

COMPARISON OF POLYFERRIC SULPHATE WITH OTHER COAGULANTS FOR THE REMOVAL OF ALGAE AND ALGAE-DERIVED ORGANIC MATTER

Jia-Qian Jiang*, Nigel J. D. Graham* and Clive Harward**

* *Environmental and Water Resource Engineering, Department of Civil Engineering, Imperial College, London SW7 2BU, UK*

** *Anglian Water Services Ltd, Chivers Way, Histon, Cambridge CB4 4ZY, UK*

ABSTRACT

This paper is concerned with the performance of a relatively new form of metal-iron coagulant, Polyferric Sulphate (PFS), which has received very little research attention to date. Laboratory experiments have been undertaken in which the coagulation performance of PFS, Ferric sulphate, Aluminium sulphate and Poly aluminium chloride have been studied using 'model' waters containing single cultures of algae (*Anabaena flos-aquae* and *Asterionella formosa*) and other 'model' waters prepared by mixing aquatic humic substances with *Asterionella formosa* at different concentration ratios. Physico-chemical variables such as colloid charge, floc number concentration and size distribution, DOC concentration and turbidity, have been determined to quantify treatment performance. The performance of PFS was found to be superior to the other coagulants and this was believed to be due to the presence of more highly charged cation species. For all coagulants there was an approximate stoichiometry between coagulant dose and the dissolved organic carbon concentration.

KEYWORDS

Polyferric sulphate; ferric sulphate; aluminium sulphate; polyaluminium chloride; coagulants; algae; *ANABAENA FLOS-AQUAE*; *ASTERIONELLA FORMOSA*.

INTRODUCTION

In conventional water treatment systems the removal of particles and dissolved materials is determined primarily by the effectiveness of coagulation, a process in which chemical reactions and physical transport processes are used to destabilize and aggregate suspended particles and to precipitate or adsorb natural organic substances so that these contaminants can be removed in subsequent sedimentation (or flotation) and filtration stages. The process of coagulation as practised in water treatment can be considered as three separate and sequential steps : coagulant formation, particle destabilization, and interparticle collisions. Conventionally, coagulant formation and coagulant reactions with contaminants in surface water sources occur in rapid mixing tanks; interparticle collisions

occur predominantly in flocculation tanks and in sludge blanket settling tanks. Coagulants are sometimes pre-formed prior to their addition to rapid-mixing facilities and one example of these is polyferric Sulphate (PFS). PFS contains pre-formed iron (III) hydrolysis species, $[\text{Fe}(\text{OH})_x]^{(3-x)+}$, and polynuclear complexes of iron (III), $[\text{Fe}_m(\text{OH})_x]_n^{(3m-x)n+}$, and the functions of these species are to provide both colloid charge neutralization and polymer bridging between floc particles.

Limited development of PFS has been carried out since 1975, when a patent defining the preparation of PFS was published; the method consisted of the catalytic oxidation of a solution containing H_2SO_4 and FeSO_4 , under very acidic conditions ($\text{pH} < 3$), followed by a period of aging. Subsequent research has been concerned with decreasing the reaction time and the dose of catalyst used (Mikami, 1976; 1980). Acid washing solutions from iron and steel manufacture and of by-products from TiO_2 production have been applied as raw materials in the preparation of PFS (Matsubayashi, 1986). It is clear that more work is required to properly evaluate PFS formulations and optimize the methods of preparation; this paper is concerned with these objectives.

This paper summarises the results of laboratory jar test experiments undertaken to assess the coagulation performance of a laboratory prepared PFS chemical in comparison with three other conventional coagulants: aluminium sulphate [AS], polyaluminium chloride [PAC], and ferric sulphate [FS]. The performance assessment was based on each coagulant's ability to remove algae and algal derived organic matter at a constant pH value of 7.5. Two kinds of algae, *Anabaena flos-aquae* (Blue green) and *Asterionella formosa* (diatom), were used in the tests since these species are very common in UK surface water reservoirs and are known to be associated with water treatment, and treated water quality, problems. The particular influence of humic substance concentration on the performance of PFS has also been investigated.

