A study of coagulation mechanisms of polyferric sulfate reacting with humic acid using a fluorescence-quenching method

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Received 18 July 2001; received in revised form 5 March 2002; accepted 1 April 2002

Abstract

A fluorescence-quenching method is developed to assess the effect of pH on the coagulation mechanism of humic acids (HA) reacting with metal ions. A polyferric sulfate (PFS) synthesized in our laboratory is adopted as the coagulant to simplify the hydrolysis process and increase the experimental precision. The following results are discovered. When the concentration of PFS increases from 2 to 10 mg/L, the effective pH range of HA removal changes from 4.0–5.0 to 4.0–7.5. At increased coagulation pH, the ferric ions may still react with HA but unable to neutralize the surface charge completely. The residual concentrations of HA measured by fluorescence spectrophotometer are lower than those by TOC, as a consequence of the fluorescence-quenching effect. This demonstrates that the coagulation of HA by PFS at low pH is mainly due to charge-neutralization. The adsorption of the HA on the pre-formed iron hydroxide flocs is accompanied by the dissociation of Fe ions from the floc structure until the equilibrium has been reached, which is evidenced by the presence of the Fe-HA complexes in the solution during adsorption experiment. This is quite different from the characteristics of flocs formed by PFS associated with HA in the coagulation. Within the pH range investigated, the complex-formation and the hydrolysis are the two competitive reactions happened between the hydroxide ions in solution and the functional groups of HA. Therefore, the removal of HA is not caused by adsorbing onto the iron hydroxide resulted from PFS hydrolysis, but through the complex-formation between the PFS and the HA.

Keywords: Coagulation; Humic acids; Polyferric sulfate; Fluorescence quenching; Charge neutralization; Adsorption

1. Introduction

Humic acid (HA) is a natural organic matter, resulting from the weathering and/or the biodegradation of dead plants and animals [1–3]. There is no specific molecular structure suggested for HA, but it has been noted that its functional groups such as carboxylic and phenolic acids can adsorb metal ions and influence its fate [4,5]. In order to reduce the concentration of HA in drinking water, coagulation is an essential method. With different coagulant (such as iron salt or aluminum salt) and dosages and different pH, HA can be removed either by complexation with the coagulant or by precipitation after being adsorbed [6–9]. Based on the stoichiometry, researchers have proposed several coagulating mechanisms for the removal of natural organic matters. The mechanisms of de-stabilization include not only the charge-neutralization and the incorporation of organic matter onto the iron hydroxide flocs but also the co-precipitation of the complexes of metal-organic matter with the metal hydroxides [10–12]. Van Benschoten and Edzwald [13] used the Times
Spectrophotometric Analysis to predict the possible chemical formula of the complex formed after the fulvic acid (FA) reacted with the aluminum sulfate. In addition, from the kinetics point of view, István [14] showed that the hydrolysis of metal ions occurred immediately after contacting with water. Therefore, most of the iron or aluminum salts before reacting with the organic matter are in the form of hydroxide. In turn, some studies have found that the species, the number, and the position of the functional groups on organic matters all have significant effect on coagulation [15,16]. By using mono- and poly-aluminum compounds as coagulants to react with FA at different pH, Rebhum and Lurie [17] proposed the following equations:

\[(\text{Charge-neutralization and precipitation})\]

\[
\begin{align*}
\text{FA} & \rightarrow \text{FA} - \text{monomeric Al}_{(s)} & \text{pH} = 4 \sim 5 \\
\text{FA} + \text{polymeric Al} & \rightarrow \text{FA} - \text{polymeric Al}_{(s)} & \text{pH} = 5 \sim 6 \\
\end{align*}
\]

(adsorption) \text{pH} > 7

\[
\begin{align*}
\text{FA} + \text{Al(OH)}_{3(s)} & \rightarrow \text{FA} - \text{Al(OH)}_{3(s)} \\
\text{FA} - \text{polymeric Al}_{(s)} + \text{Al(OH)}_{3(s)} & \\
\text{FA} - \text{polymeric Al} - \text{Al(OH)}_{3(s)}. \\
\end{align*}
\]

They concluded that the coagulation mechanism and the reaction pathway of humic substances are strongly kinetically affected. At low pH, the aluminum salt neutralized the charge on FA directly. Therefore, the flocs formed after the de-stabilization precipitated gradually. Increasing solution pH will enhance the hydrolysis of Al-salt, and thus increase the chance to form Al(OH)$_3$(s). Simultaneously, the opportunity for FA to contact with the free Al-salt decreases, so the FA is removed by adsorbing onto Al(OH)$_3$(s). On the other hand, the slow hydrolysis of the pre-hydrolyzed poly-aluminum salt could neutralize the charge of FA before the formation of the Al(OH)$_3$(s), and form the FA-polymeric Al which could be removed through adsorption. Rebhu's theory was only a deduction from their experimental result, more direct evidence must be provided to determine the actual pathway.

