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Synthesis and coagulation performance of composite poly-aluminum-ferric-silicate-chloride coagulants in water and wastewater

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ABSTRACT

The aim of this work was to study the combination of an inorganic pre-polymerized coagulant (polyaluminum chloride [PACl]) with ferric species and polysilicic acid in various mixing orders Al/Fe/Si and OH/Al molar ratios, by applying two polymerization techniques for the production of a unique reagent, representing a more efficient coagulant than the respective commercially available (PACl-18) or laboratory-prepared ($PACl_{lab}$) for water or wastewater treatment. Several of coagulants' derivatives were prepared and were examined by jar tests for the treatment of simulated surface water, contaminated by clay particles (turbidity) and humic acid (natural organic matter); pH, turbidity, $UV_{254\ nm}$ absorbance, and residual Al were measured in the treated water. $PSiFAC_{1.5:10:15}$ prepared by the co-polymerization technique was found to be the most efficient coagulant from all the tested compounds; in addition, no flocculant aid (polyelectrolyte) was required with this product. Low coagulant doses, about 1.5–2 mg/L were required for the reduction of turbidity values to lower than 1 NTU; furthermore, $PSiFAC_{1.5:10:15}$ resulted in low residual aluminum concentration (about 140 µg Al/L). The most effective coagulants obtained were also used for the treatment of tannery wastewater to evaluate their performance and it was observed that high turbidity removal (~99%) was obtained at doses of about 100 mg/L. The most effective coagulants are under study for their potential use to alleviate membrane fouling in MBRs.

Keywords: Water and wastewater treatment; Composite coagulants; Poly-aluminum-ferric-silicate-chloride coagulants (PSiFAC); Coagulation; Turbidity removal

1. Introduction

Coagulation/Flocculation is a common water treatment process to destabilize the dissolved and colloidal impurities and to produce large flocculated aggregates that can be removed during the subsequently applied clarification/filtration process. The polyaluminum chloride (PACl) is the most extensively used coagulant for water purification and eventually in wastewater treatment plants throughout the world [1]. The inorganic polymeric flocculants (IPFs) or pre-polymerized coagulants, such as PACl (in the case of Al-coagulants) represent a relatively new type of coagulation reagents, which were developed in order to increase

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the efficiency of coagulation–flocculation process. However, although the presence of polymerized metal species in IPFs (e.g. Keggin-Al_{13}) enabled them to perform more efficiently than the conventional coagulants, such as alum [2,3], there is still an increasing demand for further improvement of their properties. The main reason is the insufficient aggregation abilities of the IPFs, which usually imposes the use of a flocculant aid (polyelectrolyte) for enhancing the efficiency of flocculation process.

In order to improve the aggregating capacity of PACl, several efforts have been made during the recent few years, towards the incorporation of silica in its structure. Hasegawa et al. [4] noticed that by introducing metal ions into polymerized silicic acid solution, the molecular weight of the product was increased and the corresponding stability and coagulation performance were further improved. In this case, the product was rather an inorganic metal-polysilicate flocculant, where silica was the main component, than a pre-polymerized inorganic coagulant. More recently, research has focused in the incorporation of silica within the pre-polymerized metal solutions, aiming to produce compounds with larger molecular weight by the application of two techniques i.e. either by introducing polymerized silica in the pre-polymerized metal solution (composite polymerization), or by introducing polymerized silica in the metal solution, followed by polymerization (co-polymerization) [5]. Extensive studies on polysilicate coagulant combined with ferric salt and aluminum salt have been conducted by several researchers all over the world [6–16]. Zouboulis and Tzoupanos [12,13] systematically examined several silica-based PACl derivatives, resulting to the identification of the following optimized conditions for their preparation, according to the respective coagulation performance data: OH/Al ratio 1.5–2 and Al/Si ratio 10–15, whereas co-polymerization was found more beneficial than composite polymerization for the coagulant preparation. As a result, the final selected product exhibits better coagulation performance for the treatment of contaminated natural (surface) waters than the conventional coagulants (e.g. alum) and the pre-polymerized commercial coagulants (PACl-18) or even a laboratory-prepared PACl, presenting higher polymerization degree than the respective commercial products.

In this study, an alternative mixture of aluminum, ferric, and silicate salts incorporated together in a new product is proposed. The product is called poly-aluminum-ferric-silicate-chloride and may be pre-polymerized either by hydroxylation of individual salts or prepared by first mixing the raw products, followed by hydroxylation; aluminum, ferric, and silicate may then become the polymeric components of the new composite coagulant agent. Some investigators have achieved to retard the gelation time of polysilicates by the use of aluminum or iron [17], so the polysilicate inorganic anionic polymer can be enriched with the inorganic cationic polymers of Al(III) and Fe(III) in order to improve their aggregating function and control their hydrolysis reaction. The ferric salts can generate thicker and heavier flocs than aluminum salts, but their strong tendency to hydrolysis and polymerization may result in flocs instability and corrosion problems. Nevertheless, the combination of aluminum and ferric salts may improve the hydrolysis process, the stability of hydrolyzed ferric salts, and the formation of larger flocs. The contribution of individual components in the composite coagulant may present positive or negative effects on the coagulation–flocculation process. Recently, several investigators [18–22] have studied the simultaneous addition of Al(III), Fe(III), and polysilicic acid solution (pSi), aiming to the simultaneous polymerization of pSi and hydroxylation of metal ions would be synchronized. These results indicate that the coagulation performance of PACl in water treatment can be improved by introducing polysilicic acid and ferric salts, and the coagulation efficiency of poly-aluminum-ferric-silicate-chloride is affected by the Al/Fe/Si ratio and preparation techniques.

