

# Synthesis and coagulation performance of composite poly-aluminum-ferric-silicate-chloride coagulants in water and wastewater treatment and their potentially use to alleviate the membrane fouling in MBRs

A.K. Tolkou<sup>1</sup>, A.I. Zouboulis<sup>1</sup>, P.E. Samaras<sup>2</sup>

<sup>1</sup>Laboratory of General & Inorganic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, GREECE,

<sup>2</sup>Laboratory of Water & Wastewater Technologies, Department of Food Technology, Alexander Technological Education Institute of Thessaloniki, GR-57400 Thessaloniki, GREECE

Presenting author email: [tolkatha@chem.auth.gr](mailto:tolkatha@chem.auth.gr), Tel: +30694 4517146, +302310 997794

## Abstract

The aim of this work was the study of the combination of an inorganic pre-polymerized coagulant (PACl) with ferric species and polysilicic acid in various mixing order, Al/Fe/Si and OH/Al molar ratios, and two polymerization techniques for the production of a unique reagent representing a coagulant, more efficient than commercial PACl-18 and laboratory prepared PACl<sub>lab</sub> for water or wastewater treatment. A number of coagulants were prepared and were examined by jar tests for the treatment of simulated water; pH, turbidity and UV<sub>254nm</sub> absorbance were measured in the treated water. PSiFAC<sub>1.5:10:15</sub> prepared by co-polymerization 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<sub>1.5:10:15</sub> resulted in very low residual aluminum concentration of 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, Coagulation, Turbidity removal.

## 1. Introduction

Coagulation is a common water treatment process to destabilize dissolved and colloidal impurities and to produce large flocculated aggregates that can be removed in the subsequent clarification/filtration process. The poly-aluminum chloride (PACl) is the most extensively used coagulant at water purification and wastewater treatment plants throughout the world [1]. The Inorganic Polymeric Flocculants (IPFs), or pre-polymerized coagulants, such as polyaluminum chloride (PACl, in the case of Al-coagulants) represent a relatively type of coagulation reagents, which were developed in order to increase the efficiency of coagulation-flocculation process. However, although the presence of polymerized metal species in IPFs (e.g. keggin-Al<sub>13</sub>) enabled them to perform more efficiently than the conventional coagulants such as alum [2, 3], there is still need 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) to increase the efficiency of flocculation process.

In order to improve the aggregating power 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 polyaluminum chloride derivatives, leading to the following optimized conditions for their preparation, according to the respective coagulation performance data: OH/Al ratio 1.5–2, Al/Si ratio 10–15, whereas co-polymerization should be preferred for the coagulant preparation. As a result, the final selected product exhibits better coagulation performance for the treatment of contaminated natural waters, than the conventional coagulants (e.g. alum), the pre-polymerized commercial coagulants (PACI-18), or even a laboratory prepared PACI, presenting higher polymerization degree than commercial products.

Today, there is a prompt need for the development of new PAC-based coagulants such as poly-aluminum-ferric-silicate-chloride to improve the coagulation performance. The poly-aluminum-ferric-silicate-chloride coagulant is made of aluminum, ferric and silicate. The coagulant may be pre-polymerized by hydroxylation of individual salts, or prepared by firstly mixing the raw products followed by hydroxylation; aluminum, ferric and silicate may then become the polymeric components of the composite. Some investigators have achieved to delay the gelation time by the use of aluminum or iron [17], so the polysilicate inorganic anionic polymer can be enriched by the inorganic cationic polymers of Al (III) and Fe (III) in order to improve their aggregating function and to retard 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), so that the polymerization of pSi and the hydroxylation of metal ions would be synchronized. These results indicate that the coagulation performance of PACI 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 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 simple pre-polymerized (PACI) ones. The hydrolysis polymerization of Al (III), Fe (III) and polysilicic acid was investigated *both in different mixing order and in different Al/Fe/Si and OH/Al molar ratios and by two polymerization techniques (co-polymerization or composite polymerization)*. The coagulation efficiency of the produced coagulants was tested in contaminated tap water, 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 PACI-18 and laboratory prepared PACI. Furthermore, 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  $\mu\text{S}/\text{cm}$ ) 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 PACI-18 (containing 17.15%  $\text{Al}_2\text{O}_3$ , with 40% basicity and density 1.365  $\text{g cm}^{-3}$ ) was also examined. According to the following equation [3]:

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

the molar ratio for PACI-18 reagent with basicity 40% should be OH/Al = 1.2 (as for aluminum  $\text{zM} = 3$ )

### 2.1. Procedure for the preparation of coagulants

#### 2.1.1. Preparation of polysilicic acid solution (pSi)

The preparation of pSi was preformed according to Tzoupanos *et al.* [12]. Therefore, water glass solution (containing 10% NaOH and 27%  $\text{SiO}_2$ ) (Merk), was diluted to 0.5M  $\text{SiO}_2$  and placed in a plastic beaker. HCl (1N) (Chem Labs) was added drop wise, under magnetic stirring, until a pH of 4. The solution was left for ageing for 90 min at pH 4 followed by a pH reduction to 2, where the solution remained for 60 min before being used (containing 0.37–0.38M  $\text{SiO}_2$ ).

### 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 order and in different Al/Fe/Si and OH/Al molar ratios. The respective initial solutions were 0.5M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (Merk), 0.5M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Merk), 0.5M 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 aluminum concentration was fixed for all coagulants at 0.1 M. The following three composite coagulants were prepared under these conditions:

- *PAFSiC and PACFSi (pFSi + 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 pFSi was used to prepare two types of coagulants. According to the first procedure, pFSi was mixed with Al solution at various ratios of Al/Si+Fe; then, 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 pFSi 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 (pASi + 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, pASi was used for the preparation of two types of coagulants. According to the first procedure, Fe solution was mixed with pASi 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 (pFA + pSi)*: Fe solution was added in Al solution, under vigorous stirring at the desired ratios of Al/Fe. Then, the pFA was used to prepare two types of coagulants. pSi solution was mixed with pFA 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<sub>lab</sub>*: Polyaluminum chloride solutions were also prepared ( $\text{PACl}_{\text{lab}}$ ) for comparison reasons under the same conditions, but without the addition of silicates and ferric.

All the composite coagulants were characterized for the determination of their pH (by a Metrohm Herisau pH-Meter), turbidity (by a Hach ratio/XR Turbidity-meter) and conductivity (by a Crison CM 35 conductivity-meter) respectively.

### 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 1L glass beakers. Two types of samples were used: simulated surface water and tannery wastewater. The simulated surface water (1 L) was prepared by tap water, clay (kaolin) suspension and humic acid. The initial concentration of clay suspended particles was 10 mg/L and that of humic acid 5 mg/L. Tannery wastewater was used as a representative industrial wastewater; the sample was

collected from the influent of a 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<sub>254nm</sub>. Absorbance at UV<sub>254nm</sub> provides an indication of the amount of natural organic matter (NOM) in the water and was measured by a Hitachi UV/vis spectrophotometer.

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

Type of sample to be treated	Turbidity (NTU)	Absorbance UV <sub>254 nm</sub>	pH
Simulated surface water	17.2	0.153	7.0
Tanner Wastewater (general input)	>2000	2.711	7.4

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

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

### 2.2.1. Residual aluminum concentration

The residual aluminum concentrations were determined by the eriochrome cyanine R standard method [23], where aluminum salts 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 PACI-18.

