Coagulation of Natural Organic Matters Using Aluminum Tridecamer (Al$_{13}$) with Counter Ions

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ABSTRACT

Coagulation of natural organic matters (NOM) using coagulants is an efficient drinking water treatment process. Polyaluminum chloride (PACl) is a commonly adopted coagulant with aluminum tridecamer ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]Cl_7$, Al$_{13}$) as an important hydrolysed intermediate. This paper investigated the effects of anions on coagulation of NOM with purified Al$_{13}$ with sodium salts as counter ions.

Keywords: Al$_{13}$; humic acids; anions; stability; coagulation

1. INTRODUCTION

Polymer aluminum chloride (PACl) is one of the frequently used coagulants in water treatment for organics and colloids removal (Lin et al., 2008, 2009; Shafran et al., 2005; Yan et al., 2007; Zhao et al., 2008). Hydrolysis and condensation of aluminum ions in acidic solution can yield numerous polynuclear species, including Keggin ions such as $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (Al$_{13}$) (Akitt et al., 1985) or $[Al_{30}O_8(OH)_{36}(H_2O)_{28}]^{18+}$ (Al$_{30}$) (Chen et al., 2006; Roswell and Nazar, 2000). The Al$_{13}$ aggregates are of size of approximately 400 nm so are named nano-Al$_{13}$ (Gao et al., 2009). Although being intensively studied (Sarpola et al., 2004), the coagulant species, nano-Al$_{13}$, were mostly applied in pure coagulant process with no impurities. However, salts and natural organic matters (NOM) are present in all raw waters. Natural organic matters (NOM) are ubiquitously present in surface waters (Matilainen et al., 2010).

Salts containing high-purity Al$_{13}$ were produced (Gao et al., 2009; Liu et al., 1999; Shi et al., 2007; Wang et al., 2004; Xu et al., 2003; Zhao et al., 2002). Sulfate left in the produced Al$_{13}$ salt by conventional SO_4^{2-}/Ba^{2+} separation method may deteriorate stability of Al$_{13}$ cluster in water (Wang et al., 2002). Lin and Lee (2010a) purified Al$_{13}$ clusters by solvent precipitation technique to achieve higher stability of Al$_{13}$ clusters than those purified using the SO_4^{2-}/Ba^{2+} method. Lin and Lee (2010a) demonstrated a series of electrospray ionization mass spectrometry (EIS) results of Al$_{13}$ in the 50:50 water/acetonitrile solutions. These authors noted that acetonitrile is prone to adduct to the aluminum center and alter aluminum tridecamer to shorter polymer species. In the presence of the acetonitrile, the chloride ions could not coordinate with the aluminum center. However, Lin and Lee (2010b) demonstrated that the presence of chloride ions in water can lead to destabilization of Al$_{13}$ aggregates, suggesting the limited coordination capacity of chloride ions with the chloride ions. Lin and Lee (2011) demonstrated the EIS series of Al$_{13}$ in water/

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methanol solutions and revealed that methanol molecules were medium ligands to Al_{13} cluster. These results clearly demonstrated that anions can affect the stability of nano-Al_{13}, with effects following acetonitrile > methanol > chloride.

Coagulation-sedimentation is a cost-effective process to eliminate NOM from waters (Bratby, 2006). This study characterized the Al_{13} contents in self-synthesized product and demonstrated the possible inhibition effects of counter ions on coagulation efficiency of studied Al coagulants on humic acids removal from water.

2.   MATERIALS AND METHODS

2.1   Chemicals and materials

A laboratory synthesized Al_{13} was prepared by solvent precipitation method from $AlCl_3 \cdot 6H_2O$ and purified as previously noted (Lin and Lee, 2010a). A fixed quantity of $AlCl_3 \cdot 6H_2O$ salt (4.65 g) was dissolved in 20 ml deionized water at 353 K; aqueous NaOH (1.8 g in 20 ml deionized water) was then added drop wisely with vigorous mixing until $[OH^-]/[Al] = 2.42$. The yielded solution was turbid, but became clear after further mixing for 2 h at 353 K. Vacuum condensation at 333 K by a rotary evaporator (BÜCHI Rotavapor R-200, BÜCHI Labortechnik AG, Switzerland) was applied to the suspension to remove water until the final suspension volume was 5 ml. Then 10 ml of n-propanol was added into the suspension with mixing at room temperature for 10 min. Following this step 50 ml of acetone was added with mixing. Salt precipitated from the solution was filtered through a glass filter (Por. 4, nominal maximum pore size, 10-16 μm; Robu Glasfilter GeraȽte GmbH, Hattern, Germany) and was rinsed using tetrahydrofuran (THF) to produce an off-white powder with an 85% yield.

