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Synthesis and characterization of a novel composite pre-polymerized coagulant for water and wastewater treatment

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Abstract*— The main aim of this study was the synthesis and characterization of alternative composite inorganic coagulants, resulted from the incorporation of polysilicates and ferric salts in the structure of commonly applied polyaluminum chloride (PACl) in the coagulation–flocculation (C/F) process, in order to increase its efficiency for water and wastewater treatment. The new product is called polyaluminum ferric silicate chloride (PSiFAC) and is synthesized under various experimental conditions and two different preparation methods (co-polymerization, or composite polymerization). The major typical properties of the prepared coagulants were examined, i.e. pH, turbidity, conductivity and Al species distribution (e.g. Keggin-Al13), employing the ferron technique. The composition, structure and morphology of the composite coagulants were studied in detail using (among others) the application of FT-IR and SEM techniques. The results show that the new composite materials have high Al13 content (51%). The study of FT-IR spectra exhibit intensive peaks, among others, at around 1098–1100 and 831–833 cm−1, which can be attributed to the stretching and bending vibration of Fe–OH–Fe and Al–OH–Al bonds, respectively in the coagulant, indicating the existence of the polymerization. SEM micrographs showed amorphous structures on the surface of composite coagulant, as well as the clinging block-shaped crystals, probably because of the formed NaCl. Overall, the FTIR and SEM analysis of the different PSiFAC samples indicate that the preparation method has no effect on the structure and morphology of the samples, but indicate certain differences in their physic-chemical properties. The most effective coagulants obtained were also used for the treatment of tannery wastewater to evaluate their performance

***Keywords*— composite inorganic coagulants, poly-aluminum-ferric-silicate-chloride, wastewater treatment**

I. Introduction

Coagulation-Flocculation is an essential part of several water and wastewater treatment operations, applied usually as advanced pre-, or post-treatment process to flocculate colloidal particles and dissolved organics. The commonly applied coagulants, are mainly the inorganic salts of aluminum and iron (AlCl3, FeCl, etc.). The Inorganic Polymeric Flocculants (IPFs), or pre-polymerized coagulants, such as polyaluminum chloride (PACl) [1], as well as the polyferric chloride (PFC) [2], represent a relatively new type of coagulation reagents, which were specifically developed, in order to increase the efficiency of coagulation-flocculation process. By introducing these metal ions (Fe, Al) into the polymerized silicic acid solution [3], the molecular weight of the product can be increased and the corresponding stability and coagulation performance can be further improved. Extensive studies on polysilicate coagulant combined with ferric or aluminum salts have been conducted recently by several researchers all over the world [4-6]. Zouboulis and Tzoupanos [7, 8], systematically examined several silica-based polyaluminum chloride derivatives.

The main aim of this study was the incorporation of polysilicates and ferric salts in the structure of PACl. The new product is called polyaluminum ferric silicate chloride and it was synthesized under various experimental conditions, i.e. by applying different basicity ([OH]/[Al] molar ratio); silica and/or ferric content ([Al]/[Fe]/[Si] molar ratio) and different preparation method (co-polymerization, or composite polymerization). Their properties were mainly evaluated by means of aluminum species distribution, employing the ferron technique. The structure and the morphology of composite coagulants were studied in detail, as well with the application of FT-IR and SEM techniques.

II. Materials and Methods

A. *Synthesis of Poly-aluminum-ferric-silicate-chloride Coagulants*

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.

Composite coagulants (PSiFAC-polyaluminum ferric silicate chloride) were produced in the present study at room temperature, according to a procedure proposed by Tolkou et al., 2014 [9], under various experimental conditions, and by using different ratios of components and (inorganic) polymerization modes.

The used initial solutions were 0.5 M $AlCl_3 \cdot 6H_2O$ (Merck), 0.5 M $FeCl_3 .6H_2O$ (Merck), 0.5 M NaOH (Merck)-as the added base-and the prepared polysilicic acid solution (pSi), according to Tzoupanos et al., 2009 [7]. In particular, appropriate amount of ferric chloride solution was added to a solution of aluminum chloride, under vigorous stirring at the desired ratios of Al/Fe and in the formed solution it was added the pSi at desired ratios of Al+Fe/Si, followed by the polymerization of Al with the slowly (under magnetic stirring) addition of the appropriate amount of NaOH solution (PSiFAC co-polymerization).

