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Advances in coagulation/flocculation field: Al- and Fe-based composite coagulation reagents

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ABSTRACT

Currently, the research in the field of coagulation/flocculation process is focused on the synthesis of new composite coagulants, which are constituted of both inorganic and organic materials, so as to utilize within one reagent the advantages of both inorganic and organic components. Among possible organic additives, an anionic polymer can be used by introducing it into a pre-polymerised metal (i.e. Al or Fe) coagulant. In this study, a co-polymer of acrylamide and sodium acrylate is combined with two widely used Al or Fe based coagulants, i.e. polyaluminium chloride (PACl), and polyferric sulphate (PFS), thus producing novel composite coagulation reagents. The coagulants were characterised in terms of typical physico-chemical properties, such as the degree of polymerisation, pH, conductivity, turbidity. Finally, coagulation experiments (jar-tests) enable the comparable assessment/evaluation of coagulants efficiency, when treating model kaolin-humic acid suspensions or pre-treated tannery wastewater.

Keywords: Coagulation; Composite coagulants; Polyaluminium chloride; Polyferric sulphate; Anionic polymer

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 a cation will result in colloidal destabilisation, as they specifically interact with the negatively charged colloids and neutralise their charge. Highly charged cations, such as Al^{3+} and Fe^{3+}, are regarded as the most effective cations for such a purpose. Therefore, there are a number of conventional coagulants based on aluminium and iron such as the $Al_2(SO_4)_3$, $AlCl_3$, $Fe_2(SO_4)_3$ and the $FeCl_3$. During the last decades, the increasing demand of more efficient coagulation treatment, especially regarding the removal of NOM, has lead to the development of a new category of coagulants, the inorganic polymeric flocculants (IPFs), e.g. polyaluminium chloride (PACl), polyferric sulphate (PFS), etc. Their properties were intensively examined and it has been proved that they are more efficient in lower dosages, in natural organic matter (NOM) removal, in greater pH, temperature and colloids concentration range than the conventional non-polymerised ones, resulting in more cost-effective treatment [1]. However, despite their efficiency, IPFs are still inferior to the organic polymeric flocculants, , mainly regarding their aggregation/floc-

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culation abilities. Currently, research is focused on the synthesis/improvement of new composite coagulants, either by optimising the preparation conditions or, mainly, by adding appropriate additives with desired properties, such as polysilicic acid, organic polymers etc. [2,3]. Under this framework, the synthesis of new composite coagulants, which are constituted of both inorganic and organic materials (mainly used as flocculant aids, [4,5]) so as to utilize within one reagent the advantages of both inorganic and organic components and increase their efficiency in treating water and/or wastewater, has been attracted increasing attention. Possible additives may be classified into three categories as follows:

(i) Cationic: e.g polydimethyldiallylammonium chloride (p-DADMAC)
(ii) Anionic: e.g polyacrypamide co-polymers with acrylic acid
(iii) Non-ionic: e.g. several types of polyacrylamides

In this paper, the development of such novel reagents of both aluminium and iron is investigated by combining an inorganic pre-polymerised metal (Al or Fe-based) coagulant with an organic, anionic polymer (polyacrylamide co-polymer, AP) under different [AP]/[metal] (mg/L) ratios. Anionic polymer is a synthetic polymer which has been widely used in water treatment applications (Magnaflock LT-25). These applications include use as a coagulant/flocculant aid for water and wastewater clarification and filtration and thickening of coagulant sludge [6]. The produced composite coagulants were characterised in terms of typical properties, such as the degree of polymerisation, pH, conductivity, turbidity. Finally, coagulation experiments (jar tests) were conducted in order to evaluate the efficiency of the prepared coagulants.

