Interactions between alum and organics in coagulation

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Abstract

The coagulation–sedimentation process, i.e. a major pretreatment for filtration, has the potential to remove organic contaminants. However, interactions between coagulants and organics in the absence of suspended solids have only received limited attention. This study aims to model alum–organics' interactions corresponding to the behavior of organics during coagulation. Two typical organic materials, humic acid and salicylic acid, are investigated. Experimental results indicate that the removal of organics by coagulation is directly related to the molecular weight. The interaction of alum with humic acid involves complexation, charge neutralization, precipitation and adsorption. The coagulation of salicylic acid with alum arises from adsorption and entrapment. Results of this study confirm a stoichiometric relationship between the initial concentrations of humic acid and optimal alum dosages.

Keywords: Alum; Coagulation; Humic acid; Organic contaminants; Salicylic acid; Water treatment

1. Introduction

Sources of organics in the public water supply comprise not only natural organic matter but also industrial, stock and domestic wastewaters. Organic matter in a water source is undesirable, especially with respect to generating disinfection by-products. The coagulation–sedimentation process, i.e. a major pretreatment for filtration, has the potential to remove organic contaminants.

Humic substances are commonly found in soil, sediments and natural waters. The behavior of humic substances in the coagulation and flocculation processes has been widely investigated. Hall and Packham [1] felt that humic acid and fulvic acid removal from water by iron and aluminum coagulants could be regarded as a process of chemical precipitation forming insoluble basic aluminum/iron humates rather than coagulation. This variety of precipitates may be soluble or insoluble, depending on the coagulant dose [2]. A stoichiometry between humics' concentration and optimum dosage has been also confirmed [2–4].

Dempsey et al. [5,6] have stated that coagulation of humic substances with coagulants can be achieved through charge neutralization and adsorption. Dempsey [7] has concluded that adsorption is the most important mechanism for fulvic acid removal over the entire pH range. However, Van Benschoten and Edzwald [8] have indicated that the role of complexation of aluminum and fulvic acid in coagulation is significant. In addition, coprecipitation during organics' coagulation has been discussed [9,10]. Studies involving the domain of specific organics' removal by coagulation have found that these organic compounds with a low molecular weight are less easily eliminated than humic substances [11–13].

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Notably, preformed flocs built from the coagulation of kaolinite suspension by alum/iron salts have good adsorption characteristics for organic matter [14–16]. These results are not only valuable in water treatment but are meaningful for organic removal by coagulation.

The most representative mechanisms for the destabilization of colloids include electric-double-layer compression, adsorption and charge neutralization, enmeshment, and interparticle bridging. However, most previous work has focused on the application of those mechanisms to describe the behavior of suspended particles coagulated with chemicals. Whether the mechanisms involved in the coagulation of organics are similar to those for mineral particles still remains unclear. So far, the interaction between coagulants and organics with different molecular weight (MW) ranges in the absence of suspended solids has only received limited attention. Therefore, in this study, the characteristics of organic coagulation by alum are more thoroughly explored and the mechanism of organic substances' removal by alum coagulation is also examined. Humic acid and salicylic acid are chosen here as model organics due to the differences in their molecular weights. Humic acid is naturally widespread with an MW of a few hundred to 1 000 000. Salicylic acid is a common aromatic acid in natural water and is a strong chelating agent, like fulvic acid [7].

2. Materials and methods

Humic acid was obtained from the commercial sodium humate (Aldrich, USA) with composition C: 51.37%, H: 4.19%, N: 0.75%, as indicated by Mazet [3]. Salicylic acid (analytical grade) was obtained from the Hayashi Co. (Japan). Stock solutions of the coagulant were prepared by dissolving aluminum sulfate (alum; $Al_2(SO_4)_3 \cdot 18H_2O$; Merck) in deionized water.