Humic acid standard (Sigma-Aldrich, H16752, MO, USA) was firstly dissolved in 1 N NaOH and added deionized water as stock solution 1,000 ppm. Then, pH of the solution was adjusted to 6.36 by 0.1 N HCl and filtered through 0.45 μm filters. The solution was then diluted to 75 mg/L concentration prior testing.

All the other chemicals (NaOH, NaCl, NaBr, NaI, Na_2SO_4, Na_2CO_3, $Na_2C_2O_4$, $NaClO_4$, $NaBPh_4$, NaSCN, NaPBz, $NaPhSO_3$, NaPAc, $NaBF_4$, $NaC_{12}H_{25}SO_4$ (sodium dodecyl sulfate, SDS) and polyaluminum chloride (PACl) in 5.4% w/w Al^{3+}) were purchased from Merck Taiwan Ltd. at the highest purities available.

2.2   Titration tests

Purified Al_{13} salt was dissolved in deionized water to generate 0.0128 M of Al solution. 50 ml of the Al_{13}-NaCl solution (pH 4.78, turbidity 15 by a nephelometric turbidity unit (NTU)) was poured into a conical flask on an autotitrator and stirred vigorously. A 0.4 M NaOH aqueous solution was added to the flask at flow rate of 1 ml/min until solution pH reached 13.

2.3   Coagulation tests

Humic acids solutions were diluted from stock solution with DI water to 152 mg/L at pH 6.9. In tests with counter-ions, prescribed amount of sodium salts were mixed at 0.17 mM equivalent (e*[ion]/$[Al^{3+}]$=3.35) with the humic acid solution. The yielded humic acid solution was dosed with PACl or Al_{13} solutions at 53 mg/L in Al^{3+} with vigorous mixing (2 min) and then slow mixing (28 min). The supernatant was withdrawn from 2 cm from water surface after 30-min sedimentation. The UV spectra of each sample were scanned at the intensities of 220, 254, 280, 290, 300, 350, 400 and 450 nm recorded and averaged for humic acid content determination.

2.4 Analytical analysis

The synthesized Al_{13} powders, which were characterized by the IR spectra were determined using a Varian 640-IR spectrophotometer (FT-IR) (Varian NMR, Inc., Palo Alto, CA, USA) using KBr pellets dispersed with sample powders in the 4000-400 cm^{-1} range. The ^{27}Al NMR spectra were acquired by a Varian Unity Inova 500 spectrometer (Varian NMR, Inc., Palo Alto, CA, USA) at a resonating frequency of 130 MHz. The ^{27}Al NMR spectra were referenced to $AlCl_3 \cdot 6H_2O$ (0.5 M) at pH 2 (0 ppm). The D_2O solution of purified Al_{13} was poured into a 5-mm NMR tube. The ^{27}Al solid-state magic angle spinning (MAS) NMR spectra were acquired with a Bruker DSX 400 spectrometer. The purified Al_{13} powder (42.8 mg) was then dissolved in 0.2 ml D_2O solution (0.17 M) for ^{27}Al-NMR measurement. The number of scans was 1024. The purity of sample was characterized as peak ratio for Al_{13} and Al monomers. This purity does not count for other species such as Al_{30} or colloids formed after aging. The purified Al_{13} solution was prepared using analytical grade reagents and deionized water. The aluminum solution ($[Al_{13}]^{+7}$) concentration was adjusted to 67 mM, and final pH was 4.78.

3. RESULTS AND DISCUSSION

3.1 Produced Al_{13} salt

The SEM image of the produced Al_{13} salt is shown in Figure 1a. The sediment of Al_{13} salt is shown in Figure 2. The ^{27}Al NMR spectra had two resonance peaks - a narrow peak at 62.5 ppm corresponding to the tetrahedral core of the Al_{13} polycation, and the 0 ppm peak for octahedrally coordinated monomeric Al species (Figure 1b). The relatively broad 0 ppm peak in ^{27}Al NMR spectra was probably attributable to rapid quadrupolar relaxation of the unsymmetrical nucleus of aluminum hydroxide. The ratio between Td-Al and monomeric Al signal intensities indicates that the purified salt contained > 95% Al_{13} (top of Figure 1b). The IR spectrum for the purified Al_{13} cluster (spectrum not shown) clearly reveals the representative bands at 999 cm^{-1} for the Al-OH-Al bond; the band at 723 cm^{-1} for Keggin-AlivOOH; and 636 cm^{-1} for Al-OH. Hence, the present purified product had high purity of Al_{13}.