2. Material and methods

2.1. Preparation of Fe and Al coagulants

Firstly, the preparation of the inorganic pre-polymerised polyferric sulphate (PFS) under the r = OH/Fe molar ratio of 0.25 was accomplished. Then, to prepare PFS-APm composite coagulants with the desired AP/Fe ratios, a predetermined amount of water-based polyacrylamide co-polymer (AP) solution was injected into PFS stock solution (0.09 M) at a rate of 0.4 ml/min under magnetic stirring at temperature of 50°C to prevent the formation of insoluble products. Four new coagulants were prepared with AP/Fe ratio equal to 0.02, 0.05, 0.10 and 0.15 and r = 0.25. The concentration of the final products was within the range of 0.04–0.07 M (as Fe).

In the case of Al-based composite coagulants, firstly intermediate PACl solutions were prepared according to the following procedure: a predetermined amount of 0.5 M $AlCl_3.6H_2O$ solution was placed in a beaker on a magnetic stirrer (Al solution). Appropriate amount of 0.5 M NaOH solution in order to achieve the desired OH/Al = 1 molar ratio was slowly added (addition rate 0.1 ml/min) in the aluminium solution under intensive stirring. Then, the appropriate amount of AP was slowly added (addition rate 0.2 ml/min) as water solution under magnetic stirring in the PACl solution (temperature 50°C). The concentration of the final products was 0.1 M (as Al). The coagulants are referred in the text as follows: composite coagulant with e.g. Al/AP = 10 and OH/Al = 1 as PACAP 1/10 and PACl with OH/Al = 1 as PACl 1.

The polyelectrolyte used is a common anionic polyacrylamide (Magnaflock LT25, Ciba SC LTD, commercially available), which is used widely in the water and wastewater treatment facilities in Greece. For comparison purposes, laboratory prepared PFS and PACl with OH/Metal molar ratios of 0.25 and 1 respectively were used.

2.2. Characterisation of coagulants

The pH, conductivity and turbidity measurements were performed by using a Metrohm Herisau pH-Meter, a Crison CM 35 conductivemeter and a HACH RATIO/XR Turbimeter, respectively. The degree of aluminium and iron polymerisation and the contribution of polymeric species were determined by means of the ferron-timed spectroscopy method. According to this method, the metal (M) species can be classified into three categories, i.e. as M_a (oligomers), M_b or $M_{(pol)}$ (medium polymers) and M_c (large polymers). It is well established that the medium metal polymers (M_b or $M_{(pol)}$) contribute to the improvement of pre-polymerized coagulants efficiency [7,8].

2.3. Coagulation experiments

The coagulation experiments were carried out using a jar test apparatus with six paddles (Aqualytic). Two different samples were treated with the prepared coagulants, i.e. surface water and wastewater. In the case of Fe-based coagulants, the aqueous solution to be treated was kaolin–humic acid model suspension (5 mg/L of both kaolin and humic acid), simulating surface water. The Al-based coagulants were applied in wastewater treatment, and particularly in the post-treatment of the effluents of a tannery wastewater treatment facility. The properties of the test suspensions are summarised in Table 1, whereas the coagulation experiments conditions are given in Table 2. At the end of the experiments, a supernatant sample (100 ml) was collected for further analysis.

The coagulation efficiency of the iron based composite coagulants was compared to the respective coagulation performance of PFS and of the simultaneous addition of PFS and AP (at a ratio of AP/Fe = 0.10) as separated reagents. The coagulation efficiency was evaluated in terms of removal of turbidity, removal of humic acid content (expressed as UV_{254nm} absorbance) and concentration of residual iron.

Table 1
Properties of the samples to be treated

Type of sample to be treated	Turbidity (NTU)	Absorbance at UV_{254}	pH	Phosphates (mg/L)	Conductivity (mS/cm)
Simulated surface water	9.00–10.0	0.110–0.120	7.80–8.00	—	0.72
Wastewater	250	4.500	8.00	5.9	15.87

Table 2
Coagulation experiments conditions (surface and wastewater treatment)

Type of treatment	Rapid mixing period		Slow mixing period		Sedimentation (min)
	Duration (min)	Mixing rate (rpm)	Duration (min)	Mixing rate (rpm)	
Simulated surface water	3	200	25	40	45
Wastewater	3	200	30	40	45

In the case of Al-based composite reagents, the coagulation efficiency was compared with the respective performance of the combined addition of AP and PACl (OH/Al = 1), but as separated reagents. The addition of AP was accomplished 15 s before the beginning of the slow mixing stage. The coagulation performance was assessed by the determination of removal of turbidity, removal of organic matter (expressed as UV_{254nm} absorbance), removal of phosphate ions (o-phosphate) and final conductivity of the sample.

