Polyferric sulphate: Preparation, characterisation and application in coagulation experiments

A.I. Zouboulis *, P.A. Moussas, F. Vasilakou

Division of Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124, Greece

Abstract

The process of coagulation is a core environmental protection technology, which is mainly used in the water or wastewater treatment facilities. Research is now focused on the development of inorganic pre-polymerised coagulants. A characteristic example is PFS (polyferric sulphate), a relatively new pre-polymerised inorganic coagulant with high cationic charge. In this paper, the role of major parameters, including temperature, types of chemical reagents, ratio $r = [OH]/[Fe]$, rate of base addition in the preparation stages of PFS were investigated. Furthermore, the prepared PFS was characterised based on typical properties, such as the percentage of the polymerised iron present in the compound, z-potential, pH, etc. Moreover, dynamics of coagulation process were examined by means of the Photometric Dispersion Analyzer (PDA). Finally, the coagulation efficiency of PFS in treating kaolin suspension and biologically pre-treated wastewater was evaluated in comparison with the respective conventional coagulant agent.

The results indicate that certain parameters, such as the *r value*, the rate of base addition and the duration and temperature of the polymerisation stage, significantly affected the properties of the PFS. Additionally, the prepared PFS polymerised coagulants exhibit a significantly better coagulation performance than the respective non-polymerised one, i.e. ferric sulphate.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Coagulation; Polyferric sulphate; Inorganic pre-polymerised coagulant; PDA

1. Introduction

The process of coagulation is widely used in the wastewater treatment facilities, especially for the destabilisation of colloids suspensions and for the removal of suspended solids along with the removal of phosphate ions. It is known as a core environmental protection technology. Nearly all the colloids found in natural waters carry negative charge and therefore, they remain in suspension, due to the mutual electric repulsions. Therefore, the addition of an appropriate cation will result in colloidal destabilisation, as they specifically interact with the negatively charged colloids and neutralise their charge. Highly charged cation, such as Fe^{3+}, is regarded as one of the most effective cation for such a purpose. Therefore, there are a number of conventional coagulants based on iron, such as the $Fe_2(SO_4)_3$ or the $FeCl_3$. When, the ferric ions were dosed into the water, they hydrolysed rapidly and in an uncontrollable manner, resulting in the formation of various iron species. The range of species formed is influenced by a number of factors, such as the nature and the temperature of the water, the coagulation pH, the dosage of the coagulant, which in turn influences the treatment performance. Therefore, a considerable attention has been paid during the last 20 years to the pre-hydrolysed inorganic coagulants based on iron (or aluminium), such as polyferric chloride or polyaluminium chloride [1–4]. Their significant advantage is that the hydrolysis of iron ions occurs under specific experimental conditions during the preparation stage of the coagulant, and not after their addition to the raw water, which consequently, results in a better control of the coagulation procedure [5]. Therefore, research focuses on the development of such coagulants, which will combine superior efficiency and lower operational cost as compared with the conventional ones.

A relatively new kind of coagulation reagents is the Inorganic Polymeric Flocculants (IPFs), such as the polyferric sulphate (PFS). PFS is a pre-hydrolysed coagulant prepared by partially neutralisation of iron salts. During the neutralisation several polymerisation reactions occur resulting in the formation of various species of polymerised iron. PFS contains polynuclear

---

* Corresponding author. Tel.: +30 310 997 794.
E-mail address: zoubouli@chem.auth.gr (A.I. Zouboulis).

complex ions, such as $Fe_2(OH)_2{}^{4+}$, $Fe_3(OH)_4{}^{5+}$, formed by OH bridges and large number of inorganic macromolecular compounds. The obtained molecular weight can be as high as 10^5 [6]. Due to the presence of polymeric species the PFS carries high cationic charge, which can improve the charge neutralisation capacity and hence, it becomes more effective at a comparatively lower dose, than the conventionally applied reagents [7]. Furthermore, it has been reported by several researchers that PFS exhibits a superior efficiency in the removal of chemical oxygen demand (COD), biochemical oxygen demand (BOD), turbidity and colour, than the conventional coagulants based on iron [6–8]. Also, it can be used in a wide range of pH and temperature, due to its strong hydrolysis. Meanwhile, some preliminary toxicity studies suggested that drinking water treated with PFS is safe for human consumption [9].

Several researchers have proposed different methods for preparing the PFS in laboratory scale [10–12], suggesting that the structure and the characteristics of the hydrolysis/polymeric species are highly dependent on factors, such as the concentration of Fe(III) ions, the temperature of the hydrolysis stages and the type of added base reagent. However, there is still uncertainty about the effect that other parameters, including the temperature and the duration of the aging time, the flow rate during the base addition and the r ($r = $ OH/Fe) value, will have upon the properties of PFS as their contribution has not been yet thoroughly investigated.

The aim of this paper is to shed light on the effect that these factors have upon the structure and the quality of produced PFS in a detailed and integrated manner. The prepared coagulants were characterised in terms of typical properties, such as the degree of polymerisation, pH, z-potential, conductivity and density. Moreover, a structure and morphology analysis were carried out by obtaining FTIR, XRD spectra and SEM microphotographs. Additionally, dynamics of coagulation process were examined by means of the Photometric Dispersion Analyzer (PDA) enabling the determination of optimum experimental conditions regarding the fast mixing stage of the coagulation/flocculation process. Finally, this paper considers the coagulation performance of PFS in treating kaolin model suspension and biologically pre-treated municipal wastewater focusing on the removal of phosphate ions. The latter is of paramount importance as the coagulation process is regarded as an important option for the tertiary treatment of wastewater and therefore the efficiency in removing the phosphate ions is a crucial criteria regarding the usage of PFS coagulants for such a purpose.

2. Materials and methods

All used reagents were analytically pure chemicals. Deionized water with conductivity lower than $0.5\,\mu S/cm$ was used to prepare all the solutions.

