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# Comparative Coagulant Demand of Polyferric Chloride and Ferric Chloride for the Removal of Humic Acid

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# Comparative Coagulant Demand of Polyferric Chloride and Ferric Chloride for the Removal of Humic Acid

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**Abstract:** This paper is concerned with the potential advantages of the use of polyferric chloride as a coagulant for the removal of natural organic matter (e.g., humic acid) in water treatment. In particular, this paper assesses the effects of the basic nature of polyferric chloride, the type of water, and the coagulation pH on the humic acid removal performance. The comparative dose demand of polyferric chloride and ferric chloride was assessed in terms of a good humic acid removal efficiency (>50%) achieved. It was found that a polyferric chloride with a basic ratio of 0.3 can achieve the best humic acid removal. The water having both humic acid and colloidal particles was favorable to the floc development and a better humic acid removal. For the same coagulation conditions, the dose demand of polyferric chloride was 50% less than that of $FeCl_3$ for a >50% humic acid removal.

**Keywords:** Coagulation, humic acid, natural organic matter (NOM), prepolymerized iron coagulants

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# INTRODUCTION

Natural organic matter (NOM) such as humic acid in surface water causes many problems such as color, taste, odor, and lower efficiency in the water treatment process. In addition to this, in the chlorination process, humic acid reacts with chlorine and produces disinfection-by-products (DBPs). The World Health Organization (WHO) has recommended the maximum concentrations of DBPs and these parameters have been regulated in the Disinfectant/Disinfection-by-Products (D/DBPs) Rule by the USEPA and the environmental agencies of other developed Countries. Due to the above-mentioned factors, the effective removal of NOM is an important step which affects the quality of treated drinking water. A range of techniques can be used for the removal of NOM; including adsorption on activated carbon, coagulation followed by a suitable separation process, membrane processes, and chemical oxidation. Among these techniques, coagulation is one of the widely adapted processes. The actual reduction of NOM depends on the type and the dose of coagulants, coagulation pH, water temperature, and other raw water quality characteristics (1,2). Overall, the feature of NOM coagulation is that higher coagulant doses are required than for turbidity removal, and that there is a stoichiometry in the required coagulant dose with DOC concentration (3).

Conventional coagulation with ferric or aluminium salts is widely used to reduce the turbidity and color and a number of related researches have been reported. Some findings from these studies can be summarized as: the optimal pH value for ferric salts is within the range 3.7–4.2 and for aluminium sulphate within the range 5.0–5.5 for color removal (4–5). The optimum dose for achieving the lowest residual color, in molar terms, appears to be the same for Fe and Al (6). However, one of the drawbacks in the use of conventional metal coagulants is the inability to control the nature of the coagulating species formed during dilution under the prevailing raw water conditions and in competition with other reactions. As a result, the performance of NOM coagulation may worsen with changes in the nature of raw water, thereby requiring a change in the coagulant dose and the coagulation pH. A possible way of improving the efficiency of coagulation is the use of pre-polymerized coagulants. Considerable attention has been paid in recent years to the preparation and the performance assessment of pre-polymerized coagulants (7–9), which have been focused on poly-aluminium chloride (10), polyferric sulphate (11), and polyferric silicate sulphate (12). This paper is thus concerned with the potential use of polyferric chloride (PFC) as a coagulant for humic acid removal in water treatment. In particular, this paper assesses the NOM removal performance with PFC and $FeCl_3$ in terms of the basic ratio of PFC, coagulation pH, raw water quality characteristics, and the comparative coagulant dose demand.

## METHODS AND EXPERIMENTAL PROCEDURES

Polyferric chloride (PFC) coagulants used in this study were prepared in the laboratory following an established method (13). For a given concentrated ferric chloride solution, a given amount of $NH_4H_2PO_4$ was added as a stabilizer, then sodium hydroxide was gradually dosed to make ferric chloride polymerized through hydrolyzing reactions, and PFC was prepared after being aged for 4 hours with a basic ratio (as molar ratio of hydroxide to iron) of 0.3 to 0.8. There were no purification steps of the product PFC.