The NMR spectrum of PACl tested in the present work had a weak 62.5 ppm peak and a relatively strong 0 ppm peak. The purity of Al_{13} in the PACl salt was estimated less than 25% (middle of Figure 1b).

3.2 Stability

Initial pH of the Al_{13} solution was roughly 4.74 (Figure 3a). The pH increased with B value owing to polymerization of Al oligomers and neutralization of free H^+ in the solution (Foumier et al., 2008). At B = 5.2 − 5.8, the added OH^- primarily deprotonated the external water ligands on Al_{13} clusters. At B = 5.8, pH reached 8.2 and the titration reached equivalent point with deprotonation reaction to reduce the surface charge of Al_{13} clusters, resulting in their aggregation. The turbidities of the titration solution are an indicator for cluster stability. The particle distribution at B = 5.8 indicated that the mean particle size was 56.4 μm (Figure 3b). Over 5.8 < B < 6.4, the added OH^- deprotonated the water ligands of formed Al_{13} aggregates and polymerized deprotonated aggregates into sol-gels (Wang et al., 2002). Particle size distribution at B = 6.4 had mean particle size of 1150 μm (Figure 3c). When pH was > 10, the formed sol-gels were dissolved into $Al(OH)_4^-$ (Archer et al., 2005). These

(a)

(b)
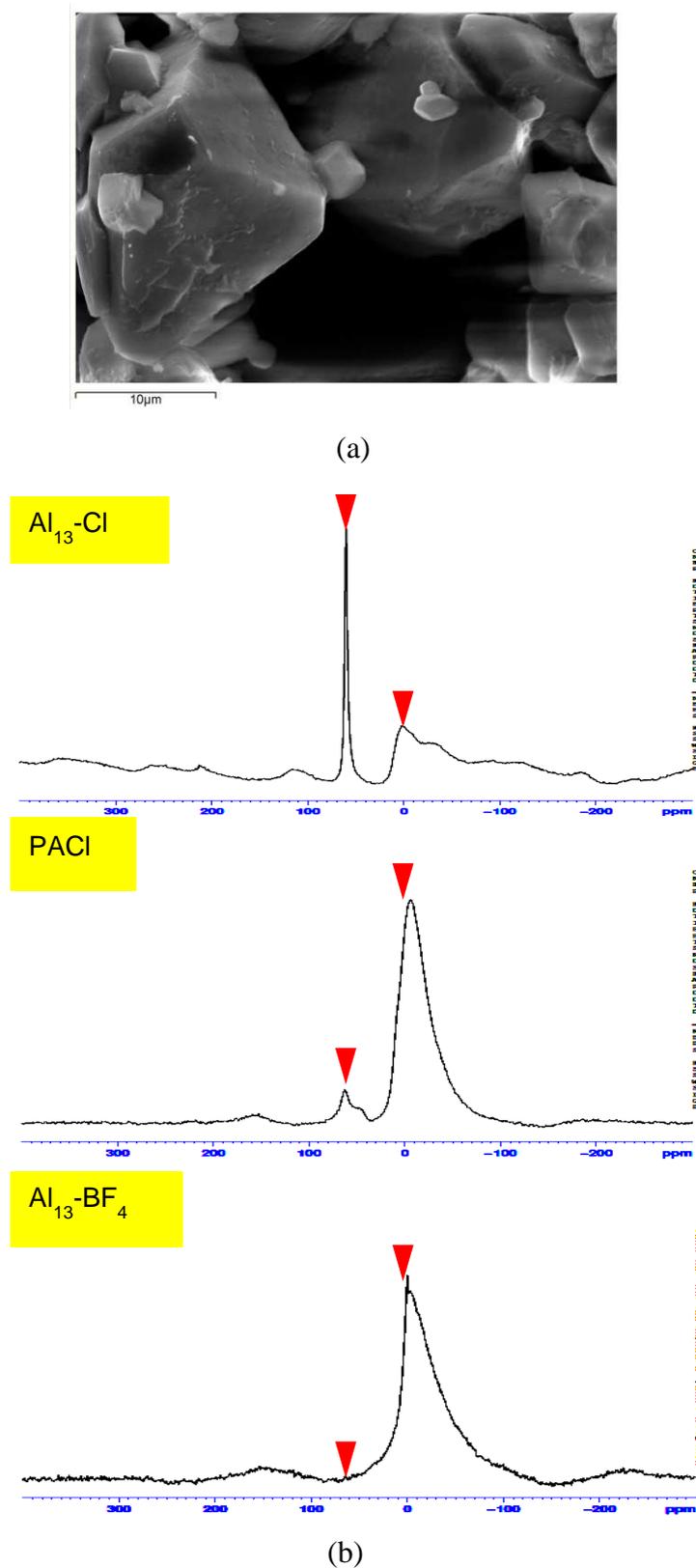
Figure 1   (a) SEM image of the purified Al_{13} salt; (b) Solid-state ^{27}Al NMR of aluminum salts. Top-down: Purified Al_{13} salt; PACl salt; purified Al_{13} + $NaBF_4$ salt, respectively. Peaks at 62.5 ppm correspond to tetrahedral core, and 0 ppm to octahedrally coordinated monomeric Al species