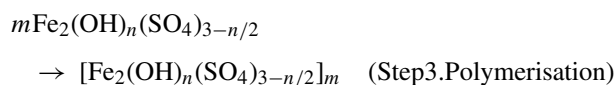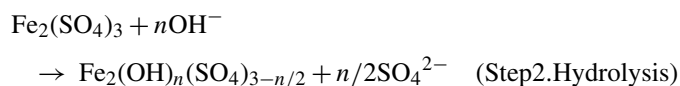### 2.1. Mechanism of PFS preparation

The synthesis of PFS commences with the oxidation of ferrous sulphate (5.59×10^{-3} M as Fe) to ferric sulphate in highly acidic conditions (H_2SO_4, 96 wt%). The oxidising agent was nitric acid (HNO_3, 65 wt%).

$$FeSO_4 + 1/2SO_4{}^{2-} + \text{oxidising agent}$$
$$\rightarrow 1/2Fe_2(SO_4)_3 \quad \text{(Step 1. Oxidation)}$$
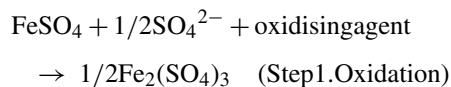
When the amount of sulfuric acid is limited, the hydroxide ion will replace the sulphate ion in the hydrolysis stage and therefore, the polymerisation will occur:

$$Fe_2(SO_4)_3 + nOH^-$$
$$\rightarrow Fe_2(OH)_n(SO_4)_{3-n/2} + n/2SO_4{}^{2-} \quad \text{(Step 2. Hydrolysis)}$$

$$mFe_2(OH)_n(SO_4)_{3-n/2}$$
$$\rightarrow [Fe_2(OH)_n(SO_4)_{3-n/2}]_m \quad \text{(Step 3. Polymerisation)}$$

2.2. Synthesis of PFS

The synthesis of the PFS was performed following in general terms the proposed method of Jiang and Graham [10]. The investigation of optimum experimental conditions was conducted by altering certain experimental parameters, such as the temperature and duration of each stage of the preparation method, the type of the base reagent, the flow rate of adding the base solution as well as the r value.

2.3. Characterisation of the liquid PFS

The total iron concentration, pH, conductivity and turbidity measurements were performed by using a PerkinElmer 2380 Atomic Spectrometer, a Metrohm Herisau pH-Meter, a Crison CM 35 conductimeter and a HACH RATIO/XR Turbimeter, respectively.

2.3.1. Determination of z-potential values

The PFS samples were diluted (about 100-fold) leading to the formation of various hydrolysis products including insoluble colloidal particles. Since the z-potential measurement of a solution cannot take place, it is suggested that, as some of the dissolved hydrolysis species of PFS can be adsorbed onto the surface of the sediment of PFS hydrolysis products, measuring the z-potential of the sediments could provide approximately similar information about the z-potential values of all hydrolysis species of PFS. The z-potential of colloidal particles was measured by a Laser Zee Meter 501.

2.3.2. Determination of polymerised iron concentration

The measurement of the Fe species by the ferron-timed spectroscopy method has been reported previously [10]. The ferron reagent (8-hydroxy-7-iodoquinoline-5-sulphonic acid) can form complexes with single ferric ions, as well as with monomeric and dimeric species, within the reaction time of 1 min, whereas it can form complexes with medium and high molecular weight iron polymers with increasing reaction time. The precipitated ferric species will not react with ferron. Based on this principle, the

visible absorbance at 600 nm of solutions was measured in pre-determined time intervals and each absorbance corresponded to the respective ferric species concentration. In particular, the oligomeric (monomeric and dimeric) iron species are determined from the absorbance reading taken 1 min after the mixing of the ferron reagent and the diluted PFS sample. The polymeric species of PFS are determined from the difference between the 24 h and 1 min absorbance reading. The concentration of precipitated iron species are calculated by subtracting the concentration of oligomeric and polymeric species from the total iron concentration.

2.3.3. Determination of the ratio r = [OH]/[Fe]

The molar ratio of OH^- to the Fe is called the r value and it can be directly related to the stability of produced PFS. It is determined by adding excess hydrochloric acid (HCl 1N) and potassium fluoride solution (KF 50 wt%) to the sample and back titrating with sodium hydroxide (NaOH 1N).

2.4. Characterisation of solid PFS

The liquid products were freeze-dried for 96 h and then were placed into a desiccator to cool for another 24 h. The solid PFS was ground using a laboratory mortar and a pestle for further characterisation.

2.4.1. FT-Infra Red Spectroscopy (FTIR)

One milligram from the freeze-dried coagulants was mixed with 250 mg KBr and the respective pellet was prepared. FTIR spectroscopy was recorded with a PerkinElmer Spectrophotometer and the spectra were recorded in the range of $4000–200\,cm^{-1}$.

2.4.2. X-ray diffraction

Samples of produced PFS powder were characterised by X-ray diffraction (XRD) for the determination of crystalline phases using a Siemens D-500 X-ray diffractometer with Cu K radiation in the range of 5–65° 2θ at a scan rate of 1°/min.

2.4.3. Scanning Electron Microscopy

The morphology of the samples was examined by SEM using a JEOL, JSM 840 scanning microscope.

2.5. Photometric Dispersion Analyzer

The extent of aggregation, as well as the kinetics of coagulation was examined with the aid of Photometric Dispersion Analyzer (PDA 2000, Rank Brothers Bottisham, UK). The PDA instrument measures the ratio R, which are directly related with the mean concentration and size of dispersed particles. The test
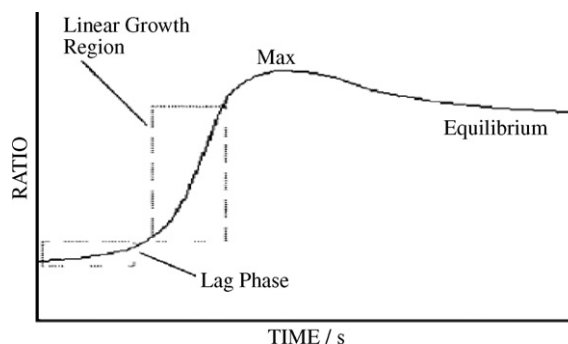

Fig. 1. Schematic representation of the typical ratio R curve.

suspension (1.5 l) was contained into a 2-l beaker and was constantly stirred by a JP SELECTA jar test device. The created microflocs passed through the measuring transparent plastic cuvette (3 mm diameter) with the aid of a peristaltic pump. The applied flow rate was 30 ml/min in order to secure laminar conditions throughout the experiment. The ratio R curves, derived from the PDA instrument have the typical form shown in Fig. 1 [13].