Three model test waters containing:

1. Kaolin particle alone, 100 mg/l,
2. Humic acid alone, 10 mg/l with dissolved organic carbon (DOC) concentration of 3.5 mg/l at pH 7 and
3. Kaolin particles (100 mg/l) mixed with humic acid (10 mg/l) with DOC concentration of 2.4 mg/l at pH 7, were prepared by mixing given amount of different components with tap water (the tap water had following quality properties: DOC concentration = 0.1 mg/l, turbidity =
   0.1 NTU and hardness (expressed as $CaCO_3$) = 155 mg/l).

Both humic acid and kaolin powder were provided by Sigma-Aldrich, UK and both are in technical grade. The coagulation pH was adjusted with the addition of a predetermined volume of either hydrochloric acid or sodium hydroxide solutions. A pre-titration technique was used to determine the required amount of HCl or NaOH against various coagulant doses in order to achieve the given coagulation pH. The solution pH was checked during the mixing and flocculation periods. Further fine adjustments to the pH can be made during the jar test if the pH is out of the ±0.2 range. The jar test was followed an established procedure (1) and carried out with rapid mixing at 275 rpm for 1 minute, slow mixing at 35 rpm for 20 minutes, and followed by a settling period of 30 minutes. The supernatant sample was withdrawn at a depth of between 15 to 20 mm from the surface for the measurement of $UV_{254}$ absorbance and color (via the vis-absorbance at 420 nm) (both by Helios Alpha UV-visible spectrophotometer, Thermo Scientific), DOC (by TOC 5000 A, Shimadzu Scientific Instruments) and turbidity (by HACH turbidity meter). Water quality parameters were measured following the standard methods (14). Zeta potential was analyzed after the model water was mixed rapidly for 1 min (by Malvern Zeta Potentiometer). A photometric dispersion analyzer (PDA2000, Rank Brothers Ltd) was used to monitor floc aggregation kinetics using an established method (15). A sample was circulated through transparent plastic tubing of 3 mm inner diameter by a peristaltic pump at a flow rate of 25 mL/min. min. The ratio value obtained by PDA is termed as the Flocculation Index (FI) and was recorded every 5 s for the duration of jar test.

## RESULTS AND DISCUSSION

### The Effect of Basic Ratio

The evidence of the existence of pre-polymerized species has been confirmed by a study on the chemical nature of precipitates formed with a polymeric iron coagulant and a ferric salt (16). The test revealed that the species in the re-dissolution solutions from ferric salt's precipitates were predominantly $Fe(OH)_3$, whilst those from polyiron precipitates were predominantly higher MW polymers. This was also evident from the investigation of their zeta potential–pH behavior. Re-suspended precipitates of polyiron carry a significantly higher cationic charge compared to those of ferric salt. It has been well addressed that the basic ratio r, defined as the molar ratio of hydroxide to iron, is the most important parameter to be controlled in the preparation of pre-polymerized inorganic coagulants (17) such as PFC.

It has been discovered (18) that when the basic ratio is 0.3, the polymeric iron species are dominant with a molecular size range of 0.5 to 10 K and possess the maximum positive charge. Consequently, a polyferric salt with a basic ratio of 0.3 should outperform to others, this has been confirmed previously (19) and in this study. Figures 1 and 2 show the comparative humic acid (HA) removal by PFCs with various basic ratios. In order to present the effect of the basic ratio of PFC on the HA removal in a realistic condition, a model water with mixed kaolin particles and HA at pH 7 was used. It can be seen that in comparison with other PFCs, the PFC with the basic ratio of 0.3 resulted in the minimum residual DOC and color in the treated supernatant. Therefore, further discussions are focused on the performance of PFC with the basic ratio of 0.3 only.

