



Transfer and transport of aluminum in filtration unit

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Abstract

Aluminum salt coagulants were used prevalently in various water works. In this article, the effects of filtration on residual aluminum concentration and species distribution were researched by determining the concentration of different aluminum species before and after single layer filter, double layer filter, and membrane filtration units. In the research, size exclusion chromatography (SEC) was used to separate colloidal and soluble aluminum, ion exchange chromatography (IEC) was used to separate organic and inorganic aluminum, and inductivity coupled plasma-atomic emission spectrometry (ICP-AES) was used to determine the aluminum concentration. The results showed that the rapid filtration process had the ability of removing residual aluminum from coagulant effluent water, and that double layer filtration was more effective in residual aluminum removal than single layer filtration, while nano filtration was more effective than micro filtration. It was found that when the residual aluminum concentration was below 1mg/L in sediment effluent, the residual aluminum concentration in treated water was above 0.2 mg/L. The direct rapid filtration process mainly removed the suspended aluminum. The removal of soluble and colloidal aluminum was always less than 10% and the natural small particles that adsorbed the amount of soluble or small particles aluminum on their surface were difficult to be removed in this process. Micro filtration and nano filtration were good technologies for removing aluminum; the residual aluminum concentration in the effluent was less than 0.05 mg/L.

Key words: aluminum species; membrane filtration; rapid filtration

Introduction

The filtration unit is indispensable in traditional water treatment system, which is important in ensuring water quality safety. Generally, the filtration system is set behind the settlement and clarification unit according to the water flow, and its main function is to remove water turbidity, partial natural organic matter (NOM), bacteria and virus, and thus provide a good water condition for the disinfection process. With the development of water treatment, various kinds of filtration tanks have emerged. The normal rapid filtration tank has the longest application history and is still being used prevalently. To enhance its ability in holding back impurities, the single layer filter, double layer filter, and homogeneous filter appear, and these are the major filter forms in most water plants.

Aluminum salts are prevalently used in the water treatment system (Qu *et al.*, 2002). In the whole coagulant market, aluminum sulfate, poly aluminum chlorine (PAC), and iron salts account for 20%, 40%, and 40%, respectively. Although these have a good coagulation effect, the application of aluminum salts in water treatment is the major factor causing high residual aluminum in most drinking water (Irina and Jeff, 2000; Peter and Gary, 2005;

Huang *et al.*, 2006). Sufficient evidences indicate that aluminum is not a neutral element to human body and is thought to be connected with several diseases (Schenk *et al.*, 1989; Crapper *et al.*, 1973). By promoting the lipid peroxidation reaction that occurs in the brain, aluminum exerts its chronic accumulation neuro toxicity. At present, most developed countries have standardized the aluminum concentration in drinking water, and the standard in China is below 0.2 mg/L.

In several water works, to increase coagulation performance and to control the coagulant process conveniently, the actual coagulant dosage is generally considerably more than the theoretical dosage (Wang and Cui, 2001). On this condition, partial aluminum will react with the pollutants and deposit in the settlement tank, while the excess part will still exist in effluent water as residual aluminum and will enter the filtration unit (Gao *et al.*, 2004; Konstantinos *et al.*, 2006; Hu *et al.*, 2006). Considering turbidity in filtration effluent is correlated with the residual Al concentration (Letterman and Driscoll, 1988), the removal of turbidity can reduce the residual aluminum concentration including suspended and colloidal aluminum. However, former studies mainly deal with the total aluminum concentration and its relation with turbidity (Liu *et al.*, 1997). The removal rule of the different aluminum species is not clear yet and requires extensive research.

Micro filtration (MF) and nano filtration (NF) are the

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new techniques in the drinking water treatment system. Micro-membrane, with a pore size of 0.02–1.0 μm , removes pollutants by mechanical selection and diffusion function. Nano filtration is more effective in removing organic matters and inorganic ions because of its considerably smaller average pore size. Therefore, membrane filtration will be an effective technology in aluminum removal, while there is no related research conducted.

The objective of this article was to study the removal rules of different aluminum species in the single layer filter, double layer filter, and membrane filtration units. The species referred in this research include total aluminum (Al_T), suspended aluminum (Al_{SUS}), colloidal aluminum (Al_C), soluble aluminum (Al_S), inorganic aluminum (Al_I), organic aluminum (Al_O), and soluble-colloidal aluminum ($\text{Al}_{(C+S)}$).

