

Effect of Fe (III) Speciation in the Polymeric Ferric Sulfate on the Treatment Performance of Surface Water Contaminated Slightly

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Abstract. Fe-Ferron method was used to investigate the role of Fe(III) speciation of the polyferric sulfate (PFS) in coagulation–flocculation the process with surface water. The experiments results show that the Fe_b components are dominant contents under a broad pH variation during the coagulation. The humic acid (HA) removal is found directly related to the aggregation of iron components in the water, the maximum removal of the HA occurs in the pH range from 7 to 8, at which the changes of zeta potential explain that charge neutralization and the compression double electric layer are the main mechanisms of coagulation. The role of adsorption and sweeping by amorphous Fe(OH)₃ that cannot be ignored in the treatment with surface water at the same time.

Introduction

Humic substances are the major components of natural organic matter (NOM) in the surface water, which are the precursors of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetates (HAAs)[1]. DBPs have been confirmed related to several types of cancer, so lots of advanced technologies including ozonation, ultrafiltration, photocatalysis, and anion exchange are adopted to remove NOM, among them, enhanced coagulation is considered to be the most convenient and economical one for minimizing DBPs[2].

PFS is a kind of pre-polymerized inorganic coagulants used to remove colloids, particles, and organics in the water. PFS is the intermediate product during the hydrolysis-aggregation-precipitation process of the iron, containing various poly-nuclear iron ions, such as Fe₂(OH)₂⁴⁺, Fe₃(OH)₄⁵⁺ [3]. It is widely agreed that Fe (III) speciation is directly connected to the coagulation behavior of PFS, so many studies have tried to optimize iron species distribution by improving the preparation conditions[4-9], but there is limited work about the relationship between coagulation efficiency and transformation of iron species during the whole coagulation–flocculation process.

In this paper, Fe-Ferron method was taken to quantitatively characterize the Fe (III) species during the treatment with surface water, the effects of dosage and pH value were studied, the mechanisms of iron polymer species on the removal of HA were discussed at the same time.

Materials and Methods

Coagulants and Test Water

The PFS was prepared in the laboratory using FeSO₄, H₂O₂, H₂SO₄ and deionized water, the content of total Fe and basicity of the liquid PFS were 15.04% (3.48mol/L as Fe) and 20.14%, respectively. The test water used in the experiments was slightly contaminated surface water (Table 1) collected from Qingnian Lake in Tianjin University in May.

Table 1 Characteristics of the surface water used in the experiments.

| T (°C) | pH | DOC (mg/L) | Turbidity (NTU) | UV ₂₅₄ (/cm) | SUVA (100×UV ₂₅₄ /DOC) |
|----------|-----------|------------|-----------------|-------------------------|-----------------------------------|
| 23.5±2.0 | 8.27±0.25 | 19.85±0.05 | 20.48±0.50 | 0.1048±0.0005 | 0.525±0.005 |

Jar Tests

Jar tests were conducted using a six-peddle stirrer at room temperature ($24\pm 2^{\circ}\text{C}$). A total 250 mL volume of test water, previously adjusted to a desired pH value with 1M NaOH and HCl, was transferred into a 500mL beaker. Predesigned amount of PFS stock solution was injected under rapid stirring conditions. After being dosed, 30s of rapid mixing at 200rpm was applied, followed by 15 min of slow stirring at 30 rpm and then 20 min for settling. After the completion, the supernatants samples were passed through a $0.45\ \mu\text{m}$ filter to measure UV_{254} and dissolved organic carbon (DOC), UV_{254} was analyzed with a UV/Vis analyzer (L6S, INESA, China) at 254nm. DOC was tested with a TOC Analyzer (TOC-L, Shimadzu, Japan). The removal of UV_{254} absorbance was used to evaluate the HA removal efficiency in this study. A small amount of sample was taken immediately to measure zeta potential using a microscopic electrophoresis apparatus (JS94H, Shanghai zhongchen digital technic apparatus Co. China) after 1 min rapid mix.