This study aims to examine the behavior of several derivatives of silica-based aluminum coagulants for the production of an efficient coagulant for wastewater or water treatment with better performance than the conventional (alum) or the simple pre-polymerized (PACl) ones. The hydrolysis polymerization of Al(III), Fe(III), and polysilicic acid was investigated *both in different mixing orders and in different Al/Fe/Si and OH/Al molar ratios and by the application of two polymerization techniques (co-polymerization or composite polymerization).* The coagulation efficiency of the produced coagulants was tested in contaminated tap water and simulating natural (surface) waters. The coagulants with the more efficient combination of OH/Al and Al/Fe/Si molar ratios were further examined and their performance was compared with the corresponding of PACl-18 and laboratory-prepared PACl. Furthermore, the selected coagulants were applied for the treatment of tannery wastewater.

2. Materials and methods

All used chemical reagents were of analytical grade. De-ionized water (with conductivity lower than 0.5 μS/cm) was used to prepare all solutions, while de-ionized carbonate-free water was used for the preparation of stock solutions of the coagulants.

For comparison reasons, commercially available PACl-18 (containing 17.15% Al_2O_3, with 40% basicity and density 1.365 g/cm^3) was also examined. Basicity is defined by the following equation (Eq. (1)), [3]:

$$\text{Basicity}\,(\%) = \left[\frac{\text{OH}}{(M)zM}\right] \times 100 \tag{1}$$

where OH is the concentration of base, M is the metal, and zM is the charge of the metal. According to this equation, the molar ratio for PACl-18 reagent with basicity 40% should be OH/Al = 1.2 (as for the case of aluminum, $zM = 3$).

2.1. Procedure for the preparation of coagulants

2.1.1. Preparation of pSi

The preparation of pSi was performed according to Tzoupanos et al. [12]: water glass solution (containing 10% NaOH and 27% SiO_2) (Merk) was diluted to 0.5 M SiO_2 and placed in a plastic beaker. HCl (1 N) (Chem Labs) was added dropwise under magnetic stirring, until a pH of 4. The solution was left for ageing (90 min at pH 4) followed by a pH reduction to 2, where the solution remained for 60 min before being used (containing 0.37–0.38 M SiO_2).

2.1.2. Synthesis of poly-aluminum-ferric-silicate-chloride coagulants

The synthesis of coagulants took place at room temperature by the application of two polymerization methods according to a modified procedure proposed by Gao et al. [7], although with certain modifications i.e. by applying the co-polymerization or the composite polymerization techniques both in different mixing orders and in different Al/Fe/Si and OH/Al molar ratios. The respective initial solutions were 0.5 M $AlCl_3{\cdot}6H_2O$ (Merk), 0.5 M $FeCl_3{\cdot}6H_2O$ (Merk), 0.5 M NaOH (Merk) (as the added base), and the prepared polysilicic acid solution. The base addition rate (achieved by a peristaltic pump) was 0.1 mL/min and the stirring speed was 700–800 rpm. The final volumes of the obtained solutions samples were about 40–65 mL and the final Al concentration was fixed for all coagulants at 0.1 M. The following three composite coagulants were prepared under these conditions, following three different mixing orders:

- *PAFSiC and PACFSi (FpSi + Al)*: Ferric chloride solution was added in an appropriate volume of pSi solution, under vigorous stirring. The concentration and volume of the ferric chloride and the pSi varied in order to achieve the desired ratio of Fe/Si for each reagent [10]. Then, the formed FpSi was used to prepare two types of coagulants. According to the first procedure, FpSi was mixed with Al solution at various ratios of Al/Si + Fe; then, the base solution was added slowly in the mixture under stirring in order to achieve the desired OH/Al molar ratio. The coagulants prepared by the co-polymerization technique are referred as *PAFSiC*. According to the second technique, the base solution was initially added to the Al solution creating an intermediate PACl solution and then, the appropriate amount of FpSi was introduced in order to achieve the desired Al/Si + Fe molar ratio. The coagulants prepared by the composite polymerization technique are referred as *PACFSi*.
- *PFASiC and PFACSi (ApSi + Fe)*: pSi solution was added in Al solution, under vigorous stirring. The concentration and volume of pSi solution used varied to achieve the desired ratios of Al/Si for each reagent [12]. Then, ApSi was used for the preparation of two types of coagulants. According to the first procedure, Fe solution was mixed with ApSi solution at desired ratios of Al + Si/Fe and in the mixture the base solution was added slowly (under magnetic stirring) at a dosage required to achieve the desired OH/Al molar ratio. The coagulants prepared with the co-polymerization technique are referred as *PFASiC*. According to the second technique, the base solution was initially added to the Al solution, creating an intermediate PACl solution and then, the appropriate amount of pSi was added at the desired Al/Si molar ratio followed by the addition of the Fe solution. The coagulants prepared with the composite polymerization technique are referred as *PFACSi*.
- *PSiFAC and PSiCAF (pAF + pSi)*: Fe solution was added in Al solution, under vigorous stirring at the desired ratios of Al/Fe. Then, the pAF was used to prepare two types of coagulants. The pSi solution was mixed with pAF solution at desired ratios of Al + Fe/Si and base solution was added slowly (under magnetic stirring) in the mixture at the desired OH/Al molar ratio. The coagulants prepared with the co-polymerization technique are referred as *PSiFAC*. According to the second technique, the base solution was initially added to the Al solution, creating an intermediate PACl solution and then, Fe solution was added at the desired Al/Fe molar ratio followed by the addition of the pSi solution. The