EXPERIMENTAL PROCEDURES

Model waters

Stock cultures of *Asterionella formosa* and *Anabaena flos-aquae* were grown under continuous lighting conditions (200 – 250 lm/m^2 with standard fluorescent light) and constant temperature (17.0 °C). The composition of growth media for both species are shown in Table 1.

Table 1. Composition of Growth Media

Constituent	Growth Media (mg/L)	
	<i>Anabaena flos-aquae</i>	<i>Asterionella formosa</i>
Ca (NO ₃) ₂ · 4H ₂ O	20	20
KH ₂ PO ₄	12.4	—
MgSO ₄ · 7H ₂ O	50	12.5
NaHCO ₃	15.9	15.9
EDTA FeNa	2.25	2.25
EDTA Na ₂	2.25	2.25
H ₃ BO ₃	2.48	2.48
MnCl ₂ · 4H ₂ O	1.39	1.39
(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	1	1
Cyanocobalamin	0.04	0.04
Thiamine HCl	0.04	0.04
Biotin	0.04	0.04
NaNO ₃	80	—
Na ₂ HPO ₄ · 12H ₂ O	36	0.036
K ₂ SiO ₃	—	0.032 ml/l
HCl (1 N)	—	0.04 ml/l

Initial coagulation experiments were undertaken with solutions of the algae in their growth media and examples of the general water quality characteristics are shown in Table 2. For the experiments concerned with the effect of humic substances on the coagulation performance, the solutions of algae (*Asterionella formosa*) and growth media were diluted to achieve a DOC of 2.5 mg/L prior to the addition of different concentrations of humic substances. Examples of the water quality characteristics are shown in Table 3. Humic material was directly extracted from an upland raw water by a method involving pre-concentration by reverse-osmosis and freeze-drying. Such material could be readily re-dissolved in high-purity water for use in the coagulation experiments.

Jar Test

A six-beaker jar test apparatus was used with each beaker containing 300 ml of solution. The 300 ml solution volume is smaller than is commonly used in jar test experiments, in order to minimize the required quantity of algae and extracted humic material. A period of 2 min was allowed for rapid mixing at 300 rpm, followed by a period of 25 min flocculation at 35 rpm. At the end of the flocculation period, the solution was allowed to settle for a period up to 2 hours and supernatant samples taken for analysis. A constant pH of 7.5 was achieved by the prior addition of either HCl or NaOH, and the solution pH was checked during the mixing and flocculation periods.

Coagulants

PFS was prepared in the laboratory by a method involving the catalytic oxidation of ferrous sulphate. The amount of ferrous sulphate, oxidant and catalyst used were as required for chemical equilibrium. The final step of the method involved a 5-7 hour aging period at a temperature in the range 45 - 75°C. The resulting PFS solution had the following properties: $[\text{Fe}^{3+}] = 160 \text{ g/L}$, $[\text{Fe}^{2+}] < 1 \text{ g/L}$, $\text{OH/Fe} = 0.4$, $\text{pH} = 0.5 \text{ to } 1.0$. For the other coagulants, ferric sulphate was analytical reagent grade (BDH Chemicals, Poole, UK), and both polyaluminium chloride (PAC, 8% Al_2O_3 , $\text{OH/Al} = 1.5$) and aluminium sulphate (8.2% Al_2O_3) were commercial grade (Alcan Chemicals Ltd, Gerrards Cross, UK).

Analysis

Algae concentration is expressed as algal cell numbers which were determined by Coulter Counter particle analysis (model TA II, Coulter Electronics Ltd, Luton, U.K.). Floc size measurements were also measured by Coulter Counter. Turbidity was measured by Turbidity meter (Model 2100A, Hach Camlab) and DOC was determined by a Dohrmann DC 80 Carbon Analyser (Envirotech, Santa Clara, Calif). Colloid and floc charge was estimated by a method of colloid titration (Kawamura and Tanaka, 1966).