The R curve can be divided into three parts: (A) immediately after the coagulant addition there is a small change in the R values. During this part, which is called "*lag phase*", the destabilisation of the particles takes place. (B) Then, the linear growth region part follows, where the collisions of previously destabilised particles result in aggregate formation. (C) Finally, in the equilibrium phase, the value of the R remains relatively constant as the rate of the formation and the breakage of flocs is rather equal. Generally, it can be concluded that the higher R values imply bigger particles size and therefore, a better separation by the application of subsequent sedimentation.

2.6. Coagulation experiments

The coagulation experiments were carried out using a jar test apparatus with six paddles. Kaolin model suspension and biologically pre-treated municipal wastewater was used as the test suspension, dosed with the appropriate amount of the coagulant. Table 1 summarises the typical properties of the kaolin suspension and of the municipal wastewater. The concentration of the stock kaolin suspension was 5 g/l. The test suspensions were prepared by diluting the stock solution with tap water to concentration of 5 mg/l and 7 NTU. A non-ionic polyacrylamide (product name: Magnafloc LT20, Ciba SC) was used as a flocculant aid. The experimental conditions were the following, as determined by the PDA analysis (Section 3.4) and in accordance with the relevant literature [7,12]: the initial fast mixing time was set to 3 min at the paddle speed of 200 rpm to allow the particles to be destabilised followed by the floccu-

Table 1
Properties of the kaolin suspension and of the municipal wastewater

	pH	NTU	z-Potential	PO_4^- (mg/l)	Conductivity (mS/cm)	UV_{254}
Kaolin suspension	7.0	7	−29	–	0.60	–
Wastewater	7.4	10	−33	3	3.31	0.200

Table 2
PFS samples prepared under different type of base addition (A–C) and under different temperature in the hydrolysis stage (D–F)

	Oxidation stage (i) oxidant; (ii) duration; (iii) temperature	Hydrolysis stage (i) base; (ii) addition rate; (iii) temperature	Polymerisation stage (i) duration; (ii) temperature	Fe total (g/l)	Fe_{pol} (%)	Density (g/l)	pH	$[OH^-]/[Fe]$	Conductivity (mS/cm)	z-Potential
A	(i) HNO$_3$; (ii) 2 h; (iii) 90 °C	(i) NaHCO$_3$ 0.5N; (ii) 0.75 ml/min; (iii) 50 °C	(i) 2 h; (ii) 50 °C	43.5	54	1102,83	1.53	0.32	43	−4.1
B	(i) HNO$_3$; (ii) 2 h; (iii) 90 °C	(i) NaOH 0.5N; (ii) 0.72 ml/min; (iii) 50 °C	(i) 2 h; (ii) 50 °C	59.5	26	1191	1.1	0.12	41,1	−2.7
C	(i) HNO$_3$; (ii) 2 h; (iii) 90 °C	(i) NaHCO$_3$ 1N; (ii) 0.75 ml/min; (iii) 50 °C	(i) 2 h; (ii) 50 °C	52.5	32	1198	1.4	0.21	40	−3
D	(i) HNO$_3$; (ii) 2 h; (iii) 90 °C	(i) NaHCO$_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) 2 h; (ii) 50 °C	47	57	1132	1.4	0.35	46	−1.9
E	(i) HNO$_3$; (ii) 2 h; (iii) 90 °C	(i) NaHCO$_3$ 0.5N; (ii) 1.6 ml/min; (iii) 70 °C	(i) 2 h; (ii) 50 °C	49	54	1144	1.4	0.36	43	−1.9
F	(i) HNO$_3$; (ii) 2 h; (iii) 90 °C	(i) NaHCO$_3$ 0.5N; (ii) 1.6 ml/min; (iii) 90 °C	(i) 2 h; (ii) 50 °C	46	46	1178	1.4	0.34	41	−3.3

lation period (set to 30 min and with paddle speed of 35 rpm) and the final sedimentation period, which lasts for 45 min. After that a supernatant sample (100 ml) was withdrawn for further analysis.

2.6.1. Determination of ortho-phosphate ions concentration

The concentration of orthophosphate is measured by means of the ascorbic acid method [14]. In this method, ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form phosphomolybdic acid, which is reduced to intensely coloured molybdenum blue by ascorbic acid. The coloured solution was measured photometrically at 880 nm with a Schimadzu spectrophotometer.

3. Results and discussion

3.1. Characterisation of the PFS products—evaluation of optimum conditions

Tables 2–4 summarise the typical properties of the PFS products produced in the laboratory. The measurements were conducted after 24 h aging at room temperature.

Table 2 shows that the addition of a strong base (coagulant B) or of a weak base with higher molarity (coagulant C) results in a significant decrease of the degree of polymerisation (Fe_{pol}) and in a shift of z-potential values towards lower negative values, as compared to the coagulant A, which was prepared with a weak base of medium molarity. In addition to this, as it is shown in Table 5, the coagulants B and C were fairly unstable as a rapid precipitation occurred within the following 2 and 3 days, respectively. Moreover, in order to evaluate the effect of temperature in the hydrolysis, coagulants D, E, and F were prepared. It was found that higher temperatures (i.e. 90 °C) result in the decrease of Fe_{pol} and of z-potential values. On the other hand, it is evident that there are no significant differences between coagulants D and E, suggesting that the application of medium temperatures facilitate the formation of polyferric sulphate. However, the temperature of 50 °C is most preferable taking into the account the energy needed to achieve that temperature, which is undoubtedly less than in the case of 70 °C.

Table 3 illustrates the effect of base addition rate on the properties of the coagulants (G–K). It is evident from the data of Table 3 that the lower the rate is, the lower the degree of polymerisation becomes. As Liu and Chian [15] proposed, this is due to the fact that an increase of duration in the preparation of coagulants may facilitate the formation of precipitated and nucleated species of iron in the earlier stages, where the r (r = OH/Fe) values are low. Additionally, Table 3 summarises the properties of the coagulants (L-N) prepared under different r values. As it is shown from the figures, an increase in the r ratio results in a slight increase of the polymerisation degree. However, as the r ratio increases, the stability of products deteriorates leading to the precipitation of amorphous iron hydroxide as shown in Table 5.