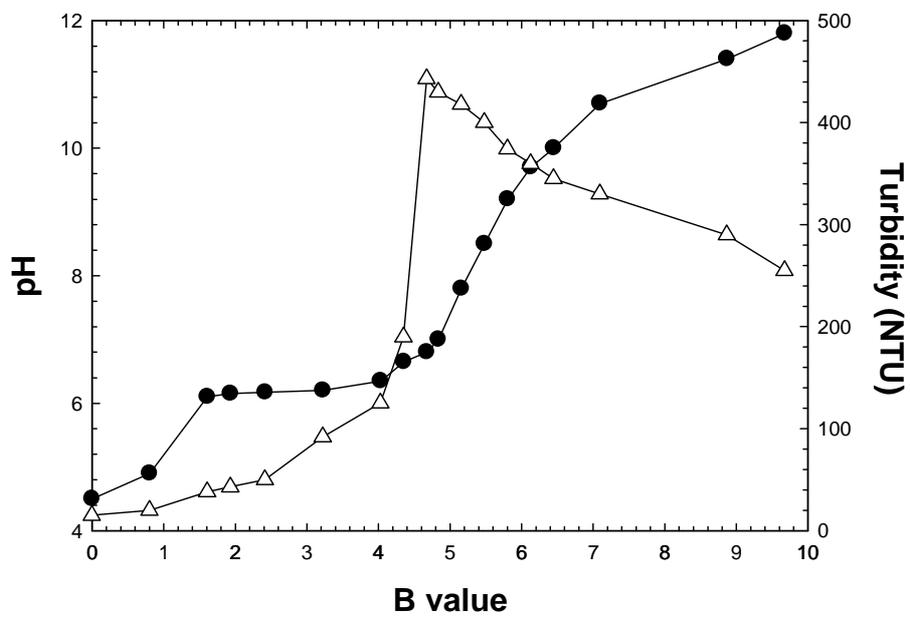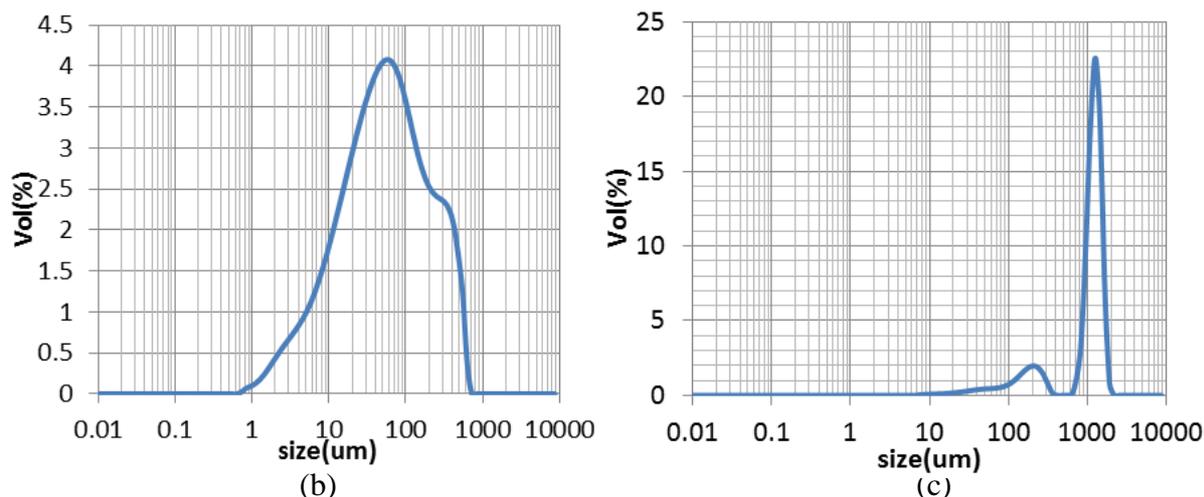**Figure 2**   Appearances of collected sediments. (a) Al_{13} salt; (b) Al_{13}-humic acid sediments

