaction pathways for Al hydrolysis and the final nature of the precipitates during PACl coagulation of HA and that the hydrolysis products are also strongly affected by the characteristics of the PACl coagulant.

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* *Corresponding author*. Tel.: +886 3 5712121x55507; fax: +886 3 5725958.
E-mail address: cphuang@mail.nctu.edu.tw (C. Huang).

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1. Introduction

Humic substances (HS) are colored and generally represent more than 50% of dissolved organic matter (DOM) in surface waters (Alborzfar et al., 1998). Many problems are associated with HS in the context of drinking water quality, including undesirable color, tastes and odors, and particularly the occurrence of carcinogenic disinfection-by-product (DBP) during chlorination (Gallard and Gunten, 2002).

In most surface waters, aquatic fulvic acid is the major component of HS, but humic acid (HA) is also present simultaneously (Edzwald and Tobiason, 1999). In water treatment, HA removal is mainly achieved by coagulation with hydrolyzed metal species (Duan and Gregory, 2003). HA removal by using various coagulants has been widely explored to determine the optimum condition for HA destabilization (Exall and Vanloon, 2000; Sieliechi et al., 2008). These studies have suggested that the optimum condition of coagulation for HA removal is closely related to pH due to effects on hydrolyzed metal species, which subsequently affect the degree of HA destabilization. The mechanisms of HA destabilization by hydrolyzed coagulant species have been well established. A combination of complexation of HA with metal ions, adsorption onto metal hydroxide precipitates, and co-precipitation with metal hydroxides are important in HA removal (Dempsey et al., 1984; Huang and Shiu, 1996).

Polyaluminum chloride (PACl) has been commonly adopted to remove organic matter by coagulation in water practices. The nature of PACl coagulant is highly related to its basicity (γ), which strongly affects the coagulation behavior. Some investigators have suggested that the basicity adjusted in the range from 2 to 2.3 during the preparation of PACl can produce high content of Al_{13} polycation (i.e., $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) (Bottero et al., 1980; Van Benschoten and Edzwald, 1990; Shen and Dempsey, 1998). Study has indicated that the major pre-hydrolyzed species of PACl is Al_{13} polycation that can subsequently destabilize HA by strong charge neutralization to effectively remove HA from water through coagulation/sedimentation process (Liu et al., 2009). However, other studies have reported that *in-situ* hydrolyzed Al_{13} shows better performance in the removal of natural organic matter (NOM) by coagulation/sedimentation (Hu et al., 2006; Zhao et al., 2008). In the presence of NOM, the Al_{13} polycation is converted into monomers catalyzed by complexation with organic ligands (Masion et al., 2000; Yamaguchi et al., 2004), and this could affect the efficiency of HA removal by PACl coagulation. The characteristics of HA and hydrolyzed metals floc governs floc density and settling rates, which dictates the efficiency of HA removal. Wang et al. (2007) have indicated that the HA flocs formed by PACl coagulation are multi-scale fractal, and their surface characteristics, such as irregularity and roughness, vary with the ratio of coagulant dosage and the quantity of HA. This implies that the structure of HA flocs could be significantly affected by Al–HA interaction. Kazpard et al. (2006) has suggested that the optimal coagulant dosage is a function of the interactions between the functional groups of HA and Al_{13} polycation. Although these studies have investigated the effect of PACl coagulation on the efficiency of HA removal through investigation into Al–HA interactions, the interaction mechanisms of hydrolyzed Al species and HA remains unclear because the pathway of Al species hydrolysis and decomposition in the presence of HA are complicated and may depend on coagulation conditions such as pH and dosage. In other words, the fate of hydrolyzed Al species in HA coagulation is the key factor to optimize HA destabilization, but it is still not fully understood.

In this study, the effect of Al species on the coagulation performance of humic acid (HA) was evaluated and the chemical interactions between hydrolyzed Al and HA were investigated. Two polyaluminum chloride (PACl) coagulants, one commercial PACl (termed PACl-C) and another custom-made PACl (designated PACl-Al_{13}) containing Al_{13} with 7% and 96% of total Al concentration, respectively, were mixed with HA in water. The Al–HA flocs that formed after coagulation at various pH values were investigated by X-ray photoelectron spectroscopy (XPS) and solid-state ^{27}Al nuclear magnetic resonance (^{27}Al NMR) to verify the nature of the reaction products and to identify the reaction mechanisms between HA and Al species. The morphology of Al–HA flocs was also examined by wet scanning electron microscopy (WSEM).

2. Materials and methods

2.1. Humic acids solution

A synthetic humic acid powder (Aldrich Co., USA) was added into distilled (DI) water and the solution was adjusted to pH 1 using HCl. After 10 min settling, the solution was centrifuged for 20 min and then the supernatant was withdrawn into DI water. After that, the solution was stirred at pH 11 by NaOH to completely hydrate and dissolve the remaining HA, followed by the filtration through 0.45-μm membrane. The filtrate was used as a synthetic stock solution, to which DI water was added to prepare the experimental HA solutions at the desired concentration of 5 mg/L. The specific conductivity of the working suspension was adjusted with 10^{-3} M $NaClO_4$ solution (Merck, Inc., USA) and the alkalinity was adjusted by adding 10^{-3} M Na_2CO_3 (Merck, Inc., USA). The conductivity and alkalinity of HA suspension is 357 μs/cm and 105 mg/L as $CaCO_3$, respectively.

2.2. Characterization of coagulants

Study reported that the content of Al_{13} polycation varies with the basicity in the preparation of PACl, and the PACl containing higher content of Al_{13} is more efficient to destabilize the organic matter by charge neutralization during coagulation (Liu et al., 2009). To investigate the effect of hydrolyzed Al species on the HA coagulation, two PACl coagulants with different basicity were used to evaluate the performance of coagulation in this study. A commercial-grade PACl (Al_2O_3 = 10%; γ = 1.4) was purchased from Showa Chemicals Inc., which was designated as PACl-C herein. Another PACl identified herein as PACl-Al_{13} contained high Al_{13} content that was separated from preformed PACl (Al_2O_3 = 29%; γ = 2.3) by sulfate precipitation and nitrate metathesis (SO_4^{2-}/Ba^{2+} separation method) (Shi et al., 2007). Based on the results of sulfate analysis by Ion Chromatography (833 Basic IC plus, Metrohm,

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