Selective binding behavior of humic acid removal by aluminum coagulation☆

Pengkang Jin [a], [*], Jina Song [a], [b], Lei Yang [a], Xin Jin [a], Xiaochang C. Wang [a]

[a] School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xi'an, Shaanxi Province, 710055, China
[b] College of Energy and Environmental Engineering, Hebei University of Engineering, Handan, Hebei Province, 056038, China

ARTICLE INFO

ABSTRACT

The reactivity characteristics of humic acid (HA) with aluminium coagulants at different pH values was investigated. It revealed that the linear complexation reaction occurred between aluminum and humic acid at pH < 7, and the reaction rate increased as the pH increased from 2 to 6. While at pH = 7, most of the dosed aluminum existed in the form of free aluminum and remained unreacted in the presence of HA until the concentration reached to trigger $Al(OH)_{3(s)}$ formation. Differentiating the change of functional groups of HA by ^1H nuclear magnetic resonance spectroscopy and X-ray photoelectron spectra analysis, it elucidated that there was a selective complexation between HA and Al with lower Al dosage at pH 5, which was probably due to coordination of the activated functional groups onto aluminium. While almost all components were removed proportionally by sweep adsorption without selectivity at pH 7, as well as that with higher Al dosage at pH 5. This study provided a promising pathway to analyse the mechanism of the interaction between HA and metal coagulants in future.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Humic acid (HA) is one of the major components of natural organic matter (NOM), arriving from weathering and/or biodegradation of dead plants and animals (Cheng and Chi, 2002). It significantly generates DBPs (disinfection by-products) with negative effects on human health during drinking water treatment and raised serious concern about water quality safety (Zhao et al., 2015; Siéliéchi et al., 2008; Bieroza et al., 2011). Currently, aluminum salts have been widely used as coagulants in coagulation-sedimentation process to remove HA in terms of high performance and low cost.

Over the past three decades, people have realized that the mechanisms involved in colloidal particle and HA removal could be significantly different. Many researchers proved interaction mechanisms of aluminium with HA by measuring the change in turbidity, Zeta potential and DOC in solution before and after coagulation at different pH values (Hundt and O'Melia, 1988; Huang and Shiu, 1996; Duan et al., 2002; Shin et al., 2008; Angelico et al., 2014). However, most studies still used the traditional coagulation mechanisms to explain the reaction between HA and aluminum.

Obviously, colloid theory was inapplicable to HA, a macromolecule with large and heterogeneous group of macromolecules. One of the most crucial factors in coagulation process is pH value, affecting the equilibrium of the reactions between organic functional groups and metal hydrolysed species. As is well known, the charge of HA can be readily affected by pH via the protonation and deprotonation of functional groups, resulting in the different reactivity and binding characteristics with metal coagulants (Browne and Drlscoll, 1993). As analytical techniques and methods progresses, various characterization methods and approaches have been applied to better understand the interaction behavior between HA and aluminum coagulants. Cheng and Chi (2002) assessed the pH effect on coagulation mechanism of HA reacting with metal ions using a fluorescence-quenching method. Other studies investigated the characteristics of Al-HA floc during coagulation process. Spectroscopic analysis by Lu et al. (1999) indicated that HA formed soluble complexes with Al^{3+} at pH < 4.5, while HA adsorbed on $Al(OH)_{3(s)}$ surface in the pH range from 5.0 to 7.0. Lin et al. (2014) compared the difference of HA destabilisation between commercial or laboratory-prepared PACl for high Al_{13} coagulation at pH 6 by investigating Al-HA floc with ^{27}Al nuclear magnetic resonance and X-ray photoelectron spectroscopy (Al 2p core-level spectra).

Although many attempts have been carried out to study the mechanism, some issues still remain poorly understood. Firstly, HA

contains high content of unsaturated conjugated functional groups, such as double bonds, aromatic rings, and oxygen-containing groups including carboxyl (-COOH), hydroxyl (-OH), and carbonyl (-C=O) (Bahemmat et al., 2016). At lower pH, the proton was unlikely to dissociate from HA. At higher pH, the functional groups of HA were deprotonated, which made HA more negatively charged. The active groups that release protons also have the high reactivity to metal ions, referred to as binding sites. The binding sites of HA would be changed due to protonation/deprotonation of functional groups at different pH value, resulting in distinctive coagulation mechanisms between coagulant and HA. Almost no research has been performed to investigate the reaction characteristics and interaction behaviour between HA and metal salts at different pH values from this point.

Secondly, aluminum salts have been widely used as coagulants for the removal of humic substances from waters, especially when the Schulze−Hardy rule states that multivalent ions destabilize colloidal suspensions much more effectively than monovalent ones (Hardy, 1900; Schulze, 1882). As is well known, aluminum is not stable in solution, and can be hydrolyzed to different dissolved species in aqueous solution depending on the pH and dosage. After dosing into water, monomeric Al species will be subject to a series of hydrolysis to form multinuclear species with different polymerization degree and finally to form amorphous hydroxide solids at a certain pH (Shi et al., 2007). Moreover, the similar reaction also occurs as pH increases at the same dosage. Thus, the reaction between HA and aluminium become more complicated, leading to more difficulties to explore the reaction mechanisms.