Polyferric sulfate (PFS), which is composed of pre-formed polynuclear complexes of iron (III), can be expressed as $[\text{Fe}_{m}(\text{OH})_{n}]^{(3m-2)n+}$. The goal of this research is to use PFS as a coagulant to investigate the mechanism of HA coagulation. There are two reasons for choosing PFS as the coagulant. (1) Aluminum-salt and iron salt have the similar mechanism in coagulation, but the former is suspected harmful to human and living organisms. Aluminum ion can lead to maladies such as Alzheimer’s Syndrome, Osteoporosis, Anemia and Anorexia after its concentration in body accumulated to a certain level (Letterman, 1985). By contrast, iron is an essential element for the formation of hemoglobin. The daily requirement of Fe is 10 mg for adult. This is one of the reasons why the application of iron salt as coagulant is becoming popular. (2) The iron salts are categorized into mono- and poly-ferric salts. When mono-ferric salt such as FeCl$_3$ is added directly into a raw water, the complicated hydrolysis reactions would be triggered and become hard to control, accompanied by the precipitation of Fe(OH)$_3$ afterwards. The hydrolysis of PFS, on the other hand, can be controlled to a specific degree during manufacturing [18]. Thus, the use of PFS can reduce the complicated reactions caused by iron-salt hydrolysis, which provide simpler and more precise control on the coagulation reactions [19,18,20].

The dissolved HA shows a strong fluorescence effect. It can be excited by a short wavelength such as UV, and then emitting the sorbed energy through fluorescence. The fluorescence intensity (FI) is proportional to the concentration of HA, which provide a detection method for HA. When the complexes of HA with metal ions are formed, the emission of fluorescence is either quenched or enhanced depending upon the associated metals. The fluorescence measurement has been adopted in the past by many researchers as an important detection method for the study of HA reacting with metal ions [21–24]. In this study, we investigate the coagulation mechanism of HA by detecting the changes in the FI of solutions. Semmens and Ayers [15] have shown that both the coagulant dosage and the solution pH are important factors in HA coagulation. Removal efficiencies of HA under different pH and coagulant dosages were determined by jar-test. The FI were also used to differentiate the complex-formation reaction of HA with amorphous iron oxide from the adsorption of HA on the flocs of iron hydroxides.

2. Materials and methods

2.1. Material

PFS: The PFS was produced in our laboratory using concentrated sulfuric acid and ferrous sulfate. Catalyst and oxidant were added with oxygen pumped into the reactor to start the hydrolysis, oxidation and polymerization [25]. The preparation was completed with an aging period of 5–7 h at 50°C to achieve the stability of the PFS. The PFS thus prepared was characterized as follows: $[\text{Fe(III)}] > 150 \text{mg/L}$; $[\text{Fe(II)}] < 1 \text{mg/L}$; $[\text{OH}^−]/[\text{Fe}] = 0.4$; pH = 0.56; basicity 13.3; specific gravity 1.48; reddish brown in color with consistent viscosity 13.5 cp. No precipitation or stratification was observed after being stored on the shelf for more than 1 year.

HA: The HA used in the experiments of coagulation and adsorption is a commercialized product bought from the Aldrich Chemical Co. (Catalog No. H1,675-2). This product is isolated from the NaOH extraction solution of brown coal. The molecular weight of the Aldrich HA is in the range of 2000–50,000 Da. The stock
HA solution was prepared by adding 1.4g of the HA into 1L 0.01M NaClO₄ solution. The pH was controlled at 8.5. After stirred for 6h, the reacted mixture was filtered to remove any particles. The total organic carbon (TOC) of the stock HA solution was 444mg/L.

2.2. Fluorescence analysis

Hitachi F-2000 fluorescence analyzer with excitation wavelength 350nm and emission wavelength 450nm was used to measure the concentration of the HA. The calibration curve of the FI vs. the concentrations of the standard HA solutions in the range of TOC 0–6mg/L has an r-square value of >0.995. The FI is influenced by the solution pH, especially in the low pH condition, but no significant pH effect on FI measurement of the Aldrich HA was detected at pH above 7.5. Therefore, the solution was adjusted to pH 7.5–8 before each measurement to minimize the experimental error.