A parallel experiment was performed to investigate the adsorption ability for HA by iron precipitates. Certain amount of PFS stock solution was first added to 250 mL of tap water with the given pH, the ionic strength of the solution was kept at 0.01M with NaCl. After that, the stirring conditions were the similar with jar tests to generate iron flocs. After being settling, the total solution was filtered to get the precipitates, then the precipitates were dried to constant weight at 40°C , and then distributed to the 250 mL of surface water respectively, and then, 15 min of slow mixing (30rpm) was conducted, followed by 20 min of settling. Finally, the supernatant was filtered to analyze the residual UV_{254} absorbance.

Analysis of Fe (III) Species Distribution during Coagulation-Flocculation

The measurement procedure of Fe (III) species by the Ferron reagent was performed as the previous reports [10, 11]. A certain amount of water sample was taken from the beakers 2 cm below the water surface to analyze iron species with the UV/Vis analyzer at 600nm as soon as every stirring step completed, the concentration of total Fe (Fe_T) was measured by the 1,10-phenanthroline spectrophotometry according to GB/T 5750.6-2006, monomeric and dimeric species (Fe_a) can be determined from the 1 min absorbance reading, medium or reactive polymers (Fe_b) were determined from 1 min to the 24 h. Nucleated and precipitated species (Fe_c) were calculated using the formula of $\text{Fe}_c = \text{Fe}_T - \text{Fe}_a - \text{Fe}_b$.

Results and Discussion

Characterization of Fe (III) Species for PFS Stock Liquid (SL)

As known to all, the solid coagulants must be dissolved to obtain a stock solution before being dosed. During this process, the Fe_T , the pH value, and other conditions will change, as well as the Fe (III) species, and these changes have a direct effect on the coagulation performance. Fig.1 presents the effect of maturing time on the iron species distribution of PFS after being diluted to the SL (1mol/L as Fe, pH=1.94). The Fe_a is the dominant content in the entire process. When PFS samples were initially diluted, the pH of SL rose slightly, indicating there was disintegration of the polymers, the hydroxyl bridge broke, resulting in hydroxide being released into the solution[12], so the Fe_b and Fe_c changed appreciably, eight hours later, the Fe_b increased to a maximum value, about 36%, soon after, a large part of the Fe_b was converted to the Fe_c . Those changes above suggested a complex species transformation took place after being diluted. In the following 18 hours, small changes happened in the distribution of iron species of the SL.

Effect of Dosage of the Coagulant on HA and DOC Removal

Fig.2 records the variation of residual UV_{254} absorbance and DOC at different dosages of PFS at the initial pH 8.27 ± 0.25 . The UV_{254} absorbance and DOC decreased sharply first and reached the minimum values at 54 mg Fe/L, then the removal efficiency deteriorated with further increasing of the dose. The overdose of PFS would not improve the remove of UV_{254} , but inhibited the coagulation

performance. When the dosage of PFS reached 72 mg Fe/L, the residual UV₂₅₄ was even higher than the initial one, which may be caused by the chromaticity induced by iron ions.

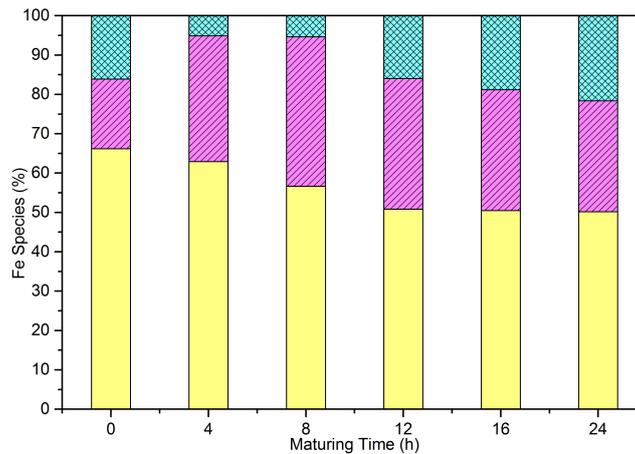


Fig. 1 Effect of the maturing time after being diluted on the iron species in SL.