1 Materials and methods

1.1 Apparatus and materials

Polypropylene filter core was supported by Shanghai Eling Filter Equipment Company, with filtration precision 0.45 μm and effective filter area 0.50–0.70 cm^2 . C70-F flat sheet membrane module was obtained from Nitto Dento, Japan. NF270 membrane was supported by Dow Chemical, USA, with effective membrane area $3.35 \times 10^{-3} \text{m}^2$, average pore size 0.36 nm, and molecular weight cut-off 150.

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, PAC, NaOH, and HCl were analytical reagents. Humic acid (HA) $3.0 \times 10^3 \text{mg/L}$ (calculated as DOC) and Kaolin soil $1.0 \times 10^5 \text{mg/L}$ (calculated as suspended solid) were prepared as storage solutions.

Besides, LP2000-turbidity meter (Hanna Instruments Srl), pH meter (ORION 710), and IRIS Intrepid-II ICP (Thermo Elemental, USA) were also used in the experiments.

1.2 Experiment methods

All experiments were conducted in the lab scale. The source waters include Kaolin soil water (water1), PAC water (water2), and HA/ AlCl_3 water (water3) prepared as Table 1, and the aluminum concentration was controlled between 0.5 and 1.5 mg/L , which had similar water quality as the settlement effluent. By applying rapid single layer filtration (SF), double layer filtration (DF), and membrane filtration units, water1, water2, and water3 were filtrated, respectively. The concentration of the different aluminum species was obtained by direct determining or material balance calculating, as described by Zhao and Jiang (2005).

1.2.1 Rapid filtration system

The rapid filtration system is shown in Fig.1. The source water was stored in a tank with a size of 510 mm \times 500 mm

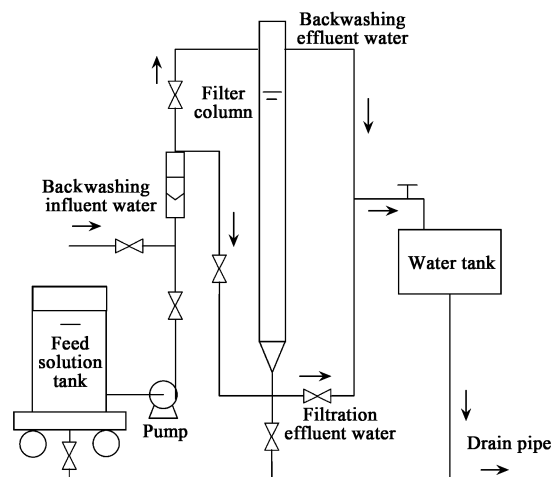


Fig. 1 Rapid filtration system.

$\times 760 \text{mm}$. A flow meter was set to control the filtration and back washing flux. The filtration column was 100 mm in inner diameter and 2500 mm in height. The bottom part of the column was the gravel supporting layer, which was 200 mm in depth. Silica sand was used as the SF media; anthracite and silica sand were used as the DF media, as shown in Table 2. The filtration rate was kept at 10 m/h.

Table 2 Rapid filtration parameters

Type	Media	Depth (mm)	Grain size (mm)	Porosity (%)
Single-layer filtration (SF)	Silica sand	800	0.5–1.2	43
Double-layer filtration (DF)	Anthracite	400	0.8–1.8	53
	Silica sand	400	0.5–1.2	43

1.2.2 Membrane filtration

The membrane filtration system is shown in Fig.2. Dead-end filtration was adopted in MF, and X-flow filtration was adopted in NF. During the whole experiment, the water temperature was maintained at 25°C. The pump output pressure and flux were maintained at 0.5 MPa and 4.6 L/min, respectively.

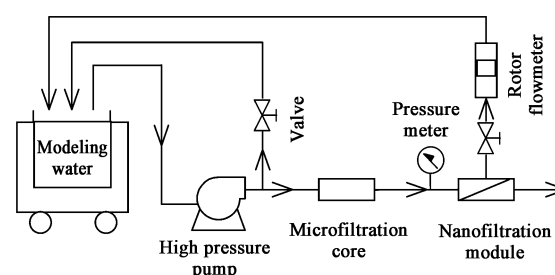


Fig. 2 Membrane filtration system.

Table 1 Waters used in filtration

Prepared water	Preparation method	Water quality index
Kaolin water	Add Kaolin-soil storage liquid into tap water and mix uniformly	$\text{Al}_T = 0.6 \text{mg/L}$
PAC water	Add PAC to tap water and mix uniformly; finally adjust the solution pH to 4 by adding HCl	$\text{Al}_T = 1.2 \text{mg/L}$
HA/ AlCl_3 water	Add HA storage liquid and 56.5 ml AlCl_3 solution to tap water and mix uniformly	DOC = 10 mg/L , $\text{Al}_T = 1.4 \text{mg/L}$

2 Results and discussion

2.1 Rapid filtration

By species analyzing, it was found that the main aluminum species was Al_{SUS} in both water1 and its filtration effluent, and $Al_{(C+S)}$ accounted for less than 8% in water1 as shown in Fig.3. The Al_T removal rate was less than 10% and the $Al_{(C+S)}$ concentration varied slightly in both SF and DF filtration processes. Therefore, rapid filtration could remove aluminum partially, and all species had residual in filtration effluent, which is consistent with the conclusion drawn by Berube and Soucy (2004).

