The transformation of aluminium species in the processes of coagulation, sedimentation and filtration

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Abstract The aluminium toxicity is closely related to aluminium species. In this work aluminium was fractionated into seven forms: Al(T), Al(Sus), Al(C + S), Al(S), Al(C), Al(O) and Al(I). Four Al-based coagulants and simulated raw water were used in the laboratory to investigate the aluminium transformation in coagulation, sedimentation and filtration processes. It is the use of Al-based coagulants that contributes more to the increase of the residual aluminium for the low-turbidity raw water, while the Al-based coagulants, especially the polymeric aluminium coagulants, work to remove the aluminium from the high-turbidity raw water. In the case of traditional coagulants, the increase of the turbidity or the dissolved organic carbon (DOC) concentration in the raw water results in a high concentration of Al(C + S). The removal rate of aluminium species in the filtration process is not only related to its size: R_{Al(Sus)} > R_{Al(C+S)}, R_{Al(Cl)} > R_{Al(O)}, but also to the physicochemical properties of aluminium species and filter. For the kaolin-polyaluminium chloride system, a lower removal rate of aluminium species results is due to the complexation of humic acid and aluminium species.

Keywords Al-based coagulant; aluminium species; coagulation and sedimentation; filtration; residual aluminium

Introduction
Coagulation, sedimentation, filtration and disinfection are conventional water treatment processes for the municipal supply of drinking water. The Al-based coagulants are widely used in the coagulation process because of their excellent coagulation performance. However, their use in water treatment draws increasing attention due to the residual aluminium in water and aluminium toxicity (McLachlan et al., 1996; Nayak, 2002). Many countries and organisations have established regulations on residual aluminium in drinking water. The maximum allowable concentration of Al in drinking water is limited to 0.2 mg/L in China. Many researches have made great progress in total aluminium control (Vanbenschoten et al., 1994; Kvech and Edwards, 2002; Frommell et al., 2004; Gao et al., 2004; Wang and Cui, 2004).

Aluminium exists in various species in water. Based on the kinetic difference of the reactions between aluminium and Ferron reagent, the soluble aluminium species in Al-based coagulant can be partitioned into Al_{a}, Al_{b} and Al_{c}, respectively (Smith, 1971; Jardine and Zelazny, 1986; Hsu and Cao, 1990). According to its scattering form or ligand in water, aluminium can also be categorised into suspended aluminium, colloidal aluminium, organically bound aluminium and inorganic bound aluminium (Baba and Okazaki, 2000; Srinivasan and Viraraghavan, 2002). The toxicity of aluminium is not only determined by the total aluminium concentration, but also closely related to the aluminium species (Levesque et al., 2000; Berthon, 2002; Suwalsky et al., 2002). Hence, understanding the distribution and transformation of the aluminium species in the water...
treatment process plays a significant role in controlling the toxicity of residual aluminium and safeguarding the quality of drinking water.

Methods and materials

Coagulants and chemical reagents

All reagents used were of analytical reagent grade except those being pointed out. Four Al-based coagulants (Table 1), including aluminium sulphate, aluminium chloride, polymeric aluminium chloride (PACl) with high content of Alb (PACl-b), and PACl with high content of Alc (PACl-c), were investigated in the present study. The first two are reagent grade, and the last two are prepared and purified in the laboratory (Zhao et al., 2002). A stock suspension of purified kaolin (Imerys, St. Austell, UK) was prepared in deionised water to a concentration of 100 g/L. By dissolving pre-weighed quantities of humic acid (HA, Aldrich Chemical Co.) in deionised water, a stock HA solution with a dissolved organic carbon (DOC) concentration of 3.038 g/L was prepared. The solution pH was measured by an Orion 720A pH meter and adjusted to 7.0 by the addition of 0.1 mol/L NaOH as needed during the preparation process.

Coagulation

According to the required turbidity and DOC concentration, the simulated raw water was prepared by adding some stock kaolin solution and stock HA solution to tap water and then mixing to homogeneity. Some dilute HCl or NaOH solution is needed to adjust the pH value of the raw water to 7.5. The character of the four kinds of raw water is described in Table 2. For the coagulation tests, a conventional jar test procedure was applied by using a PB-700 Jar tester (Phipps & Bird Co.). To 800 mL of the raw water, a known quantity of coagulant was added. The raw water was then rapidly stirred at 250 rpm for 1 min, slowly stirred at 40 rpm for 15 min, and then settled quiescently for 10 min (Wang et al., 2002). Supernatant samples of 40 mL were then withdrawn from a position of approximately 2 cm below the water surface for the analysis of aluminium species.