### The Effect of the Type of Water

In natural surface water, both NOM such as humic acid and colloidal particles are present. Whilst in the presence of both colloidal particles

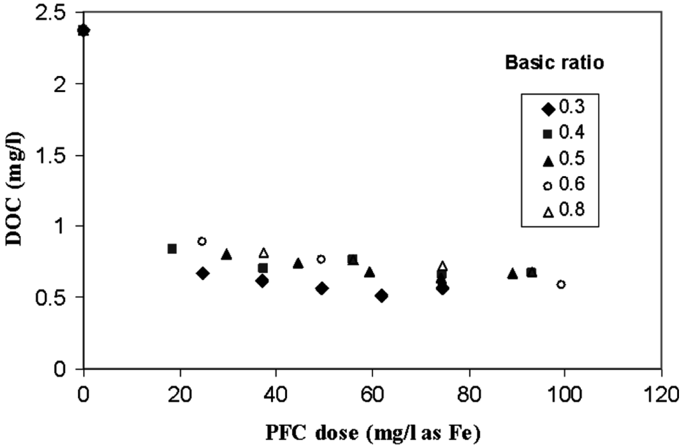

*Figure 1.* The residual DOC vs. PFC dose at pH 7 (mixed kaolin particle and humic acid water, the raw water DOC = 2.4 mg/l).

and humic acid, a more negative charge of the water sample is expected and this is the case in this study (Fig. 3a); however, this is not correlated to the dose required in order to achieve the maximum removal of humic acid and particles. The results clearly demonstrated that for the coagulation pH 7 and a PFC dose of less than 60 mg/l, $UV_{254}$ reduction was greater (Fig. 3b) and residual turbidity was lower (Fig. 4) when both the colloidal particles and humic acid were presented than that when

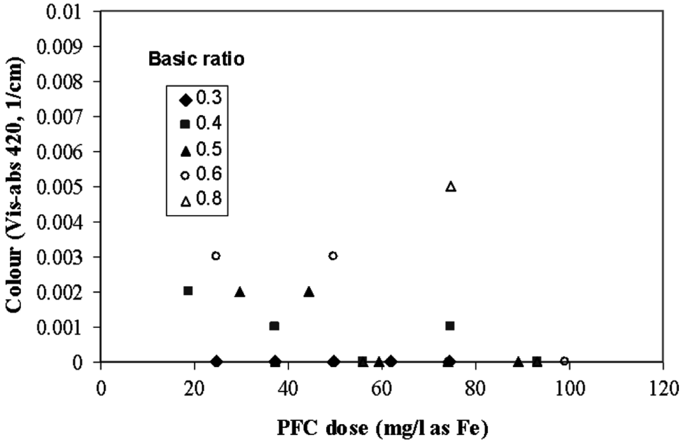

*Figure 2.* The residual color vs. PFC dose at pH 7 (mixed kaolin particle and humic acid water, the raw water color = 0.028 $cm^{-1}$ as vis-abs at 420 nm).