A synthetic sample was prepared to contain a desired concentration of humic acid. Non-purgeable dissolved organic carbon (NPDOC) in the synthetic sample was measured by means of a TOC analyzer with UV/persulfate oxidation (Dohrmann DC-180, USA). The synthetic water

alkalinity was created by using 100 mg l^{-1} $NaHCO_3$. The initial ionic strength of water was controlled at 10^{-2} M. Therefore, $NaClO_4$ was also added to the synthetic water to compensate for a deficit in ionic strength provided by the alkalinity. This study was in two parts. In the first part, a series of jar tests was performed in 1 l beakers at room temperature. Next, according to the direction of the jar-test results, further experiments were designed to investigate the relationship between the initial concentrations of organics and optimal alum dosages, as well as organics' adsorption by aluminum hydroxide precipitates.

In the jar tests, the coagulant was added to the beaker containing the synthetic water and the pH was immediately adjusted to a given value with NaOH. Rapid mixing (150 rev min^{-1}) for 3 min was followed by 20 min of slow mixing (20 rev min^{-1}) and 2 h of quiescent settling. The pH values were recorded at the end of the settling period, after the completion of which the supernatants were analyzed by means of a UV analyzer (1 cm cell; Hitachi model U-3210, Japan) at a wavelength of 254 nm for humic acid or 231 nm for salicylic acid. Next, the supernatant samples were passed through a 0.45 μm filter (cellulose nitrate, Whatman) and again analyzed by UV spectrophotometry. The material, as collected by the 0.45 μm filter, was operationally defined as a "precipitate" in this study.

In the adsorption experiment, the alum precipitates generated by undergoing rapid mixing for 30 min were used as adsorbents for the organics. A given concentration of organic compound was added to the alum suspension for the adsorption. Finally, the suspension was filtered and the filtrate was analyzed by means of the UV analyzer after 24 h at 25°C.

A comparison of sequential dosing with single dosing was performed to determine the effects of different dosing methods on the organics' removal. A 25 ml amount of alum reagent was prepared with a suitable concentration and this was then divided into five parts. Each of the 5 ml portions of the alum reagent was transferred to the synthetic sample after the mixing–settling process had been completed in each time interval. For each time

interval, a supernatant sample was collected for UV absorbance measurements.

3. Results and discussion

Suspended solids are absent in our synthetic waters, and the removal of dissolved organic matter occurs with a phase change in which precipitates are produced.

3.1. Elementary jar testing

Jar testing has been performed using alum to coagulate humic acid and salicylic acid. Residual organics after jar settling are shown in Fig. 1 as a function of pH at a given dosage. The upper curves
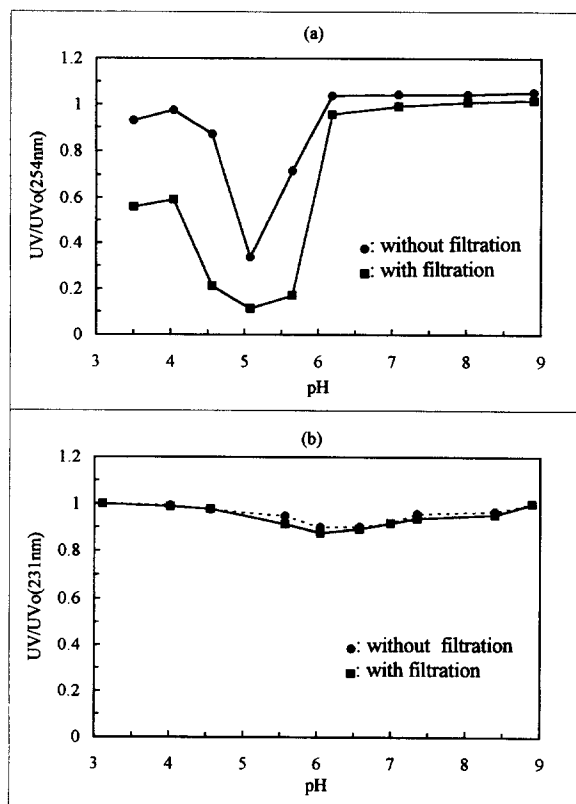

Fig. 1. Residual organics after jar mixing–settling as a function of pH at given dosages. (a) Humic acid: initial concentration, 4 mg NPDOC l^{-1}; alum, 0.8 mg Al l^{-1}. (b) Salicylic acid: initial concentration, 4 mg C l^{-1}; alum, 5 mg Al l^{-1}.