**Table 3:** Properties of laboratory prepared coagulants.

Coagulant type	OH/Al	Al/Fe/Si molar ratios		pH	Turbidity (NTU)	Conductivity (mS/cm)
PACI-18	1.2	-		0.4	6.8	49.5
PACI <sub>1</sub>	1	-		3.7	1.2	20.9
PACI <sub>1.5</sub>	1.5	-		3.8	2.1	21.0
PAFSiC <sub>1.5:15:10</sub>	1.5	<i>pFSi + Al</i>		3.9	117.0	24.0
PACFSi <sub>1.5:15:10</sub>	1.5	Fe/Si: 15	Al/Si+Fe: 10	3.6	8.6	22.9
PFASiC <sub>1.5:15:10</sub>	1.5	<i>pASi + Fe</i>		3.9	256.0	24.4
PFACSi <sub>1.5:15:10</sub>	1.5	Al/Si: 15	Al+Si/Fe: 10	3.7	141.6	23.4
PSiFAC <sub>1.5:10:15</sub>	1.5	<i>pFA + pSi</i>		3.9	211.0	23.7
PSiCAF <sub>1.5:10:15</sub>	1.5	Al/Fe: 10	Al+Fe/Si: 15	3.7	144.0	23.7

It can be observed that the addition of the metals in a PACI solution for formation of composite coagulants, results in increase of its turbidity, attributed potentially to the increase of the components size. Furthermore, the increase of turbidity is higher when the co-polymerization technique is used, due to simultaneous polymerization technique of the raw materials.

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

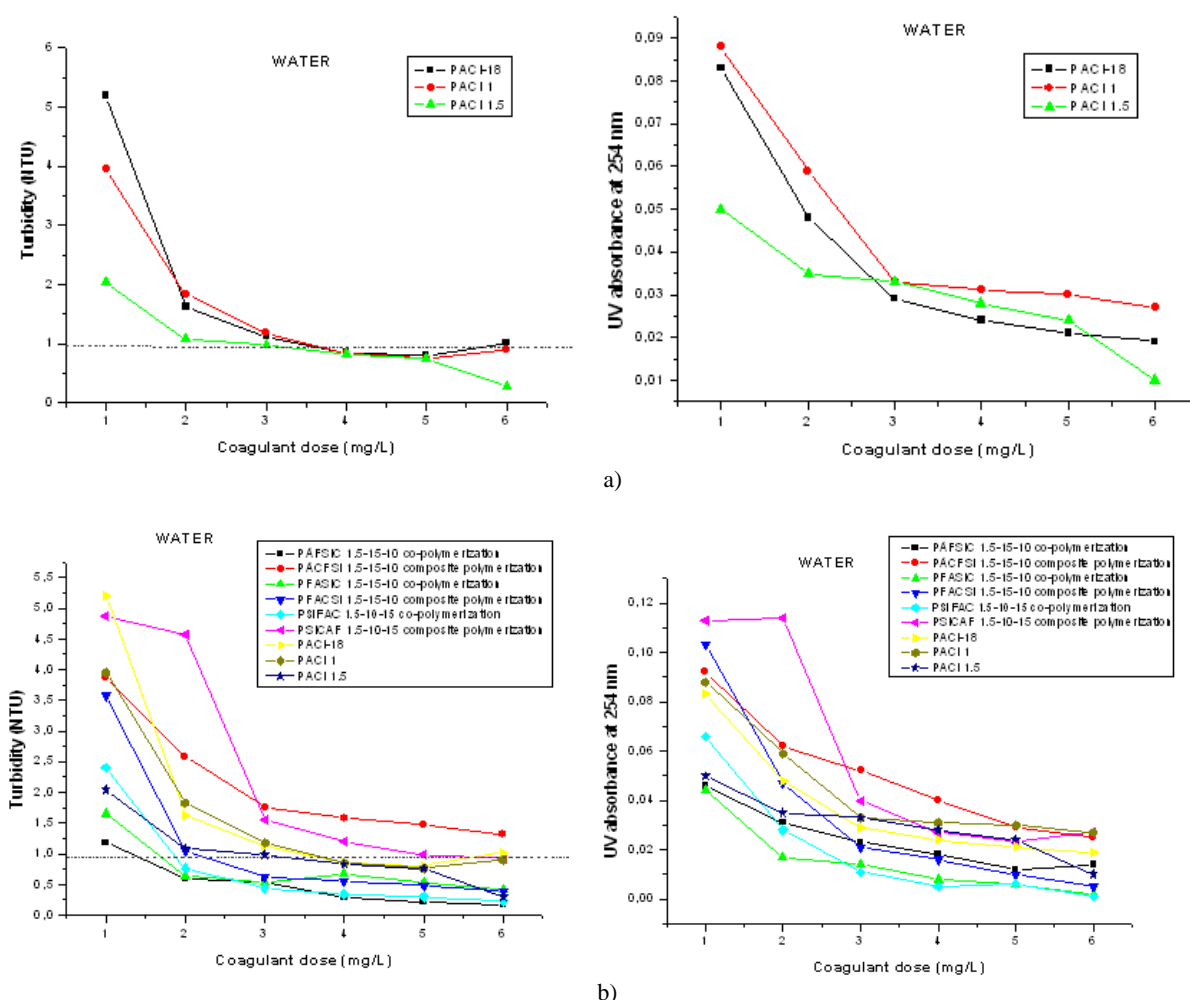
#### 3.2.1 Coagulation performance in simulated surface water