In the case of composite polymerization (PSiCAF), the base solution was initially added to the Al solution, creating an intermediate PACl solution. A solution of polyaluminum chloride ($PACl_{lab}$) was also prepared for comparison purposes under the same conditions.

Table I indicates the respective experimental conditions used for the preparation of certain, specific composite coagulants. The molar ratios used, were resulted from optimization processes, performed during preliminary experiments [9], noting that only selected results will be presented in the following (probably the best ones), from the full series of several obtained inorganic polymeric coagulants.

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TABLE I.

TABLE II. EXPERIMENTAL CONDITIONS OF PREPARED COAGULANTS

Coagulant type	Experimental conditions	
	Polymerization technique	*Molar ratio*
$PACl_{1.5(lab)}$		OH]/[Al] = 1.5
$PSiFAC_{1.5\text{-}10\text{-}15}$	Co-polymerization	OH]/[Al] =1.5 [Al]/[Fe] = 10 [Al+Fe]/[Si] = 15
$PSiCAF_{1.5\text{-}10\text{-}15}$	Composite polymerization	OH]/[Al] =1.5 [Al]/[Fe] = 10 [Al+Fe]/[Si] = 15

B. Characterisation Methods

- *Physico-chemical properties*. All the composite coagulants were characterized by measuring the pH value (using a Metrohm Herisau pH-Meter), the turbidity (using a Hach ratio/XR Turbidity-meter) and the conductivity (using a Crison CM 35 conductivity-meter).
- *Aluminum species distribution*. Aluminum species distribution was determined with the application of Al-ferron timed spectrophotometric method, which is based on the different reaction time of aluminum species with ferron reagent (8-hydroxy-7-iodoquinoline-5-sulphonic acid) to form water soluble complexes. These complexes absorb light with a maximum at 370 nm, hence absorbance measurements at this wavelength allow the calculation of the different species of aluminum (i.e. Al_a-monomers, Al_b-Al_{13} and Al_c-$Al(OH)_3$). A Hitachi UV/vis spectrophotometer was used for this purpose.
- *Scanning electron microscopy (SEM)*. Small portions of coagulant powders were obtained after drying in the oven (~40^o C); they were used to observe the morphology of the products, by employing a ZEISS EVO 50 scanning microscope.
- *FT-infrared spectroscopy (FTIR)*. FTIR spectra were recorded in the range of 4000–400 cm^{-1} by using a Nicolet 380 FT-IR Spectrometer-Thermo Scientific spectrophotometer.

C. Coagulation performance

A jar-test apparatus (Aqualytic) equipped with six paddles (employing 1L glass beakers) was used, to examine the coagulants efficiency in tannery wastewater. The relative properties of the used tannery wastewater were turbidity 668 NTU, 2.981 absorbance at UV254nm, 6800 mg/L COD, and 1.76 mg/L PO_4^{3-}. Water samples were collected from the supernatant of each beaker for further analysis.

III. Results and Discussion

A. Physico-chemical properties

Table II displays the major physicochemical properties of laboratory prepared composite coagulants. It can be observed that the addition of pSi in an Al-Fe solution to induce the formation of composite coagulants, results in the increase of turbidity, possibly due to the hydrolyzed silicon.

From the results in Table II, it appears that the polymerization method affects the percentage of medium-sized forms of polymerized aluminum (Al_b), wherein contained Al_{13}, and specifically in the case of $PSiFAC_{1.5\text{-}10\text{-}15}$, prepared by the method of co-polymerization, an increased content was found (Al_{13} 51%). Comparing this value with the corresponding value of laboratory prepared $PACl_{lab}$, it seems to exhibit rather similar behavior.

TABLE III. PROPERTIES OF LABORATORY PREPARED COAGULANTS

Coagulant type	Physic-chemical properties			Aluminum species distribution		
	pH	*Turbidity (NTU)*	*Conductivity (mS/cm)*	*Al_a (%)*	*Al_b (%)*	*Al_c (%)*
$PACl_{1.5(lab)}$	3.8	2.1	21.0	39	47	14
$PSiFAC_{1.5\text{-}10\text{-}15}$	3.9	211.0	23.7	44	51	5
$PSiCAF_{1.5\text{-}10\text{-}15}$	3.7	144.0	23.7	81	12	7

B. Structure Analysis

The possible chemical bonds present in the prepared coagulants were examined. Figure 1 illustrates the FT-IR spectra of composite coagulants prepared with the composite polymerization method ($PSiCAF_{1.5\text{-}10\text{-}15}$) and also prepared with the co-polymerization method ($PSiFAC_{1.5\text{-}10\text{-}15}$), whereas for comparison reason the corresponding spectra for $PACl_{1.5}$ at Figure 2 is also presented. As it is noticed from the study of relative spectra, there are similar absorption bands, regardless the applied polymerization technique.