Table 4 demonstrates the effect of temperature and of aging time (maturation) on the polymerisation stage. The data of

Table 3
PFS samples prepared under different addition rates of the base solution (G–K) and under different r values (L–N)

	Oxidation stage (i) oxidant; (ii) duration; (iii) temperature	Hydrolysis stage (i) base; (ii) addition rate; (iii) temperature	Polymerisation stage (i) duration; (ii) temperature	Fe total (g/l)	Fe_{pol} (%)	Density (g/l)	pH	$[OH^-]/[Fe]$	Conductivity (mS/cm)	z-Potential
G	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) *7.5 ml/min*; (iii) 50 °C	(i) 2 h; (ii) 50 °C	43.5	54	1102,83	1.53	0.32	43	−4.1
H	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) *3.2 ml/min*; (iii) 50 °C	(i) 2 h; (ii) 50 °C	39	57	1093,45	1.5	0.28	44.4	−4.4
D	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) *1.6 ml/min*; (iii) 50 °C	(i) 2 h; (ii) 50 °C	47	57	1132	1.4	0.35	46	−1.9
I	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) *0.8 ml/min*; (iii) 50 °C	(i) 2 h; (ii) 50 °C	41.1	46	1105,60	1.44	0.36	46.6	−4.1
J	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) *0.4 ml/min*; (iii) 50 °C	(i) 2 h; (ii) 50 °C	46	42	1129	1.43	0.3	46.4	−1.5
K	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) *0.2 ml/min*; (iii) 50 °C	(i) 2 h; (ii) 50 °C	43	42	1120	1.45	0.3	45.5	−2.9
L	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) 2 h; (ii) 50 °C	47	48	1150	1.2	*0.16*	60.6	−3.6
D	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) 2 h; (ii) 50 °C	47	57	1132	1.4	*0.35*	46	−1.9
M	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) 2 h; (ii) 50 °C	49	60	1116	1.5	*0.42*	43.3	−3.1
N	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) 2 h; (ii) 50 °C	43	53	1101	1.7	*0.53*	46.9	−1.8

Table 4
PFS samples prepared under different temperature and duration of the polymerisation stage (D–P) and (D–R), respectively

	Oxidation stage (i) oxidant; (ii) duration; (iii) temperature	Hydrolysis stage (i) base; (ii) addition rate; (iii) temperature	Polymerisation stage (i) duration; (ii) temperature	Fe total (g/l)	Fe_{pol} (%)	Density (g/l)	pH	$[OH^-]/[Fe]$	Conductivity (mS/cm)	z-Potential
D	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) 2 h; (ii) *50 °C*	47	57	1132	1.4	0.35	46	−1.9
O	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) 2 h; (ii) *70 °C*	40	43	1107	1.45	0.32	44	−2.7
P	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) 2 h; (ii) *90 °C*	39	45	1116	1.34	0.2	53	−2.5
D	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) *2 h*; (ii) 50 °C	47	57	1132	1.4	0.35	46	−1.9
Q	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) *4 h*; (ii) 50 °C	46	57	1132	1.4	0.32	46	−2
R	(i) HNO_3; (ii) 2 h; (iii) 90 °C	(i) $NaHCO_3$ 0.5N; (ii) 1.6 ml/min; (iii) 50 °C	(i) *7 h*; (ii) 50 °C	47.5	59	1121	1.5	0.3	44	−2.1

Table 5
The stability of PFS samples

N_o	$[OH^-]/[Fe]$	Stability
A	0.25	/
B	0.12	2[a]
C	0.21	3[a]
D	0.35	/
E	0.36	/
F	0.34	/
G	0.32	/
H	0.28	/
I	0.36	/
J	0.30	21[a]
K	0.30	14[a]
L	0.16	/
M	0.42	124[a]
N	0.53	58[a]
O	0.32	/
P	0.20	/
Q	0.32	/
R	0.30	/

/: No precipitation occurs within 6 months.
[a] Destabilised time (day) – precipitation occurs.

[Table 4](#) suggest that an increase of the temperature at this stage has a detrimental effect on the polymerisation of Fe species, possibly leading to the breakage of Fe−Fe bonds or of Fe−O−Fe bonds. On the other hand, the duration of polymerisation stage has practically no influence on the properties of products whereas the degree of polymerisation, the *z*-potential and the pH values remain steady. Therefore, it can be suggested that the polymerisation yield is not significantly affected by the duration of polymerisation stage of the preparation method due to the active iron species, which are produced during the hydrolysis/polymerisation process.

3.2. Stability of the PFS products

The stability of the samples was observed under room temperature and the results are summarised in [Table 5](#). The results show that when the coagulants were prepared by the addition of NaOH or 1 M NaHCO$_3$, there was a rapid precipitation within the following 2–3 days, although the corresponding *r* value is significantly low. This can be attributed to the fact that during the base addition, the concentration of base can locally exceed the critical value resulting in the formation of iron hydroxide. Consequently, the formed iron hydroxide acts as nuclei on which the further formation of precipitates is facilitated. Additionally, it is worth noting that the majority of the PFS products stand for more than 6 months without any precipitation to be observed. However, for *r* values exceeding 0.4 there were a significant production of precipitate within a time period of 4 months while for *r* > 0.5 precipitates were observed in the PFS product within the following 2 month period. Additionally, [Table 5](#) illustrates that the slow addition rate of the base results in the observation of precipitates in the respective PFS products (J and K) due to the fact described in Section [3.1](#).
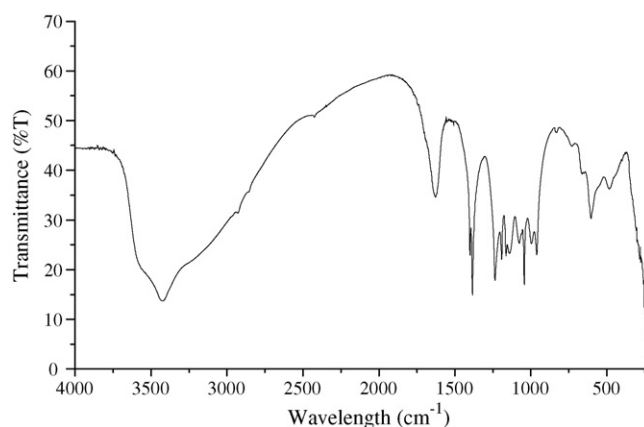

Fig. 2. FTIR spectra of PFS sample (D).

3.3. Structure and morphology analysis

FTIR, XRD and SEM analysis were carried out in order to identify the structure of PFS and, particularly, to elucidate whether the *r* value affects the structure and morphology of PFS and identify any possible connection between the differences in the structure and the stability of the samples. Therefore, coagulants D and M were selected for such a purpose, as they were prepared under the same experimental conditions but they possess a different *r* value, i.e. 0.35 and 0.42, respectively. Additionally, coagulant M is less stable than D, producing precipitates 4 months after its preparation, while coagulant D produces no precipitates for a time period more than 6 months.