Fig.4 shows the results of aluminum species removal of water2 in rapid filtration. It can be concluded that SF and DF had different aluminum removing capacities. The Al_T removal rate was about 33% and 40%, respectively; the Al_{SUS} removal rate was about 40% and 45% respectively. $Al_{(C+S)}$ had a lower removal rate in both SF and DF processes, and in both filtration types, the Al_{SUS} removal rate was higher than that of $Al_{(C+S)}$ and Al_T . Al_S had the least removal rate less than 10%. Accordingly, Al_{SUS} was the form that could be removed from the solution in the filtration process and DF was more effective in removing aluminum than SF.

The experiment with water3 had similar results. However, the Al_O concentration was considerably higher than that in water1 and water2. Al_O had a similar removal rate with

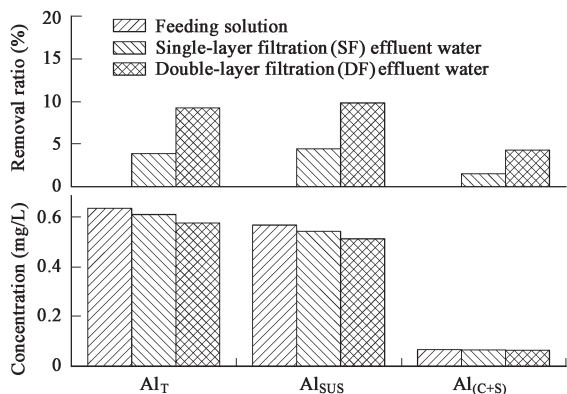


Fig. 3 Residual aluminum species concentration and the removal rate of water1 before and after the SF and DF processes.

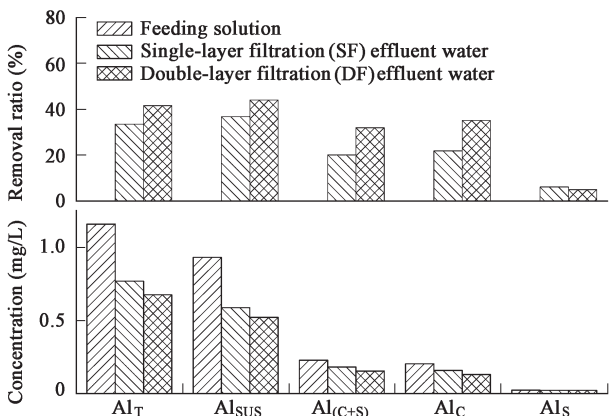


Fig. 4 Residual aluminum species concentration and the removal rate of water2 before and after the SF and DF processes.

Al_I in both SF and DF processes, of about 40%.

Generally, most of the small natural particles were non-leachable in sand filtration (Berube and Soucy, 2004). In this experiment, the suspended aluminum in water1 originated from Kaolin-soil, which contained several small natural particles, and these particles were difficult to be removed from water without coagulant agent. The particulate aluminum in water2 and water3 originating from fresh-forming aluminum flocs were easier to be removed in the filtration process (Duffy and Vanloon, 1994; Fukushi and Tsukimura, 2004; Furrer *et al.*, 2002). As mentioned above, suspended and colloid aluminum were the major forms that could be removed by general rapid filtration, and thus, the removal rate of total aluminum in water1 effluent was lower than that in water2 and water3. When compared with water3, water2 had a lower pH value, which prevented suspended aluminum formation. Besides, HA in water3 could react with aluminum ions and its hydrolysis species forming colloid matters and suspended flocs, which had special chemical characteristic and were easier to be removed from water solution enhancing filtration capacity (Srinivasan and Viraraghavan, 2004; Gu and Karthikeyan, 2005). Consequently, water3 (Fig.5) had a higher total aluminum removal rate than water2.

In conclusion, the aluminum removal rate (R) was not only connected with the filtration media's chemical character, but was also related to the particle diameter of the different aluminum species. It can be arranged as $R_{Al_{SUS}} > R_{Al_C} > R_{Al_S}$.