in Figs. 1(a) and 1(b), representing organics remaining after coagulation and settling, are termed "settled curves" in the following description. The lower curves in Figs. 1(a) and 1(b), indicating organics remaining after coagulation, settling and membrane filtration, are defined here as "filtered curves". The difference between the two curves is the quantity of precipitate that fails to settle. Experimental results indicate that optimal pH values for humic acid and salicylic acid removal are different (equivalent to 5 and 6, respectively). Generally, the ionization of carboxyl groups ($pK_a \approx 4.5$ [17]) leads to a situation in which humic acid possesses a negative charge. Under the 0.8 mg Al l^{-1} condition, the positively charged mononuclear or polynuclear species of Al(III) is predominant at pH 5 after hydrolysis. Such Al(III) species induce a complexation reaction with humic acid, the latter functioning as a strong organic ligand for Al(III). The latter species can also neutralize the negatively charged sites on humic acid, which subsequently forms aluminum humate. Fig. 1(b) also indicates that an insignificant removal occurs with salicylic acid by alum coagulation, even with a relatively higher dosage than that applied for the humic acid removal as shown in Fig. 1(a).

The ratios of residual and original UV absorbances are shown in Fig. 2 as a function of alum dosage. This figure clearly indicates that the optimal dosage for humic acid is about 1.0 mg Al l^{-1}, which corresponds to 90% removal. Aluminum humate may be water-soluble or water-insoluble, depending on its molecular size. As the alum dosage is increased, aluminum humate may aggregate and form precipitates after jar mixing. These results also indicate that restabilization occurs in the settled curve of humic acid, as shown in Fig. 2(a). This implies that the destabilization of humic acid by alum cannot be attributed to the compression of the electric double layer but to charge neutralization. As the dosage is increased, the fraction of aluminum hydroxide precipitated as the hydrolyzed Al(III) species increases. Therefore, more humic acid or aluminum humate can be adsorbed onto the aluminum hydroxide precipitates, causing removal by jar settling or membrane filtering. As the alum dosage increases
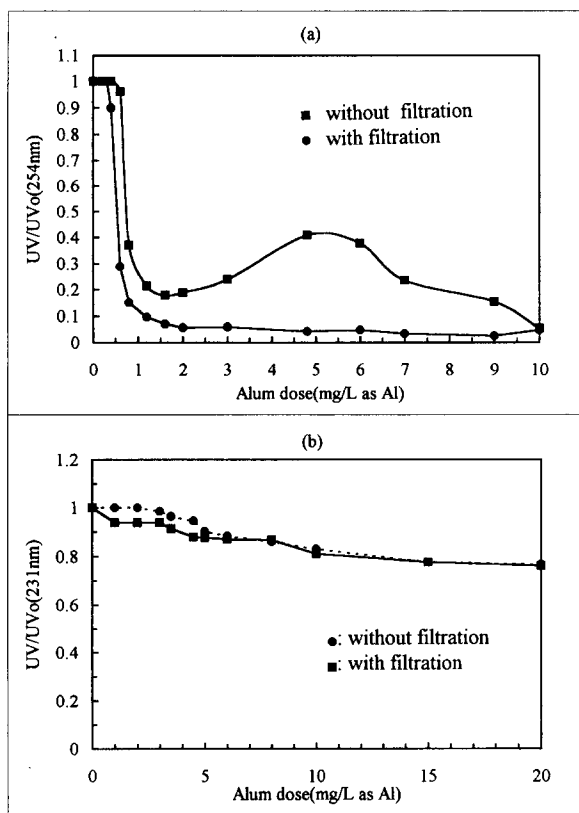
Fig. 2. Residual organics after jar mixing–settling as a function of dosage at a given pH. (a) Humic acid: initial concentration, 4 mg NPDOC l^{-1}; pH 5. (b) Salicylic acid: initial concentration, 4 mg C l^{-1}; pH 6.

over a certain level at which a large quantity of aluminum hydroxide precipitate is produced, the major mechanism of humic acid removal by alum coagulation can be expected to shift from complexation–charge neutralization–precipitation to adsorption. The result in Fig. 2(b) shows that justifying an optimal dosage for salicylic acid is relatively difficult. The difference between the settled curve and the filtered curve appears only at an alum dosage of less than 6 mg Al l^{-1}. A higher dosage of alum gives a settled curve that corresponds with the filtered curve. This phenomenon is discussed in the following section. Although the functional groups (–COOH and –OH) of salicylic acid are similar to those of humic acid, the behavior of salicylic acid in alum coagulation is different from that of humics. It is postulated that the

molecular weight of the organic compound is an important factor for organics' coagulation.