coagulants prepared with the composite polymerization technique are referred as *PSiCAF*.

- *$PACl_{lab}$*: PACl solutions were also prepared ($PACl_{lab}$) for comparison reasons under the same conditions, but without the addition of silicates and ferric.

All composite coagulants were characterized by means of pH value (by a Metrohm Herisau pH-Meter), turbidity (by a Hach ratio/XR Turbiditymeter), and conductivity (by a Crison CM 35 conductivity-meter).

The afore-mentioned procedure for the production of the composite coagulants has the benefits of energy and time saving during the manufacture of them, resulting in lower operating cost, which may compensate for the higher cost of metallic Al, used as raw material. Considering that various aluminum byproducts (e.g. those found in wastes from recycling refreshment cans, fly ash etc.) could be used for creating the intermediate PACl solution after the appropriate treatment, the cost-effectiveness option could be further improved.

2.2. Jar tests

Jar tests were used for the examination of the coagulants efficiency. A jar test apparatus (Aqualytic) equipped with six paddles was used, employing 1 L glass beakers. Two types of samples were used: simulated surface water and tannery wastewater. The simulated surface water (1 L) was prepared by using tap water, clay (kaolin) suspension, and humic acid. The initial concentration of clay suspended particles was 10 mg/L and that of humic acid was 5 mg/L Tannery wastewater was used as a representative industrial wastewater; the sample was collected from the influent of tannery wastewater treatment plant. The properties of both samples are given in Table 1, while the conditions used in the jar test runs are shown in Table 2.

Water samples were collected from the supernatant of each beaker and were analyzed for the determination of pH, turbidity, conductivity, and $UV_{254\ nm}$. Absorbance at $UV_{254\ nm}$ provides an indication of the amount of natural organic matter in water and was measured by a Hitachi UV/Vis spectrophotometer.

The experiments were repeated two to three times and the average values are shown in the figures; usually, the variance between the obtained separately values were within 3–5%.

2.2.1. Residual aluminum concentration

The residual aluminum concentrations were determined by the eriochrome cyanine R standard method [23], where aluminum species react with eriochrome cyanine R dye at pH 6, resulting to a colored compound with maximum absorbance at 535 nm.

3. Results and discussion

3.1. Comparison of prepared coagulants

Table 3 displays the major physicochemical properties of laboratory-prepared composite coagulants and of commercially available PACl-18.

It can be observed that the addition of metals in a PACl solution for the formation of composite coagulants results in increase in turbidity, attributed potentially to the increase in components size. Furthermore,

Table 1
Initial sample properties (simulated surface water and wastewater samples)

Type of sample to be treated	Turbidity (NTU)	Absorbance $UV_{254\ nm}$	pH
Simulated surface water	17.2	0.153	7.3
Tannery wastewater (general input)	>2,000	2.711	7.4

Table 2
Coagulation experimental conditions (simulated surface water and wastewater samples); [according to 12]

	Rapid mixing period		Slow mixing period		
Type of treatment	Duration (min)	Mixing rate (rpm)	Duration (min)	Mixing rate (rpm)	Sedimentation (min)
Simulated surface water	2	160	10	45	45
Tannery wastewater (general input)	3	200	30	40	45

Table 3
Properties of laboratory-prepared coagulants (different mixing orders were applied for the composite coagulants)

Coagulant type	OH/Al	Al/Fe/Si molar ratios		pH	Turbidity (NTU)	Conductivity (mS/cm)
PACl-18	1.2	–		0.4	6.8	49.5
$PACl_1$	1	–		3.7	1.2	20.9
$PACl_{1.5}$	1.5	–		3.8	2.1	21.0
$PAFSiC_{1.5:15:10}$	1.5	*FpSi + Al*		3.9	117.0	24.0
$PACFSi_{1.5:15:10}$	1.5	Fe/Si: 15	Al/Si + Fe: 10	3.6	8.6	22.9
$PFASiC_{1.5:15:10}$	1.5	*ApSi + Fe*		3.9	256.0	24.4
$PFACSi_{1.5:15:10}$	1.5	Al/Si: 15	Al + Si/Fe: 10	3.7	141.6	23.4
$PSiFAC_{1.5:10:15}$	1.5	*pAF + pSi*		3.9	211.0	23.7
$PSiCAF_{1.5:10:15}$	1.5	Al/Fe: 10	Al + Fe/Si: 15	3.7	144.0	23.7

the increase in turbidity is higher, when the co-polymerization technique is used, due to simultaneous polymerization technique of raw materials.