Fe_a (■), Fe_b (■), Fe_c (■)

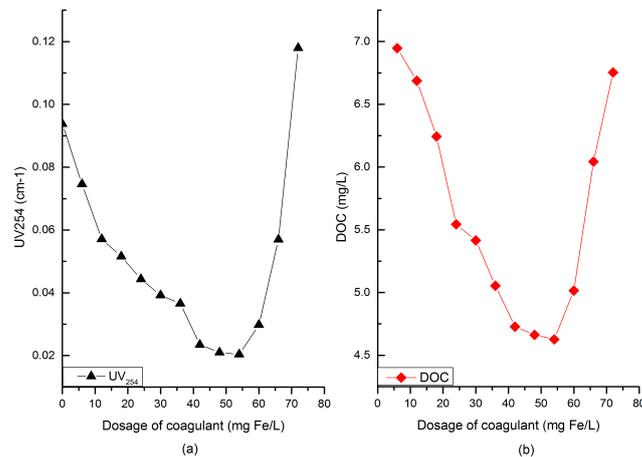


Fig. 2 Effect of the dose on the removal efficiencies of UV₂₅₄ and DOC. (a) The residual UV₂₅₄, (b) The residual DOC.

Conversion of Fe (III) Species during Stirring under Different pH Values

Fig. 3 shows the distribution of different iron species in the test water with pH ranging from 3.5 to 9.5. The coagulant dosage was of 54 mg Fe/L, which was confirmed to be the suitable value according to the Fig. 2. The distribution indicated that iron species were pH dependent, the monomers (Fe_a) decreased sharply with the pH rising for all the three stages, whereas the Fe_b rose and then declined after achieving the maximum point when the pH equal to 6.5-7.5, the Fe_c increased gradually and dominated at the last stage. Compared with the iron speciation in the SL, as the coagulant being dosed, Fe_b was generated immediately, and in a dominant position subsequently in the stirring process.

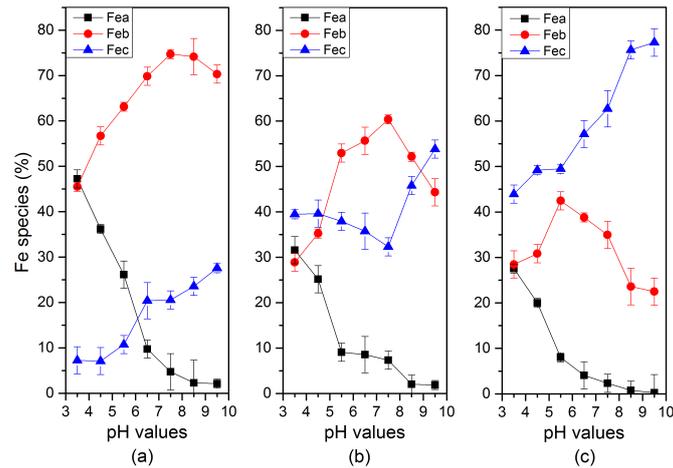


Fig. 3 Transformation of iron species under different pH values during the coagulation-flocculation process. (a) Rapid mixing stage, (b) Slow mixing stage, (c) settling stage.