Thirdly, although the same removal efficiency was found at the optimal pH (pH 5) and neutral pH (commonly used in water treatment) (Wang et al., 2002), the residual organic matters after coagulation showed significantly different characteristics in our previous studies (Jin, 2005). We consider that the selectivity characteristics may highly influence the removal of HA at different pH values. According to Model V/VI/VII proposed by Tipping, HA binding sites have different pKa values (Tipping and Hurley, 1992; Lofts and Tipping, 2011; Tipping et al., 2011), which is similar to the selective complexation we suggested, *i.e.*, hydrolyzed Al species selectively bind to binding sites at different pH values. However, reports can be barely found related to this phenomenon.

In this study, to characterize the pH-dependent interaction between Al and HA, fluorescence spectroscopy and morin fluorescence technique were applied. Photometric dispersion analyser (PDA) was used to investigate the $Al(OH)_{3(s)}$ formation by observing the scattering intensity of transmitting light through the aqueous solution (Gregory, 1985). Moreover, to investigate the reactivity of HA with coagulants, ^{1}H NMR and XPS techniques were employed to monitor the structural change in characteristic functional groups of HA during coagulation. Based on experimental data, this study provides the insight into the reactivity characteristics of humic acid and its reaction mechanism with aluminum coagulants at different pH values.

2. Materials and methods

2.1. Materials and reagents

Humic acid was obtained from Sigma-Aldrich. The stock HA solution was prepared by adding 1 g HA into 1 L 0.1 mol/L NaOH solution. After stirred for 12 h, the samples were filtered through a 0.45-μm membrane to remove suspended materials.

2.2. Jar test procedure

Coagulation studies were performed in a conventional jar-test apparatus, equipped with six 1-L beakers. The stock HA solution was diluted with ionized water to reach the designated concentration (DOC = 10 mg/L). In addition, $NaNO_3$ was added to adjust the ionic strength of the solution to 0.1 mM. The phosphate buffer was also added into the solution. Aluminum chloride (41.4 mM Al^{3+}) was used in the study. The calculated volume of coagulation stock solution (to achieve the required dosage) and 0.1 M NaOH solution (to achieve the required pH) was added to the HA (DOC = 10 mg/L) solution. The coagulation procedure involved rapid mixing at 200 rpm for 1 min, followed by slow stirring at 20 rpm for 30 min. After 50 s, approximately 30 mL of the solution was taken to determine the Zeta potential and fluorescence intensity of the coagulating suspension. A 60-min settling period followed. The flocs were separated from the solution by centrifugation at 6000 rpm for 10 min.

2.3. Reacted aluminum analysis

Usually, free Al (unreacted Al) can be easily detected due to its reaction with some substances to form fluorescent complexes. The free Al refers to soluble Al hydrolysis species that do not react with HA or adsorb HA. In this study, the amount of free and complexed Al (aluminium formed complex with HA) can be determined via the morin (2,3,4,5,7-pentahydroxyflavone, $C_{15}H_{10}O_7 \cdot 2H_2O$) fluorescence analysis. A constant morin concentration (1.00 μM) and different Al concentrations were prepared. The fluorescence intensity of each solution was measured with an emission wavelength at 510 nm and excitation wavelength at 420 nm. Under this condition, the binding of A1 to HA has no fluorescence absorption. Moreover, no reaction was observed between HA and morin (Browne and Drlscoll, 1993).

Then, aluminum and 10 mg/L (DOC) HA were combined with the aqueous fluorescent reagent morin (1.00 μM). Each solution was coagulated according to the jar test procedure. After settling period, the supernatant were filtered through 0.45-μm membrane to measure the fluorescence intensity. The concentrations of the free Al and reacted Al were determined by comparing the fluorescence intensity of the two. The fluorescence spectra were collected using an FP-6500 fluorescence spectrophotometer (Jasco, Japan).

2.4. Dissolved aluminum hydrolysed species or amorphous aluminum hydroxide detection

Different concentrations of aluminum chloride solution without HA contained in a 1-L beaker (ionic strength was adjusted to the same as in HA solution) were stirred by following the above jar test procedure to online monitor the formation of amorphous aluminum hydroxides using the Photometric Dispersion Analyser (PDA-2000, Rank Brothers, UK). The PDA procedure was described by Yukselen and Gregory (2004). The PDA measures the average transmitted light intensity (dc) and the root mean square (rms) value of the fluctuating component of the intensity. The ratio (rms/dc) is often called the Flocculation Index (FI), which provides a sensitive measure of particle aggregation (Yu et al., 2015). For a given system, the FI value is strongly correlated with the aggregate (floc) size and increases as particles aggregate (Gregory, 2009). If the aluminium coagulants were hydrolysed into dissolved species, the FI curve was a line parallel to the X axis. For amorphous aluminium hydroxides, the curve was a rising fluctuated line, which indicated the formation of particles.

2.5. ^{1}H NMR analysis

Each samples for ^{1}H NMR analysis was pre-treated by solid phase extraction (SPE). Before coagulation, the HA solution was