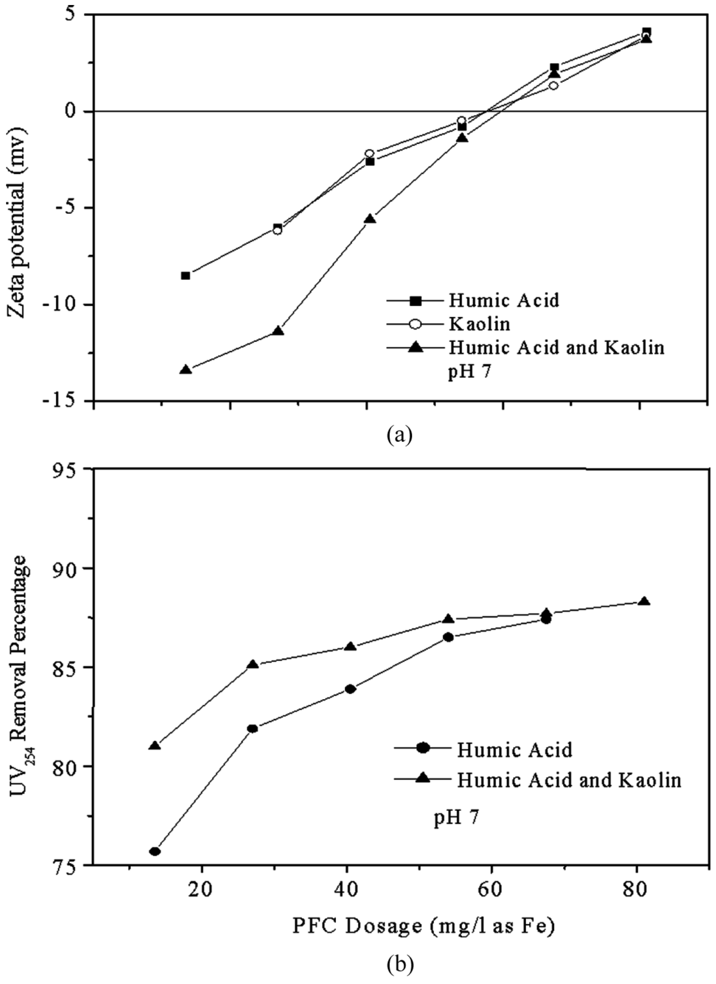

***Figure 3.*** (a) Zeta potential vs. PFC doses and (b) $UV_{254}$ reduction vs. PFC doses at pH 7.

there was humic acid alone in water. These observations could be explained as that the presence of particles in NOM water will enhance the inter-particle collisions and then a good aggregation. On the other hand, NOM could complex with coagulating species to form large flocs which then co-precipitate the colloidal particles; both are favorable to the floc development and then achieve a better settling performance. The evidence of a great floc development in the coagulated water consisting both humic acid and colloidal particles can be seen in Fig. 5. A higher

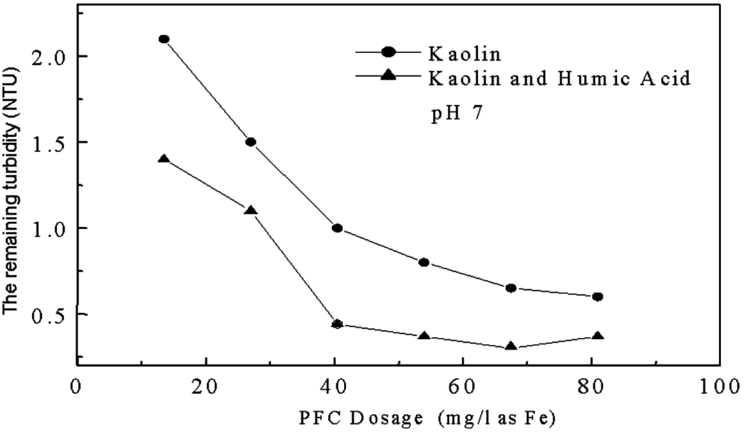

*Figure 4.* The residual turbidity vs. PFC dose at pH 7.

flocculation index was achieved for the water having both humic acid and particles in comparison with that having humic acid alone and for the same coagulation conditions.

It is interesting to note that the DOC of kaolin-HA mixed model water (2.4 mg/l) was lower than that of HA alone model water (3.5 mg/l) for a given solution pH (pH 7). This indicates that kaolin clay possesses an affinity to HA; almost 30% HA was adsorbed by kaolin without coagulation. This finding is consistent with that from a previous study

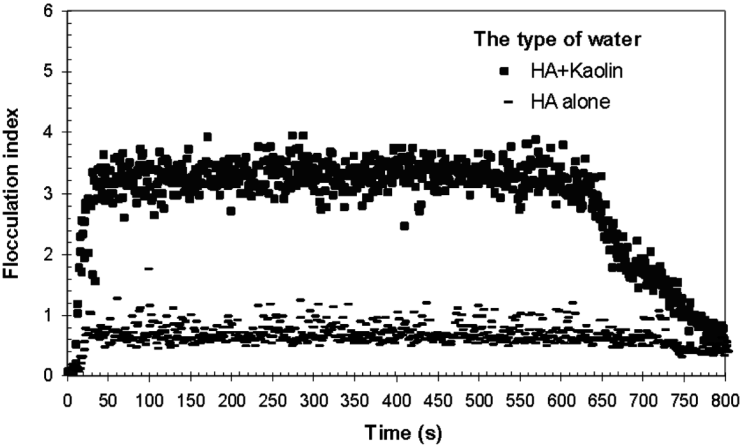

*Figure 5.* Coagulation floc development vs mixing time. PFC dose = 24.6 mg/l, coagulation pH = 7.

where the use of clay as adsorbent for adsorption of HA was reported (20). Kaolin powder has a clay-like structure and possesses features of interlayer expansion when mixing with solution which could host HA in certain level.