RESULTS

Initial Experiments

The results of the coagulation experiments for each algal species carried out in solutions of their growth media are highlighted in Figures 1 and 2, and in Table 2. Figures 1 and 2 show the total algal cell reduction with coagulant dose for each of the four coagulants. The results show the well-established phenomena of an increasing treatment performance with coagulant dose up to a maximum value that is then independent of increasing coagulant dose. For both algal species, PFS was found to achieve the greatest cell reduction and was clearly superior to the other pre-formed polymeric coagulant (PAC).

To compare the relative water treatment performance of the four coagulants in terms of other water quality parameters, Table 2 shows the results corresponding to one coagulant dose (0.20 m mol Al³⁺ or Fe³⁺ per litre). The results given in Table 2 in particular demonstrate a superior performance by PFS in removing the soluble algae-derived organic matter (Extracellular products) with DOC reductions of approximately 70%.

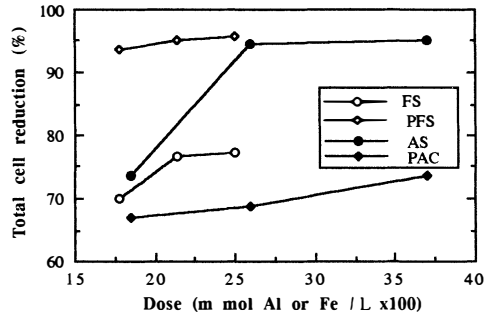


Fig.1 Comparison of four coagulants for *Anabaena* cell removal.

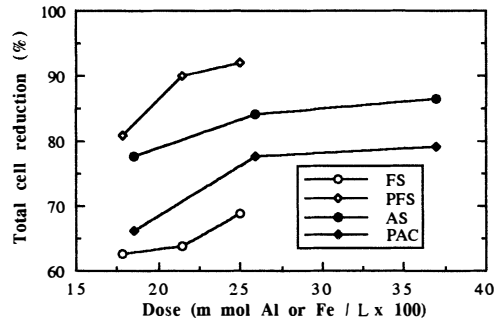


Fig.2 Comparison of four coagulants for *Asterionella* cell removal.

Table 2. Comparative Coagulation Performance

Coagulant	Total cell removal%		DOC removal%		Turbidity removal%		pH		Colloid (Floc) charge ^a	
	X*	Y*	X	Y	X	Y	X	Y	X	Y
PFS	94	87	70	63	96	70	7.5	7.5	60	45
FS	74	63	45	44	62	—	"	"	19	12
PAC	68	68	34	40	52	—	"	"	25	21
AS	78	79	56	46	72	55	"	"	40	29

X: *Anabaena flos-aquae*, Y: *Asterionella formosa*.

^a the unit is (meqL⁻¹ 10⁻⁴),

Coagulant dose for X and Y is 20 m mol Al³⁺ or Fe³⁺L⁻¹ 10⁻².

* Initial water quality characteristics:

Total *Anabaena* conc. = 2.0·10⁵ cells ml⁻¹,

dp = 5 μm, conc. = 2·10⁴ cells ml⁻¹,

dp = 10 μm, conc. = 3.6·10⁴ cells ml⁻¹,

DOC = 26.5 ppm, Turbidity = 34 NTU,

pH=8.5, Colloid charge = - 128 meqL⁻¹ 10⁻⁴.

Total *Asterionella* conc. = 2.1·10⁵ cells ml⁻¹,

dp = 5 μm, conc. = 2.5·10⁴ cells ml⁻¹,

DOC = 22.5 ppm, Turbidity = 12 NTU,

pH = 8.5, Colloid charge = - 140 meqL⁻¹ 10⁻⁴.

