Zeta potentials and sizes of aluminum salt precipitates – Effect of anions and organics and implications for coagulation mechanisms

Jinming Duan [a,c,*], Junsheng Wang [a], Tingting Guo [a], John Gregory [b]

[a] Key Laboratory of Northwest Water Resources, Environment and Ecology, MOE, Xi'an University of Architecture and Technology, 13 Yanta Road, Xi'an 710055, China
[b] Department of Civil and Environmental Engineering, University College London, Gower Street, WC1E 6BT, UK
[c] Centre for Water Management and Reuse, University of South Australia, Mawson Lakes Campus, SA 5095, Australia

ARTICLE INFO

ABSTRACT

Zeta potentials and sizes of aluminum salt precipitates were examined as a function of solution pH at different concentrations, based on laser Doppler velocimetry and dynamic light scattering techniques. A great difference was observed in zeta potential and size of the aluminum hydroxide precipitates from aluminum nitrate and aluminum sulfate (alum) solutions. While the isoelectric point (IEP) of aluminum nitrate precipitate has a fixed value (9), that of alum precipitates decreased with the salt concentration. The size of the early-formed fresh hydroxide precipitates of aluminum nitrate was around a few hundred nm in the acidic pH range, but increased from neutral pH up to 15 μm at the IEP. The particles of precipitates are colloidally stable in the pH range 5–6. In comparison, the size of alum precipitates was comparatively larger in the acidic up to neutral pH, and are colloidally unstable in the whole pH range. Relative influences of anions such as sulfate and phosphate, silicic acid, as well as citrate and oxalate on zeta potential and precipitate size are explicitly revealed experimentally. The results also indicate important roles of van der Waals attraction, as well as hydration force in the aggregation of the primary precipitates. Sulfate ions appear to significantly promote Al^{3+} precipitation in humic acid water. Overall, this work provides further insight on coagulation mechanisms of clay particles and natural organic materials (NOM) in water treatment, particularly in sweep coagulation.

1. Introduction

Hydrolysis and precipitation of aluminum salts are of essential importance for elucidating the coagulation mechanisms of colloidal particles and dissolved natural organic matter (NOM) in water and wastewater treatment [1–4]. Al^{3+} ions undergo hydrolysis reactions, leading to spontaneous precipitation under supersaturation conditions [5,6]. The precipitation process consists of nucleation and crystal growth, and aggregation (or agglomeration) [7]. Al^{3+} hydrolysis reactions are fast (<1 s), while nucleation and crystal growth take a few seconds [8,9]. However, the aggregation of incipient precipitates may take a long time depending on their colloidal stability. The colloidal stability of the primary precipitate can be described by the classical DLVO theory, if only electrical and van der Waals forces are important [7]. Nevertheless, non-DLVO forces

such as hydration force may also be involved at small separations. The colloidal and electrical properties of aluminum salt precipitates attracted considerable attention in the past, but with only preliminary observation on the sizes and the values for the isoelectric point (IEP) of the precipitates being reported controversially [10–12]. This creates some problems in understanding of coagulation mechanisms under certain circumstances.

Solution chemistry, such as pH and inorganic anions as well as organic acids, can profoundly affect Al^{3+} hydrolysis and precipitation. Anions, such as sulfate and phosphate, modify the electrical potential and settleability of Al^{3+} precipitates [10,13–15]. The influence was considered to be related to their basicity, or co-ordinative binding affinity for Al compared with hydroxyl ion [14,16]. Further, organic acids affect the precipitation through chemical complexation and physical adsorption [12,17].

Coagulation of clay particles and NOM in water treatment is closely related to hydrolysis and precipitation of the hydrolyzing metal salts [18]. For colloidal particles coagulation mechanisms proposed include adsorption and surface complexation of hydrolysis products [19,20], precipitation charge neutralization (PCN) [1,21], and 'sweep coagulation' [22]. For NOM coagulation

* Corresponding author at: School of Municipal and Environmental Engineering, Xi'an University of Architecture and Technology, Xi'an, China.
Tel.: +86 02982201354.
E-mail address: jinmingduan@xauat.edu.cn (J. Duan).

mechanisms supposedly involve charge neutralization precipitation (CNP) [3] or co-precipitation, and adsorption [3,12]. Both the PCN and CNP emphasize the importance of charge neutralization. In PCN mode formation of positive Al(III) precipitates on particle surfaces neutralizes the negative surface charge to prompt aggregation of the particles, while in CNP binding of Al(III) species to anionic sites of humic acids neutralizes the negative charge leading to precipitation of the Al-OH–HA complex (or co-precipitation) [18]. However, it has been found that optimum coagulation often deviates from the isoelectric point (IEP) of flocs [23,24] and it can occur under charge reversal conditions (e.g. pH 6) at higher coagulant dosages [18,21,24]. This suggests the significance of coagulation mechanisms other than charge neutralization, particularly at high coagulant dosages or in 'sweep coagulation'. A systematic characterization of zeta potential, size and aggregation of the fresh precipitates can provide new information for the coagulation mechanisms of colloidal and dissolved contaminants.

The objective of this study is to examine the electric properties, sizes and aggregation of fresh precipitates of aluminum salts in water, especially in the early-stages of precipitation, under the influence of pH, inorganic and organic anions, and NOM. A discussion of coagulation mechanisms is carried out based on the experimental findings, particularly with respect to the model of PCN and 'sweep coagulation' in water treatment.

2. Experimental

2.1. Materials

Ultra-pure water ($18.2\,M\Omega\,cm^{-1}$ at $25\,^\circ C$) was sourced from a Milli-Q Ultrapure water system (Millipore, Bedford, MA, USA).

Aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), sodium silicate ($Na_2SiO_3 \cdot 9H_2O$), Na_2SO_4, $NaClO_4$, $NaHCO_3$, HCl, and NaOH were of analytical grade (Xi'an Chemicals Ltd., China). Stock solutions of aluminum nitrate and aluminum sulfate were prepared at $0.2\,mol\,L^{-1}$ as Al, and stored in refrigerator at $4\,^\circ C$. A $0.1\,mol\,L^{-1}$ stock solution of sodium silicate was used. Sodium oxalate ($Na_2C_2O_4$) and trisodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) were purchased from Kermel Chemical Corporation Limited (Tianjin, China).

Humic acid (HA) was purchased as a commercial product (Technical grade, Aldrich, USA). A stock solution was prepared by dissolving 1 g of dry humic acid product in 1 l of ultra-pure water using a magnetic stirrer at a temperature of $60\,^\circ C$ for 2 h, and the filtrate (dissolved organic carbon (DOC) approximately $150\,mg\,L^{-1}$) from a $0.45\,\mu m$ membrane filter (Mixed Cellulose Esters Membrane Filters (MCE), Xinya Shanghai Ltd, China) was stored for use. The average hydrodynamic size of HA is $14 \pm 4.6\,nm$. The DOC concentration of the humic acid solutions was determined by a TOC analyser (Shimadzu TOC-VCPH, Japan).

2.2. Instruments and methods

Zeta potentials (ζ) and sizes of Al precipitates were measured by a Zetasizer Nano ZS (Malvern, UK). The hydrodynamic diameter (D) of the precipitated particles was measured by dynamic light scattering, while electrophoretic mobility was measured by the laser Doppler micro-electrophoretic light scattering technique. The zeta potentials were calculated from electrophoretic mobility (u_E) using Henry's equation ($u_E = (2\varepsilon\zeta/3\eta)f_1(\kappa a)$) ($\kappa$ is the Debye–Hückel parameter and a is the particle radius; $f_1(\kappa a)$ is Henry correction factor taken from Table 3.1 in [25]). The values of permittivity (ε) and viscosity (η) were used as supplied by the instrument computer program). The value of κ was calculated using total 1–1 electrolytes in solutions including those added for pH adjustment.

For aluminum sulfate precipitates, corrections were made using the method of Wiersema et al. [26], assuming all the SO_4^{2-} to be in solution. The measurement size ranges of the instrument for particle size and zeta potential are $0.3\,nm$–$10\,\mu m$ and $3.8\,nm$–$100\,\mu m$ in diameter, respectively, as specified by the instrument manual. Measurements were made at a water temperature of $20 \pm 0.1\,^\circ C$. The measurements were reproducible and average values of triplicate measurements for each condition are reported.

Precipitation tests of aluminum salts were carried out in a 100 mL beaker using Milli-Q water with addition of $1\,mmol\,L^{-1}$ $NaHCO_3$ and $1\,mmol\,L^{-1}$ $NaClO_4$. In the experiment, a pre-determined amount of HCl or NaOH was first added in the Milli-Q water, a pre-calculated volume of aluminum salt stock solution was then added, reaching a target pH after reaction. The solution was then stirred for 10 s using a glass rod (no further agitation was performed) and 2 mL of the resultant suspension was transferred to each of two cuvettes. Measurement for the size of 'early-formed precipitates' was conducted at the end of the first minute reaction time except when a continuous monitoring of the growth in precipitate size was required. The zeta potential of the suspension was measured after the size measurements. For aggregates in the size range of 10–$20\,\mu m$, the measured sizes were close to the measurements by a laboratory microscope, as examined regularly for larger aggregates (BX51, Olympus Corporation, Japan).

Scanning electron microscopy (SEM) imaging of the metal salts precipitates was conducted using an FEI Quanta 200 instrument (FEI Company, USA). In the samples preparation, one drop of the metal salts suspension at each condition was transferred by a pipette to a clean glass slide and covered by a glass beaker. The drop of suspensions was dried for 24 h at ambient temperature and measured under the low vacuum mode with the samples sputter coated in gold.

3. Results and discussion

3.1. Zeta potentials and sizes of aluminum hydroxide precipitates

3.1.1. Precipitates in nitrate solutions

The results of aluminum nitrate solutions at three different concentrations (1, 5, $10\,mmol\,L^{-1}$) are presented in Fig. 1. The zeta potentials of the aluminum hydroxide precipitates at a fixed final pH showed rather small differences ($<3\,mV$) at these concentrations (Fig. 1(a)). They were the highest in pH range 5–6, and decreased with the increase of pH. The IEP was at pH 9, which coincides with the one previously reported by microelectrophoresis of aged aluminum nitrate precipitates [11] but different from the value (pH 8) for freshly precipitated $Al(NO_3)_3$ solutions ($5.0 \times 10^{-4}\,mol\,L^{-1}$) measured by a streaming current detector [10].

The size of the precipitates also varies with solution pH and it increases noticeably with the concentration of the metal salts at a fixed pH (Fig. 1(b)). In the acidic pH range of 5–6, where $\zeta \geq 40\,mV$, the diameter of the precipitates was in the range of 200–$500\,nm$. However, at neutral pH and above, the diameter increased greatly with pH, reaching a maximum of about $14\,\mu m$ at pH 9 (i.e. the IEP). The precipitates in the size of 200–$500\,nm$ at low pH must have been responsible for the Tyndall beam observed by [10].

At a fixed aluminum nitrate concentration, the supersaturation degree varies at different pHs due to the variation of Al^{3+} solubility [6]. The results show that the largest precipitate sizes did not occur at the pH of highest supersaturation (pH = 6). This indicates that the surface properties rather than the amounts of primary precipitates decide the aggregation rate.