3.2. Impact of Al/Fe/Si ratio and preparation technique on coagulation performance

3.2.1. Coagulation performance in treating simulated surface water

A preliminary study was carried out by the application of all produced coagulant samples aiming to obtain an initial concept of their coagulation behavior and to define the most efficient one. Fig. 1 displays the results of coagulation experiments, related to the treatment of "model" water sample (simulating surface water), applying all the laboratory-prepared coagulant agents. The concentration of coagulants varied between 1 and 6 mg/L and the experiments were conducted at the initial pH (7.0) of water sample.

As shown in Fig. 1(a), PACl-18 and $PACl_{lab}$ exhibit similar behavior, regarding turbidity reduction, while $PACl_{1.5}$ proved to be the most efficient: the concentration required to reduce the final turbidity under 1 NTU (according to the respective legislation limit, EU Directive 98/83/EC) is about 2–3 mg/L, whereas with the other coagulants the respective concentration was found to be higher than 3 mg/L. Therefore, the desired OH/Al molar ratio is 1.5 and that was an indicator for the preparation of the new composite Al/Fe/Si coagulants with 1.5 OH/Al molar ratios.

Fig. 1(b) displays the results of coagulation experiments with all composite Al/Fe/Si laboratory-prepared coagulants (1–6 mg/L/pH 7.0) by the two polymerization techniques. It can be observed that *$PSiFAC_{1.5:10:15}$*, prepared with the method of *co-polymerization*, was found as the most efficient between them. Regarding turbidity removal, it is remarkable that the concentration needed to reduce the final turbidity under 1 NTU is about 1.5–2 mg/L, while the respective concentration for PACl is higher. The second more efficient composite coagulant was the $PAFSiC_{1.5:15:10}$ followed by $PFASiC_{1.5:15:10}$. The least efficient composite coagulants are those prepared with the method of composite polymerization.

The differences between the three most efficient composite Al/Fe/Si coagulants and $PACl_{1.5}$ are shown in Fig. 2, where the percentage removal of turbidity is presented. The respective removal rate with $PSiFAC_{1.5:10:15}$ was 97%, whereas with $PACl_{1.5}$ the highest removal rate achieved was 93% for a coagulant dose of 2 mg/L.

Similar conclusions can be drawn about the reduction of $UV_{254\ nm}$ absorbance (Fig. 1(b)); *$PSiFAC_{1.5:10:15}$* seems to be the most efficient and $PFASiC_{1.5:15:10}$ seems to be the second for concentrations higher than 2–3 mg/L. The least efficient composite coagulants are those prepared by composite polymerization, similar to the turbidity results. Nevertheless, the respective UV reduction rate with $PSiFAC_{1.5:10:15}$ was 93%, whereas with $PACl_{1.5}$ the highest removal rate achieved was 78%, using 3 mg/L of coagulant.

In addition, the most effective coagulant resulting from the above experiments of different mixing orders of Al, Fe, and Si components, as described in Table 3, such as the case of PSiFAC (*pAF + pSi*), was examined by using different Al/Fe/Si and OH/Al molar ratios and by the two polymerization techniques (co-polymerization or composite polymerization) and as shown in Fig. 3, $PSiFAC_{1.5:10:15}$ prepared with the method of co-polymerization was also found as the most efficient between them.

Specifically, Fig. 3 displays the results of coagulation experiments using different Al/Fe/Si and OH/Al molar ratios and as shown both the 1.5 and 2.0 OH/Al molar ratios exhibit better coagulation performance for the treatment of contaminated natural waters among the derivatives; but this one with the molar ratio of 1.5 has some additional advantages apart from the low levels of residual turbidity, such as:

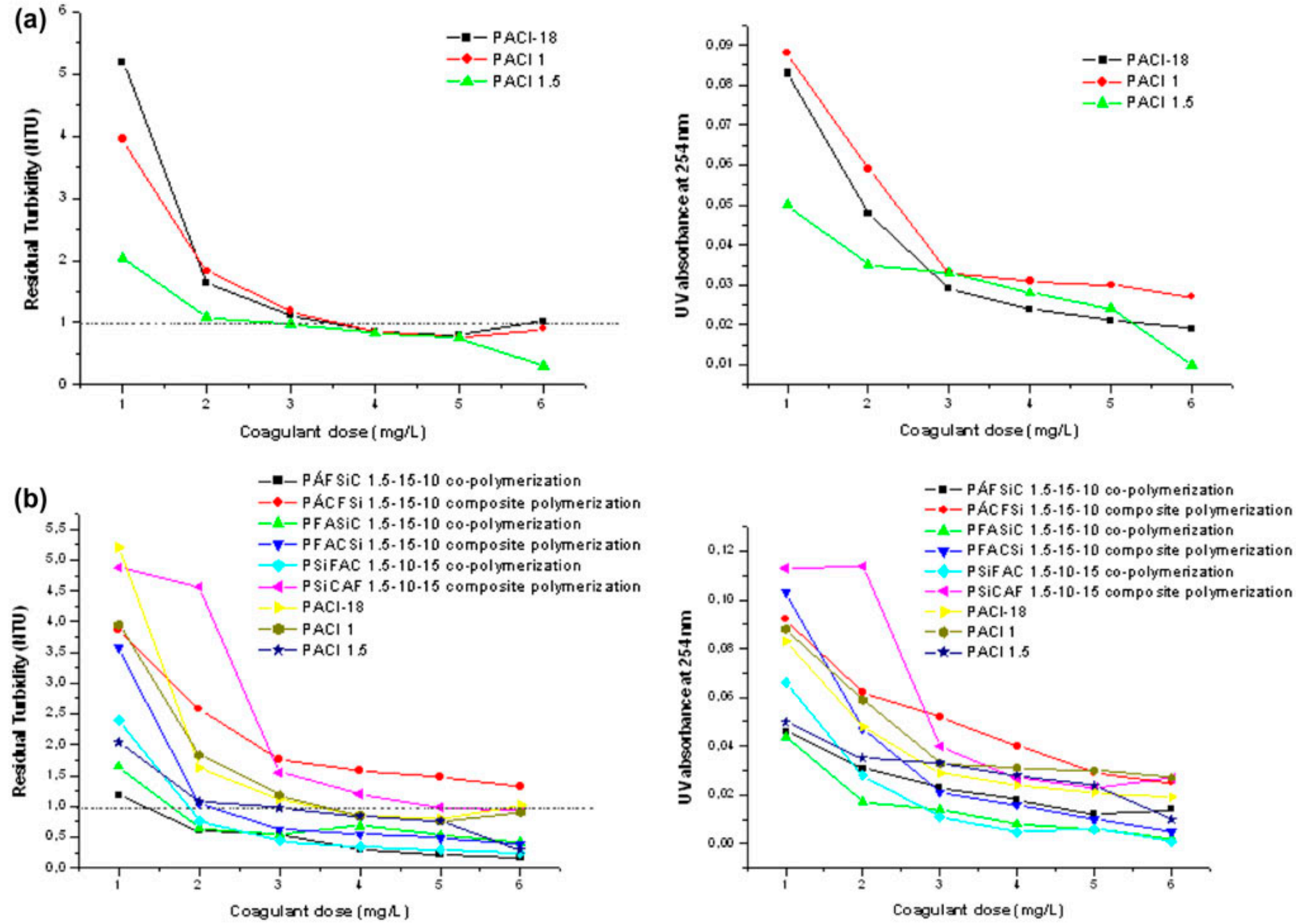

Fig. 1. Comparative coagulation experiments for turbidity and $UV_{254\,nm}$ absorbance of water samples for all laboratory-prepared coagulants: (a) PACl coagulants and (b) composite Al/Fe/Si coagulants.

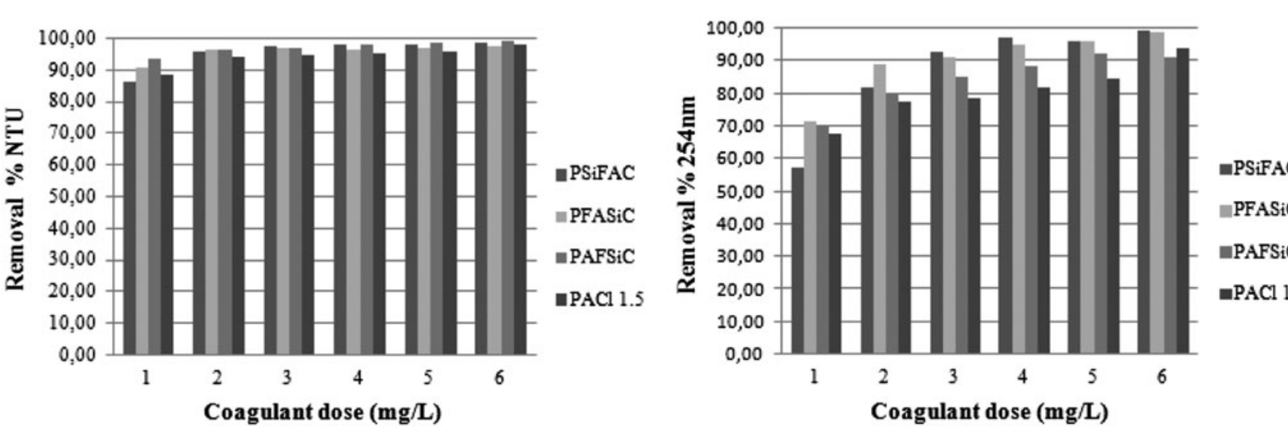

Fig. 2. Turbidity and $UV_{254\,nm}$ absorbance removal rates of the most efficient composite Al/Fe/Si laboratory-prepared coagulants for water samples.