The first step in this study was the preliminary application of all produced coagulant samples, aiming to obtain an initial concept of their coagulation behavior and to define the most efficient one. Figure 1 displays the results of coagulation experiments, related to the treatment of model water sample (simulating surface water)

with all laboratory prepared coagulants. 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 Figure 1a PACI-18 and PACI<sub>lab</sub> exhibit similar behavior regarding turbidity reduction, while PACI<sub>1.5</sub> 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 is 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.

Figure 1b displays the results of coagulation experiments with all composite Al/Fe/Si laboratory prepared coagulants (1 – 6 mg/L / pH 7.0) by two polymerization techniques. It can be observed that *PSiFAC*<sub>1.5:10:15</sub> 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 PACI is higher. The second more efficient composite coagulant was the *PAFSiC*<sub>1.5:15:10</sub> followed by *PFASiC*<sub>1.5:15:10</sub>. The least efficient composite coagulants are those prepared with the method of composite polymerization.

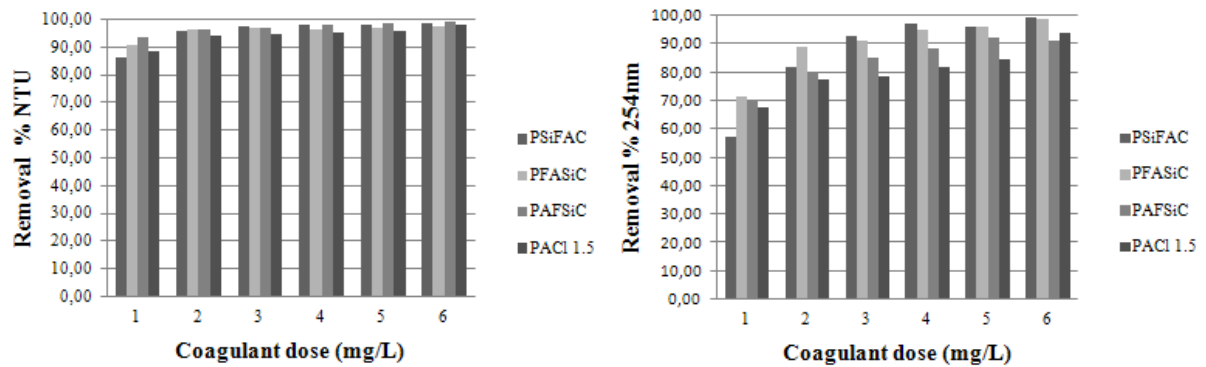


**Figure 1:** Comparative coagulation experiments for turbidity and 254 nm absorbance of water samples, for all laboratory prepared coagulants. a) PACI coagulants, b) composite Al/Fe/Si coagulants

The differences between the three most efficient composite Al/Fe/Si coagulants and PACI<sub>1.5</sub> are shown in Figure 2 where the percentage removal of turbidity is presented. The respective removal rate with *PSiFAC*<sub>1.5:10:15</sub> was 97%, whereas with PACI<sub>1.5</sub> the highest removal rate achieved was 93% for a coagulant dose of 2 mg/L.