Both spectra exhibit two characteristics bonds at 3500–3300 and 1641–1638 cm^{-1}, which can be attributed to the stretching vibration of –OH and to the bending vibration of water absorbed, polymerized and crystallized in the coagulant. As shown in Figure 1, the band at 1038 cm^{-1} is believed to be indicative of the high degree of polymerization of silica and it is assigned to the asymmetric Si–O stretching vibrations of Si–O–Si bonds. Moreover, the peaks at 1100 cm^{-1} could be attributed to the asymmetric stretching vibration of Fe–O–Fe or Al–O–Al, and around 1080-980 cm^{-1} corresponds to symmetrical stretching vibrations of Si–O–Fe and Si–O–Al respectively. In addition, there are strong absorption peaks at 1098–1100 and 831–833 cm^{-1} wave number, which can be attributed to the stretching vibrations and bending vibration of Fe–OH–Fe or Al–OH–Al respectively, indicating that the respective polymers are formed in the samples.

C. *Morphology Analysis*

Figure 3 illustrates the SEM images of the dried $PSiCAF_{1.5\text{-}10\text{-}15}$ sample (Figure 3a), prepared by the composite polymerization method, as well as the same sample $PSiFAC_{1.5\text{-}10\text{-}15}$ sample, but prepared by the different (co-polymerization) method (Figure 3b). Several different morphologies were observed, whereas the most predominant were a cubic-like morphology and a separated compact solid surface. Initially, the cubes were considered to be NaCl crystals, separated from the other constituents. Atomic analysis with SEM/EDS however, revealed that these cubes consist of the sum of the elements (Na, Al, Si, O, Cl, Fe) with % (per weight) relative content of 2.2, 17.0, 1.4, 43.9, 26.9, 5.8 for $PSiFAC_{1.5\text{-}10\text{-}15}$ and 4.7, 14.6, 0.7, 43.4, 28.5 and 5.1 for $PSiCAF_{1.5\text{-}10\text{-}15}$ respectively (Table III).

TABLE IV. ATOMIC ANALYSIS WITH SEM/EDS OF CUBIC CRYSTALS OF DRIED COMPOSITE COAGULANTS

% (w/w)	**Coagulant type**	
	$PSiFAC_{1.5\text{-}10\text{-}15}$	***$PSiCAF_{1.5\text{-}10\text{-}15}$***
Na	2.2	4.7
O	43.9	43.4
Cl	26.9	28.5
Al	17.0	14.6
Fe	5.8	5.1
Si	1.4	0.7

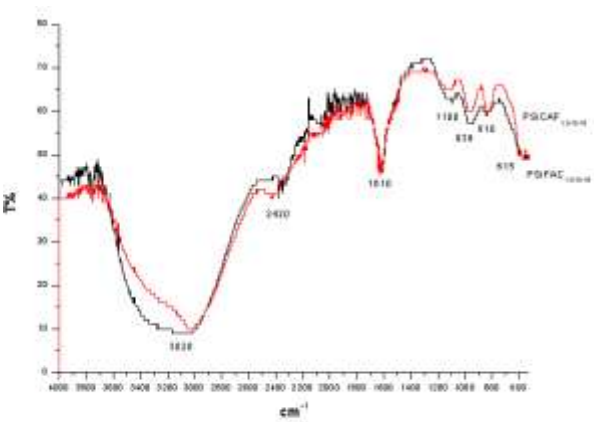


Figure 1. FT-IR spectra of composite coagulants prepared with the composite polymerisation method ($PSiCAF_{1.5\text{-}10\text{-}15}$) and prepared with the co-polymerisation method ($PSiFAC_{1.5\text{-}10\text{-}15}$)