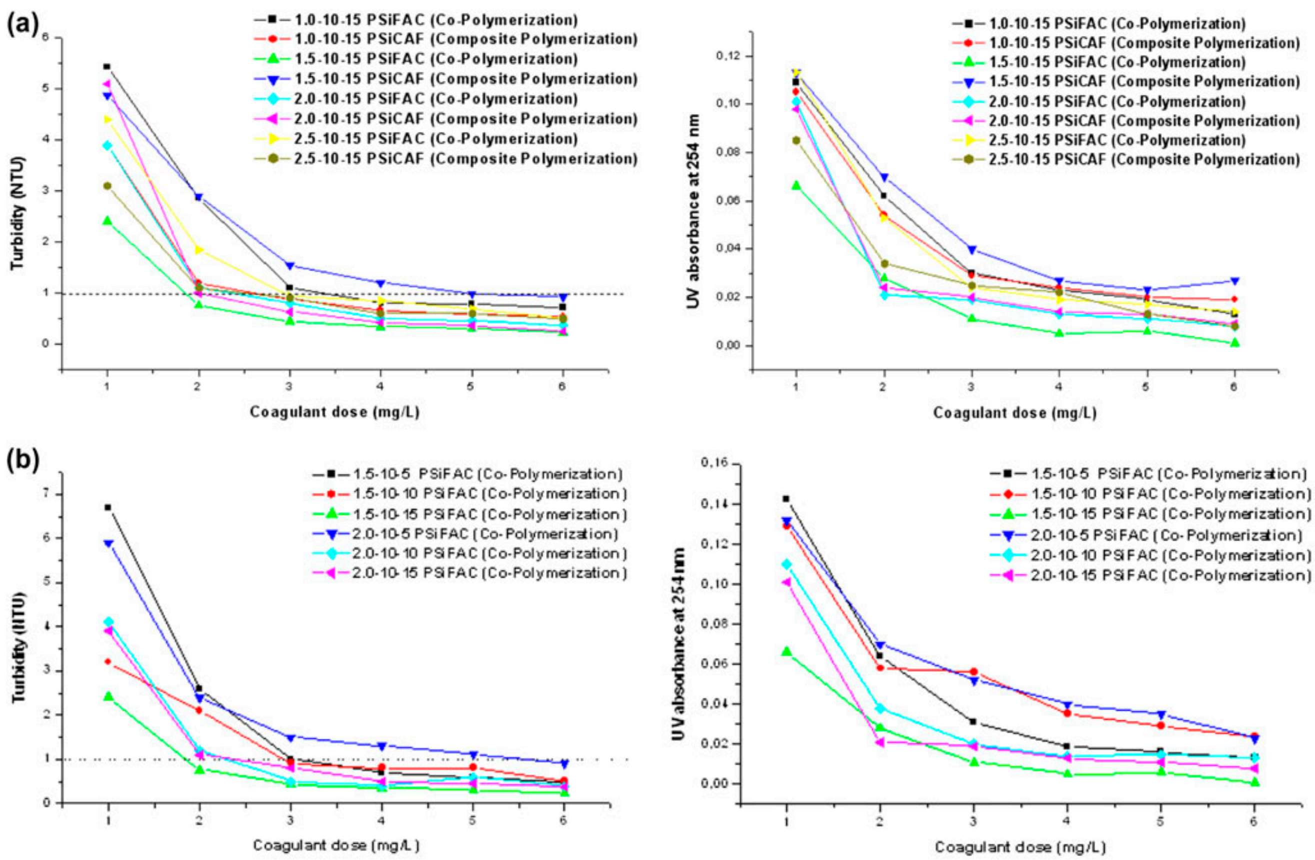

Fig. 3. Comparative coagulation experiments for turbidity and 254 nm absorbance of water samples for all laboratory-prepared derivatives of PSiFAC (*pAF* + *pSi*) coagulants, in (a) different Al/Fe/Si ratios and (b) different OH/Al ratios.

- cost-effectiveness, while there is no need for further amount of the base (NaOH) for the polymerization;
- time saving during the preparation procedure (less time for the addition of the base); and
- as resulted from the two above advantages, another one is energy saving for the preparation.

Residual aluminum concentration is a very important parameter from health perspectives and should be carefully considered, when an aluminum coagulant is applied in water treatment. According to Fig. 4, it can be seen that the Al concentration remaining in the sample after treatment varies significantly, depending upon the initially applied concentration of the examined coagulants. The lowest residual Al concentration was achieved by the addition of 2 mg/L $PSiFAC_{1.5:10:15}$. This specific coagulant seems to be the most efficient composite coagulant, as for almost all applied concentrations, and residual Al concentration remains under the respective legislation limit of 200 μg Al/L (EU Directive 98/83/EC). The highest residual Al concentration with the specific coagulant is 150 μg/L for an initial coagulant concentration of 6 mg/L. The second most efficient composite coagulant is $PFASiC_{1.5:15:10}$, as the residual Al concentration remains also under the respective limit.