2.3. PFS coagulation of the HA

The stock HA solution was diluted with ionized water to reach the designated concentration for the coagulation experiment (jar-test). NaClO₄•H₂O was added to adjust the ionic strength of the solution to 0.01 M. The pH of the bulk solution was adjusted to the desired value using NaOH or HCl before the coagulation and also after each addition of PFS. The jar-tests were conducted by rapid mixing at 120rpm for 2min, followed by a 20-min flocculation period at 30rpm and a 30-min settling period. The final solution pH in each experiment was recorded. Samples taken from 3 cm below the water surface were filtered through 0.45μm filters. The filtrates were adjusted to pH 7.5–8, and their FI and non-purgeable dissolved organic carbon (NPTOC) were determined. The amount of HA remaining after precipitation, coagulation, and filtration were calculated.

2.4. Humic acid adsorption on Fe(OH)₃

The ionic strength of the Milli-Q water (1L) was adjusted to 0.01 M as described in Section 2.3. After the PFS (10mg/L as Fe) was added, the reaction was adjusted to pH 5–6 with NaOH and stirred the same way as in the coagulation. After that the sample was distributed into 10 polyethylene bottles and adjusted to each designated pH. Ten mg/L HA was added into each bottle. After shaken for 24 h at 150 rpm, the mixture was filtered through a 0.45μm filter paper and the pH and the concentration of HA of filtrate from each bottle was measured.

2.5. Changing solution pH after coagulation to measure the removal rates

This test was conducted to determine the effect of pH on the removal rate. The pH was first adjusted to 5 after the 10mg/L coagulant was added to the HA. After coagulation, the content was equally distributed into 10 polyethylene bottles. In each bottle, the pH was adjusted to a designated value between 4 and 5, stirred at 150 rpm for 8h, and then filtered. The TOC and FI was used to determine the residual concentrations of HA in the filtrates.

3. Results and discussion

3.1. pH Effect on HA removal

The removal of HA by PFS is related to the solution pH. Under the same dosage of coagulant, it was observed a lower removal rate at higher solution pH (Fig. 1). But all the removal rates decrease in the three coagulant dosages at pH <4.5. This is because that the proton was not likely to dissociate from HA at lower pH, and the HA is more neutral, whereas PFS is more positively charged at low pH. After HA react with PFS, a small portion of the complexes have a charge reverse (from negative to positive charge), which prevents the complexes from removal. However, the variation of removal rates in the pH range studied has shown that the removal of HA is still favored at low pH. In addition, the effective range of pH enlarged (from pH 4–5 to 4–7.5) as the dosage of coagulant increased (from 2 to 10mg/L). This is because that (1) at higher pH, the functional groups of HA, carboxylic or phenolic...
Acids were deprotonated, and that resulted in a greater portion of negatively charged HA. As a result, more iron salt was consumed to neutralize the charge to reach higher removal rate. (2) The hydrolysis of PFS was enhanced at high pH, which resulted in less positive iron salt. And more PFS was needed for HA removal.

The polynuclear species of PFS \( ([\text{Fe}]_m(\text{OH})_x(\text{3m-x})n^+) \) will not be the same when it is hydrolyzed or associated with HA. From the dynamic point of view, the hydrolysis of PFS and the complex-formation of PFS with HA could be explained as follows:

1. Hydrolysis

\[
R_1 = k_1 \left\{ [\text{Fe}_n(\text{OH})_x(3m-x)(y/n)]^{(3m-x)/(3m+y-n)} \right\} \text{OH}^{-}\cdot
\]

2. Complex-formation

\[
R_2 = k_2 \left\{ [\text{Fe}_n(\text{OH})_x(3m-x)(y/n)]^{(3m-x)/(3m+y-n)} \right\} \text{HA}^{y-}\cdot
\]