Absorbance at 254 nm as a convenient indicator of organic matter presence was measured with a Schimadzu UV/Vis spectrophotometer using a 1 cm path length quartz cuvette, while the residual turbidity was measured by a HACH RATIO/XR Turbimeter. The concentration of phosphates was determined with the ascorbic acid method, according to APHA [9], while the residual dissolved iron concentration was determined by means of atomic absorption spectroscopy, after filtration by 0.2 μm membrane (Perkin Elmer, AAnalyst 400).

2.4. *Study of coagulation kinetics*

The coagulation dynamics as well as the extent of aggregation was studied by using a continuous flow optical flocculation monitor (PDA 2000, Rank Brothers, UK). The test suspension of 1.5 L tap water, containing 5 mg/L kaolin and 5 mg/L humic acid, was placed in a 2 L beaker and stirred with the paddle of a jar-test apparatus. The suspension flows through the measuring transparent plastic cell (with 3 mm diameter), where it was illuminated by a narrow light beam (of 850 nm wavelength), with the help of a peristaltic pump. The pump was placed after the PDA apparatus for preventing the eventual floc breakage caused by the mechanical forces of the pump. The applied flow rate was 30 mL/min in order to have laminar conditions in the sampling tube, hence avoiding flocs breakage. Concentration of coagulants was 6 mg/L and pH 7.75 (initial). The PDA instrument measures the *R* values, which are directly related with the mean concentration and size of dispersed particles. Therefore,

Table 3
Typical properties of Fe- and Al-based coagulants

Fe-based coagulants PFS – AP_m					Al-based coagulants				
[AP]/[Fe]	Fe_{pol} (%)	pH	Turbidity (NTU)	Conductivity (mS/cm)	[Al]/[AP]	Al_{pol}* (%)	pH	Turbidity (NTU)	Conductivity (mS/cm)
0 (PFS)	14	1.93	1.5	17.6	0 (PACl)	31	3.91	0.9	24.5
0.02	13	2.00	4.5	15.4	20	30	3.97	3.1	24.1
0.05	13	2.00	6.3	14.8	15	27	4.00	4.6	23.5
0.10	12	2.05	6.5	14.1	10	25	4.05	7.0	23.2
0.15	12	1.96	6.5	13.0	—	—	—	—	—

* corresponding to medium size Al polymers, e.g. Al_{13} (Al_b according to ferron method)

the *R* value can be effectively utilized to describe the aggregation progress of the particles [10]. Generally, it is worth noting that the higher *R* values imply bigger particles size for a given suspension.

3. Results and discussion

3.1. Properties of the prepared coagulants

Table 3 shows the typical properties of the reagents produced in the laboratory. The measurements were conducted after 24 h aging at room temperature.

The degree of metal polymerisation was determined by means of the ferron-timed spectroscopy method. The data of Table 3 suggests that the addition of AP has a minor influence on the degree of iron polymerization, as the respective values remain almost steady. Additionally, it is worth mentioning that a minor increase of turbidity values is also noted, however, this increase is not associated with any observed precipitate within the solution of the prepared coagulants. Additionally, the pH remains almost constant regardless of the applied AP/Fe ratio during the preparation stage, thus allowing the direct comparison between those reagents.

Regarding the Al-based coagulants, it can be seen from Table 3 that the addition of AP results in a small decrease of Al_{pol} content, in contrast to Fe-based coagulants. The interaction of AP and Al species is thought to be responsible for this behaviour, leading to the formation of larger Al species (i.e. Al_c). The existence of larger Al species in the composite coagulants is also evident from the increase of turbidity in the composite coagulants compared to PACl. It should be mentioned that this increase is not due to solids formation, as the solutions remain clear liquids. Finally, the pH and conductivity are affected in a relatively small extent (slight increase and decrease respectively).