The stability of precipitates formed during jar tests has been evaluated by measuring the turbidities of the supernatant at three different settling times (Fig. 3). These results indicate that the turbidity increases with dosage when there is no settling. In addition, the turbidity decreases as the settling time increases. As shown in Fig. 3(a), precipitates are very stable when the alum dosage is close to an optimal amount (1 mg Al l^{-1}) for humic acid. Besides, the occurrence of restabilization shown in Fig. 2(a) imparts a rise in turbidity at 2 h settling in Fig. 3(a). A comparison with the blank test results (sample without organics), shown in Fig. 3(b), reveals that higher turbidity values are obtained in the sample containing humic acid
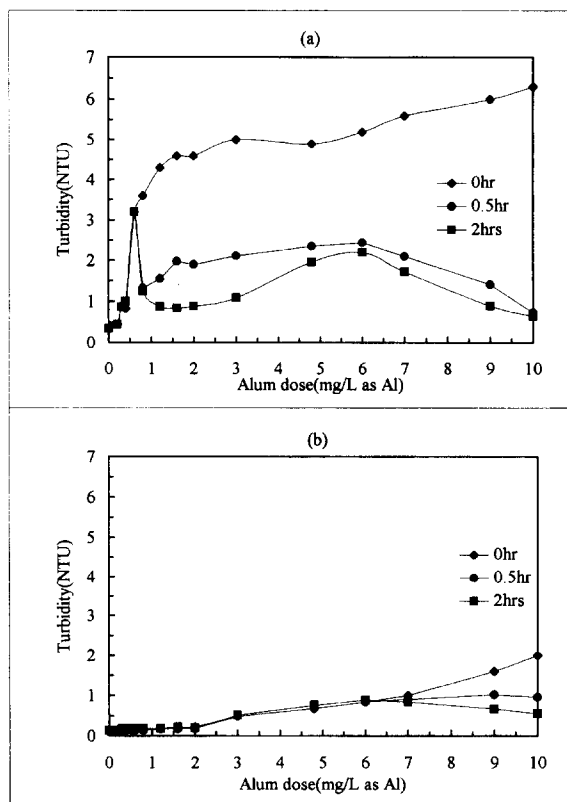

Fig. 3. Turbidity of the supernatant of three different settling times as a function of dosage at pH 5. (a) With humic acid (initial concentration, 4 mg NPDOC l^{-1}); (b) without humic acid.

for alum doses below 9 mg l^{-1}. This indicates that precipitates not only result from $Al(OH)_3(s)$ adsorption but from complexation–charge neutralization in the alum coagulation with humic acid, since precipitates in blank tests can only be generated by the presence of aluminum hydroxide. However, such a distinction of turbidity between blank and organic water is absent for salicylic acid, as shown in Fig. 4. This implies that the floc formed during the alum coagulation is primarily a result of amorphous $Al(OH)_3$, and is not a result of complexation. Although salicylic acid carries a negative charge ($pK_{a1} = 2.97$) in natural water, due to the low molecular mass of salicylic acid ($MW = 138.12$), it is still almost impossible to form an organic–Al(III) precipitate larger in size than 0.45 μm by the complexation of salicylic acid with positively hydrolyzed Al(III) species.
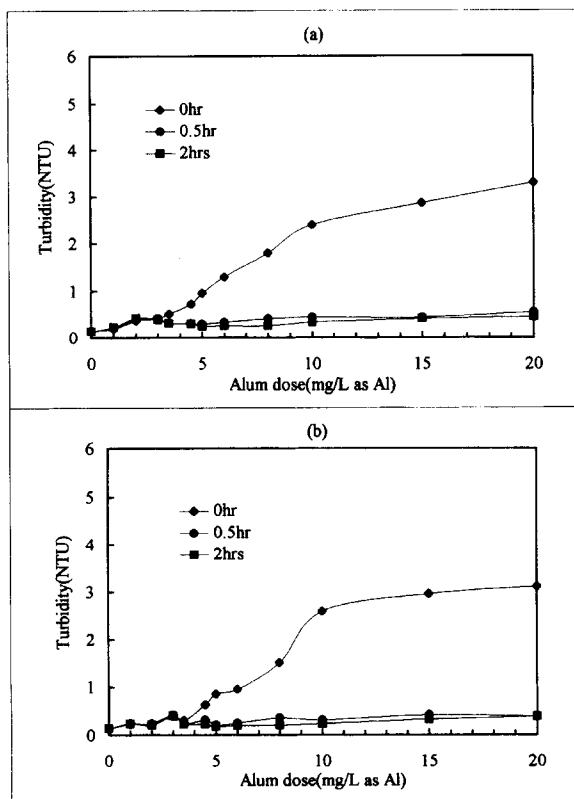

