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Effect of different coagulants on the ultraviolet light intensity attenuation

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ABSTRACT

The effect of different coagulants added to deionized water on ultraviolet (UV) light intensity at the wavelength of 253.7 nm was investigated in this study. It was demonstrated that iron salts had a greater negative effect on the UV transmittance (UVT) of the solution, but aluminum salts had little effect on the UVT of the solution except polyaluminium chloride (PAC). Polyferric sulfate (PFS) and PAC, as highly effective inorganic-polymer coagulants, had a greater negative effect on the UVT of the solution than the related metal salts. UV light attenuation of iron salts and aluminum salts existing in the solution were in good agreement with the Lambert-Beer law, except PAC and PFS. The UV absorption coefficients of different coagulants were obtained and compared below: PFS>$FeCl_3$>$Fe_2(SO_4)_3$>$FeSO_4$>PAC>$AlCl_3$>$Al_2(SO_4)_3$. If the coagulation pretreatment with PFS was added before UV disinfection of water, it would lead to stronger UV light attenuation than that with PAC. It means that more UV light can reach and inactivate bacteria in water to accomplish a better water disinfection after coagulation with PAC, compared with PFS. Therefore, these results can give guidance on the coagulants used in the pretreatment before UV disinfection process.

Keywords: Ultraviolet transmittance; Coagulant; UV absorption coefficient; Polyaluminium chloride; Polyferric sulfate; UV disinfection

1. Introduction

Ultraviolet (UV) disinfection is being used increasingly as an alternative to chlorine disinfection for the treatment of drinking water or wastewater [1,2]. The main advantage of this technology is the absence of toxic by-products which are usually generated and identified during chlorine disinfection [3]. UV disinfection is also characterized as a short contact time and a more efficient germicidal technology [4,5]. In addition, UV disinfection needs no addition of chemicals and does not alter water quality [6].

However, there are many factors which have effects on UV disinfection efficiency. The most critical wastewater quality parameter generally used in mathematical models describing UV disinfection efficiency is the UV transmittance (UVT) of wastewater at 253.7 nm [7,8]. Other important water quality parameters that can affect UV disinfection performance include: suspended solids, turbidity, particle size distribution and colour [9]. The lower the UVT is, the lower UV disinfection efficiency is. UVT is related to pretreatment, source and chemical composition of water. Some authors suggested the performance of UV disinfection was influenced by water turbidity and UV lamp intensity, which may be reduced by lamp age and fouling caused by some compounds in

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the wastewater [10,11]. Moreover, UV can be absorbed by some ions, such as $Fe^{2+}$and Fe^{3+}, which have molar absorption coefficients at 253.7 nm of 466 l/mole/cm and 3069 l/mole/cm, respectively [12]. This reduces the UV dose available for UV disinfection of water.

Coagulation or filtration is often used for particle removal in wastewater treatment plants before UV disinfection [13,14]. The purpose of adding coagulant to water supply is to make present contaminants unstable and cause them to be removed in subsequent sedimentation and filtration processes [15]. Gehr and Wright (1998) assessed the disinfection performance of a municipal wastewater which had been pretreated by ferric chloride coagulant followed by sedimentation [8]. The wastewater in the UV systems contained high levels of ferric ion (often above 3 mg/l), suspended solid and UVT values at wavelength of 254 nm were also not ideal (approximately 30 mg/l and 0.32 respectively). The target level of fecal coliforms could not be reached, and the pilot tests revealed significant UV intensity attenuation after only a few hours.

The effectiveness of UV disinfection is directly related to UV dose absorbed by microorganisms [1]. UV dose (mWatts sec/cm^2) is defined as UV light intensity (mWatts/cm^2) times the exposure time (seconds). When time is constant, the UV dose will depend on the UV intensity. There are many factors affecting UV intensity. The concentration, varieties of coagulants and solution depth are the main factors.

Hence, the objectives of this research were: to investigate the effects of the solution depth and the concentration of various coagulants, such as ferrous sulfate, ferric sulfate, ferric chloride, aluminum sulfate, aluminum chloride, polyferric sulfate (PFS) and polyaluminium chloride (PAC) on the UVT of the solution; to compare the UV absorbance of various coagulants; to study the relationship between different concentrations of coagulant and UV absorption coefficients.