3.2. Evaluation of coagulation efficiency

3.2.1. Treatment of simulated surface water

Fig. 1a illustrates the coagulation performance of composite coagulation reagents PFS – AP_m, $r = 0.25$, AP/Fe = 0.02, 0.05, 0.10, 0.15. For comparison reasons the respective coagulation performance of simple PFS and of mixed PFS + AP (as separated reagents) is also included.

Regarding turbidity removal (Fig. 1a), the best coagulation performance was achieved with the coagulant PFS –AP_m, $r = 0.25$ and AP/Fe = 0.10 for a dosage equal to 8 mg/L as Fe. Overall, the composite coagulants PFS – AP_m is more efficient that the non-modified PFS, for all coagulant dosages, except for the coagulant with AP/Fe = 0.10, which for low applied dosages exhibits a slightly worse performance than PFS.

Regarding the removal of organic content (Fig. 1b), it is evident that the composite coagulants PFS – AP_m exhibits a highest efficiency compared to the non-modified PFS for all applied coagulant dosages. The best performance is again achieved with the coagulant PFS – APm, r = 0.25 and AP/Fe = 0.10 for a dosage equal to 8 mg/L as Fe. Fig. 1c illustrates the residual iron concentration after the coagulation process. It is concluded that for almost all cases the level of iron concentration is below the legislation limit for potable water (0.20 mg/L Fe) (EC Directive, 1998).

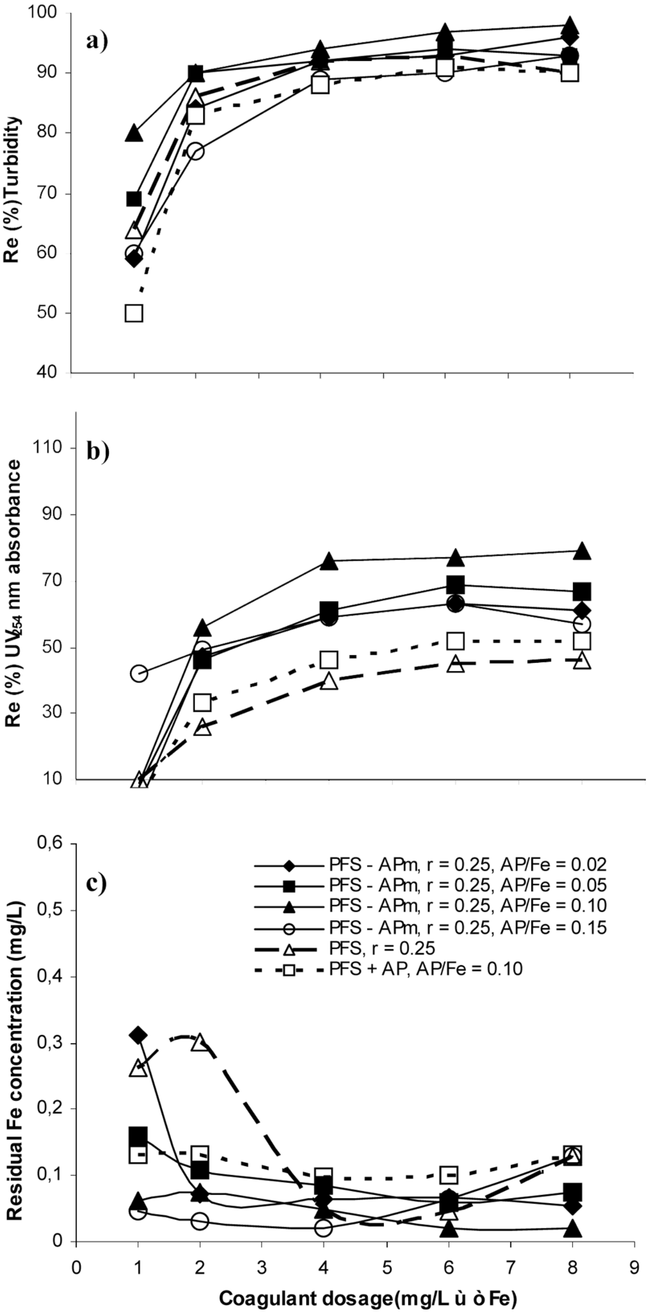

Fig. 1. Comparative coagulation performance of PFS-AP_m, PFS and PFS + AP samples for a kaolin–humic acid suspension.