Fig. 4. Turbidity of the supernatant of three different settling times as a function of dosage at pH 6. (a) With salicylic acid (initial concentration, 4 mg C l^{-1}); (b) without salicylic acid.

Figs. 5(a) and 5(b) show isoremoval lines for humic acid with the various alum dosages and pH values by jar mixing–settling and jar mixing–settling–filtering, respectively. There is a similar trend for three isoremoval lines (60, 80, and 90%) in Fig. 5(a). It shows that the alum dosage required to reach an equivalent percentage of organic removal is decreased with a pH increase from 3 up to around 6.3, and then is increased if the pH is higher than 6.3. In addition, two regions of 80% removal of humic acid after the jar tests are found. These two regions consist of a low dosage of alum around pH 5 and a high dosage of alum at pH above 6. The first region mentioned is attributed to the occurrence of complexation–charge neutralization, and the second region covers the area in which the adsorption is a predominant mechanism for the destabilization of humic acid. It is also found that restabilization is absent at pH above 6. Results in Fig. 5(b) indicate that a progressive increase occurs for optimal alum dosage at pH 6 and 7 as compared to that at pH 5. As salicylic acid removal is less than 25% under our experimental conditions, the results of its isoremoval lines are not discussed here.

3.2. Relationship between initial concentrations of organics and optimum dosage

Fig. 6 shows the residual concentrations of humic acid after jar mixing–settling–membrane filtering with various alum dosages at an optimal pH 5. Three initial concentrations of humic acid have been used to investigate the existence of a stoichiometric relationship between humic acid and alum dosage. This relationship at pH 5 indicates that destablization can be achieved by charge neutralization resulting from a specific chemical interaction between positively charged aluminum species and negative functional groups of the humic acid, as shown in the inset graph.