3.3.1. FTIR analysis

FTIR spectra of the coagulants D and M are presented in [Figs. 2 and 3](#). Both spectra exhibit two characteristics bonds at 3430–3421 and 1628 cm^{-1}, which can be attributed to the stretching vibration of −OH and to the vibration of water absorbed, or complexed in the coagulant. The different peaks in the region of 1400–1000 cm^{-1} can be assigned to the stretch vibrations of the S=O and/or the O=S=O bonds, which in particular, presents two strong peaks near 1350–1300 cm^{-1}
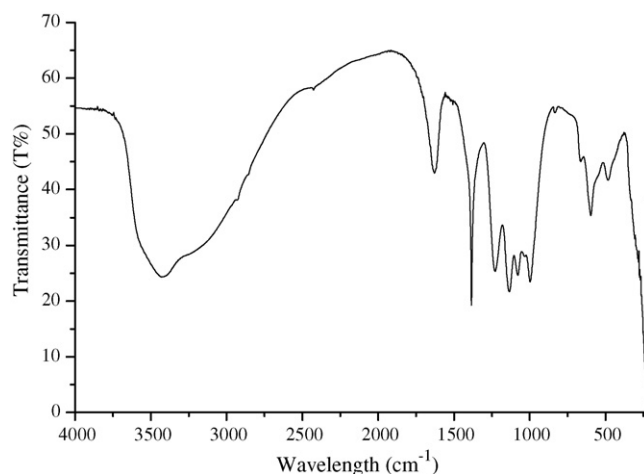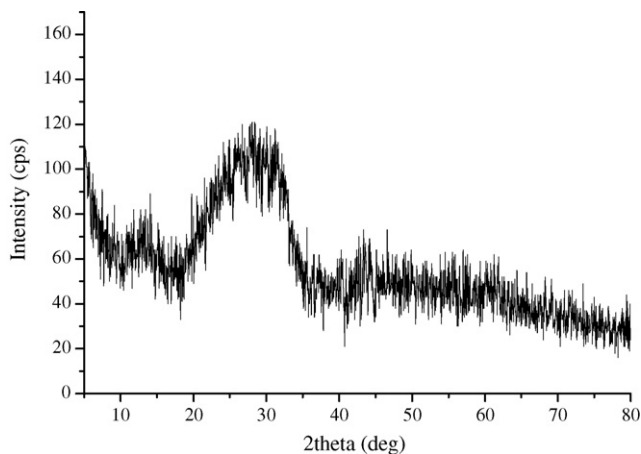

Fig. 3. FTIR spectra of PFS sample (M).

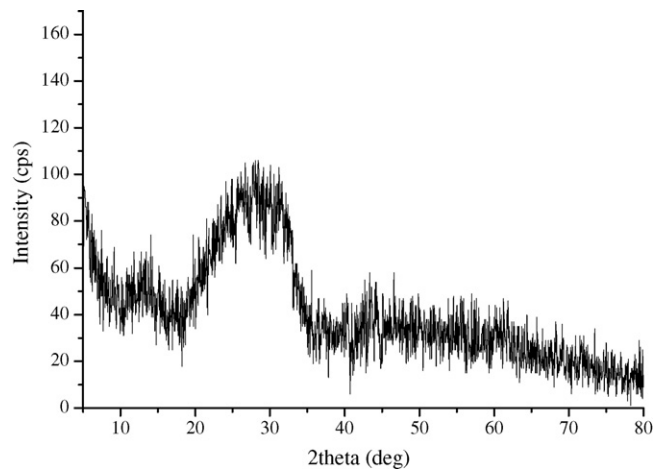Fig. 4. X-ray diffractometer scan of PFS sample (D).

Fig. 5. X-ray diffractometer scan of PFS sample (M).

(asymmetric stretch) and 1160–1120 cm^{-1} (symmetric stretch). Additionally, the sulphates (SO$_4{}^-$) exhibit a very strong band in the range 1130–1080 cm^{-1} and a considerably weaker band in the region 680–610 cm^{-1} [16–18].

They also exhibit a characteristic peak at 825–830 cm^{-1}, which is attributed to the Fe−OH−Fe oscillation peak, while the characteristic peak around 500 cm^{-1} are assigned to the stretch vibration of Fe−O bond. It is worth noting that the ferric ions (Fe(III)) are octahedrally coordinated by OH$^-$ in acidic environment, as Flynn [19] recorded. In conclusion, the experimental findings indicate that there is no significant difference in the structure of the samples as both spectra exhibits similar peaks of the same magnitude.

3.3.2. XRD and SEM analysis

As illustrated in Figs. 4 and 5, X-Ray diffraction studies indicate that PFS samples D and M have a largely amorphous structure with small traces of crystallinity. This observation is also supported by the examination of Scanning Electron Microscopy. As shown in Fig. 6, the PFS samples D and M behave as an amorphous material in general, randomly forming aggregates of various sizes and shapes.

Overall, the FTIR, XRD and SEM analysis of PFS samples indicate that the *r* value has no effect on the structure and morphology of the samples and, consequently, the deterioration of stability, caused by the increase of *r* value, is not due the different chemical structure.