Finally, in comparison with the mixed PFS + AP, it is evident that the composite coagulants PFS – AP_m exhibit a better performance in terms of removal of turbidity and organic matter, even for the cases that the composite coagulants contain a lower concentration of anionic polymer (e.g. PFS – AP_m with AP/Fe = 0.02 and 0.05). The latter confirms the suggestion that the properties and eventually the coagulation efficiency of the composite coagulants PFS – AP is not the simple sum of the properties of each reagent but that the various interactions occurred during the optimised preparation process between the reagents result in the improvement of the coagulation efficiency.

3.2.2. Treatment of wastewater

Fig. 2 displays the results of the coagulation experiments with Al-based coagulants regarding the post-treatment of biologically pre-treated tannery effluents. Regarding turbidity removal (Fig. 2a), it can be seen that the composite coagulants exhibit better performance, than PACl and AP as separated reagents for all the applied concentrations. Between the composite coagulants, PACAP 1/15 seems to be more effective, especially in relatively low dosage (i.e. 100 mg/L). Organic matter removal (expressed as UV absorbance at 254 nm, Fig. 2b) is also higher with the use of the composite coagulants. In this case, it can be observed that all composite coagulants exhibit similar behavior, with the PACAP 1/10 showing a slightly better performance, than the other composite coagulants. Regarding phosphates, it can be seen from Fig. 2c that for all the tested coagulants their removal rate is over 90%, even with relatively low concentration of coagulants (i.e. 100 mg/L). Removal rate over 90% corresponds to final phosphates concentration lower than 1 mg/L, which is the respective legislation limit for ecologically sensitive areas. However, again the composite coagulants exhibit better performance, than PACl and AP, with the PACAP 1/15 to be slightly more effective, achieving removal rate of 99% for the highest coagulant dosage applied (i.e. 250 mg/L). Fig. 2d illustrates the variation of the samples conductivity after the treatment with all the tested coagulants. It can be noticed that the application of all coagulants results in an increase in the samples conductivity. This increase is more intense in the case of the composite coagulants.

It should be mentioned that the AP was used in a ratio (w/w) of 1:20 compared to PACl (application as separated reagents). This ratio resulted after preliminary experiments (data not shown), which showed that use of higher concentrations of AP leads to excessive sludge production and worsening of the coagulation performance.