Experimental results also showed that the zeta potential was converted from negative to positive with increasing of PFC's dosage; one example of this can be seen in Fig. 3a. At pH 7, a charge reversal occurred at a dose of 60 mg/l for the three types of waters, which was consistent with that of $UV_{254}$ reduction and turbidity removal. When the solution charge reversed from the negative to the positive, the $UV_{254}$ percentage removal gradually increased (Fig. 3b). For the kaolinite and humic acid water, the residual turbidity was <0.5 NTU for a dose of 40 mg/l (Fig. 4).

## The Effect of Coagulation pH and Comparative Dose Demand

The effects of coagulation pH on the removal of NOM with either Fe(III) or Al coagulants are considered for three reasons. First, decreasing the pH of HA containing waters leads to the HA precipitation and then reducing raw water DOC concentrations. This can be seen in Fig. 6 where the DOC concentrations in raw model water (dose = 0) at pH7 was 2.4 mg/l whilst at pH5 was 1.2 mg/l. The second aspect of interest is that pH influences the ionisation of carboxylic and phenolic functional groups associated with the HA and this results in a reduction of the net molecular charge of the HA, which then requires less coagulant dose and leads to a greater removal of NOM. Lastly, a lower pH favours sustaining

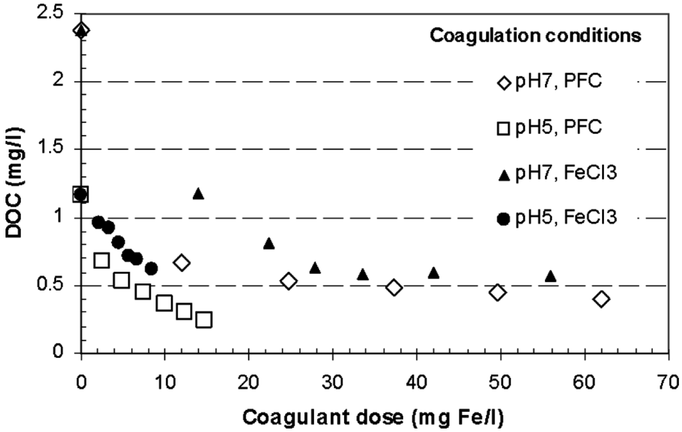

*Figure 6.* The effect of coagulation pH on the DOC reduction.

polymeric coagulant species with high positive charge and offsets the acceleration of hydroxide precipitation caused by higher coagulant doses.

It has been well established that for the iron-based coagulants, the optimum pH for the humic acid removal is at 4 to 5 (21) and this has been confirmed in this study. Fig. 6 shows that for both PFC and $FeCl_3$, the minimum residual DOC was achieved at pH5; a high dose was required at pH7 in order to reduce the DOC into a lower level.

It is interesting to see from Fig. 6 that PFC can reduce DOC with lower doses than $FeCl_3$. To reduce DOC by 50% (from 1.2 to 0.6 mg/l) at pH 5, the dose required was 4 mg/l for PFC but 8 mg/l for $FeCl_3$. This is also the case when pH was 7; 15 mg/l for PFC vs. 34 mg/l for $FeCl_3$. It has been claimed previously (19) that polyferric sulphate can remove more NOM from colour-causing waters at relative low doses. This study has confirmed the same for PFC.

In general, there are two major mechanisms of NOM coagulation (19),

1. Charge neutralisation at lower pH and doses of coagulant, whereby positive charged coagulating species complex the negative charged NOM followed by precipitation and
2. Sweep coagulation at relative high pH and doses of coagulant, by the formation of metal hydroxide precipitates first and followed by the adsorption/co-precipitation of NOM.