Based upon these results, it is suggested that a poly-aluminum-ferric-silicate-chloride coagulant with improved properties should have a medium basicity (i.e. OH/Al molar ratio 1.5), relatively low silica and ferric content (i.e. Al/Si molar ratio 15 and Al/Fe 10) and should be prepared preferably by the co-polymerization technique, similarly to the relevant observations of Tzoupanos et al. [12] for silica-based aluminum coagulants. Furthermore, the introduction of the appropriate amount of ferric chloride in the already efficient silica-based aluminum coagulants seems to improve their efficiency even more, than the commonly applied polymers.

Table 4 displays the major physicochemical properties of water samples produced by coagulation with $PSiFAC_{1.5:10:15}$.

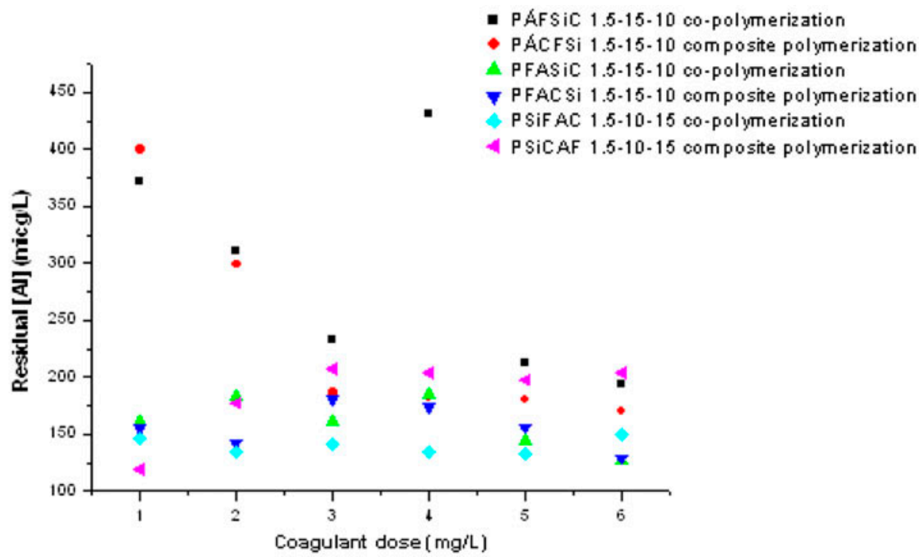

Fig. 4. Comparative coagulation experiments for residual aluminum concentration of water samples for composite Al/Fe/Si laboratory-prepared coagulants.

Table 4
Physicochemical properties of water samples after the coagulation performance of $PSiFAC_{1.5:10:15}$ laboratory-prepared coagulant

Coagulant dose (mg/L)	pH	Turbidity (NTU)	Absorbance $UV_{254\ nm}$	Residual [Al] (μg/L)
1	7.2	2.4	0.066	146.3
2	7.2	0.8	0.028	135.0
3	7.2	0.4	0.011	141.3
4	7.1	0.3	0.005	135.0
5	7.2	0.3	0.006	132.5
6	7.1	0.2	0.001	150.0

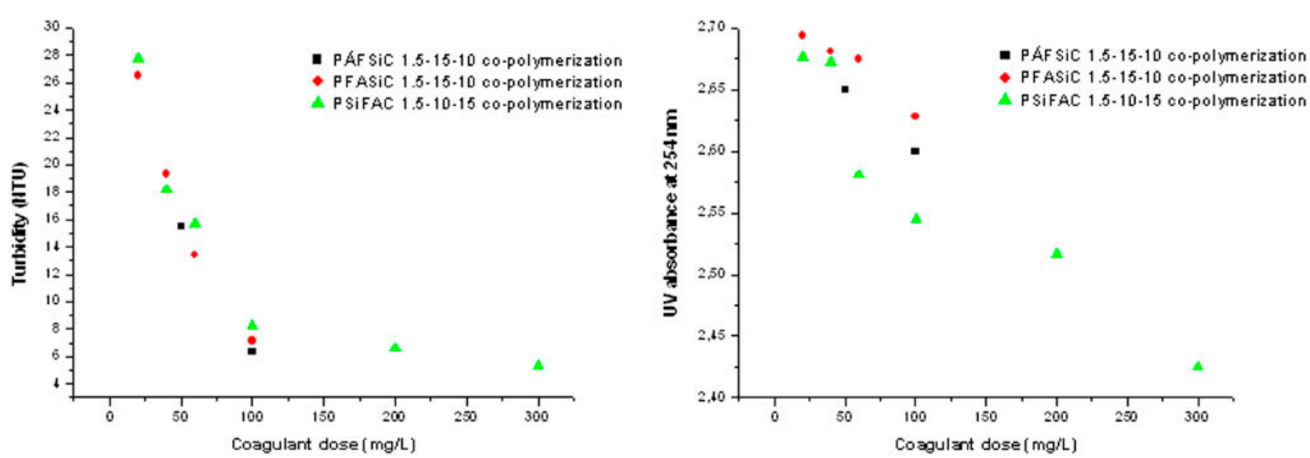

Fig. 5. Comparative coagulation experiments for turbidity and $UV_{254\ nm}$ absorbance of wastewater samples for selected laboratory-prepared coagulants.