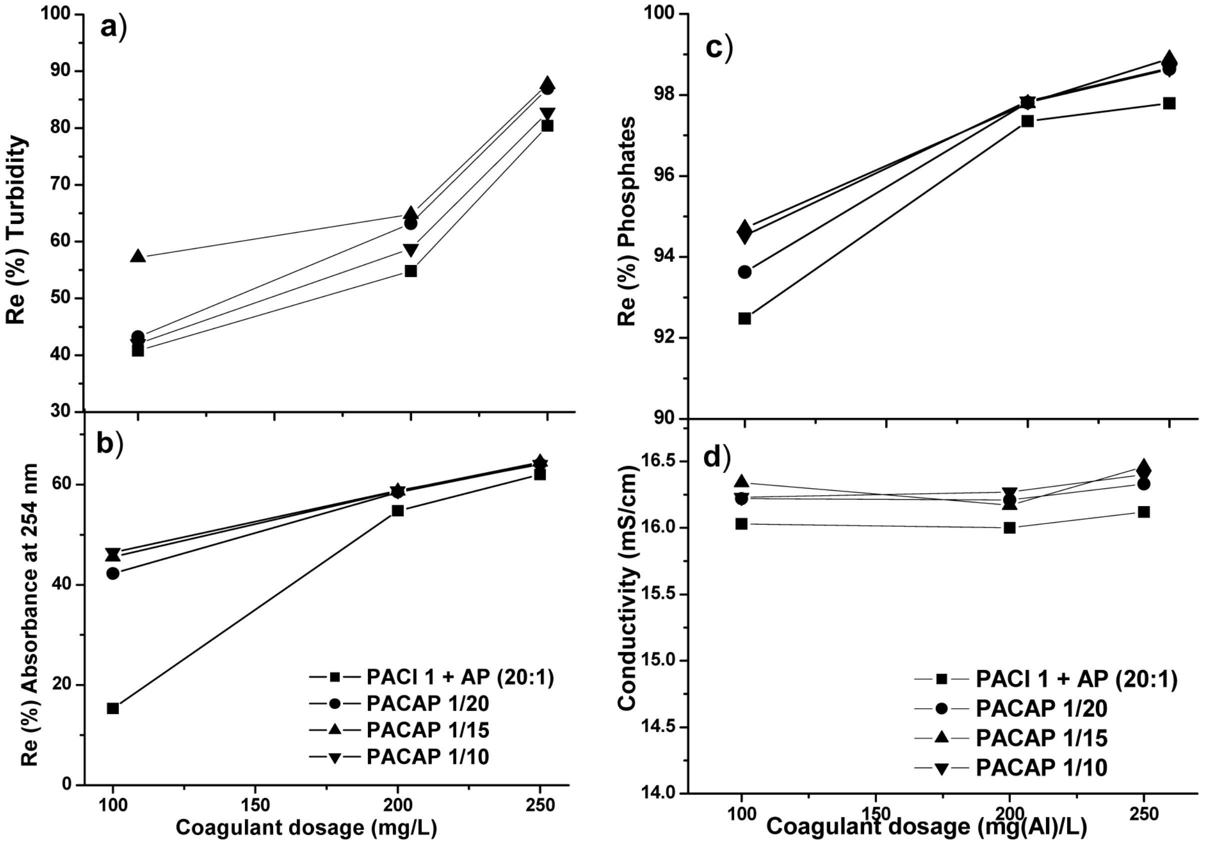

Fig. 2. Comparative coagulation performance of PACl 1 and several composite Al-based coagulants for the post-treatment of biologically pre-treated tannery effluents.

Comparing the treatment efficiency of PACl and AP as separated reagents with the respective performance of PACAP 1/20 (same AP concentration), it can be seen that the composite coagulant is superior in all examined cases. Moreover, with the composite coagulants it is possible to use higher amounts of AP, in order to improve the treatment performance.

3.3. Coagulation kinetics

The effect of AP/Fe ratio on the coagulation kinetics, as well as on the extent of aggregation, is demonstrated in Fig. 3. The speed and the duration of fast mixing stage were 200 rpm or 282 s^{-1} (expressed in velocity gradient units, G) and 180 s, respectively. The tested coagulation reagents were: the PFS-AP_m, $r = 0.25$ with AP/Fe = 0.02, 0.05, 0.10 and the simple PFS and AP at a dosage of 6 mg/L each.

In this study, three parameters were calculated for the analysis of the experimental data collected during the coagulation experiments. These parameters included the slope of the initial growth region, a time-weighted average steady state ratio value (ratio) and a time-weighted variance of the steady-state ratio value, as proposed by Hopkins and Ducoste [12] and used by several researchers [12,13]. The slope of the initial growth region is an indicator of the rate at which flocs are developing, the ratio represents the average extent of aggregation obtained during the steady state time interval and finally the time-weighted variance is an indicator of the extent of flocs break up, as well as a measure of flocs size.

Table 4 displays the calculated parameters for each tested coagulation reagent after the treatment of the kaolin–humic acid suspension.