The above equations show that when the concentration of the hydroxide ion is decreased but with constant PFS concentration, the reaction rate of Eq. (1) will decline. Since the negative charge on the HA (\( \text{HA}^{y-} \)) preferably conjugates the PFS, the complexes formed will precipitate out of the solution through charge neutralization (Eq. (2)). Hence, it can be concluded that the removal rate of HA is higher at acidic solution. Other evidences were observed from the turbidity of the solution. The turbidity of the filtrate increased dramatically with increasing pH in a narrow range of pH, followed by a gradual decrease (Fig. 2). The dosage of the coagulant also affected the turbidity. As mentioned above, at low pH there is enough positive charge on PFS to neutralize the negative charge on HA. Therefore, the HA could precipitate through charge neutralization. Conversely, the hydrolysis of PFS increases as the solution pH increase. In this case, the PFS could still react with HA, but its ability to neutralize the negative charge on HA decreased, resulting in the slightly negatively charged complexes of PFS-HA in solution, which repelled each other. Because no floc could be filtered out, the solution turbidity increased. As pH increased, more \( \text{Fe(OH)}_3 \) flocs or \( \text{Fe(OH)}_4 \) ions formed, which reduced the chance for HA to associate with PFS. At this time the number of soluble PFS-HA complexes decreased, so did the turbidity. As a whole, we could divide the relationship between the coagulant dosage and the solution pH into three sections (Fig. 3). In the low pH range, the removal of HA was due to charge neutralization which formed the complex of PFS-HA. In the middle pH, although the PFS could still complexes with HA, the residual negative charges on the complexes prevented them from flocculation and precipitation. The small fraction of positively charged flocs of iron hydroxide resulted in less PFS-HA adsorbed on the limited number of flocs, and the removal rate was then small. In the high pH range, the negatively charged flocs of \( \text{Fe(OH)}_3 \) or the \( \text{Fe(OH)}_4 \) ions formed from PFS before it could associate with HA. In short, the increase of pH favored the hydrolysis of PFS, and decreased the formation of positively charged ions. Thus the ability for

![Graph](image_url)

**Fig. 2.** The changes of turbidity under different coagulation conditions (the initial humic acid concentration is 6 mg/L).

**Fig. 3.** The possible patterns of flocs existed in the coagulation of PFS with humic acid. ( ● ) PFS (●) humic acid ( ○ ) \( \text{Fe(OH)}_3 \).
PFS to neutralize the negative charge on HA became small, and the HA could not be removed effectively. This was the reason why more coagulant was necessary to destabilize HA, and the effective pH range became large as shown in Fig. 1.

3.2. The mechanism of PFS coagulating with HA

(1) There are many aromatic rings in the structures of HA. Ultraviolet rays can excite those components, and the fluorescence will be emitted from it afterwards. However, if the carboxylic or phenolic groups on HA form complexes with iron ions, the FI would be reduced, which is called the fluorescence-quenching effect. In this study, the residual rate of HA were calculated with TOC and FI measurement, represented by

\[ \frac{R_T}{\text{HA}} = \frac{\text{HA}_T}{\text{HA}_{T0}} \]

and

\[ \frac{R_F}{\text{HA}} = \frac{\text{HA}_F}{\text{HA}_{F0}} \]

respectively. [HA]_{T0} and [HA]_{F0} are the initial concentrations of HA and [HA]_{T0} and [HA]_{F0} are the final concentrations of HA measured by FI and TOC.

Since a good correlation was discovered between the values of FI and TOC in synthetic solutions (Fig. 4), both methods were used to determine the concentration of HA. The results of the experiments conducted with different coagulant dosage and the solution pH showed that most of the \( R_F < R_T \) (Fig. 5), except in the regions close to 1 and 0. Since the iron salt did not affect the measurement of TOC, the \( R_T \) indicated the actual residual rate of HA. The \( R_F \), on the other hand, was affected by the fluorescence-quenching effect, which was less than the actual concentration of HA. When more and more HA associated with iron ions (as shown in Fig. 3b), the effect of fluorescence quenching became apparent. The results were indicated in region (b) of Fig. 5. After the complex-formation reaction occurred, as shown in Fig. 3b, the soluble complexes repelled each other and remained suspended. Due to the quenching effect, the FI decreased and the residual concentration measured was less than that by TOC. Therefore the \( R_T/R_F \) ratio deviated from the 1:1 linear relationship (region (b) in Fig. 5). As the solution pH continued to increase, the formation of Fe(OH)$_3$ or Fe(OH)$_4$ (as shown in Fig. 3c) diminished the possibility of complex-formation. Most of the HA in solution was unable to associate with iron salt. The effect of fluorescence quenching became less important, and the values of \( R_T \) and \( R_F \) approached 1:1 correlation again (region (c) in Fig. 5). Generally speaking, the effect of pH on coagulation is same as the assumption shown in Fig. 3, at low pH, the mechanism of charge neutralization is important. As pH increased, the ability for PFS to neutralize HA was reduced, and the rate of iron ion reacting with the hydroxyl groups was accelerated.