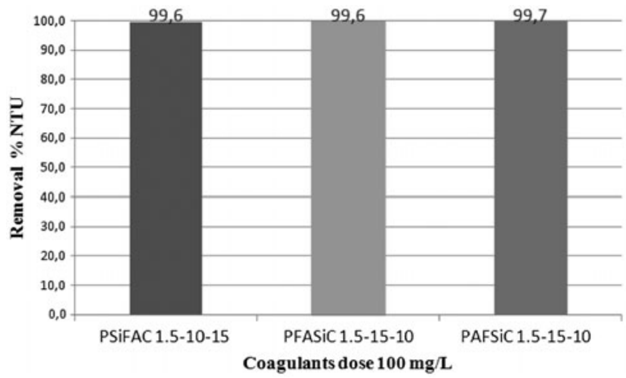

Fig. 6. Turbidity removal rates of the most efficient composite Al/Fe/Si laboratory-prepared coagulants for wastewater samples.

3.2.2. Coagulation performance in tannery wastewater

The most effective coagulants obtained by the treatment of simulated water, i.e. *$PSiFAC_{1.5:10:15}$*, $PAFSiC_{1.5:15:10}$, and $PFASiC_{1.5:15:10}$ were applied for the treatment of tannery wastewater to evaluate their coagulation efficiency for industrial wastewater.

The results of turbidity removal and UV absorbance reduction during the treatment of tannery wastewater are given in Fig. 5; as shown, all three coagulants greatly reduced sample turbidity and absorbance for doses higher than 100 mg/L. Furthermore, as the wastewater sample was not subjected to any pre-treatment stage, it is a highly contaminated sample and coagulation was beneficial to the improvement of its quality.

In Fig. 6, the turbidity removal rates of the most efficient composite Al/Fe/Si coagulants for wastewater samples are presented and all three coagulants greatly reduced the turbidity (~99%) and the absorbance at doses higher than 100 mg/L. From this, it is resulted that the optimum coagulant for water treatment (i.e. *$PSiFAC_{1.5:10:15}$*) is also capable of being used for the wastewater treatment, as an additional field of their application.

4. Conclusions

The primary target of this study was to combine an inorganic pre-polymerized coagulant (PACl) with ferric species and polysilicic acid in one unique reagent, examining both different mixing orders and Al/Fe/Si and OH/Al molar ratios by the application of two different polymerization methods; the main conclusions drawn are the following:

- Several poly-aluminum-ferric-silicate-chloride derivatives were examined, leading to the following optimized conditions for their preparation:

  (1) *PAFSiC and PACFSi (FpSi + Al)*—OH/Al ratio 1.5, Fe/Si ratio 15, and Al/Si + Fe ratio 10,

  (2) *PFASiC and PFACSi (ApSi + Fe)*—OH/Al ratio 1.5, Al/Si ratio 15, and Al + Si/Fe ratio 10,

  (3) *PSiFAC and PSiCAF (pAF + pSi)*—OH/Al ratio 1.5, Al/Fe ratio 10, and Al + Fe/Si ratio 15.

- The application of co-polymerization process for producing poly-aluminum-ferric-silicate-chloride coagulants proved to produce more effective coagulants than the composite polymerization method with the same Al/Fe/Si ratio.
- Overall, it is suggested that a poly-aluminum-ferric-silicate-chloride coagulant with improved properties should have medium basicity (i.e. OH/Al molar ratio 1.5), relatively low silica and ferric content (i.e. Al/Si molar ratio 15 and Al/Fe 10) and should be prepared preferably by the co-polymerization technique.
- $PSiFAC_{1.5:10:15}$ prepared by *co-polymerization* was found the most efficient coagulant regarding water treatment. The concentration required to reduce the final turbidity under 1 NTU is about 1.5–2 mg/ L. The second more efficient composite coagulant was the $PAFSiC_{1.5:15:10}$, followed by the $PFASiC_{1.5:15:10}$.
- As a result, the final selected product (referred as $PSiFAC_{1.5:10:15}$ coagulant) exhibits better coagulation performance for the treatment of contaminated natural waters than the pre-polymerized commercial coagulants (PACl-18) or even the laboratory-prepared $PACl_{lab}$.
- The great advantage in the use of $PSiFAC_{1.5:10:15}$ coagulant seems to be the lower level of residual aluminum concentration, remaining in the treated water sample. The control of residual Al is necessary, due to the respective legislation limits (EU < 200 μg Al/L) and it can be problematic, when conventional coagulants are being used.
- In the case of composite poly-aluminum-ferric-silicate-chloride coagulants, no further flocculants aid and polyelectrolyte are required; as a result additional cost-benefits may arise by the utilization of this material including the avoidance of specific equipment for handling

the polyelectrolyte (e.g. dissolution system and pumping system).

- The most effective coagulants obtained for water samples i.e. *$PSiFAC_{1.5:10:15}$*, $PAFSiC_{1.5:15:10}$, and $PFASiC_{1.5:15:10}$ were applied for the treatment of tannery wastewater to evaluate their coagulation efficiency. All three coagulants greatly reduced the turbidity (~99%) and the absorbance at doses higher than 100 mg/L.

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