2. Methods

2.1. Experimental equipment

As shown in Fig. 1, the size of glass box was 20 × 10 × 15 cm^3, and there was a waterproof UV sensor (GUVC-T11GC-3LW5, Genicom Inc., Korea) at the bottom of the box. UV intensity could be measured with a UV meter. The radiation source for the system was a low pressure mercury lamp with a power of 15 W. The main wavelength of the low pressure mercury lamp was 253.7 nm. The UV lamp housed in a lamp box was connected with a wooden tube (diameter 5.8 cm, height 40 cm) so as to minimize the possibility of reflected radiation reaching the glass box [16]. The properly designed, collimated beam apparatus provided a well-behaved, quantifiable radiation source.

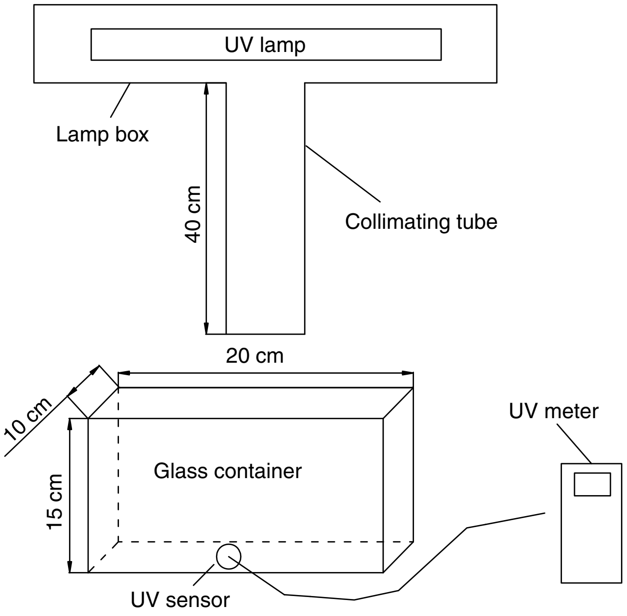

Fig. 1. Collimated beam apparatus.

2.2. The test method of UVT

The UV lamp should be preheated 30 min before the experiment, and make UV incidence intensity become stable. Firstly, UV incidence intensity I_0 was measured, then solution of given volume ranging from 0.3 l to 2.2 l, was sequently added to glass container, and the height of container was adjusted to keep the constant distance (20 cm) between the solution surface and the lamp. Finally, UV irradiation meter (TN-2254, Taiwan Taina Inc.) was used to measure the UV intensity at the given solution depth. Adjusting the solution depth between 0 and 7.2 cm and varying the coagulant, the UV intensity of different solution depths was measured for various coagulants. Each experiment was performed at least three times. The results were expressed as the mean, and the standard errors were calculated. Deionized water was used as the control solution.

2.3. The test method for total aluminum content in PAC

Hydrochloric acid was added to the sample for depolymerization, and then excess Ethylenediaminetetraacetic acid (EDTA) solution of 0.05 mol/l was added to the sample in order to form complex with aluminum ion. Finally, standard titrate solution of zinc chloride was added to the sample to determine the amount of EDTA. In the titration process, semixylenol orange was used as the indicator of the sample with the colour changes from yellow to reddishness at the end point. The total aluminum content in

PAC was determined by the amounts of EDTA and standard titrate solution of zinc chloride used in the experiment [17].

2.4. The test method for total iron content in PFS

Hydrochloric acid was added to the sample, and the sample was heated to boiling. Meanwhile, excess stannous chloride was added to the sample in order to completely reduce ferric ion to ferrous ion. Then, mercuric chloride was added to the sample to remove excess stannous chloride. Finally, standard titrate solution of potassium dichromate was added to the sample to determine the amount of ferric ion. In the titration process, sodium diphenylamine sulfonate was used as the indicator, whose colour changed to purple at the end point. The total iron content in PFS was determined by the amount of standard titrate solution of potassium dichromate used in the experiment [18].