3.4. Study of kinetics of the coagulation using the PDA

3.4.1. Effect of mixing speed (or velocity gradient G (s^{-1})) in the kinetics of coagulation

The effect of speed during the initial fast mixing period on the coagulation process is shown in Fig. 7. The mixing speed is expressed in rpm, as well as in velocity gradient units G (s^{-1}). The test suspension is kaolin suspension (5 mg/l) and the coagulant used is PFS D (coagulant dosage: 5 mg/l as Fe). For the mixing speed of 200 rpm, the "lag" phase is limited and this results in a faster flocculation. Additionally, a relatively higher speed of coagulation is achieved and the final flocs after the equilibrium of the system have a larger size. In the contrary, for the initial mixing speed of 160 rpm, the "lag" phase is larger and therefore the formation of destabilised microflocs is delayed. The coagulation of suspended particles proceeds in lower speed
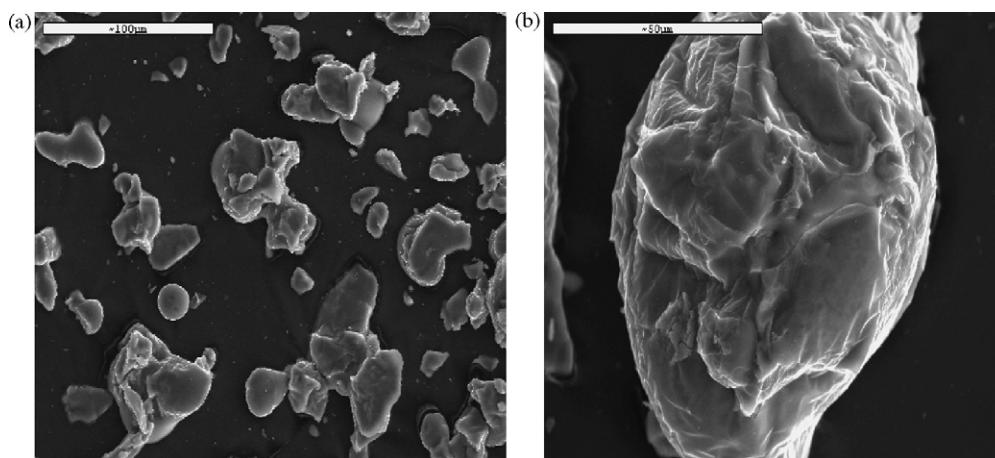

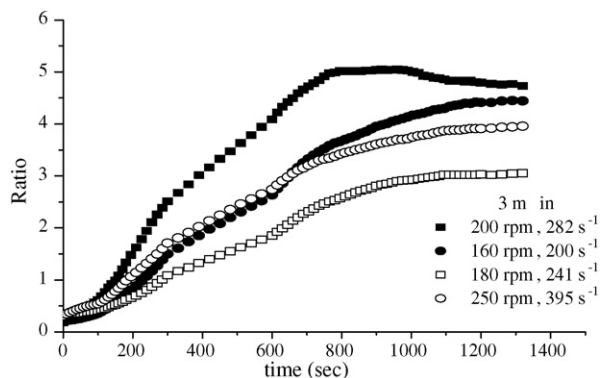Fig. 6. SEM microphotographs of PFS samples (D and M).

Fig. 7. Impact of fast mixing speed (or velocity gradient G (s^{-1})) on the coagulation of kaolin suspension (5 mg/l); PFS 5 mg/l, pH 7.

and the final size of flocs is smaller. The same happens in the case of very high mixing speed (250 rpm). The small size of flocs is due to the fact that the smaller flocs, which are formed during the fast mixing period, are destroyed by the shear stress which develops during that stage and therefore, it is impossible to obtain a bigger size in the coagulation stage.

3.4.2. Effect of mixing time in the kinetics of coagulation process

Fig. 8 illustrates the effect of mixing time in the kinetics of coagulation process. The test suspension is kaolin suspension (5 mg/l) and the coagulant used is PFS D (coagulant dosage: 5 mg/l as Fe). The speed in the fast mixing stage is 200 rpm, which found to be the optimum as shown in the previous section 3.4.1. The higher values of ratio, which correspond to the bigger size of formed flocs, were achieved, when the initial fast mixing time was 180 s. It is worth noting that the "lag" phase in both cases is similar and the fact which distinguishes the two curves is the bigger size of the flocs in the slow mixing period. On the other hand, the fast mixing time of 60 s seems to be inadequate as the lag phase is significantly bigger than in the previous cases, while the low *R* values suggest that the size of flocs are undoubtedly smaller, than in the case of 120 and 180 s.
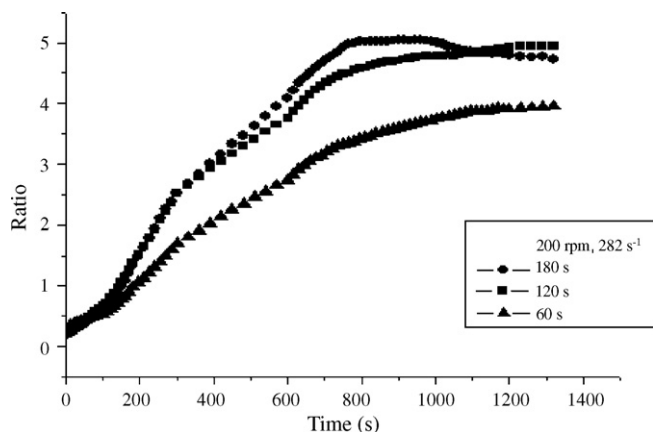

Fig. 8. Impact of time during the initial fast mixing period on the coagulation of kaolin suspension (5 mg/l); PFS 5 mg/l, pH 7.

3.5. Evaluation of coagulation efficiency

3.5.1. Comparative jar tests for the removal of turbidity

Section 3.5.1 discusses the performance of produced coagulants in removing the turbidity of a kaolin suspension and, particularly, investigates the effect of polymerisation degree in the coagulation efficiency. In the jar tests, the coagulants were used in concentrations 1–6 mg/l as Fe and the polyelectrolyte used was Magnafloc LT20, in concentrations equal to 1/10 of the coagulant concentration each time. Overall, it is worth noting that the degree of polymerisation of each coagulant is the most significant factor, which influences their coagulation efficiency. In particular, it is concluded that the lower the degree of polymerisation is, the higher the turbidity that remains in the suspension. Thus, it is suggested that the presence of polymeric species will enhance the coagulation efficiency due to the fact that longer molecular chains not only carries a higher cationic charge, but also provides a suitable substrate for the adsorption of colloidal matter, as well as facilitate the formation of aggregates. This conclusion is in total agreement with that withdrawn from previous researches [7,11,20], therefore no further details including the respective figures and tables are presented in this paper.