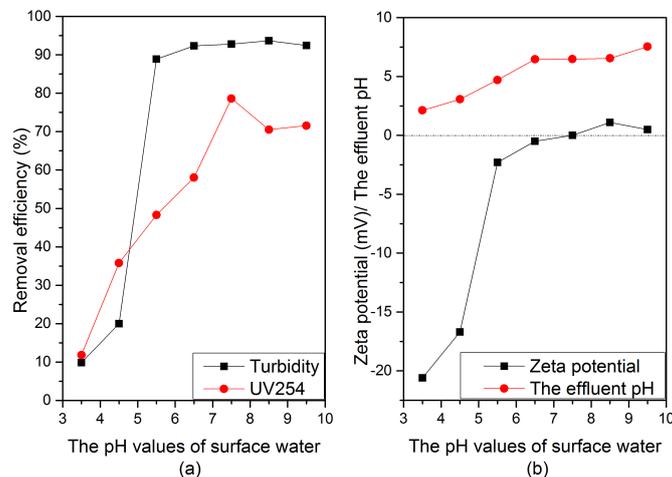


Fig.4 Effect of the pH value on the coagulation performance. (a) The turbidity and UV₂₅₄ removal, (b) Zeta potential of the flocs and the effluent pH.

Electrostatic Interaction between Coagulants and HA

The initial pH value of treated water has been found to affect the quality of the effluent at the dosage of PFS of 54 mg Fe/L (Fig.4). The removal of turbidity and UV₂₅₄ increased steadily with higher pH in the range from 3.5 to 7.5. Correspondingly, the variation of zeta potential ranging from 3.5 to 7.5 in Fig.4 (b) indicated the charge neutralization and compression electric double layer dominated the remove of UV₂₅₄, coincide with the fact that the high-density cation Fe_b increased steadily at the elevated pH.

In addition to the charge neutralization, the adsorption by amorphous hydroxide precipitates formed during the coagulation process contributes to the HA removal[13]. In general, charge neutralization occurs at slightly acidic pH, while adsorption occurs at the appearance of precipitation at high pH values or at high coagulant doses.

Fig. 5 (a) compares the turbidity removal differences between the whole coagulation-flocculation process and the adsorption process by iron precipitates. Because the colloidal particles in the water causing turbidity are mostly negatively charged, the iron precipitates with little charges has low removal efficiency of turbidity. At pH 5.5, the turbidity removal efficiency reached the maximum, which was consistent with distribution of Fe (III) species in Fig. 3 (c) that Fe_b accounted for the most at pH 5.5. Fig. 5 (b) compares the UV₂₅₄ removal between the whole coagulation- flocculation

process and the adsorption by iron precipitates at different pH conditions at the dosage of 54 mg Fe/L. The removal efficiency of UV₂₅₄ by adsorption was pH dependent. At pH from 4 to 6, the dominate iron species in the solution were the monomers, the adsorption capacity of these species was lower than that of the iron precipitates, which was abundant when the pH value exceed 6.0. With pH increasing from 4 to 6, the removal of HA by adsorption was relatively stable. However, the UV₂₅₄ removal was significantly improved at pH 7.2, and the maximal removal efficiency of 70% was achieved.

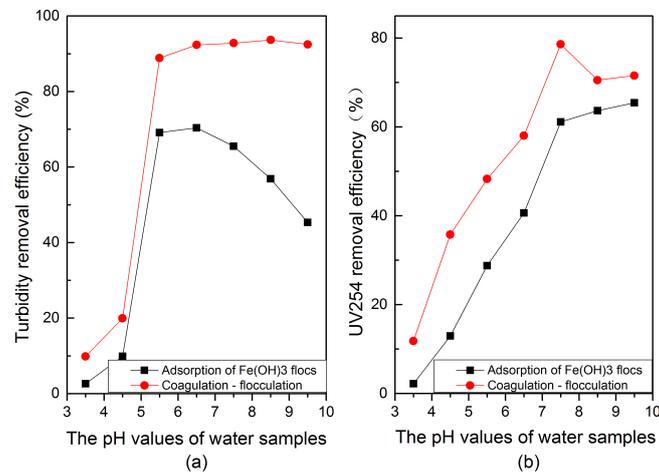


Fig. 5 Comparison of removal efficiency between coagulation-flocculation and adsorption by iron precipitates. (a) The turbidity removal efficiency, (b) The UV₂₅₄ removal efficiency