Filtration

To get the tested water with different dominant aluminium species, three kinds of simulated raw water, including kaolin suspension, PACl solution, and HA/AlCl3 system, were used and prepared by adding 250 mL of stock kaolin suspension, 370 mL of PACl-c (Table 1), and 640 mL of stock HA solution and 56.5 mL of AlCl3 (Table 1) to 193.8 L of tap water and then mixing to homogeneity, respectively. For the second raw water (PACl solution), the pH value of the tap water was adjusted to 4.0 with concentrated HCl before the PACl-c was added.

The effluents from the coagulation and sedimentation processes were also filtrated. The last two types of raw water in Table 2, low turbidity with and without DOC, were

Table 1 Character of the Al-based coagulants

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Al concentration (mg/L)</th>
<th>Basicity (β)</th>
<th>Distribution of aluminium species (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al_b Al_h Al_c</td>
</tr>
<tr>
<td>PACl-c</td>
<td>608</td>
<td>2.6</td>
<td>2.5 11.4 86.1</td>
</tr>
<tr>
<td>PACl-b</td>
<td>1,523</td>
<td>2.4</td>
<td>0.7 93.9 5.4</td>
</tr>
<tr>
<td>Aluminium chloride</td>
<td>4,747</td>
<td>0</td>
<td>95.2 1 3.0</td>
</tr>
<tr>
<td>Aluminium sulfate</td>
<td>10,480</td>
<td>0</td>
<td>96.5 1.2 2.3</td>
</tr>
</tbody>
</table>
coagulated in a larger scale. PACI-c (Table 1, most widely used in China) was used as coagulant and dosed at its optimal dose obtained in the coagulation part (2 mg/L as Al).

The experimental filter column is 100 mm in diameter and 2,500 mm in length. The filter bed consists of 200 mm of support media of gravel. On top of this lay the 800 mm of sand as single-layered media, or 400 mm of sand and 400 mm of anthracitic coal as double-layered media. The sand and anthracitic coal have a size of 0.5–1.2 mm and 0.8–1.8 mm, and a porosity of 43 and 53%, respectively. A 10 m/h filtration rate was maintained in the filtration process.

Analytical methods
According to a method modified from what is described by Srinivasan and Viraraghavan (2002), the aluminium was fractionated into seven forms: (1) total aluminium (Al(T)), (2) colloidal and soluble aluminium (Al(C + S)), (3) colloidal aluminium (Al(C)), (4) organically bound aluminium (Al(O)), (5) suspended aluminium (Al(Sus)), (6) soluble aluminium (Al(S)), and (7) inorganically bound aluminium (Al(I)). The procedure for analysing aluminium species and the relationship between aluminium species are illustrated in Figure 1.

Al(C + S) was fractionated into Al(C) and Al(S) by using gel-filtration chromatographic technique, which was similar to that described by Changui et al. (1990). The chosen gel was Sephadex G-10 (Pharmacia), which was packed in a column made of quartz glass with an internal diameter of 26 mm and a gel length of 222 mm. A 2.5 mL volume of the studied sample was injected and eluted with deionised water at a rate of 1 mL X min⁻¹ by using a peristaltic pump. The effluent between 40 and 60 mL of eluted volume was collected and analysed for Al(C). A strongly acidic cation exchange resin of Amberlite IR

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**Table 2** Character of the simulated raw water

<table>
<thead>
<tr>
<th>Raw water</th>
<th>DOC (mg/L)</th>
<th>Turbidity (NTU)</th>
<th>Total aluminium (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High turbidity without DOC</td>
<td>0</td>
<td>105</td>
<td>0.7117</td>
</tr>
<tr>
<td>High turbidity with DOC</td>
<td>5.0</td>
<td>128</td>
<td>0.7888</td>
</tr>
<tr>
<td>Low turbidity without DOC</td>
<td>0</td>
<td>19.7</td>
<td>0.1863</td>
</tr>
<tr>
<td>Low turbidity with DOC</td>
<td>5.0</td>
<td>27.5</td>
<td>0.3085</td>
</tr>
</tbody>
</table>

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**Figure 1** Procedure for analysing aluminium species and the relationship between aluminium species
120 plus was used to fractionate Al(C + S) into Al(O) and Al(I) (Srinivasan and Viraraghavan, 2002). All the concentrations of the above aluminium species were determined by inductively coupled plasma (ICP) spectrometer (IRIS Intrepid II).