Effect of Humic Substances

Jar test coagulation experiments were undertaken in solutions containing *Asterionella formosa*, to which different quantities of humic substances were added. Figure 3 shows the effect of different concentrations of humic substances on the removal of algal cells with PFS.

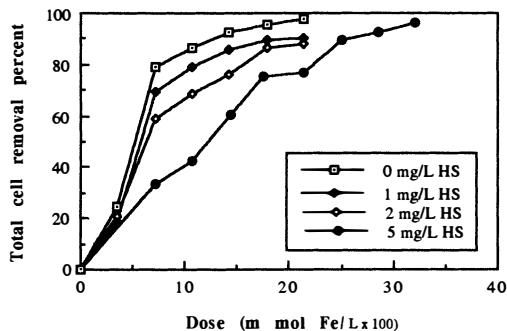


Fig.3 Influence of humic substances (HS) concentration on the removal of *Asterionella formosa* with PFS.

The results shown in Fig.3 clearly show a systematic reduction in coagulation performance with increasing concentration of humic substances for a given dose of PFS. This was the case for DOC removal (Fig.4) as well as for total algal cell removal.

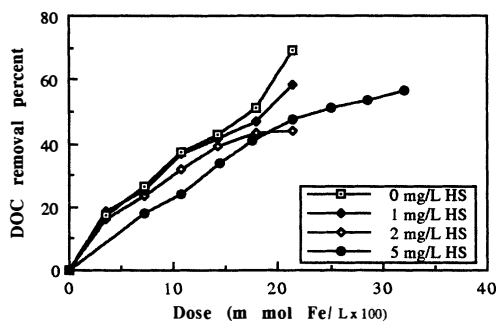


Fig.4 Influence of humic substances (HS) concentration on the removal of DOC with PFS.

The observed behaviour demonstrated by Fig.3 and Fig.4, whereby increasing levels of humic substances correspond to a systematic reduction in the removal of particulate and dissolved species at a given coagulant dose, but with an unchanged maximum removal, strongly suggests the importance of charge interaction. Measurements of colloid charge by colloid titration (Fig.5) confirm the trend that higher PFS doses are required to achieve overall charge neutralisation in solutions with greater humic substances concentration.

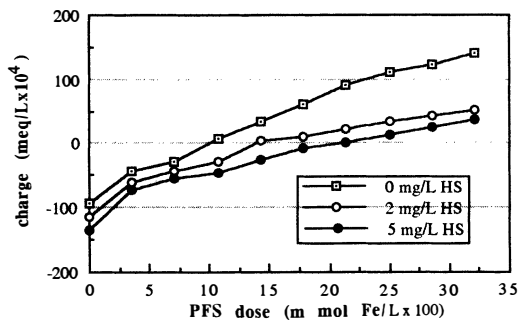


Fig.5 Influence of humic substances (HS) concentration on the overall colloid charge.

A similar behaviour was observed for the other three coagulants regarding the effect of humic substances and the corresponding results for aluminium sulphate are shown in Figs 6 - 8.

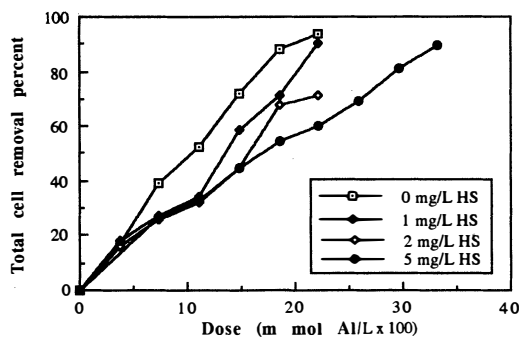


Fig.6 Influence of humic substances (HS) concentration on the removal of *Asterionella formosa* with aluminium sulphate.