The above discussion suggests that there are some points needed to be clarified further. For example, what percentage of PFS form the flocs of Fe(OH)$_3$ before HA adsorb onto it. Since PFS is a PFS salt, it has a higher alkalinity than other iron ions. It could easily form the flocs of iron hydroxide even in low pH. Thus, when PFS is used as coagulant, pH is likely to affect the adsorption reaction, not the charge neutralization. To prove this, the flocs of Fe(OH)$_3$ were prepared by stirring PFS solution at pH 5–6, adjusting the pH of the solutions to a desired value and adding HA. After shaking for 24 h, the removal rates were checked. If the surface structure of the colloid could be represented by FeOH, the adsorption and desorption of hydrogen ions at the interface between iron oxide and solution depend
on the solution pH. This is because that FeOH can release hydrogen ion to neutralize the hydroxide ion in solution and become FeO⁺ on the colloidal surface in the condition of high pH.

FeOH + OH⁻ ⇌ FeO⁺ + H₂O.

At low pH, however, the oxygen in FeOH can be viewed as Lewis base, which can provide free electron pair and it could react with hydrogen ion to form a positively charged FeOH₂⁺ on the surface of colloids.

FeOH + H⁺ ⇌ FeOH₂⁺.

According to Le Chatelier’s principle, the surface charge of oxides will become more negative at high pH, but more positive at low pH. It was observed that the removal of HA decreased as the solution pH increased (Fig. 6). This is due to the increase in the negative charges on both the HA and the Fe(OH)₃ surfaces, so increased the repulsion force. A large difference between the removal rates of adsorption and coagulation was found at pH < 7.5. This demonstrated that the removal of HA by PFS coagulation at low pH range was due to the charge neutralization instead of HA adsorbed by the flocs of Fe(OH)₃. At pH above 7.5, two removal rates became close to each other. The removal of HA by adsorption was a little higher than that by coagulation in the range of pH 7.5–9 (Fig. 6). As shown in Fig. 3b, at median pH, the addition of PFS resulted in the hydrolysis of iron salt, and the charge on the complexes of PFS-HA was not neutralized completely. On the other hand, the adsorption at pH above 7.5 shows that the amorphous flocs of Fe(OH)₃ could still adsorb HA through its positive surface charge. From these results we concluded that at pH 7.5–9.0 with PFS 10 mg/L, the possible coagulation mechanisms between PFS and HA were both charge neutralization (forming the not completely neutralized and soluble complex of PFS-HA) and adsorption (the PFS-HA complex adsorption on the flocs of iron hydroxide). The negative charge of HA is reduced by the adsorption of positively charged PFS, and then forming the soluble complex of PFS-HA with slightly negative charge. As shown in Eq. (3), a small fraction of complexes could then be removed by adsorbing on the positively charged flocs of iron hydroxide which has a pH_{pzc} around 8.3 [26].

PFS-HA + Fe(OH)₃(s) → PFS-HA – Fe(OH)₃(s). (3)

However, not all the added PFS can result in the flocs of iron hydroxide for HA adsorption, part of the PFS reacts with HA to form the soluble complex of PFS-HA. When the coagulation and the adsorption experiments were compared, as shown in Fig. 6, only a small fraction of iron hydroxide formed were able to adsorb HA in the coagulation. Most of the HA was in the state of soluble complexes of PFS-HA. Therefore, in the pH range of 7.5–9, the fraction of HA removed by coagulation was less than that by adsorption. However, it should be noted that at pH above 7.5, the possibility to form the complexes of PFS-HA decreased dramatically, and the chance to form the flocs of Fe(OH)₃ increased. When compared with the result of coagulation, as shown in Fig. 2, more soluble complexes of PFS-HA were produced at pH 7.5, at which the surface charge of the HA was not neutralized completely. Therefore, the solution after filtration still had the highest turbidity.
As solution pH increased, the possibility to form the flocs of Fe(OH)_3 increased, and the turbidity after coagulation and filtration decreased.