3. Results and discussion

3.1. Effects of iron salts on UVT

In Fig. 2 and Fig. 3, we have represented the value of I/I_0 versus solution depth for various iron coagulants. In the figures, I represents UV intensity measured at different solution concentrations and depths, while I_0 represents incident UV intensity at 20 cm from the lamp, which was average 0.64 mW/cm^2. I/I_0 means UVT in the solution [19]. Fig. 2 and Fig. 3 indicated that iron salts had great effect on UVT in solution. It was also found that UVT varied with different iron salts. The UVT in the solution significantly decreased as the solution depth increased. The concentration of iron salts had negative effect on UVT as the solution depth. When the concentration of iron ion in non-polymer iron salts and PFS were respectively 1.0 mg/l and 1.2 mg/l at the solution depth of 6.0 cm, UVT (I/I_0) of ferrous sulfate, ferric sulfate, ferric chloride and PFS was respectively 0.49, 0.34, 0.30 or 0.11. The higher the UVT in the solution was, the weaker the UV absorption in the solution was. These results were in good agreement with the research of Asano et al. [12], who reported that any of the three compounds, iron salts, natural organic matter (NOM) and manganese salts presented in reclaimed water had a significant impact on the use of UV. It is indicated in the Lambert-Beer law:

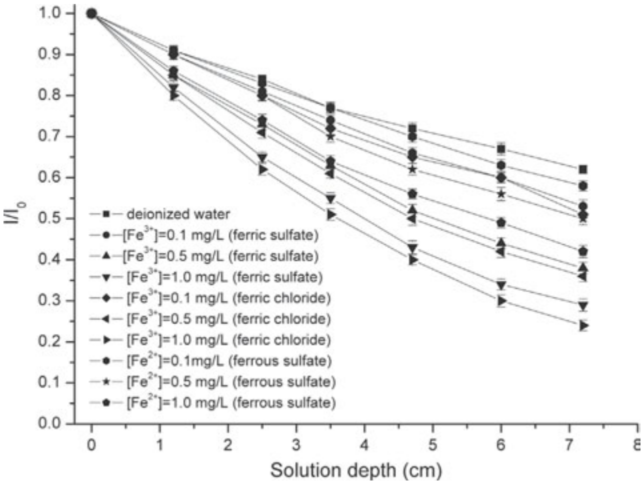

Fig. 2. UV transmittance curves of ferrous sulfate, ferric sulfate and ferric chloride.

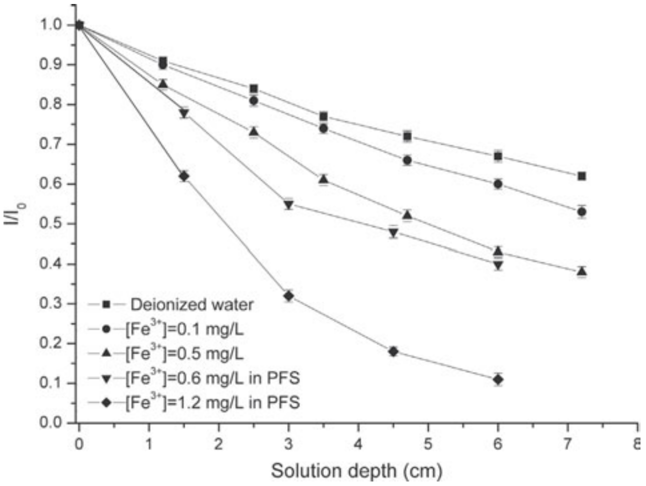

Fig. 3. UV transmittance curves of polyferric sulfate (PFS) and ferric chloride.

$$T = \frac{I}{I_0} = 10^{-\varepsilon \cdot C \cdot L} \tag{1}$$

where T represents UVT of the solution; where I_0 and I are the intensity of the incident UV light (mW/cm^2) and the transmitted UV light at different absorber concentrations and path lengths (cm); where ε represents molar absorptivity of the absorber (l/mg/cm), and C, L respectively represent the concentration of absorber in the solution (mg/l) and the distance the UV light travels through the solution (cm). As described in the law, the concentration C and the path length L are negative factors for the UVT. Therefore, it was demonstrated that UVT variations in the solution of various iron salts were in agreement with the Lambert-beer law.

3.2. Effects of aluminum salts on UVT

Fig. 4 showed the value of I/I_0 versus solution depth for various aluminum coagulants. It indicated that aluminum salts had no effect on the UVT in solution except

PAC, which had a greater effect. At various concentrations of 0.5 and 2.5 mg/l for aluminum chloride and aluminum sulfate, the largest differences of UVT between the aluminum ion solution and deionized water (control group) were less than 0.1. However, for the solution with PAC, the UVT significantly decreased as the solution depth increased. Also, the UVT decreased as the concentration of PAC increased.