Conclusion

The role of Fe (III) speciation in the coagulation of surface water by PFS was studied for the first time in this paper. The results showed that Fe_b polymers were stable in the dilute solution and dominant during the stirring process at pH of 5.5~8.0, while the Fe_b is the content rich in high density cation charges. The Fe (III) speciation directly influenced the mechanisms of HA removal. The maximum removal efficiency of the UV₂₅₄ was found to occur in the pH ranging from 7 to 8. The changes of zeta potential explained that charge neutralization and compression electric double layer were the main mechanisms of coagulation, thus high Fe_b should be necessary to obtain an efficient removal of the the UV₂₅₄, but adsorption and sweeping of HA by amorphous Fe(OH)₃ (s) played an important role at pH > 7.0 as well.

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References

- [1] S.D. Richardson, Disinfection by-products and other emerging contaminants in drinking water, *Trac-Trends in Analytical Chemistry* 22 (2003) 666-684.
- [2] Z. Yang, B. Liu, B. Gao, Y. Wang, Q. Yue, Effect of Al species in polyaluminum silicate chloride (PASiC) on its coagulation performance in humic acid-kaolin synthetic water, *Separation and Purification Technology* 111 (2013) 119-124.
- [3] A.I. Zouboulis, P.A. Moussas, F. Vasilakou, Polyferric sulphate: preparation, characterisation and application in coagulation experiments, *Journal of hazardous materials* 155 (2008) 459-468.

- [4] X. Zhang, X. Wang, Q. Chen, Y. Lv, X. Han, Y. Wei, T. Xu, Batch Preparation of High Basicity Polyferric Sulfate by Hydroxide Substitution from Bipolar Membrane Electrodialysis, *ACS Sustainable Chemistry & Engineering* 5 (2017) 2292-2301.
- [5] H. Dong, B. Gao, Q. Yue, H. Rong, S. Sun, S. Zhao, Effect of Fe (III) species in polyferric chloride on floc properties and membrane fouling in coagulation–ultrafiltration process, *Desalination* 335 (2014) 102-107.
- [6] W. Xu, B. Gao, Effect of shear conditions on floc properties and membrane fouling in coagulation/ultrafiltration hybrid process—The significance of Alb species, *Journal of Membrane Science* 415-416 (2012) 153-160.
- [7] B. Gao, B. Liu, T. Chen, Q. Yue, Effect of aging period on the characteristics and coagulation behavior of polyferric chloride and polyferric chloride-polyamine composite coagulant for synthetic dyeing wastewater treatment, *Journal of hazardous materials* 187 (2011) 413-420.
- [8] G. Lei, J. Ma, X. Guan, A. Song, Y. Cui, Effect of basicity on coagulation performance of polyferric chloride applied in eutrophicated raw water, *Desalination* 247 (2009) 518-529.
- [9] Y. Wang, B. Gao, Q. Yue, J. Wei, Q. Li, The characterization and flocculation efficiency of composite flocculant iron salts–polydimethyldiallylammonium chloride, *Chemical Engineering Journal* 142 (2008) 175-181.
- [10] B. Wang, Y. Shui, P. Liu, M. He, Preparation, characterization and flocculation performance of the inorganic-organic composite coagulant polyferric chloride and polydimethyldiallylammonium chloride, *Journal of Chemical Technology & Biotechnology* 92 (2017) 884-892.
- [11] P.A. Moussas, A.I. Zouboulis, Synthesis, characterization and coagulation behavior of a composite coagulation reagent by the combination of polyferric sulfate (PFS) and cationic polyelectrolyte, *Separation and Purification Technology* 96 (2012) 263-273.
- [12] K.E. Lee, N. Morad, T.T. Teng, B.T. Poh, Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: A review, *Chemical Engineering Journal* 203 (2012) 370-386.
- [13] B. Shi, Q. Wei, D. Wang, Z. Zhu, H. Tang, Coagulation of humic acid: The performance of preformed and non-preformed Al species, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 296 (2007) 141-148.