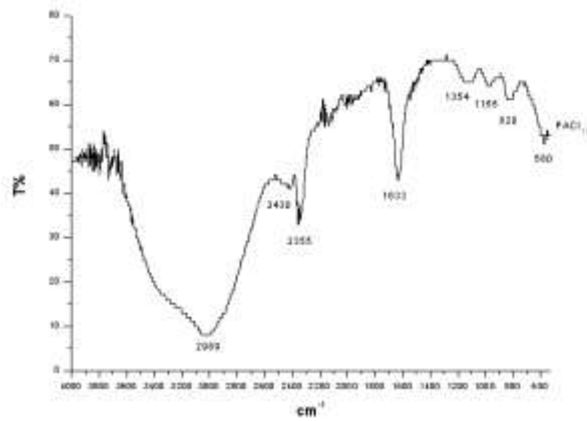
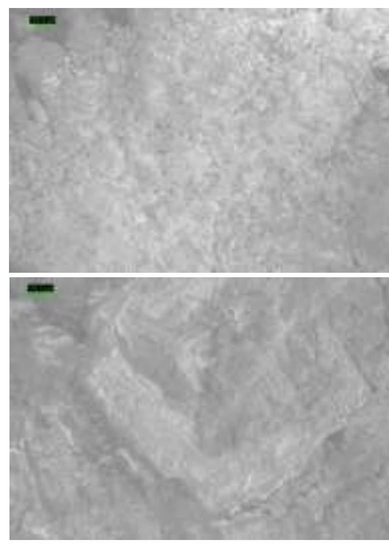


Figure 2. FT-IR spectra of laboratory prepared coagulant $PACl_{1.5}$



(a)

(b)

Figure 3. SEM images of composite coagulants, obtained after drying in an oven under constant low temperature (~40^{o} C). (a) prepared with the composite polymerisation method ($PSiCAF_{1.5\text{-}10\text{-}15}$) and (b) prepared with the co-polymerisation method ($PSiFAC_{1.5\text{-}10\text{-}15}$)

IV. Coagulation performance in tannery wastewater

The most effective coagulant obtained during preliminary experiments [9] i.e. PSiFAC1.5:10:15, was applied for the treatment of the aforementioned wastewater samples to evaluate its coagulation efficiency against these (considered as) relatively high-strength industrial wastewaters.

The results of coagulation experiments for (%) turbidity, absorption at UV254nm, COD and phosphates removals of wastewater samples are given in Figure 4; the experimental results indicated that, the addition of 30 mg/L of $PSiFAC_{1.5\text{-}10\text{-}15}$ in tannery wastewater, resulting to a reduction of COD 67%, and 96% for turbidity and 62% for phosphates. Although regarding the UV absorbance at 254 nm, the rates were found to be rather small (10%), as the wastewater sample was not subjected to any pre-treatment stage this is a highly contaminated sample, but coagulation was beneficial to the improvement of its quality.

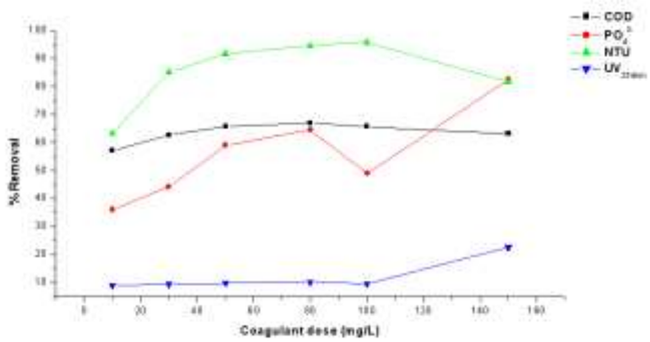


Figure 4. Coagulation experiments of $PSiFAC_{1.5\text{-}10\text{-}15}$ for tannery wastewater

V. Conclusions

The introduction of polysilicates and ferric salts in the structure of commonly applied polyaluminum chloride (PACl) affect its properties and characteristics. The results show that the new composite material, especially the one prepared with the co-polymerization technique, i.e. $PSiFAC_{1.5\text{-}10\text{-}15}$ have high Al_{13} content (51%). Overall, the FTIR and SEM analysis of the aforementioned composite coagulants indicate that the preparation method has no effect on the structure and morphology of the samples, however indicate certain differences in their major physic-chemical properties. In addition, both spectra exhibit intensive peaks, among others, at around 1098–1100 and 831–833 cm^{-1} which can be attributed to the stretching and bending vibration of Fe–OH–Fe and Al–OH–Al respectively, hence indicating the existence of polymerization. SEM micrographs show the resulting amorphous structures on the surface of the composite coagulant, as well as clinging block-shaped crystals, probably because of the formed NaCl. Finally, the most effective coagulant obtained were also used for the treatment of tannery wastewater to evaluate its performance, resulting to a reduction of COD 67%, of turbidity 96%, of phosphates 62%, but only 10% of UV_{254} nm absorbance.

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