3.3. Effects of polymer and non-polymer on UVT

Both Fig. 3 and Fig. 4 have given the information that PFS and PAC have stronger UV absorption ability at the wavelength of 254 nm than related metal salts. As shown in Fig. 3, UVT of PFS solution was lower than that of ferric chloride solution. For example, at the solution depth of 6 cm, UVT values in the PFS solution, were 0.40 for 0.6 mg/l iron ion (PFS) and 0.11 for 1.2 mg/l iron ion (PFS), respectively. However for ferric chloride solution, the values were 0.42 for 0.5 mg/l ferric ion and 0.30 for 1.0 mg/l ferric ion, higher than those in the PFS solution. The higher the UVT, the weaker absorption ability to UV radiation at 254 nm the coagulants had. Fig. 4 also indicated that UVT of PAC solution was lower than that of aluminum chloride solution. At the solution depth of 6 cm, UVT values in the PAC solution were 0.45 for 2.5 mg/l aluminum ion (PAC) and 0.36 for 5.0 mg/l aluminum ion (PAC), respectively. However, for aluminum chloride solution, the UV attenuation value was 0.06 for the highest aluminum-ion concentration of 2.5 mg/l. Similar results were obtained by some authors, who reported that the silicon-based inorganic polymer exhibited strong absorption to UV at wavelengths ranging from 205–240 nm [20]. The reasons for this are complicated and can only be speculated on. The PFS and PAC can be regarded as various middle products during the course of the hydrolysis of the ferric sulfate and aluminum chloride, the polymerization and forming sediment of ferric hydroxide and aluminum hydroxide. Their surface activity and charge neutralizing capacity make them more competitive than the conventional coagulants. PFS contains a range of preformed hydrolysis colloids, including $[Fe_2(OH)_3]^{3+}$, $[Fe_2(OH)_3]_2^{6+}$, and $[Fe_8(OH)_{20}]^{4+}$ etc [21]. PAC also contains a range of preformed hydrolysis colloids, including $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, and $Al_{13}O_4(OH)_{24}^{7+}$ etc [22]. The preformed hydrolysis products contained in polymers, PAC and PFS, possibly lead to stronger UV light scattering, and thus reduce the UVT in the solution. Fenstermacher (1980) also reported that charge transfer absorption caused by ferric iron ligands must be taken into account in order to explain the UV absorption of polymers [23].

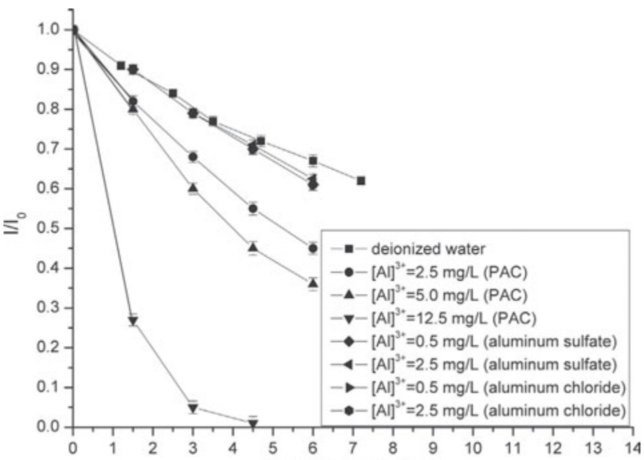

Fig. 4. UV transmittance curves of aluminum salts.

3.4. Effects of cations on UVT

Existence of $AlCl_3$ and $Al_2(SO_4)_3$, ranging from 0.5 mg /l to 2.5 mg/l Al^{3+}, had no effect on UVT in the solution (Fig. 4). These results further demonstrated that aluminum ion had almost no effect on the UVT in the solution. However, both ferric sulfate and ferrous sulfate strongly absorbed UV light. The absorptions of UV radiation by the two salts were different. Fig. 2 indicated that at different solution depths and iron concentrations, the UVT of ferric ion was lower than that of ferrous ion in the solution. At 7.2 cm, the differences of absolute UVT values between Fe^{3+} and Fe^{2+} in the solution were 0.07 for 0.1 mg/l iron ion and 0.14 for 0.5 mg/l iron ion, respectively. Asano et al. (2007) had reported that the UV light molar absorption coefficient at wavelength of 254 nm for Fe^{2+} was 466 l/mole/cm and Fe^{3+} had a stronger UV absorption ability with a molar absorption coefficient of 3069 l/mole/cm [12].