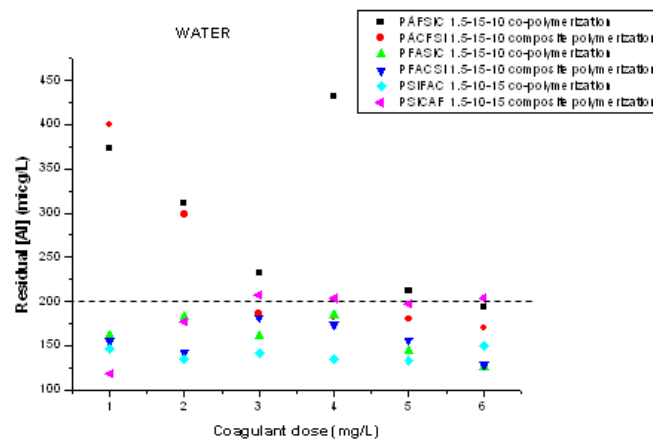
Similar conclusions can be drawn about the reduction of UV<sub>254nm</sub> absorbance (Figure 1b); *PSiFAC*<sub>1.5:10:15</sub> seems to be the most efficient and *PFASiC*<sub>1.5:15:10</sub> seems to be the second one for a concentration higher than 2-3

mg/L. The least efficient composite coagulants are those prepared by composite polymerization, similarly to the turbidity results. Nevertheless, the respective UV reduction rate with  $\text{PSiFAC}_{1.5:10:15}$  was 93%, whereas with  $\text{PACl}_{1.5}$  the highest removal rate achieved was 78% for 3 mg/L of coagulant.



**Figure 2:** Turbidity and UV absorbance at 254 nm removal rates of the most efficient composite Al/Fe/Si laboratory prepared coagulants for water samples.

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 Figure 3 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  $\text{PSiFAC}_{1.5:10:15}$ . This specific coagulant seems to be the most efficient composite coagulant, as for the almost all applied concentrations, residual Al concentration remains under the respective legislation limit of 200  $\mu\text{g Al/L}$  (EU Directive 98/83/EC). The highest residual Al concentration with the specific coagulant is 150  $\mu\text{g/L}$  for an initial coagulant concentration of 6 mg/L. The second most efficient composite coagulant is  $\text{PFASiC}_{1.5:15:10}$ , as the residual Al concentration remains under the respective limit.



**Figure 3:** Comparative coagulation experiments for Residual Aluminum Concentration of water samples, for composite Al/Fe/Si laboratory prepared coagulants.

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.  $\text{OH/Al}$  molar ratio 1.5), medium silica and ferric content (i.e.  $\text{Al/Si}$  molar ratio 15 and  $\text{Al/Fe}$  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 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  $\text{PSiFAC}_{1.5:10:15}$ .

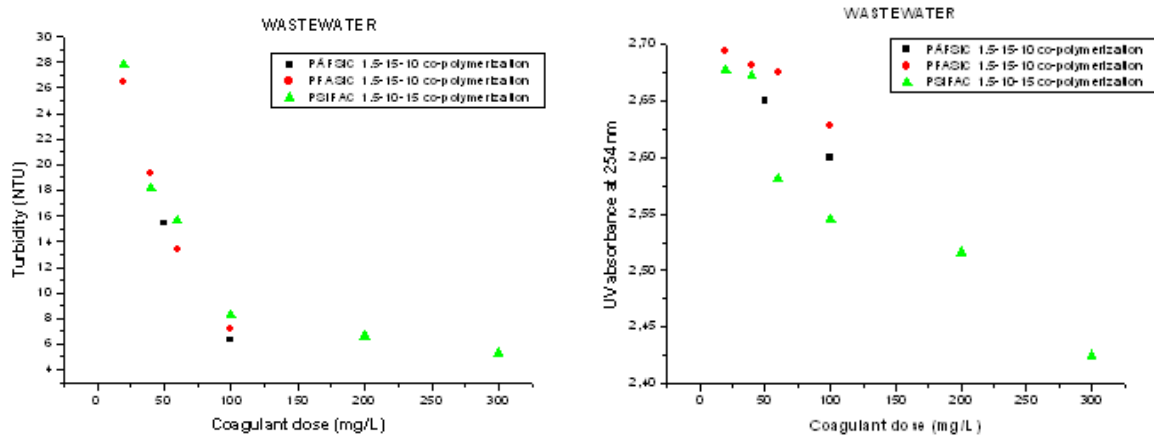
**Table 4:** Physicochemical properties of water samples after the coagulation performance of PSiFAC<sub>1.5:10:15</sub> laboratory prepared coagulant