3.3. Adsorption study

Fig. 7 shows the adsorption isotherms of salicylic acid by amorphous aluminum hydroxide flocs. The coagulation capacity of salicylic acid by jar mixing–settling–filtering is also included to make a com-
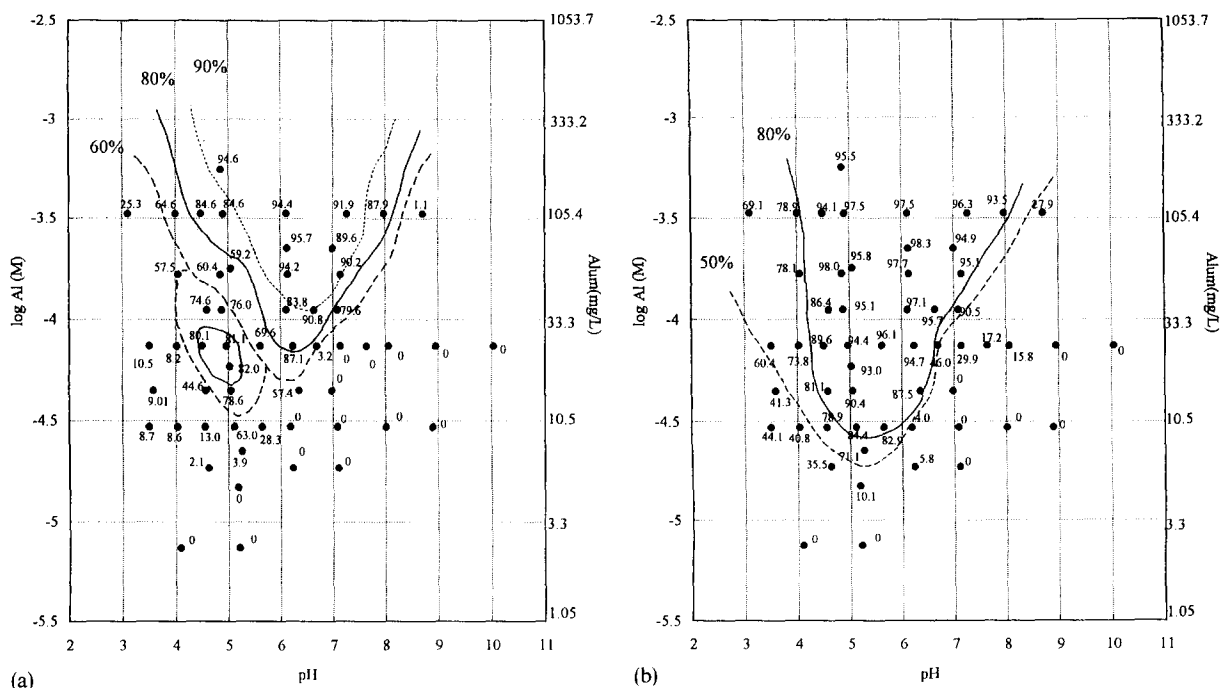
Fig. 5. Isoremoval lines of humic acid by (a) mixing and settling, and (b) mixing, settling, and membrane filtering with an initial concentration of humic acid of 4 mg NPDOC l^{-1}.
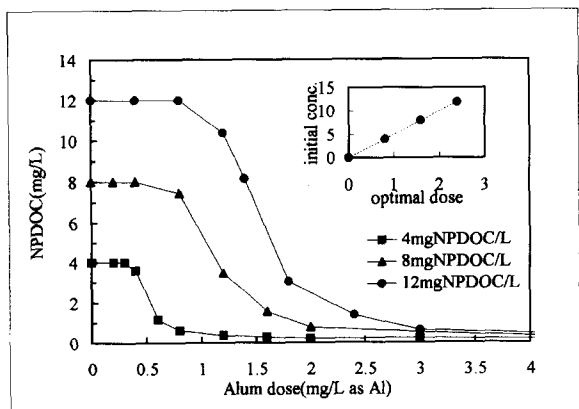

Fig. 6. Residual concentration of humic acid after mixing, settling, and membrane filtering with various alum dosages at pH 5.

Fig. 7. Adsorption isotherms of salicylic acid by amorphous aluminum hydroxide precipitates (alum, 10 mg Al l^{-1}; pH 6).