Results and discussion

Transformation of aluminium species in coagulation and sedimentation processes

As is shown in Figure 2, in the raw water with low turbidity, it is the use of Al-based coagulants that contributes more to the increase of the residual aluminium while in the one with high turbidity, the Al-based coagulants, especially the polymeric aluminium coagulants work to remove the aluminium from the water. The residual aluminium concentration of traditional aluminium coagulants is higher than that of the polymeric ones.

From Tables 3 and 4, it can be seen that all the residual aluminium from polymeric coagulants is Al(Sus). Besides Al(Sus), there are Al(C) and Al(S) in the residual aluminium from traditional coagulants. The DOC concentration of the raw water has a significant influence on the distribution of aluminium species in the effluent. When the DOC concentration rises, the sites or groups to complex the traditional coagulant (Srinivasan and Viraraghavan, 2004) increase, which may enhance the formation of Al(C) and Al(S).

Another very important factor to influence the distribution of aluminium species is the turbidity arising from the kaolin particles. Usually, Al(Sus) will be formed if the traditional coagulant is dosed in water due to its hydrolysis. There is a correlation between turbidity and Al(Sus) in raw water or effluent (Driscoll and Letterman, 1995; Cui et al., 2002). From the point of chemical equilibrium, the increase of Al(Sus) in the system will retard the production of Al(Sus), that is, the increase of kaolin particles in the raw water may result in less Al(Sus) and more Al(C + S) in the system by influencing the hydrolysis of traditional coagulant. The concentrations of Al(C) and Al(S) rise when the turbidity or the concentration of DOC increases.

Figure 2 Total residual aluminium of Al-based coagulants in different raw water. Raw water: (a) high turbidity without DOC; (b) high turbidity with DOC; (c) low turbidity without DOC; (d) low turbidity with DOC.
Transformation of aluminium species in filtration process

It can be seen from Figure 3 that the dominant aluminium species in the kaolin suspension is Al(Sus). The removal rates of both Al(T) (R_{Al(T)}) and Al(Sus) (R_{Al(Sus)}) are not more than 10%, and the removal rate of the Al(C + S) (R_{Al(C+S)}) is even lower. Usually, the industrialised liquid PACl product has a high concentration of aluminium and its dominant aluminium species is Al(C + S) (Luan et al., 1997). When the PACl product is diluted, some Al(C + S) species may transform into Al(Sus) due to the hydrolysis of aluminium (Figure 4). It is also found that the removal rate of aluminium species is related to its size: R_{Al(Sus)} > R_{Al(C+S)} > R_{Al(C)}. The R_{Al(Sus)} in the PACl diluted solution (approximately 40%, Figure 4) is more than that in kaolin suspension (10%, Figure 3) because the Al(Sus) in the PACl solution consists of freshly precipitated amorphous aluminium hydroxide, which has a high reactivity with the Ferron reagent and has a floccular structure with a more hydrophilic group such as hydroxyl (Duffy and Vanloon, 1994; Fukushi and Tsukimura, 2004). For all the species in the raw water (Figures 3–6), the removal rate in the double-layered filtration is higher than that in the single-layered filtration, as the coal filter with a porous structure can absorb more aluminium species than the sand filter. All the above results show that the removal rate of aluminium species in the filtration process is not only related to its size, but to the physicochemical properties of the aluminium species and filter.