In the meanwhile, it can be found that the residual aluminum concentration derived from water1, water2, and water3 were considerably higher than the national standard, 0.2 mg/L in both single-layer and double-layer filtration. This was mainly because the filtration system could not remove all particle matter, especially when the particle diameter was adequately small. Water1 was prepared by Kaolin-soil, as mentioned above, which was difficult to be removed from raw water. Water2 and water3 were prepared with PAC and $AlCl_3$, which restrained small particles congregating into leachable particles.

The residual aluminum in filtration effluent has relation with Al_T in raw water and residual turbidity in filtration

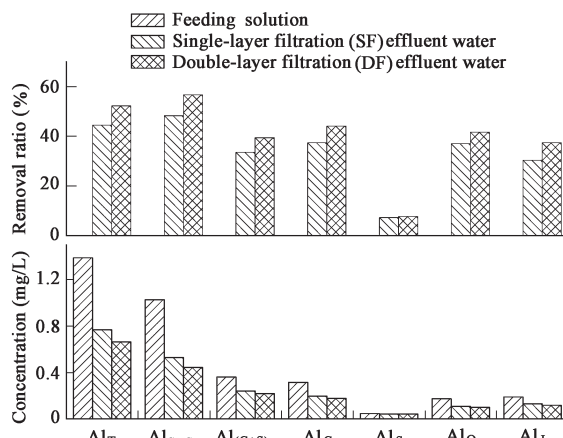


Fig. 5 Residual Al species concentration and removal rate of water3 before and after the SF and DF processes.

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effluent, which can be expressed by the following equation (Letterman and Driscoll, 1988):

$$Al_e = 0.1Al_r^{0.36} T_e^{0.32} \quad (1)$$

where, Al_e represents the residual aluminum concentration in filtration effluent water, Al_r is the total aluminum concentration in raw water, and T_e is the residual turbidity in effluent water. According to the experiential equation, we can obtain the total residual aluminum concentration in filtration effluent. Considering water3 for example, the calculating value obtained was 0.134 mg/L, which was considerably lower than the experiment result of 1.4 mg/L. Similarly, the same problem was encountered in water2 and water3. However, it should be noticed that the equation was obtained based on the experiment data of the integrated water treatment system, and not only on the filtration process. The water quality and the aluminum species distribution condition showed various differences between self-prepared water and coagulation effluent water. Considering the effects of other treatment units, we put PAC into water3 and simulated the coagulation and settlement processes, and then pumped the coagulation effluent water into the filtration unit. The residual aluminum concentration in filtration effluent water after the coagulation and settlement processes significantly decreased below 0.2 mg/L after equilibrium, which was close to the calculated value, as shown in Fig.6.

Consequently, DF and SF could not remove small particles or soluble aluminum. It is necessary to maintain certain turbidity in raw water to accelerate the formation of large settleable or leachable particles in the treatment process.

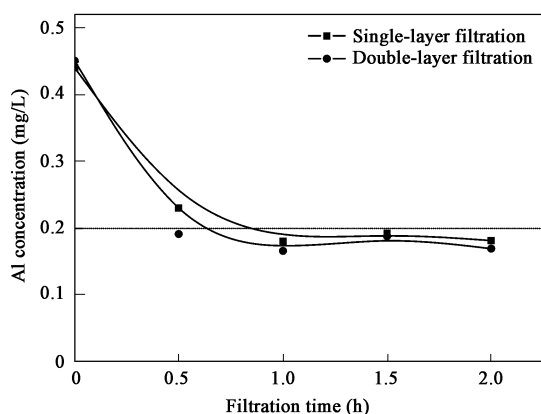


Fig. 6 Residual aluminum concentration in water3 filtration effluent after coagulation-settlement pretreatment.

2.2 Membrane filtration

In this experiment, $Al_{(C+S)}$ was defined as the part of aluminum that can pass through 0.45 μm membrane filter. Therefore, in the membrane filtration process, only Al_S and Al_C were analyzed.

Residual aluminum could not be detected in NF effluent water. Nano filtration, with small membrane pore size, could remove most multi valence salts. In the meanwhile, aluminum ion could change into species with larger molecular weight and higher electric charge by polymerization, and aluminum ion could react with humic acid and other soluble organic matters through the hydrolyzation and polymerization processes. Thus, NF achieved nearly 100% aluminum removal rate.