3.5.2. Application of PFS in biologically pre-treated municipal wastewater for the removal of phosphate ions

Coagulation experiments were also conducted for the evaluation of PFS capability to treat biologically pre-treated municipal wastewater, mainly for the removal of phosphate ions, as well as turbidity and of NOM (expressed as absorbance at 254 nm). The wastewater used for these tests was received from the exit of the biological treatment plant of Thessaloniki, Greece. Due to analytical limitations only the coagulants with the higher degree of polymerisation were applied to the treatment of this wastewater. In particular, the PFS samples used were the following: PFS D, G, H and M. In the jar tests, the coagulants were used in concentrations 5, 10, 20, 30 mg/l as Fe and the polyelectrolyte used was Magnafloc LT20, in concentrations equal to 1/10 of the coagulant concentration each time. In order to compare the efficiency of PFS samples, similar experiments were conducted by using the conventional non-polymerised coagulant, ferric sulphate. The results are illustrated in Fig. 9. It is of paramount importance to note that the pH of raw water after the coagulation treatment remains relatively steady (around neural pH) regardless of the coagulant dosages and the different reagents.

As far as the removal of phosphate ions is concerned the highest removal percentage was achieved when the PFS samples M and H were applied, while the ferric sulphate solution exhibits the worst performance. Furthermore, the higher the applied coagulant dosage was, the higher the removal percentage achieved. However, the objective of this treatment was not only to achieve the highest removal percentage, but simultaneously to lower the concentration of the phosphate ions below 1 mg/l, which is the limit concentration value in wastewaters to be discharged in sensitive to eutrophication surface waters, according to the respective legislation [21]. In particular, the treatment of wastewater with PFS (D, H, M) samples, led to
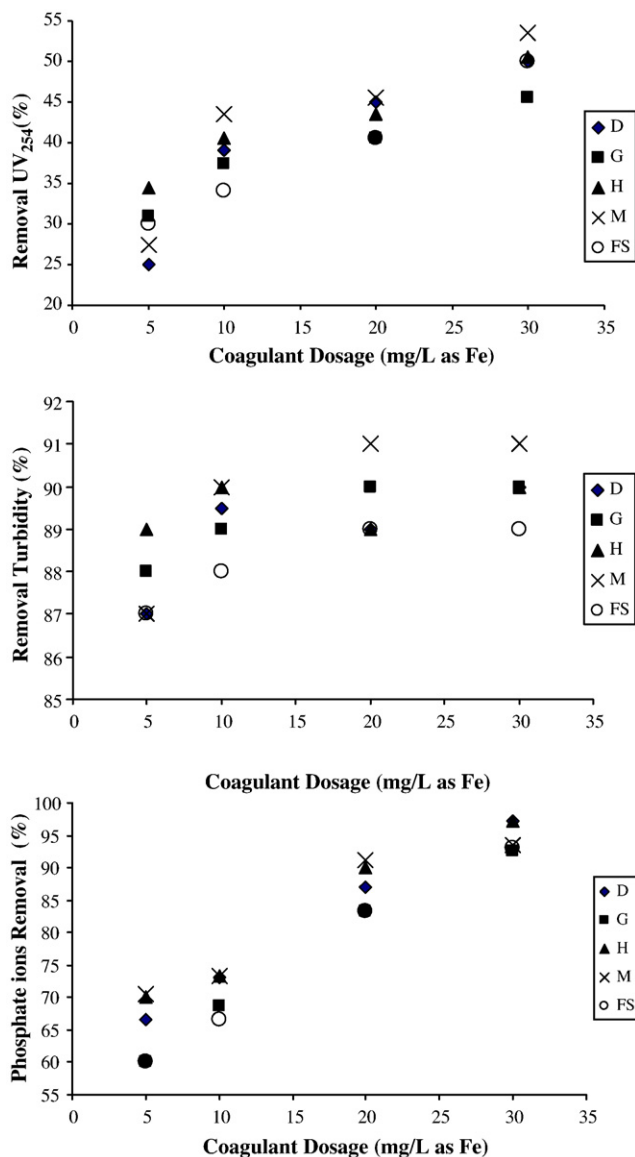
Fig. 9. Comparative results regarding the treatment of biologically pre-treated municipal wastewater for the removal of phosphates. (PFS 5, 10, 20, 30 mg/l; polyelectrolyte addition equal to 1/10th of the coagulant dosage, pH 7.4).

the successful removal of phosphate ions (well below 1 mg/l) even with the lower applied coagulant dosages (5 mg/l). On the contrary, the respective ferric sulphate dosage required to achieve residual phosphate ions concentration below the limit was higher than 10 mg/l, highlighting the superior performance of the pre-polymerised coagulants under the specific experimental conditions, notably around neutral pH, low coagulants dosages (<35 mg/l) and certain initial phosphate ions concentration.

Such findings might shed a light on the mechanism through which the removal of phosphate ions takes place. At pH value 7, where the coagulation experiments were conducted, the Fe^{3+} ion hydrolyses rapidly, forming ultimately an iron hydroxide. So, in the case of a conventional coagulant such as ferric sulphate, amorphous $Fe(OH)_3$ are the main hydrolysis species and due to reduced cationic charge the mechanism of removal of PO_4^{3-}

ions is the adsorption of them onto the surface of these species. On the contrary, in the case of pre-polymerised coagulants such as PFS, a wide range of polymeric species are predominant and the removal of PO_4^{3-} ions takes place through a combination of two mechanisms as the polymeric species not only provide a surface for adsorption, but also carry sufficient cationic positive sites for forming Fe–hydroxo-phosphate complexes [5].

It is evident, through the experimental results that the removal of phosphate ions are not completely attributed to the chemical reaction forming an insoluble compound, but it is also due to the adsorption of PO_4^{3-} ions onto the various Fe polymeric species, otherwise the conventional coagulant (FS) should have exhibited similar or better performance than the PFS under the specific experimental conditions. Therefore, as the PFS coagulants consist mainly of polymeric species, they exhibit better coagulation behaviour. It is worth noting that for a 90% removal efficiency, only 20 mg/l of PFS are required, whereas the respective dosage of ferric sulphate in this case is much higher, i.e. 30 mg/l. Overall, PFS is highly efficient in removing the phosphate ions and, particularly, achieving the limit concentration in wastewater to be discharged in sensitive areas, even with the lower applied dosage, thus illustrating the potential of PFS for efficient employment in the tertiary treatment of municipal wastewater.

Additionally, Fig. 9 presents the coagulation behaviour of PFS in terms of removing the turbidity and the NOM (expressed as UV_{254}). In both cases, the PFS coagulants exhibit a markedly better performance, than the conventional coagulant under the specific experimental parameters, i.e. around neutral pH, low dosages of coagulants and initial NOM concentration of the wastewater. As it is expected, the higher the coagulant dosage is, the better the coagulation performance is, although, in respect of turbidity removal, the increase of coagulant dosage from 20 to 30 mg/l as Fe produces no further improvement. However, it should be noticed that the removal of NOM is not sufficient enough, compared with the removal of the other parameters, regardless of the coagulant dosage and that should be a new objective for the further improvement of PFS coagulants.