The experimental data of Table 4 demonstrate that the presence of AP within the composition of PFS-AP significantly affects the formation of the flocs and the extent of their subsequent aggregation. It is evident that the increased concentration of anionic polymer results in the production of flocs that are bigger in size and in number, indicated by the higher ratio values, and relatively tenacious to continuous mechanical stirring, as the values of variance remain relatively steady, in comparison with the non modified PFS and the mere AP. The latter further confirms the suggestion that the presence of anionic polymers enhances the aggregation capacity of the composite coagulants, thus facilating the formation of more and bigger flocs via the adsorption-bridge formation mechanism.

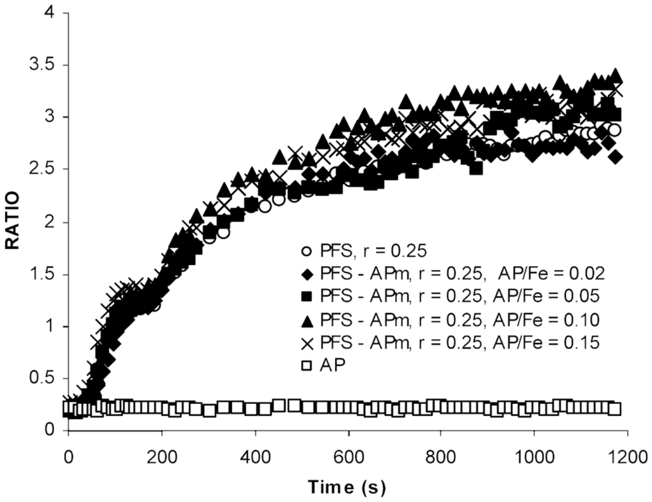

Fig. 3. Coagulation kinetics of PFS-APm, PFS and AP in kaolin–humic acid suspension.

Additionally, for the non-modified coagulant PFS, the data of Table 4 show that the formation of flocs is retarded (low value of slope) resulting, eventually, in the formation of smaller flocs, as the ratio values are lower. Finally, it is evident that the usage of mere AP resulted in a completely different coagulation performance. Practically, no flocs were formed, as a result of the anionic character of the organic polymer, which does not facilitate the destabilisation of the particles, especially in a low turbid suspension, where the concentration of the particles is low.

4. Conclusions

Overall, the results show that a) the preparation of a novel coagulation reagent with the combination of a pre-

Table 4
Parameters of coagulation kinetics for kaolin – humic acid suspension.

Coagulation reagents	Slope	Ratio	Variance
PFS – AP_m, $r = 0.25$, AP/Fe = 0.02	0.0090	2.6734	0.0045
PFS – AP_m, $r = 0.25$, AP/Fe = 0.05	0.0096	3.0271	0.0039
PFS – AP_m, $r = 0.25$, AP/Fe = 0.10	0.0099	3.2352	0.0098
PFS – AP_m, $r = 0.25$, AP/Fe = 0.15	0.0127	3.0998	0.0183
PFS, $r = 0.25$	0.0095	2.6560	0.0011
AP	—	0.2100	—

polymerised coagulant and an anionic polyelectrolyte is successfully conducted and that they possess improved properties than the conventional, non-modified reagents, b) The AP/M ratio affects the properties and the efficiency of the reagents, and c) Coagulation experiments suggested that the new coagulants exhibit a very good coagulation performance compared to the non modified coagulants, i.e. PFS and PACl and to the addition of PFS or PACl and AP as separated reagents. Their better performance can be attributed to the formation of flocs of bigger size, as revealed from the coagulation kinetics study. Moreover, apart from their better performance, the use of the composite coagulants exhibits several additional cost benefits. Particularly, the coagulation/flocculation process is simplified, as no addition of a flocculant aid in a second step is required, and the treatment costs decrease significantly, as there is no need to obtain separately the polyelectrolyte and specific equipment for handling the polyelectrolyte can be also avoided (e.g. dissolution system, pumping system). These advantages, together with the better coagulation performance should compensate by far the eventually higher preparation cost of the composite coagulants compared to the preparation cost of the simple metal salts. However, a detailed preparation cost analysis would clarify the exact extent of cost saving.

The promising results presented in this paper could serve as a basis for further research regarding the development of the inorganic-organic composite coagulants.

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