Figure 3 (a) (to be continued)

Figure 3 Titration of Al_{13} solution containing 50 ml of 0.0128 M Al_{13}-NaCl solution at pH 4.78, 15 NTU by 0.4 M NaOH. (a) Titration curve; (b) particle size distribution at B=4.8; (c) particle size distribution at B=9.8. Flow rate: 1 mL/min

experimental observations agree with those reported by Lin and Lee (2011) with purified Al_{13} without residual chloride. When chloride ions were presented in the solution, the B value triggering precipitation would be much lower, indicating the destabilizing role of chloride on Al_{13} clusters.

Some titrated samples at pH 8 were back-titrated using HCl to pH 4. Clear solution was formed, indicating de-aggregation of the Al_{13} cluster. The so-yielded solid has identical IR spectra as Al_{13} monomer. Hence, the aggregation of Al_{13} cluster is a reversible process depending on solution pH.

Titration with Na_2SO_4 showed that the Al_{13} solution was destabilized at $[SO_4^{2-}]/[Al^{3+}] > 0.65$ (Figure 4). In this test the pH ranged between 4.74 and 4.78, thus were not shown in the figure. Sulfate was presented in excess in purified Al_{13} salt by conventional SO_4^{2-}/Ba^{2+} method. This observation clearly demonstrated that the residual sulfate ions can induce structural deterioration of Al_{13} clusters.

Sodium salts (NaOH, NaCl, NaBr, NaI, Na_2SO_4, Na_2CO_3, $Na_2C_2O_4$, $NaClO_4$, $NaBPh_4$, NaSCN, NaPBz, NaPhSO_3, NaPAc, $NaBF_4$, $NaC_{12}H_{25}SO_4$ and PACl) of 0.17 mM equivalent were added to the Al_{13} salt to confirm their role on cluster stability. The NMR spec-

trum of Al_{13}-$NaBF_4$ solids is shown in Figure 1b. Clearly the addition of $NaBF_4$ completely destroyed the tetrahedral core of the Al_{13} polycation.

3.3 Coagulation tests

Fresh Al_{13} solution was prepared and used immediately in coagulation test. The removal efficiency of using 53 mg/L Al_{13} (in Al^{3+}) on 152 mg/L humic acid solution were high (100% in Figure 5a). The yielded sediment is shown in Figure 2. The presence of OAc^- and BF_4-significantly inhibited coagulation capability of Al_{13} on humic acids. The inhibition capability of dosed sodium salts on coagulation capability of Al_{13} follows: $BF_4^- > OAc^- > PhSO_3^- > I^- > SCN^- > BPh_4^- > Br^- > OBz^- > Cl^- > ClO_4^- \sim SO_4^{2-}$.