It has been well established (22) that charge neutralization is the major mechanism of humic substances removal by coagulation at lower

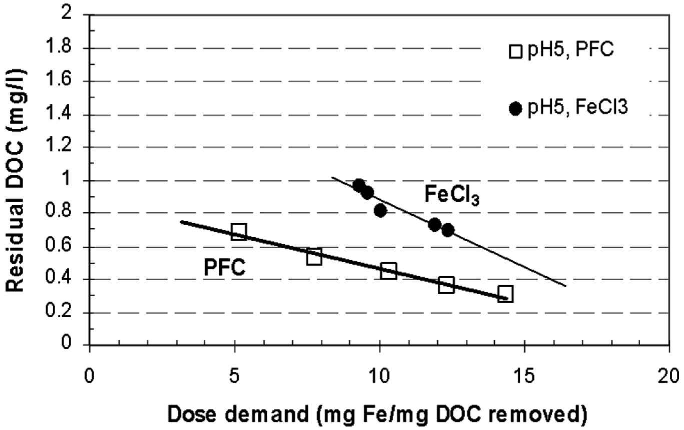

*Figure 7.* Comparative coagulant demand vs. residual DOC concentration.

**Table 1.** Dose demand vs. DOC percentage removal at pH5 (initial [DOC] = 1.2 mg/l)

| Coagulant DOC removal (%) | Dose demand for the coagulation of NOM at pH5 (mg Fe/mg DOC removed) | |
|---|---|---|
| | PFC | $FeCl_3$ |
| 50 | 6.5 | 13.5 |
| 60 | 8.5 | 15.5 |
| 70 | 14 | 18 |

pHs (4–6); relatively low doses of metal coagulants are required and dosages are proportional to humic substance concentrations. In this study, both PFC and $FeCl_3$ operated at low doses and achieved good humic acid removal. However, the dose demand of PFC was almost as half as that of $FeCl_3$ in order to achieve 50 or 60% of DOC removal at pH5 and this can be seen in Fig. 7 and Table 1.

Less dose demand with PFC cannot be attributed to low pH effect alone; the nature of the polymeric coagulating species of PFC should play the major role. As stated previously that polymeric coagulant contains pre-polymerized species which has a higher molecular size and carries higher cationic charge compared to a conventional ferric salt such as $FeCl_3$. For pH7 in this study, the sweep coagulation mechanism is obvious in the NOM coagulation as the dose required for the NOM removal was much greater than that for pH5 (Fig. 6). However, PFC still outperformed to $FeCl_3$ under such circumstances and this is due to the existence of preformed polymeric iron species with high positive charge, which offsets the acceleration of hydroxide precipitation caused by higher coagulant doses.

## CONCLUSIONS

The superior performance of PFC has been demonstrated in terms of removing both humic acid and particulate materials. The superior performance of PFC can be attributed to the presence of a range of polymeric species with a high cationic charge, which enhance the rate of the colloid charge neutralization and coagulant floc development and settlement.

This study also confirmed that a PFC with a molar ratio of 0.3 (as hydroxide to iron) can achieve the best humic acid removal. The water having both humic acid and colloidal particles was favorable to the floc development and then a better humic acid removal efficiency. For the same coagulation conditions, the dose demand of PFC was 50% less than that of $FeCl_3$ for a >50% humic acid removal.