Coagulant dose (mg/L)	pH	Turbidity (NTU)	Absorbance UV <sub>254 nm</sub>	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

### 3.2.2 Coagulation performance in tannery wastewater

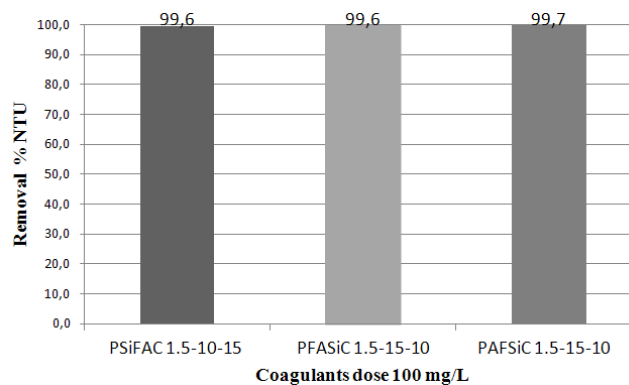
The most effective coagulants obtained by the treatment of simulated water i.e. P*SiFAC*<sub>1.5:10:15</sub>, PAFSiC<sub>1.5:15:10</sub>, PFASiC<sub>1.5:15:10</sub> were applied for the treatment of tannery wastewater to evaluate their coagulation efficiency for industrial wastewater.

The results of turbidity removal and UV absorbance reduction during the treatment of tannery wastewater are given in Figure 4; as shown the three coagulants reduce greatly the turbidity and the 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.



**Figure 4:** Comparative coagulation experiments for turbidity and 254 nm absorbance of wastewater samples, for selected laboratory prepared coagulants.

In Figure 5, the turbidity removal rates of the most efficient composite Al/Fe/Si coagulants for wastewater samples are presented, for a coagulant dose of 100 mg/L, where the high turbidity removal (~99%) was obtained.



**Figure 5:** Turbidity removal rates of the most efficient composite Al/Fe/Si laboratory prepared coagulants for wastewater samples.

#### 4. Membrane fouling control in Membrane Bioreactor Systems (MBRs)

The recently years, the use of flocculants and coagulants such as aluminum or ferric chloride has been investigated in an attempt to minimize fouling. Also, the addition of adsorbent reagents such as powdered activated carbon (PAC) has been found to improve the membrane performance by decreasing the level of organic compounds with potential for membrane fouling [24]. The trend in coagulation–flocculation field nowadays is the preparation of new, composite coagulants by the introduction of several additives to produce the so called pre-polymerized coagulants, in order to improve their efficiency and to make them equal, or even more efficient than the commonly applied organic polymers. [7-16]

By the aforementioned results about the effective coagulation performance of  $\text{PSiFAC}_{1.5:10:15}$  coagulant, is being studied its possibility (among others efficient coagulants [10, 12]) to alleviate significantly the cake layer and adsorption resistance and thus the membrane fouling, by using for the wastewater treatment in combination the coagulation and MBRs.