In addition, a distinctive difference occurred between the effect of fluorescence quenching on the experiments of adsorption and that of coagulation (Fig. 7). It implied that the mechanism of the coagulation was not adsorption. It should be noted that the adsorption was conducted after the flocs had formed, and the HA was added afterwards. Therefore, the HA did not have any chance to associate with any free iron ion in the experiment of adsorption, and the effect of fluorescence quenching should not be observed. However, the results in Fig. 7 show the reaction of HA with free iron ion occurred actually. One explanation from Furrer and Stumm [27] suggested that when the organic matter adsorbed onto the flocs of Fe(OH)_3, the bidentate ligand with two oxygen donor atoms reacted as follows at the acidic condition.

\[
\begin{align*}
\text{Fe(OH)}_3 + \text{HA} &\rightarrow \text{Fe(OH)}_2\text{O} + \text{R}\
\text{Fe(OH)}_2\text{O} + \text{R} &\rightarrow \text{Fe(OH)}_3\text{O} + \text{R}.
\end{align*}
\]

Is the HA with bidentate ligand.

After the oxygen on the ligand of HA was adsorbed by the floe of the iron hydroxide, the electron pair was pushed to the side of Fe(III) which acted as a Lewis acid. The atom of Fe(III) became unstable and dissociated afterwards. In addition, the formed hexagonal ring, which was more stable than other parts of the compound, enhanced the adsorption of Fe to dissociate from the original structure of iron hydroxide until equilibrium was reached. This is why the complexes of dissolved iron-organic matter were found in the solution. There are quiet a few bidentate ligands of carboxylic and phenolic in the HA, therefore, the possibility to form iron-HA complexes is high. As a result, the phenomenon of fluorescence quenching would undoubtedly happen, especially in low pH condition.

To further demonstrate the coagulation at low pH is mainly charge neutralization, experiments were conducted to show that the phenomenon of fluorescence quenching is more obvious in the coagulation experiments than in the adsorption experiments. The experimental procedure was the same as that for the coagulation experiments except that the pH of the solutions was adjusted to the range between 4 and 5. After 24 h of reaction, the TOC and F1 of solutions were checked. No significant difference was found (Fig. 8) when compared to the result from the coagulation experiments. Apparently, the complexes of PFS-HA were not likely to dissolve in solution. In other words, the flocs formed in coagulation did not dissolve, but the flocs of iron hydroxide produced in the adsorption experiment dissolved in acidic condition. The possible explanation is that the flocs formed in coagulation were

\[
\begin{align*}
\text{Fe(OH)}_3\text{O} + \text{R} &\rightarrow \text{Fe(OH)}_2\text{O} + \text{R} \\
\text{Fe(OH)}_2\text{O} + \text{R} &\rightarrow \text{Fe(OH)}_3\text{O} + \text{R}.
\end{align*}
\]

Fig. 8. After changing solution pH, the residual rates of humic acid in solutions were measured by fluorescence vs. those by TOC (subsequent to the coagulation process, the initial concentration for humic acid is 6 and 10 mg/L as Fe for PFS).
caused by charge neutralization, which is different from the flocs formed of iron hydroxide. Therefore, pH has less effect on the dissolution of flocs formed in coagulation process. Also, these two flocs are noticeably different in their fluorescence quenching. In conclusion, the major coagulation mechanism is definitely not adsorption of HA onto flocs of hydrolyzed PFS.

4. Conclusions

In this research, we explored the coagulation mechanisms of PFS on HA through the fluorescence-quenching effect. From the kinetics point of view, the highly positively charged PFS can coagulate HA through charge neutralization at low pH. When solution pH increased, hydroxide ions lowered the potential of complex-formation of PFS for associating HA. In the range of high pH, HA did not adsorbed easily onto the flocs of Fe(OH)$_3$ or Fe(OH)$_4$, resulting in less HA removal. Due to fluorescence quenching, the FI decreased, and the residual concentration measured by TOC was higher than that by fluorescence. This demonstrated that the complex formation of PFS-HA through charge neutralization was the major coagulation mechanism between PFS and HA at both low and middle pH range. A major change in FI measurement after coagulation and adsorption, which proved that the removal of HA was not by adsorbing onto the flocs of iron hydroxide. Changing solution pH after coagulation showed that flocs would not dissolve in acidic condition. The fact that flocs formed in adsorption experiment were more likely to dissolved in acidic condition suggesting these two flocs have different structures and charge neutralization is the predominant mechanism for HA removal by PFS.

Acknowledgements

We thank Miss. C.J. Chang and J.W. Zhang for assistance with laboratory work. The author also acknowledge the financial support of National Science Council, Taiwan, ROC for this work (NSC 89-2211-E-239-002).

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