The Al_{13} solution was prepared and aged at room temperature for 48 h. The removal efficiency of using 53 mg/L Al_{13} (in Al^{3+}) on 152 mg/L humic acid solution were still high (99.3% in Figure 5b). The presence of 0.17 mM sodium salts inhibited coagulation capability of Al_{13} on humic acids. Adding NaCl, NaBr or NaI led to 11-21% reduction of coagulation efficiency. The presence of Na_2SO_4, NaOAc, EDTA and NaC_2O_4 would
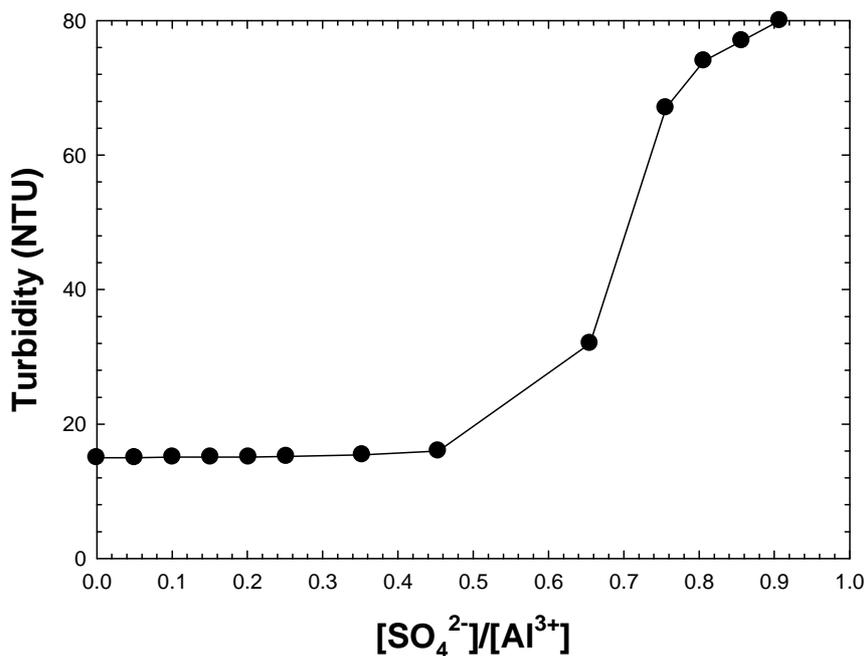
Figure 4   Titration curve of Al_{13} solution containing 50 ml of 0.0128 M Al_{13}-NaCl solution at pH 4.78, 15 NTU by (a) 0.4 M NaOH (b) 0.25 M $Na_2SO_4^{2-}$. Flow rate: 1 mL/min
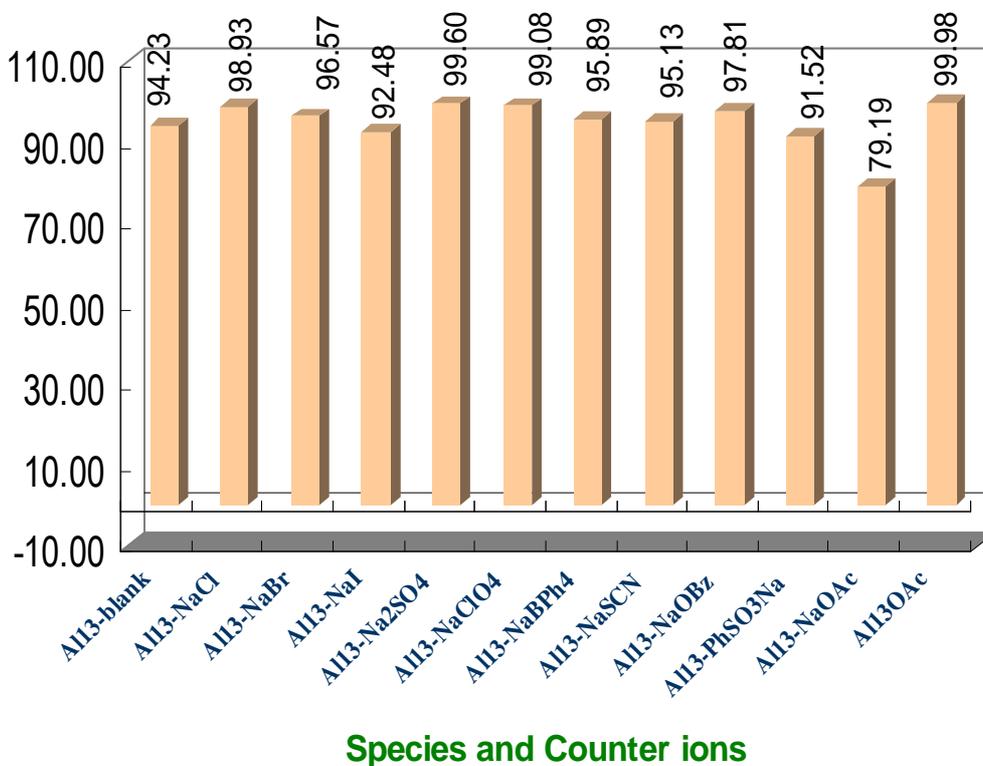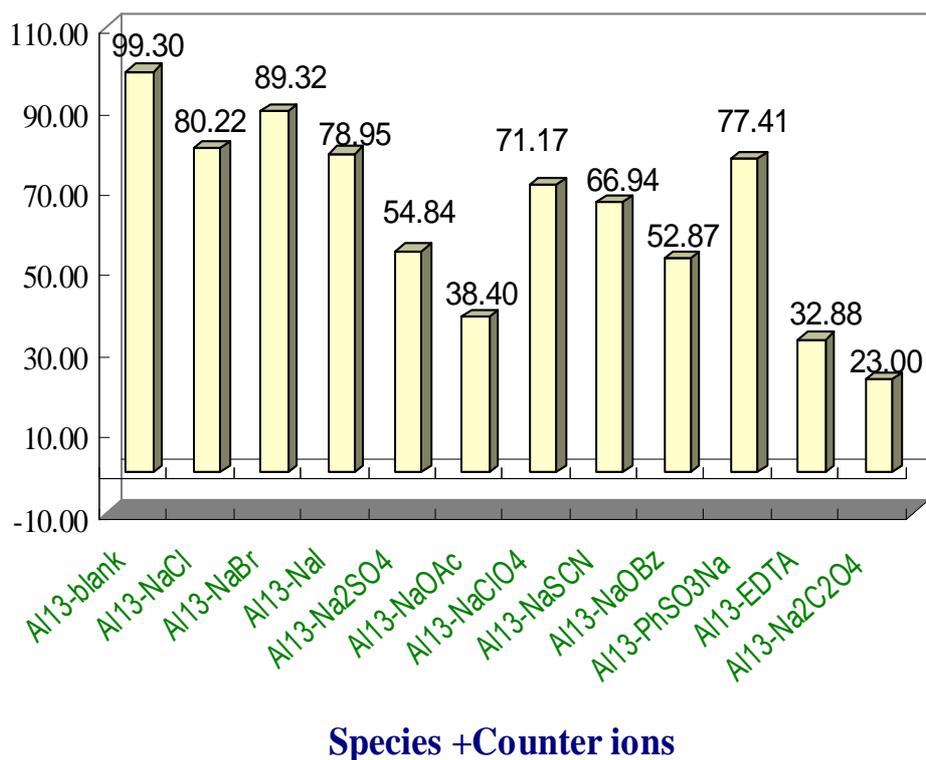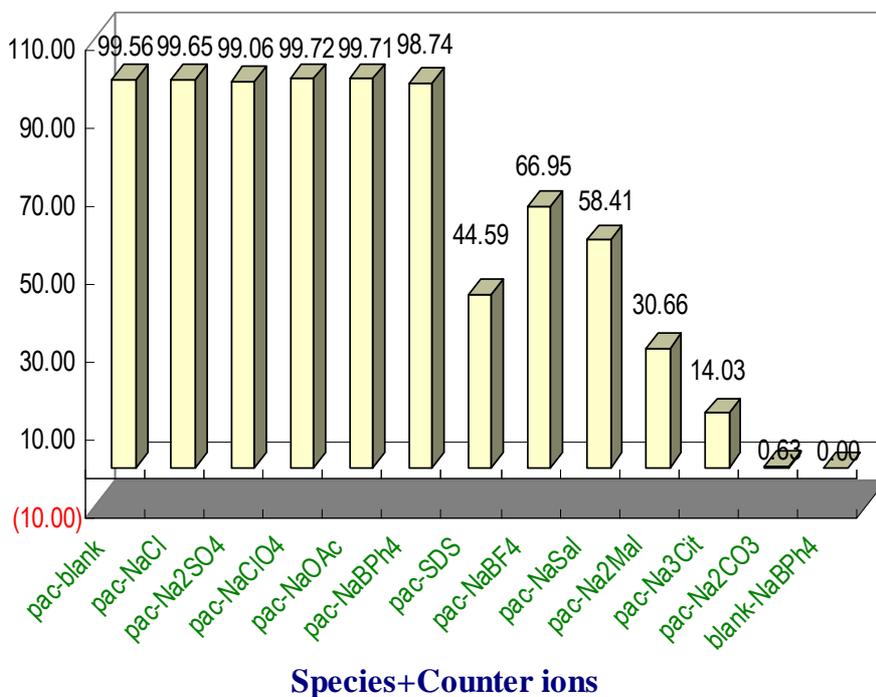