#### 5. Conclusions

The primary target of this study was to combine an inorganic pre-polymerized coagulant (PACI) with ferric species and polysilicic acid in one unique reagent both in different mixing order 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.  $\text{PAFSiC}$  and  $\text{PACFSi}$  ( $p\text{FSi} + \text{Al}$ ) - OH/Al ratio 1.5, Fe/Si ratio 15, Al/Si+Fe ratio 10
  2.  $\text{PFASiC}$  and  $\text{PFACSi}$  ( $p\text{ASi} + \text{Fe}$ ) - OH/Al ratio 1.5, Al/Si ratio 15, Al+Si/Fe ratio 10
  3.  $\text{PSiFAC}$  and  $\text{PSiCAF}$  ( $p\text{FA} + p\text{Si}$ ) - OH/Al ratio 1.5, Al/Fe ratio 10, 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), medium 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.
- In general, poly-aluminum-ferric-silicate-chloride coagulants are more effective than PACI in water and wastewater treatment, especially at lower doses.
- $\text{PSiFAC}_{1.5:10:15}$  prepared with by *co-polymerization* was found the most efficient coagulant from jar test experiments. 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  $\text{PAFSiC}_{1.5:15:10}$  followed by the  $\text{PFASiC}_{1.5:15:10}$ .
- As a result, the final selected product (referred as  $\text{PSiFAC}_{1.5:10:15}$  coagulant) exhibits better coagulation performance for the treatment of contaminated natural waters, than the pre-polymerized commercial coagulants (PACI-18), or even the laboratory prepared  $\text{PACI}_{\text{lab}}$ .
- The great advantage in the use of  $\text{PSiFAC}_{1.5:10:15}$  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 $\mu\text{g}$  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, pumping system).



- The most effective coagulants obtained for water samples i.e. *PSiFAC*<sub>1.5:10:15</sub>, *PAFSiC*<sub>1.5:15:10</sub>, *PFASiC*<sub>1.5:15:10</sub> 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.
- Because of their significant efficiency in coagulation performance in wastewater treatment, the new most effective coagulants are under study for their potentially use to alleviate the membrane fouling in MBRs.

## Acknowledgments

The financial support through the co - Financed by the European Union and the Greek State Program EPAN-II (OPC-II)/ ESPA (NSRF): 'SYNERGASIA II', Project (FOUL-MEM) - "New processes for fouling control in membrane bioreactors (11SYN-8-1084), is gratefully appreciated.



## References

1. T. Viraraghavan and C.H. Wimmer, Polyaluminum chloride as an alternative to alum coagulation: A case study. Proc. Canadian Soc. Civ. Engr. Annu. Conf. (1988) 480–498.
2. S. Sinha, Y. Yoon, G. Amy and J. Yoon, Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes. Chemosphere 57 (9) (2004) 1115–1122.
3. J.C. Crittenden, R.R. Trussel, D.W. Hand, K.J. Howe and G. Tchobanoglous, Coagulation, mixing and flocculation, in Water Treatment: Principles and Design, 2<sup>nd</sup> edition, John Wiley & Sons, New Jersey, 2005.
4. T. Hasegawa, K. Hashimoto, T. Onitsuka, K. Goto and N. Tambo, Characteristics of metal-polysilicate coagulants, Water Sci. Technol. 23 (1990) 1713–1722.
5. Y.U. Ning, Discussion of silica speciation, fouling, control and maximum reduction, Desalination 151 (2002) 62–73.
6. Z.K. Luan and Y.H. Song, Preparation and flocculation of polysilicate-metals (PSMS) flocculants. Environmental Chemistry, 16(6) (1997) 534–539.
7. B. Y. Gao, Q. Y. Yue, B. J. Wang and Y. B. Chu, Polyaluminum silicate chloride (PASiC) – A new type of composite inorganic polymer coagulant. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 229(1-3) (2003) 121–127.
8. A.I. Zouboulis and G. Traskas, Comparable evaluation of various commercially available aluminum-based coagulants for the treatment of surface water and for the post-treatment of urban wastewater, J. Chem. Tech. & Biotech. 80 (2005), 1136-1147
9. A.I. Zouboulis, G. Traskas and A. Ntolia , Comparable evaluation of iron-based coagulants for the treatment of surface water and of contaminated tap water”, Separ. Sci. Tech. 42 (2007) 803–817
10. A.I. Zouboulis and P. A. Moussas, Polyferric silicate sulphate (PFSiS): Preparation, characterization and coagulation behavior. Desalination, 224 (2008) 307–316.
11. A.I. Zouboulis, G. Traskas and P. Samaras, Comparison of Efficiency between Poly-aluminium Chloride and Aluminium Sulphate Coagulants during Full-scale Experiments in a Drinking Water Treatment Plant, Separation Science and Technology, 43 (2008), 1507
12. A.I. Zouboulis and N.D. Tzoupanos, Polyaluminium silicate chloride – A systematic study for the preparation and application of an efficient coagulant for water or wastewater treatment. Journal of Hazardous Materials, 162 (2009) 1379– 1389.
13. N.D. Tzoupanos, A.I. Zouboulis and C. A. Tsoleridis, A systematic study for the characterization of a novel coagulant (polyaluminium silicate chloride). Colloids and Surfaces A: Physicochemical and Engineering Aspects, 342 (2009) 30–39.
14. N.D. Tzoupanos and A.I. Zouboulis, Novel inorganic-organic composite coagulants bases on aluminum. Desalination and Water Treatment 13 (2010) 340-347
15. P. A. Moussas, N.D. Tzoupanos and A.I. Zouboulis, Advances in coagulation/flocculation field: Al- and Fe based composite coagulation reagents, Desalination and Water Treatment 33 (2011) 140-146