4. Conclusions

The main conclusions withdrawn from this study are as follows:

1. Certain parameters, such as the rate of base addition, the duration and temperature of the polymerisation stage and the r value significantly affected the formation and the properties of the PFS products. The optimum preparation conditions as determined from this study are: usage of 0.5 M $NaHCO_3$ solution as a base reagent, medium temperature (50 °C) at the hydrolysis stage, addition rate of the base reagent equal to 1.6 ml/min, ratio $r = 0.3$, temperature and duration of polymerisation stage 50 °C and 7 h, respectively. The coagulant produced under these conditions has a high degree of polymerisation, higher z-potential values, exhibits superior coagulation efficiency than the other prepared samples and the respective conventional non-polymerised reagent and is very stable as no precipitates observed for more than 6 months.

2. The presence of polymeric species in the coagulant significantly affects its coagulation performance. It is suggested that the higher the degree of polymerisation is, the higher the coagulation efficiency is in both treating kaolin suspension for the removal of turbidity and biologically pre-treated municipal wastewater mainly for the removal of phosphate ions.

3. A structure and morphology analysis of PFS samples, carried out by FTIR, XRD spectra and SEM microphotos, indicate that the *r* value has no effect on the structure and morphology of the samples and, consequently, the deterioration of stability, caused by the increase of *r* value, is not due the different chemical structure.

4. PFS is highly efficient in removing the phosphate ions from biologically pre-treated municipal wastewater. Moreover, PFS samples exhibit a significantly better coagulation performance, than the respective conventional coagulant, i.e. ferric sulphate, in treating such a wastewater under the applied experimental conditions. In particular, treating the wastewater with certain PFS samples removed the phosphate ions successfully (well below 1 mg/l, which is the limit concentration in wastewaters to be discharged in sensitive areas) even by using the lower coagulant dosages (5 mg/l). On the contrary, the ferric sulphate dosage required for achieving a phosphate ions concentration below this limit was higher than 10 mg/l, highlighting the superior performance of the pre-polymerised coagulants. Additionally, treating the wastewater with PFS results also in better removal of turbidity, as well as of reducing the NOM concentration, when compared to that achieved by employing a conventional coagulant, for the given experimental conditions, i.e. around neutral pH and low dosages of coagulants (<35 mg/l) and certain initial NOM concentration.

Acknowledgements

References

[1] B. Dempsey, R. Ganho, C. O'Melia, The coagulation of humic substances by means of aluminium salts, J. Am. Water Works Assoc. 76 (1984) 141–149.

[2] A. Leprince, F. Flessinger, J.Y. Bottero, Polymerised iron Chloride: An improved inorganic coagulant, J. Am. Water Works Assoc. 76 (1984) 93–97.

[3] N. Parathasarathy, J. Buffle, Study of polymeric aluminium (III) hydroxide solutions for application in wastewater treatment, Water Res. 19 (1) (1985) 25–36.

[4] H.X. Tiang, B.Z. Tian, Z.K. Luan, Y. Zhang, Inorganic polymer flocculant polyferric chloride, its properties, efficiency and production, in: H. Hahn, R. Klute (Eds.), Chemical Water and Wastewater Treatment, vol. III, Springer–Verlag, Berlin, Germany, 1994, pp. 57–69.

[5] J.-Q. Jiang, N.J.D. Graham, Pre-polymerised inorganic coagulants and phosphorus removal by coagulation—a review, Water SA 24 (3) (1998) 237–244.

[6] Q. Chang, H. Wang, Preparation of PFS coagulant by sectionalised reactor, J. Environ. Sci. 14 (3) (2002) 345–350.

[7] J.-Q. Jiang, N.J.D. Graham, Coagulation of upland coloured water with polyferric sulphate compared to conventional coagulants, J. Water Supply Res. Technol. 45 (3) (1996) 143–154.

[8] J.-Q. Jiang, N.J.D. Graham, Observations of the comparative hydrolysis/precipitation behavior of polyferric sulphate and ferric sulphate, Water Res. 32 (3) (1998) 930–935.

[9] S. Hendrich, M. Fan, S. Sung, R.C. Brown, R. Semakaleng, G. Myers, Toxicity evaluation of polymeric ferric sulphate, Int. J. Environ. Technol. Man. 1 (2001) 464–471.

[10] J.-Q. Jiang, N.J.D. Graham, Preparation and characterisation of an optimal polyferric sulphate (PFS) as a coagulant for water treatment, J. Chem. Technol. Biot. 73 (1998) 351–358.

[11] W.P. Cheng, Comparison of hydrolysis/coagulation behavior of polymeric and monomeric iron coagulants in humic acid solution, Chemosphere 47 (2002) 963–969.

[12] M. Fan, S. Sung, R.C. Brown, T.D. Wheelock, F.C. Laabs, Synthesis, characterization and coagulation of polymeric ferric sulphate, J. Environ. Eng. 128 (6) (2002) 483–490.

[13] D. Hopkins, J. Ducoste, Characterising flocculation under heterogeneous turbulence, J. Colloid Interface Sci. 264 (2003) 184–194.

[14] L. Clesceri, A. Greenberg, R. Trussell, Standard Methods for the Examination of Water and Wastewater, 17th ed., APHA-AWWA-WEF, Washington DC, 1989.

[15] T.K. Liu, E.S.K. Chian, Effect of base addition rate on the preparation of partially neutralised ferric chloride solutions, J. Colloid Interface Sci. 284 (2005) 542–547.

[16] L.J. Bellamy, The Infra-Red Spectra of Complex Molecules, John Wiley, New York, 1975.

[17] K. Nakanishi, Infrared Absorption Spectroscopy, Holden-Day, San Francisco, 1977.

[18] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley, New York, 1997.

[19] C.M. Flynn, Hydrolysis of inorganic iron (III) salts, Chem. Rev. 84 (1984) 31–41.

[20] W.P. Cheng, Hydrolytic characteristics of polyferric sulphate and its application in surface water treatment, Sep. Sci. Technol. 36 (10) (2001) 2265–2277.

[21] Greek National Legislation, "ΦΕΚ 82B/10-2-94".