3.5. Effects of anions on UVT

Fig. 2 shows UVT curves of ferric chloride and ferric sulfate with different concentrations in the solution at different solution depths. When the concentration of ferric ion in both $FeCl_3$ and $Fe_2(SO_4)_3$ solutions was 0.5 mg/l in the solution, the difference of UVT between $FeCl_3$ and $Fe_2(SO_4)_3$ was more than 0.03 at each solution depth. The difference of UVT can reach 0.05 at the solution depth of 7.2 cm. It was demonstrated that $FeCl_3$ had stronger absorption ability than $Fe_2(SO_4)_3$. Since iron ion in the two salts had the same concentration and valence, the difference of UVT may depend on anions or ligands formed by Fe^{3+} and either Cl^- or SO_4^{2-}. Some authors also demonstrated that UV absorbance of chloride ion was higher than that of sulfate ion at 254 nm measured with a UV detector [24]. Therefore, Cl^- had stronger absorption ability than SO_4^{2-}, which was one of the main reasons for these results. According to the Pearson acid base theory, hard acids react faster and form stronger coordination compounds with hard base. Fe^{3+} is a hard acid metal ion and Cl^- is also a hard base. Among halogen ions, Cl^- is a relatively stronger hard base. Consequently, they can form stable metal complex, such as $FeCl_4^-$. This may lead to stronger absorption to UV light for ferric chloride.

3.6. Comparison of the UV absorption coefficients of various coagulants

Fig. 5 and 6 presented the UV absorption coefficients in dependence on the concentrations of iron ion and aluminum ion. Using the Lambert-Beer law, the UV absorption coefficients can be calculated. It can be shown in the Eq. (2):

$$T = \frac{I}{I_0} = 10^{-\alpha \cdot L} \qquad (2)$$

After a simple transformation, the UV absorption coefficient in the Eq. (2) is obtained in the Eq. (3):

$$\alpha = \frac{-\lg(I / I_0)}{L} \qquad (3)$$

where T represents UVT in the solution; where I_0 and I are the intensity of the incident UV light (mW/cm^2) and the transmitted UV light at different absorber concentrations and path lengths; where α represents absorption coefficient of the absorber (cm^{-1}), and L represents the distance the UV light travels through the solution (cm). In the presence of different coagulant concentrations, there was a good linear relationship between $\lg(I/I_0)$ and L. Therefore, the UV absorption coefficient α depending on the metal ion concentration can be described in Fig. 5 and Fig. 6. The UV absorption coefficient significantly increased as the concentration of iron ion increased in the solution with various iron salt coagulants, especially with PFS (Fig. 5). The UV absorption coefficient increased slightly as the concentration of aluminum ion increased in the solution with various aluminum salt coagulants, but the UV absorption coefficient of PAC increased significantly as the concentration of aluminum ion increased (Fig. 6). There were good linear relationships between the UV absorption coefficient α and the metal ion concentration C for all iron salts and aluminum salts except PFS and PAC. They can be defined as in Eq. (4):

$$\alpha = \varepsilon C + \alpha_0 \qquad (4)$$

where ε represents molar absorptivity of the absorber (l/mole/cm), and C represents the concentration of absorber in the solution (mg/l), and α_0 represents the UV absorption coefficient of deionized water (control group). UV light attenuation of iron salts and aluminum salts existing in the solution are in good agreement with the Lambert-Beer law, with regardless of deionized water's UV absorption. The relationships can be described as Eq. (1). However, UV light attenuation of PAC and PFS existing in the solution did not agree with the Lambert-Beer law. Since the preformed hydrolysis products contained in PAC and PFS, and they lead to stronger scattering of UV light, that made the Lambert-Beer law invalid. Absorbing medium must be non-scattering substance, which is one of the prerequisites that need to be fulfilled in order for the Lambert-Beer law to be valid. Therefore, the UV attenuation of PAC and PFS existing in the solution were stronger than the related salts existing in the solution. The UV absorption coefficients of various iron salt coagulants at the same iron-ion concentrations are listed in a decreasing order: PFS, ferric chloride, ferric