Micro filtration, with an average pore size of 0.02–1.0 μm , could remove the particles between 0.05–10 μm . The Kaolin soil's average diameter used in experiment was about 1.69 μm . Therefore, most aluminum species in water1 could be removed. Table 3 shows the membrane filtration experiment results on water1, water2 and water3, respectively. $Al_{(C+S)}$, Al_C , and Al_S of water2 decreased notably when compared with the raw water at the initial time of filtration. Al_C could be removed effectively and the removal rate was about 49%. However, the Al_S removal rate was considerably lower when compared with Al_C . In the following 3 h, the $Al_{(C+S)}$ concentration in the filtration effluent water decreased with time and the final aluminum concentration was stable at a considerably lower level with 91% aluminum removal rate. This can be explained by the fact that the micro membrane pore size can become smaller with the filtration continuing, and finally a layer of gel will form on the membrane surface, which will enhance the filtration performance. Similar to PAC, $Al_{(C+S)}$ in water3 decreased in the filtration process as shown in Table 3. As the filtration continued, $Al_{(C+S)}$ decreased gradually and stabilized at a lower level. Al_C had a higher removal rate when compared with Al_S . As the initial concentration of Al_T was 0.28 mg/L lower than that of water2, its final removal rate of 72% was lower than that of water2. However, the removal rates of Al_O and Al_I were similar, about 70%.

The filtration effect was not only connected with the filtering mechanism but was also related to other factors such as the pore shape and diameter of the membrane and the aluminum species molecular weight. The smaller the membrane pore and the larger the molecular weight, the higher was the removal. Al_C was larger than Al_S in size, and therefore, the former removal rate was higher. Al_O and Al_I were different in ligand leading to similar diameter, and

Table 3 Membrane filtration results on water1, water2, and water3 (unit: mg/L)

Sample	Water1				Water2			Water3		
	$Al_{(C+S)}$	$Al_{(C+S)}$	Al_C	Al_S	$Al_{(C+S)}$	Al_C	Al_S	Al_O	Al_I	
Source water	0.0633	0.4465	0.3796	0.0669	0.2802	0.2443	0.0359	0.1338	0.1464	
Initial time	0	0.252	0.195	0.057	0.274	0.238	0.035	0.129	0.145	
1 h later	0	0.040	–	–	0.10	0.073	0.033	0.053	0.054	
2 h later	0	0.039	–	–	0.084	–	–	0.043	0.042	
3 h later	0	0.038	–	–	0.077	–	–	0.035	0.042	

“–”: Concentration is lower than the detection limit.

therefore, their removal rates were similar. As the filtering continued, the $Al_{(C+S)}$ concentration decreased and finally stabilized.

2.3 Comparison between the different filtration processes

From the above experiment results, it can be concluded that to a certain extent, influent water rapid filtration was effective in Al_{SUS} removal, while the Al_S removal rate was considerably lower, which was determined by the physical characteristics. Generally, the aluminum removal rate was higher in the DF process than that in the SF process. However, the residual aluminum after direct rapid filtration was still above the national standard, 0.2 mg/L. Considering the difference in water quality and aluminum species distribution between direct filtration and rapid filtration influents, the latter was more effective in aluminum removal. MF and NF were new techniques in the water treatment system and were more effective in aluminum removal than rapid filtration. NF could remove almost all the aluminum species, while MF with larger membrane pore diameter allowed partial $Al_{(C+S)}$ passing through the system. Also, as the filtration continued, the filtration performance could be enhanced.

3 Conclusions

Different filtration processes had different removal effects on residual aluminum species, which were mainly connected with the filtration media characteristics; generally, $SF < DF < MF < NF$. DF and SF could remove particles with sufficiently large diameters and failed in removing small particles or soluble aluminum. It was necessary to maintain certain turbidity in raw water to accelerate the formation of large settleable or leachable particles in the treatment process. MF and NF had good removing effect on residual aluminum. On direct filtration condition, the Al_{SUS} removal rate was approximately 100% and the $Al_{(C+S)}$ removal rate was over 70%; the final Al_T concentration in filtration effluent water was about 0.05 mg/L.

Different water quality will lead to different aluminum residual and species distribution. Natural small particles that adsorbed some amount of soluble or small particle aluminum on their surface were difficult to be removed by direct fast filtration, such as SF and DF. The experiment results showed that coagulation and settlement will accelerate the removal of aluminum in the filtration process.

The traditional water treatment filtration process could not solve the high residual aluminum phenomenon; after filtration the Al_T concentration may still be above 0.2 mg/L. If the coagulant dosage was excessive, the aluminum residual in filtration effluent water may exceed the national standard, but when the residual aluminum concentration in coagulant effluent water was not larger than 1 mg/L, the aluminum residual concentration in filtration effluent water could be controlled within 0.2 mg/L. However, when the residual aluminum concentration was

larger than 1 mg/L, MF or NF may be required to ensure the water quality safety.

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