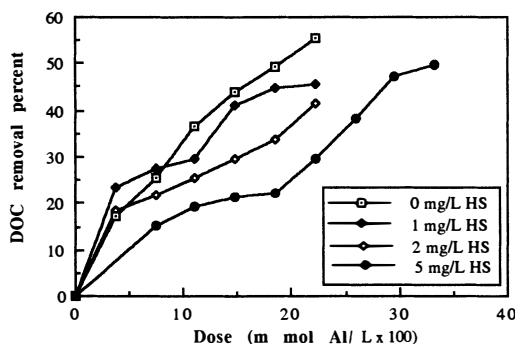


Fig.7 Influence of humic substances (HS) concentration on the removal of DOC with aluminium sulphate.

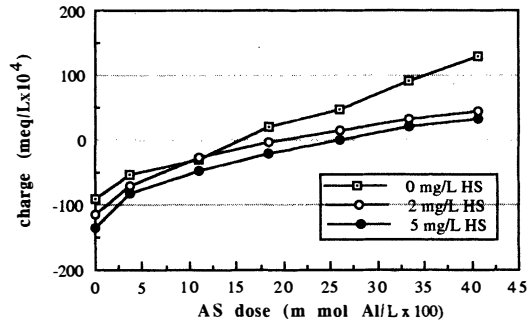


Fig.8 Influence of humic substances (HS) on the overall colloid charge.

To compare the relative water treatment performance of the four coagulants in terms of the principal water quality parameters, Table 3 shows the results corresponding to one coagulant dose (0.20 m mol Al³⁺ or Fe³⁺ per litre) and a humic substances solution concentration of 0 mg/L and 2 mg/L.

Table 3. Comparative Coagulation Performance

Coagulants	Total cell removal%		DOC removal%		Turbidity removal%		UV-Abs (254nm) removal%		Vis-Abs (420nm) removal%		Colloid (floc) charge ^a	
	X*	Y†	X	Y	X	Y	X	Y	X	Y	X	Y
PFS	96	86	61	45	88	79	50	48	54	48	65	20
FS	80	61	33	24	69	60	40	36.5	45	36.5	28	-8
PAC	72	55	30	25	70	58	38	30	40	30	26	-4
AS	90	70	52	32	84	72	45	40	54	40	30	0

^a The unit is (meqL⁻¹ 10⁻⁴),

Coagulant dose for X and Y is 20 m mol Al³⁺ or Fe³⁺·L⁻¹ 10⁻².

* X – The ‘model’ water quality characteristics :
 Total cell conc. = 4.8·10⁴ cells ml⁻¹,
 DOC = 2.5 ppm, UV-Abs (254 nm)=9.6 m⁻¹,
 pH=8.3, Turbidity = 4 NTU,
 Colloid charge = - 92 meqL⁻¹ 10⁻⁴.

† Y – The ‘model’ water + 2mg/L humic substances :
 Total cell conc. = 5.0·10⁴ cells ml⁻¹,
 DOC = 4.8 ppm, UV-Abs (254 nm)=21.0 m⁻¹,
 pH = 7.92, Turbidity = 4.5 NTU,
 Colloid charge = - 115 meqL⁻¹ 10⁻⁴.

The greater treatment performance with PFS appears to arise due to its greater ability to influence the rate and extent of floc development. Figure 9 demonstrates this in terms of floc size.

The ability of PFS to produce a more rapid floc growth, and possibly a greater floc density (to be examined in subsequent studies), leads to greater settling rates (Fig. 10).