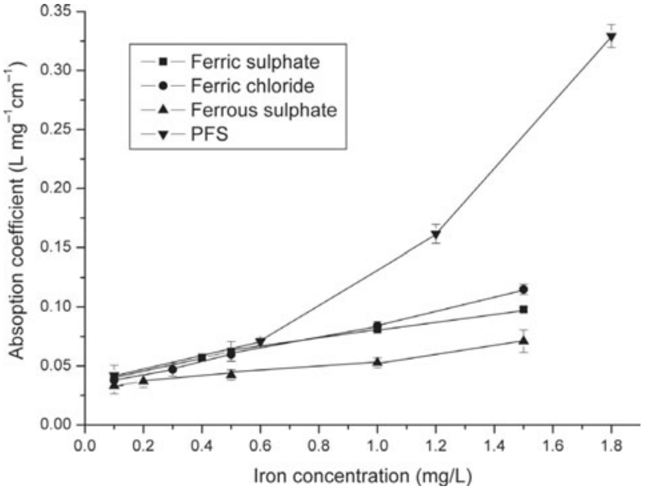

Fig. 5. The UV absorption coefficients in dependence on the concentrations of iron ion.

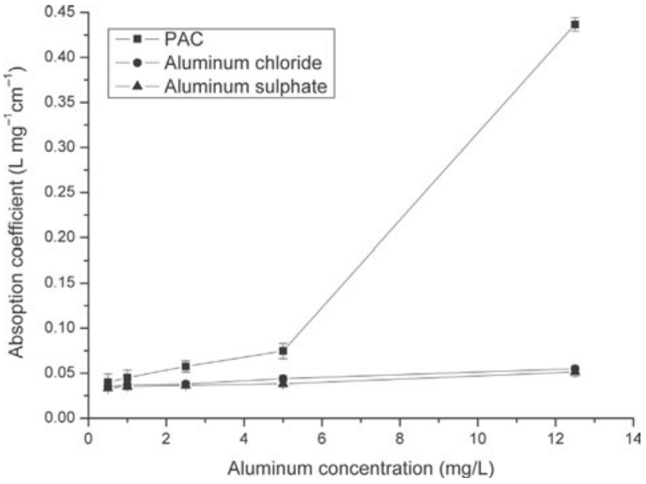

Fig. 6. The UV absorption coefficients in dependence on the concentrations of aluminum ion.

sulfate, ferrous sulfate. The UVT in the solutions with various iron coagulants can also be listed in a decreasing order ($P<0.05$): ferrous sulfate, ferric chloride, PFS. At the same concentration of metal ion, the UV absorption coefficient of PAC was lower than those of the four varieties of iron salts and was higher than those of the other aluminum salts. It means the UVT in the solution with PAC coagulant was higher than those with all the iron coagulants and lower than those of other aluminum salts.

4. Conclusions

The most common coagulants used in water-treatment facilities are aluminum sulfate, ferric chloride, ferric sulfate, PAC, PFS and etc. It was demonstrated that iron salts had greater effect on the UVT of the solution, but aluminum salts had little effect on the UVT of the solution except PAC. The verified strong UV absorption ability of Fe^{2+} and Fe^{3+} was the main reason why iron-salt coagulants absorbed more UV light than aluminum-salt coagulants. PFS and PAC, as inorganic polymer coagulants, are highly effective in water purification. The results showed that the polymer coagulants had greater effect on the UVT of the solution than the related metal salts. UV light scattering caused stronger UV attenuation of PAC and PFS than the related metal salts existing in the solution. According to the Lambert-Beer law, the UV absorption coefficients of various coagulants with different metal-ion concentrations were obtained, and it was found that UV light attenuation of iron salts and aluminum salts existing in the solution are in good agreement with the law, except PAC and PFS. The UV absorption coefficients at the same metal-ion concentration were compared and listed below: $PFS > FeCl_3 > Fe_2(SO_4)_3 > FeSO_4 > PAC > AlCl_3 > Al_2(SO_4)_3$. Therefore, aluminum salts could be a better option as coagulants to be used prior to UV disinfection compared to iron salts. These results will be a promising guidance for water coagulation before UV disinfection. Further research is needed in order to obtain essential information about the effect of different coagulants on the UV inactivation of various waterborne bacteria.

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