parison with the adsorption capacity. It is found that a linear correlation occurs with salicylic acid between the adsorption capacity and equilibrium concentration as well as the coagulation capacity and equilibrium (residual) concentration. Elzerman and Coates [18] indicated that the linear isotherm
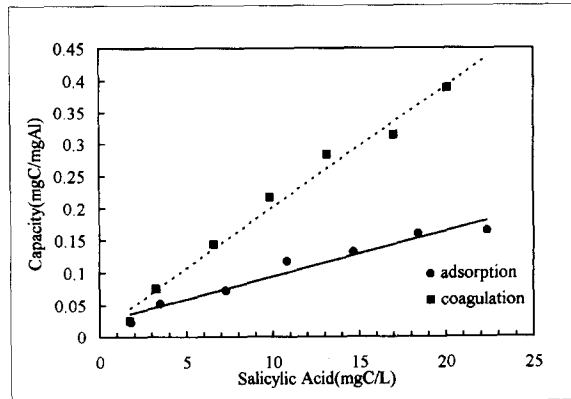
can frequently describe the sorption of hydrophobic organic contaminants in soil and sediment environments. From Figs. 4 and 7, we can infer that the removal of low molecular weight organics such as salicylic acid by coagulation is attributed primarily to adsorption. This contradicts the work reported by Semmens and Ayers [11] in which
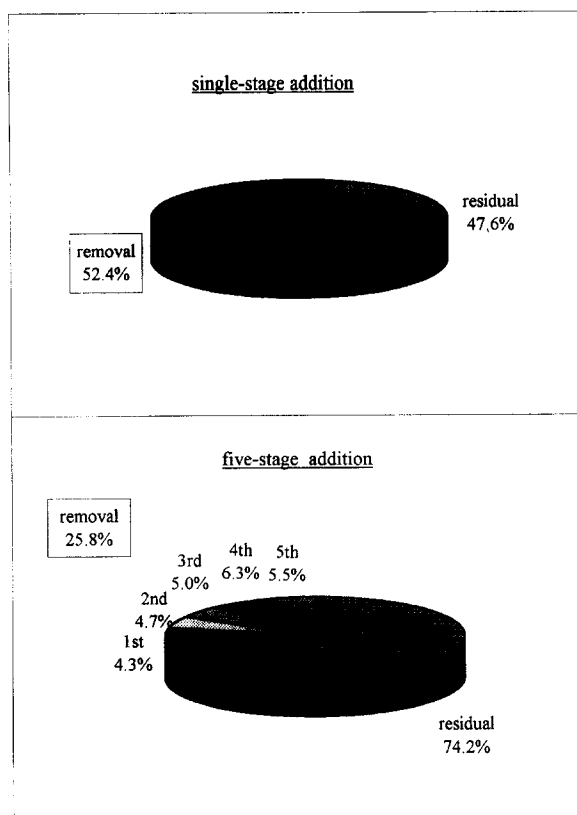
Fig. 8. Removal percentage of salicylic acid by mixing, settling, and membrane filtering with five-stage alum addition and a single alum addition while maintaining pH 6 during rapid mixing (salicylic acid, 12 mg C l^{-1}; alum, 10 mg Al l^{-1}).
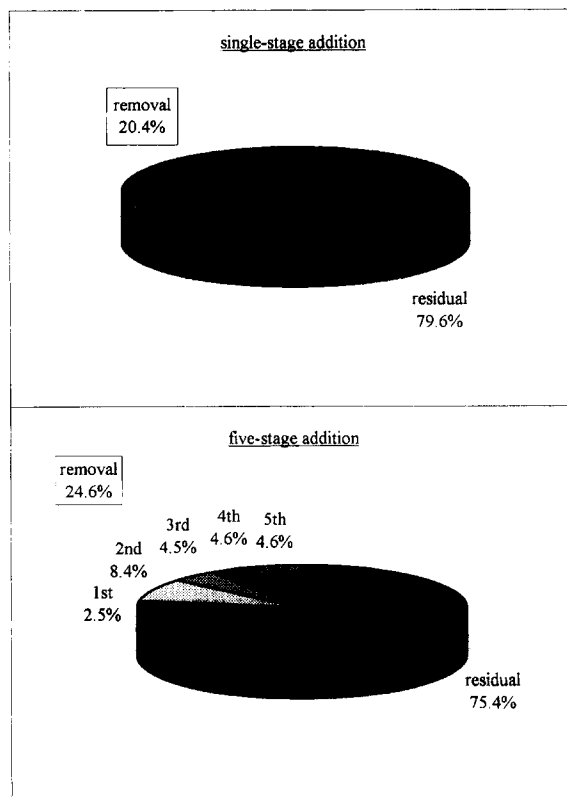

Fig. 9. Removal percentage of humic acid by mixing, settling, and membrane filtering with five-stage alum addition and a single alum addition at pH 7 during rapid mixing (humic acid, 12 mg NPDOC l^{-1}; alum, 3.5 mg Al l^{-1}).

complexation is postulated as a major mechanism, not adsorption. The result also indicates that the difference in capacity between the adsorption and coagulation curves implies that the type of interaction between salicylic acid and alum is not only adsorption but also arises from mechanism. This is verified by the results in Fig. 8, as discussed in the following section.