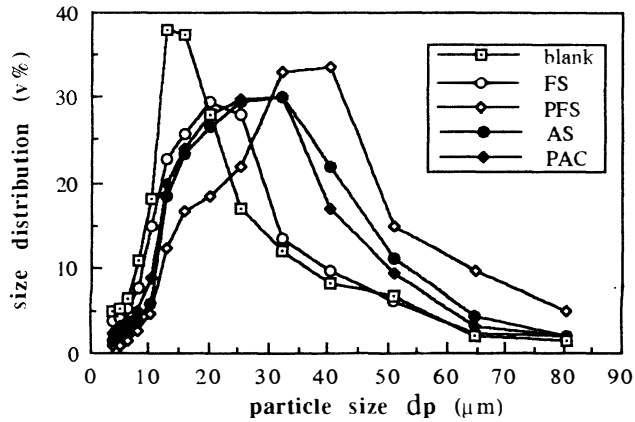


Fig.9 Comparison of floc size distributions after 10 min of flocculation (water containing *Asterionella formosa* + 1 mg/L humic substances, the quality characteristics are: Total cell conc. = $4.5 \cdot 10^4$ cells ml^{-1} , DOC = 3.9 mg/L, UV-Abs (254 nm)= 12.8 m^{-1} , pH=8.0, Turbidity = 4 NTU, Coagulant dose 0.18 m mol Al^{3+} or Fe^{3+} per litre).

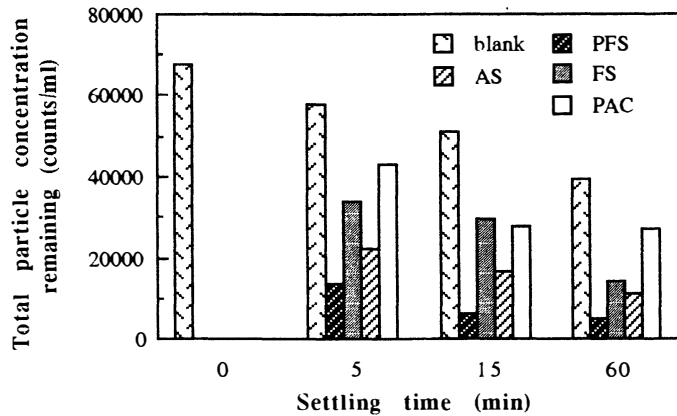


Fig.10 Comparison of settling rates for the four coagulants (water containing *Asterionella formosa* + 1 mg/L humic substances, the quality characteristics are: Total cell conc. = $4.5 \cdot 10^4$ cells ml^{-1} , DOC = 3.9 mg/L, UV-Abs (254 nm)= 12.8 m^{-1} , pH=8.0, Turbidity = 4 NTU, Coagulant dose 0.18 m mol Al^{3+} or Fe^{3+} per litre).

DISCUSSION

In general it is claimed that prepolymerized coagulants have the following advantages over metal salt coagulants: better overall treatment efficiency; better floc separation; wider working pH range; lower sensitivity to low temperatures; lower residual metal-ion concentration (Odegaard *et al.*, 1990). Prepolymerisation of the metal salt coagulant is principally to enhance the charge interaction mechanism of colloid destabilization as a consequence of the slowing down of the hydrolysis of the metal salt. Prepolymerized metal salt coagulants are produced by the controlled basification (hydrolysis) of a metal salt solution and the basicity of the polymerized coagulant is expressed in terms of the OH/M ratio (M – metal ion). In general, the higher the OH/M ratio, the lower the stability of the solution will be (especially in the presence of sulphate ions), and commercial polyaluminium products are typically in the OH/Al range 0.5 – 2.0 (Odegaard *et al.*, 1990). The PFS used in this study (OH/Fe = 0.4) has been found to be stable for a period up to six months.

The experiments undertaken in this study have been carried out at constant pH of 7.5 in order to simulate a typical algal-laden raw water. At this pH, moderate doses of aluminium or ferric salts (> 0.1 m mol/L) lead to rapid precipitation of $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$. In this case, the removal of dissolved organic species is attributed to adsorption onto $\text{Al}(\text{OH})_3$ (or $\text{Fe}(\text{OH})_3$) particles and/or, together with algal cells, enmeshment by precipitated metal hydroxide ("sweep" coagulation). In contrast, prepolymerized metal salt coagulants are believed to interact initially by charge, with cationic species adsorbing on to particle surfaces (eg. algae) and precipitating dissolved organic species (eg. humic substances). Figure 11 shows the different cationic species believed to be present in the PFS solution. Species A is a monomer, species B is a dimer, species C is an example of a medium molecular weight polymer, and species D and E represent high molecular weight polymers.