For the raw water containing HA and AlCl₃, there are similar results which are shown in Figure 5: R_{Al(Sus)} > R_{Al(C+S)}, R_{Al(OH)} > R_{Al(O)}. Moreover, the removal rates of aluminium species in Figure 5 are even higher than those in Figures 4 and 3. The HA can complex with Al³⁺ and other hydrolysis species of aluminium to form suspended flocs and colloidal particles, which is similar to the coagulation process of removing HA from water by using Al-based coagulant. The flocs and particles have different physicochemical characteristics from the hydrolysis products of aluminium alone (Figure 4), and are more easily removed by filtration. As a result, the removal rates of aluminium species in the HA/AlCl₃ system are enhanced in the filtration process. Al(C + S) can be divided into Al(O) and Al(I). When Al(O) is formed during the complexation of HA and aluminium species many, suspended flocs and colloidal particles are produced in the HA/AlCl₃ system, which results in a considerable amount of Al(C) in Al(O). In Al(I), on the contrary, there is much more Al(S) due to the unhydrolysed...
Table 4 Species distribution of residual aluminium in high-turbidity raw water with/without DOC

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Al dose (mg/L)</th>
<th>Concentration of aluminium species (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw water without DOC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al(Sus)</td>
<td>Al(C + S)</td>
</tr>
<tr>
<td>Aluminium chloride</td>
<td>0.1542</td>
<td>0.6302</td>
</tr>
<tr>
<td></td>
<td>0.6171</td>
<td>0.6272</td>
</tr>
<tr>
<td></td>
<td>0.9197</td>
<td>0.5945</td>
</tr>
<tr>
<td></td>
<td>1.2282</td>
<td>0.5353</td>
</tr>
<tr>
<td></td>
<td>1.5368</td>
<td>0.5762</td>
</tr>
<tr>
<td></td>
<td>2.1480</td>
<td>0.5022</td>
</tr>
<tr>
<td>Aluminium sulfate</td>
<td>0.1300</td>
<td>0.4077</td>
</tr>
<tr>
<td></td>
<td>0.5931</td>
<td>0.5044</td>
</tr>
<tr>
<td></td>
<td>0.9967</td>
<td>0.3672</td>
</tr>
<tr>
<td></td>
<td>1.5316</td>
<td>0.3088</td>
</tr>
<tr>
<td></td>
<td>1.8521</td>
<td>0.3725</td>
</tr>
<tr>
<td></td>
<td>2.2443</td>
<td>0.3440</td>
</tr>
</tbody>
</table>

Note: n.d = not detectable
or incompletely hydrolysed $\text{Al}^{3+}$. Since $R_{\text{Al(O)}} > R_{\text{Al(S)}}$, the removal rate of Al(O) is more than that of Al(I) in the HA/AlCl$_3$ system.

The kaolin suspension with/without HA was coagulated by PACl-c, and then underwent the sedimentation and filtration processes. Only the concentrations of total residual aluminium are shown in Figure 6, because there is only Al(Sus) in the effluent with PACI.
as coagulant. The concentration of the total residual aluminium decreases abruptly after filtration. The HA has a negative influence on the filtration performance so that some of the total residual aluminium concentrations are over 0.2 mg/L (the regulation on residual aluminium in China), especially under the condition with the single-layered filter used. There is more Al(S) in the AlCl₃ system and more Al(Sus) in the kaolin-PACl system, and the complexation of HA and aluminium species results in an increase of Al(C+S), whose removal rate is higher than that of Al(S) but lower than Al(Sus). As a result, HA has a positive influence on the removal rate of aluminium species in the former system (R_{Al(O)} > R_{Al(I)}, Figure 5) and a negative influence on that of the latter one (Figure 6).

Since the AlCl₃ system is rare, while the kaolin-PACl system is common in water treatment plant, much more attention should be paid to the influence of HA on the transformation of aluminium species.

**Conclusions**

In the coagulation and sedimentation processes, for the system of low turbidity, the addition of Al-based coagulants is the main cause leading to an increase of residual aluminium in effluent water, while for the system of high turbidity, it is the Al-based coagulants, especially polymeric aluminium that work to remove aluminium from the water. All the residual aluminium of polymeric aluminium was Al(Sus). Al(C) and Al(S) also exist in the residual aluminium of traditional coagulants. The contents of Al(C) and Al(S) in residual aluminium can be enhanced by the increase of turbidity and the concentration of DOC of raw water. The removal rate of aluminium species in the filtration process is not only related to its size: R_{Al(Sus)} > R_{Al(C+S)}, R_{Al(C)} > R_{Al(S)}, but to the physicochemical properties of aluminium species and filter. The removal rate in the double-layered filtration is higher than that in the single-layered filtration. HA has a positive influence on the removal rate of aluminium species in the AlCl₃ system and a negative influence on that in the kaolin-PACl system.

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References