16. P. A. Moussas and A.I. Zouboulis, Synthesis, Characterization and coagulation behavior of a composite coagulation reagent by the combination of Polyferric Sulphate (PFS) and cationic polyelectrolyte", *Separation and Purification Technology*, 96 (21) (2012) 263-273
17. H.X. Tang, Z.K. Luan, D.S. Wang and B.Y. Gao, Composite inorganic polymer flocculants. In *Chemical Water and Wastewater Treatment (II)*; Hahn, H.H.; Klute, R. Eds.; Springer-Verlag: Berlin, Germany (1998) 3–17.
18. B. Y. Gao, Q. Y. Yue and B. J. Wang, Properties and Coagulation Performance of Coagulant Poly-Aluminum-Ferric- Silicate-Chloride in Water and Wastewater Treatment, *Journal of Environmental Science and Health Part A*, 41 (2006) 1281–1292.
19. X. Niu, X. Li, J. Zhao, Y. Ren, and Y. Yang, Preparation and coagulation efficiency of polyaluminum ferric silicate chloride composite coagulant from wastewater of high-purity graphite production, *Journal of Environmental Sciences* 23(7) (2011) 1122–1128
20. R. Li, C. He and Y. He, Preparation and characterization of poly-silicic-cation coagulants by synchronous-polymerization and co-polymerization, *Chemical Engineering Journal* 223 (2013) 869-874
21. T. Sun, L.L. Liu, L.L. Wan and Y.P. Zhang, Effect of silicon dose on preparation and coagulation performance of poly-ferric-aluminum-silicate-sulfate from oil shale ash, *Chem. Eng. J.* 163 (2010) 48–54.
22. T. Sun, C.H. Sun, G.L. Zhu, X.J. Miao, C.C. Wu, S.B. Lv and W.J. Li, Preparation and coagulation performance of poly-ferric-aluminum-silicate-sulfate from fly ash, *Desalination* 268 (2011) 270–275.
23. L. Clesceri, A. Greenberg and R. Trussell, *Standard Methods for the Examination of Water and Wastewater*, 17th ed., APHA–AWWA–WEF, Washington, DC, 1989.
24. J. Radjenović, M. Matošić, I. Mijatović, M. Petrović and D. Barceló, Membrane Bioreactor (MBR) as an Advanced Wastewater Treatment Technology , *Hdb Env. Chem* 5 Part S/2 (2008) 37–101.