Species and Counter ions

Figure 5 (a) (to be continued)

(b)

Figure 5   Removal efficiency of humic acids from waters: (a) Fresh Al_{13} solution; and (b) 48-h aged Al_{13} solution (152 mg/L humic acids at pH 6.9 dosed with 53 mg/L Al_{13})

Figure 6   Removal efficiency of humic acids from waters (152 mg/L humic acids at pH 6.9 dosed with 53 mg/L PACl in Al^{3+})

inhibit > 50% of coagulation capability. The inhibition capability of dosed sodium salts on coagulation capability of Al_{13} follows: $C_2O_4^{2-}$ > EDTA > OAc^- > OBz^- > SO_4^{2-} > SCN^- > $PhSO_3^-$ > I^- ~ Cl^- > Br^-.

Tests with 53 mg/L PACl (in Al^{3+}) on 152 mg/L humic acid solution were conducted as a reference (Figure 6). Inhibition effects on coagulation followed: CO_3^{2-} > citrate > malate > dodecylsulfonate > salicylate > BF_4^- >> BPh_4^- > SO_4^{2-} ~ Cl^- ~ ClO_4^- ~ OAc^-. The trend of inhibition of sodium salts on PACl was close to that on fresh Al_{13} rather than aged Al_{13}.

Experimental results revealed that aging of Al_{13} solution deteriorated coagulation capability of the Al_{13} clusters. Aged Al_{13} solutions in general had lower Al_{13} contents (data not shown). The poorer coagulation performance of aged Al_{13} solution as compared to fresh Al_{13} solution suggested that the anion-Al_{13} interaction is weaker than anion-$Al(OH)_3$ interaction. Comparatively, the PACl was much more stable in solution form during aging. When using Al_{13} as coagulants, the possible aging effects in chemical preparation and operation should be taken into account.

Experimental results also revealed that the better the coordination capability of the anions, the higher the inhibition capability of the anions on Al_{13}/PACl coagulation with humic acids. However, the inhibition effect of $C_2O_4^{2-}$ was greater than that of EDTA, indicating that the five-membered ring complex by N-atom on EDTA is not as stable as that by oxalate-Al. Distinct chemical properties of added salts led to very different coagulation behavior. The sizes and charge are close for ClO_4^- and BF_4^- ions, but their capability to inhibit coagulation with humic acids are very different. Likely the hydrolyzed products, fluoride ions, of tetrafluoborate ions under acidic condition may bind to Al cluster to form stable AlF_6^{3-} leading

to deterioration of the cluster structure. Acetate is generally considered as a weak ligand in water. However, its presence at [OAc]/[Al] > 3 could lead to deterioration of Al_{13} cluster (Figure 1c). At [OAc]/[Al] = 1, aggregation of Al_{13} was produced but the structure of Al_{13} cluster remained intact (data not shown). Benzoate is regarded as a weaker ligand than acetate, which has minimal effects of Al_{13} in PACl solution. However, benzonate has a significant effect on coagulation efficiency with humic acids. Benzensulfonate is commonly applied in water as a counter ion. Its inhibition on coagulation of Al_{13} is not as high as benzonate. Hence, many chemical properties of anions affect the coagulation effects of Al_{13} with humic acids. Coagulation behavior without considering effects of counter ions is not possibly predicted correctly from first principles.

CONCLUSIONS

This study synthesized and characterized Al_{13} salts, giving a purified Al_{13} product of purity > 95% w/w. The Al_{13} salt could be reversibly transformed between dispersed and aggregates states at pH < 8.2. Fresh and aged Al_{13} solutions had different coagulation behaviors. The inhibition capability of dosed sodium salts on coagulation capability of fresh Al_{13} follows: BF_4^- > OAc^- > $PhSO_3^-$ > I^- > SCN^- > BPh_4^- > Br^- > OBz^- > Cl^- > ClO_4^- ~ SO_4^{2-}. The inhibition capability of dosed sodium salts on coagulation capability of aged Al_{13} follows: $C_2O_4^{2-}$ > EDTA > OAc^- > OBz^- > SO_4^{2-} > SCN^- > $PhSO_3^-$ > I^- ~ Cl^- > Br^-. PACl tests behaved closely with fresh Al_{13} solution. To use Al_{13} as coagulants, it is necessary to consider the possible aging effects and role of counter ions in chemical preparation and operation.

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