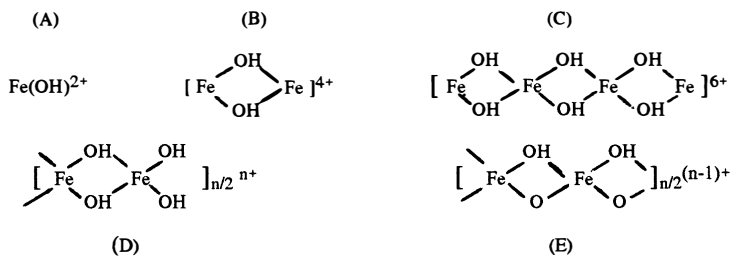


Fig.11 Cationic hydrolysis species in PFS solution.

The superior coagulation performance by PFS, for both algal cells and dissolved organic species (extracellular material and humic substances) is partly attributable to charge effects. Thus, a significantly smaller dose of PFS is required to achieve colloid neutralization (0.1 m mole Fe/L) than for the other three coagulants (0.15 m mole Al/L for AS and PAC, 0.15 m mole Fe/L for FS). However, greater coagulation performance is achieved at PFS doses above that required for colloid charge neutralization which cannot be explained by charge effects alone. Since this behaviour was observed with all four coagulants, it suggests that appreciable metal hydroxide precipitation occurs in all cases, to a greater extent with increasing coagulant dose. Nevertheless, the importance of charge interactions is clear from the results showing a dose stoichiometry with DOC concentration (Figs 3-5).

The comparatively poorer performance by PAC relative to aluminium sulphate was unexpected. Approximately the same dose (as m mol Al^{3+}/L) of PAC and AS achieved colloid charge neutralization which suggests that the PAC contained hydrolysis species of less cationic charge. In the literature there are very few reported studies of the relative performance of PAC versus AS for the treatment of algae. Zabel (1985) compared the algae removal rates achieved by flotation with three different coagulants at their optimum pH for minimum coagulant residuals, and indicated that an equivalent dosage of PAC, in terms of aluminium, was required to achieve an algae removal similar to that of aluminium sulphate.

In conclusion, the PFS used in this study was able to achieve a high degree of removal of algal cells and algae-derived organic matter, and was superior to other typical coagulants. The nature of the cationic species in the PFS solution needs to be investigated (eg. molecular weight, charge density) in order to interpret the coagulation behaviour (destabilization mechanisms) and assess the effect of changes to the method of preparation. This will be the subject of future work.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support of Anglian Water Services Ltd for this work. Thanks are expressed to Dr. P. J. Matthews, Director of Quality Anglian Water Services Ltd, for permission to publish this paper.

REFERENCES

- Kawamura, S. and Tanaka, Y. (1966). Applying colloid titration techniques to coagulant dose control. Water and Sewage Works, 9, 348-357.
- Matsubayashi, K. (1986). Japanese Patent. No. 215222.
- Mikami, Y. (1976). Japanese Patent, No. 17516.
- Mikami, Y. (1980). Japanese Patent, No. 842085.
- Odegaard, H., Fettig, J. and Ratnaweera, H. C. (1990). Coagulation with prepolymerized metal salts. In: Chemical water and wastewater treatment (Eds H. H. Hahn and R. Klute), Springer-Verlag, Berlin Heidelberg, pp. 189-220.
- Zabel, T. (1985). The advantages of dissolved- air flotation for water treatment. Journal of American Water Works Association, 77(5), 42-46.