3.4. Sequential dosing tests

Fig. 9 shows the removal percentage of humic acid by jar mixing–settling–membrane filtering with five-stage alum addition and a single alum addition while maintaining a fixed pH during the rapid mixing. The removal percentages of salicylic acid are presented in Fig. 8. These results indicate

that a 52.4% removal of humic acid is achieved by single-stage alum addition compared to 25.8% removal by five-stage coagulation. Single-stage coagulation is obviously more favorable for removing humic acid than five-stage coagulation. However, this is in contrast to the case of salicylic acid, in which five-stage coagulation possesses a higher removal percentage than single-stage coagulation. The single-stage alum addition can momentarily produce 3.5 mg Al in 1 l of the solution. Because a larger amount of OH^- ions is required for adjusting the final pH to 7 in a single addition, it is favorable for the formation of aluminum hydroxide precipitates to adsorb humic acid. In the case of salicylic acid removal by five-stage coagulation, most of the 2 mg Al l^{-1} addition at pH 6 in each stage can generate aluminum hydrox-

ide precipitates, which can subsequently adsorb salicylic acid. Successive alum addition produces fresh $Al(OH)_3$ precipitates which can become incorporated into old $Al(OH)_3$ precipitates to form an aggregate, which is accompanied by the entrapping of salicylic acid into the aggregate. Actually, such an "entrapment" is present not only in sequential dosing but also in single alum dosing, so that sequential dosing enhances the effect.

4. Conclusions

The molecular weight of the organic compounds is an important factor in organics' removal by coagulation. The optimal pH values for humic acid and salicylic acid removal are different (equivalent to 5 and 6, respectively). An insignificant removal occurs with salicylic acid by alum coagulation, even with a relatively higher dosage than that applied in humic acid removal. The major mechanisms of humic acid removal by alum coagulation involve complexation–charge neutralization–precipitation and adsorption. The predominant mechanisms of salicylic acid removal by coagulation include adsorption and entrapment. This conclusion may be described schematically, as in Fig. 10.

Precipitates are not only caused by $Al(OH)_3(s)$ adsorption, but by complexation–charge neutralization in alum coagulation with humic acid; precipitates are very stable when the alum dosage is close to the optimal amount for humic acid. For salicylic acid, the floc formed during alum coagulation is primarily a result of amorphous $Al(OH)_3$ and does not result from complexation.

A stoichiometric relationship exists between the initial concentration of humic acid and optimal alum dosage. Also, a linear correlation occurs with salicylic acid between '1'213adsorption capacity and equilibrium concentration as well as coagulation capacity and equilibrium (residual) concentration. Single-stage coagulation is more favorable than five-stage coagulation for removing humic acid, but is less favorable for removing salicylic acid.
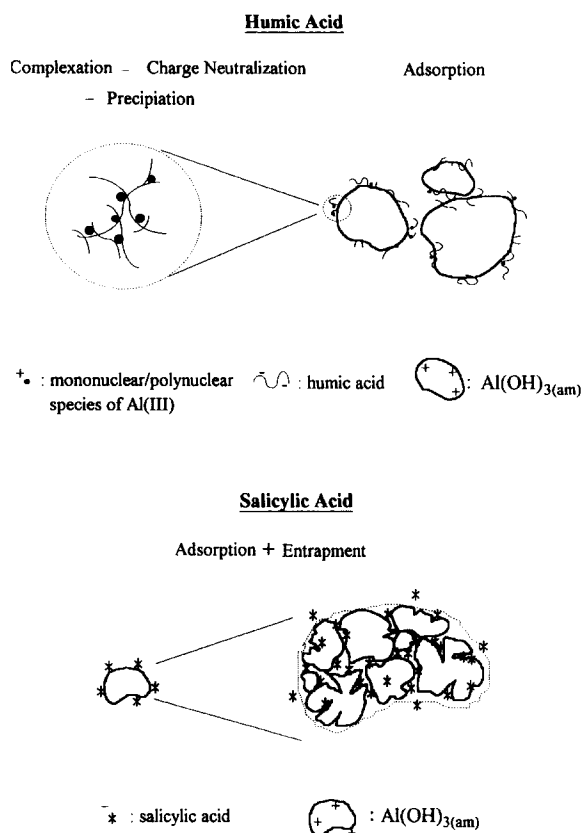

Fig. 10. Schematic diagram of mechanisms of alum coagulation: (a) humic acid; (b) salicylic acid.

Acknowledgments

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