## REFERENCES

1. Jiang, J.Q.; Graham, N.; Harward, C. (1996) Coagulation of upland coloured water with polyferric sulphate compared to conventional coagulants. *J. Wat. Supply Res. Technol.-AQUA*, *45* (3): 143–154.
2. American Water Works Association Committee Report on Coagulation. (1979) Organics removal by coagulation: a review and research needs. *J. AWWA*, *71*: 558–603.
3. Edwards, G.A.; Amirtharajah, A. (1985) Removing colour caused by humic acids. *J. AWWA.*, *77*: 50–57.
4. Black, A.P.; Singley, G.P.; Whittle, G.P.; Maulding, J.S. (1963) Stoichiometry of the coagulation of colour-causing organic cpompounds with ferric sulphate. *J. AWWA*, *55*: 1347–1366.
5. Dempsey, B.A.; Ganho, R.M.; O'Melia, C.R. (1984) The coagulation of humic substances by means of aluminium salts. *J. AWWA*, *76*: 141–150.
6. Edwards, G.A.; Amirtharajah, A. (1985) Removing colour caused by humic acids. *J. AWWA*, *77*: 50–57.
7. Fettig, J.; Ratnaweera, H.C.; Odegaard, H. (1990) Simultaneous phosphate precipitation and particle destabilisation using Al coagulants of different basicity. In: *Chemical Water and Wastewater Treatment I*, Hahn, H.H.; Klute, R. eds.; Springer-Verlag: Berlin, pp. 221–242.
8. Jiang, J.Q.; Graham, N. (1998) Preliminary evaluation of the performance of new pre-polymerised inorganic coagulants for lowland surface water treatment. *Wat. Sci. Technol.*, *37* (2): 121–128.
9. Jiang, J.Q. (2001) Development of coagulation theory and pre-polymerized coagulants for water treatment. *Separation Purif. Methods*, *30* (1): 127–141.
10. Parthasarathy, N.; Buffle, J. (1985) Study of polymeric Al hydroxide solutions for application in wastewater treatment. Properties of the polymer and optimal conditions of preparation. *Water Res.*, *19*: 25–36.
11. Jiang, J.Q.; Graham, N. (1998) Preparation and characterisation of an optimal polyferric sulphate (PFS) as a coagulant for water treatment. *J. Chem. Technol. Biotech*, *73* (4): 351–358.
12. Gao, B.; Yue, B.Q.; Zhao, H.; Song, Y. (2000) Properties and evaluation of polyferric silicate sulfate (PFSS) as a coagulant for water treatment. In: *Chemical Water and Wastewater Treatment VI*, Hahn, H.H.; Hofmann, E.; Odegaard, H., eds.; Springer-Verlag: Berlin, 15–22.
13. Jiang, J.Q.; Graham, N.; Harward, C. (1993) Comparison of polyferric sulfate with other coagulants for the removal of algae and algae-derived organic-matter. *Wat. Sci. Technol.*, *27* (11): 221–230.

14. American Public Health Association/American Water Works Association/ Water Environmental Federation, (1998) *Standard Methods for the Examination of Water and Wastewater.* 20th Ed.; Washington, DC.
15. Gregory, J.; Chung, H.J. (1995) Continuous monitoring of floc properties in stirred suspensions. *J. Wat. Supply Res. Technol.-AQUA*, *44*: 125–131.
16. Jiang, J.Q.; Graham, N. (1998) Observations of the comparative hydrolysis/ precipitation behaviour of polyferric sulphate and ferric sulphate. *Water Res.*, *32* (3): 930–935.
17. Jiang, J.Q.; Graham, N. (1997) Pre-polymerised inorganic coagulants for treating water and wastewater. *Chem. and Industry*, *10*: 388–391.
18. Jiang, J.Q. (2001) Development of coagulation theory and new coagulants for water treatment: Its past, current and future trend. *Wat. Sci. Technol.: Wat. Supply*, *1* (4): 57–64.
19. Jiang, J.Q.; Graham, N. (1996) Enhanced coagulation using Al/Fe(III) coagulants: Effect of coagulant chemistry on the removal of colour-causing NOM. *Environ. Technol.*, *17* (9): 937–950.
20. Jiang, J.Q.; Cooper, C. (2003) Preparation of modified clay adsorbents for the removal of humic acid. Environ. *Eng. Sci.*, *20* (6): 581–586.
21. Dolejs, P. (1992) The effects of temperature, pH and rapid mixing gradient on the formation of particles in treatment of humin water. In: *Chemical Water and Wastewater Treatment II*, Hahn, H.H.; Klute, R.; eds.; Springer-Verlag: Berlin, 65–77.
22. Stumm, W.; O'Melia, C.R. (1968) Stoichiometry of coagulation. *J. AWWA*, *59*: 514–539.