NOVEL FERRIC SULFATE – BASED COAGULANTS[♦]

Ingrid Bucişcanu[*], Melinda Pruneanu, Vasilica Maier

"Gh.Asachi" Technical University of Iaşi, Department of Leather Chemical Technology, O.P. Iasi 10, CP 2070 Iasi, 700050, Romania

*Corresponding author: iiacomi@ch.tuiasi.ro

Abstract: This paper is dealing with the obtaining of some coagulants from the polyferric sulfate (PFS) and Fe-based metal-polysilicate (PFSiS) classes and the preliminary assessment of the products performances. A series of partially hydrolyzed ferric solutions were obtained starting from copperas ($FeSO_4 \cdot 7H_2O$), using exclusively hydrogen peroxide (H_2O_2) as oxidation – basification agent, in a molar ratio $FeSO_4/H_2O_2 = 1:1$ and $FeSO_4/H_2SO_4$ molar ratios, from 20:1 to 2:1. The basification degree and stability of the basic Fe(III) salt solutions are mainly controlled by the $FeSO_4/H_2SO_4$ ratio; $FeSO_4/H_2SO_4$ ratios between 2.03:1 and 5:1 result in extremely stable solutions. The PFSiS coagulants were obtained through a modified copolymerization technique, involving the *in-situ* generation of silicic acid (SA) at a Si/Fe molar ratio of 1:10, followed by oxidation-basification. Stable solutions were obtained over a narrow $FeSO_4/H_2SO_4$ range, located around 2.5:1. All the solutions were characterized in terms of Fe(III) and residual Fe(II) concentration, free acidity, density, stability and time evolution of basicity. The coagulation tests indicate improved coagulation ability of the prehydrolized coagulants over the ferrous salt.

Keywords: *water, wastewater, coagulation, prehydrolyzed coagulants, iron-silicate coagulant*

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INTRODUCTION

Coagulation is a reliable and efficient method for the treatment of water and wastewater, which lowers the suspended solids and some dissolved compounds concentration of the treated water. The use of aluminum and iron salts, usually associated with flocculation adjuvants, is well-established in the field of water and wastewater primary treatment.

Studies on hydrolysis and coagulation mechanisms showed that it is not the salt itself, but the mono-, oligo- and polymeric hydrolysis products (generated *in situ*) which act as active species in the separation process. From this observation, the idea to prepare these active species separately from the medium to be treated has arisen and a new class of coagulants – **pre-hydrolyzed, preformed** or **polymeric Al** and **Fe salts,** also known as inorganic polymeric coagulants (IPCs) – has been launched on the market in the 80's.

At present, the prehydrolyzed Al and Fe salts dominate the coagulating agents market, due to many advantages over the conventional ones [1]: (1) treatment is less sensitive to water *pH* and temperature variations and does not require such strict *pH* control through supplemental chemical addition; (2) treatment with IPCs promotes enhanced coagulation at lower dosages, which is costly efficient and advantageous especially for drinking water treatment, where low residual metal concentrations are required; (3) treatment may be performed without flocculant addition, as big flocs arising from voluminous polymeric species are easily settleable.

The Al-based pre-hydrolyzed coagulants are preferred because hydrolysis proceeds via a controllable pathway, while ferric coagulants are not very easy to obtain due to Fe(III) sensitivity to hydrolysis and precipitation. Lately, the interest in Fe-based coagulants has increased, due to several advantages over the Al-based similar products [2]: higher versatility, lower costs, phosphorous and arsenic removal, better settling behavior, lower effective dosages and residual concentrations, lower toxicity, mainly when related to drinking water; the most common product of this range is the polyferric sulfate (PFS), for which the quality standards are imposed, as given in Table 1 [3].

*Table 1. General quality standards for pre-hydrolyzed **PFS** coagulants*

Appearance	Total Fe [%]	Fe^{2+} [%]	Basicity [%]	Density at 20° [g/cm^3]	pH (sol. 1%)	Insoluble matter [%]
Limpid, viscid, reddish-brown liquid	≥ 11	≤ 0.1	9-14	> 1.33	2-3	≤ 0.3

Polyferric sulfate can be produced starting from Fe(II)-containing minerals (pyrite FeS_2, copperas $FeSO_4 \cdot 7H_2O$ or magnetite $FeO \cdot Fe_2O_3$); PFS synthesis can be performed in two ways: (1) a two-step procedure, as described in [4], in which oxidation of Fe^{2+} to Fe^{3+} and basification occur consecutively. Protected oxidizing reaction takes place in the presence of sulfuric acid in excess; basification agents are weak bases such as Na_2CO_3 and $NaHCO_3$. During a subsequent ageing step, polymeric species arise. (2) selecting appropriate oxidizer and reaction conditions, PFSs synthesis can take place in one step only, by simultaneous oxidation and basification [3, 5]. Common oxidizing agents are: nitric acid, peroxides, alkaline chlorates and perchlorates, ozone, persulfates, with or without a catalyst.

Several stabilization attempts were made during the IPCs obtaining, by introducing different organic or inorganic anionic ligands that prevent excessive hydrolysis/polymerization. The combination with alkali silicates, especially with sodium silicate or waterglass (WG), generated a new class of inorganic polymer coagulants: metal-polysilicate coagulants, which exhibit superior efficiency in turbidity, COD and color removal [6]. The polysilicic acid (**PSA**), prepared through partially neutralization of alkali silicates is well-known as an effective aggregation agent and its beneficial effects in conjunction with metal salts were pointed out by Baylis [7].

The metal-polysilicate coagulants are mainly prepared by two techniques: copolymerization and the composite technique [2]. The speciation and transformations of metal-polysilicate coagulants are different from those of simple pre-hydrolyzed coagulants due to the interaction between PSA and the Fe (III) oxyhydroxy species: the silanol groups can compete with the free OH^- anions for the coordination sites and have a great impact on the hydrolysis-polymerization scheme, leading to stable polymeric species [8]. It is known that iron precipitation is significantly delayed in the presence of silicic acid, due to a soluble $FeOSi(OH)_3^{2+}$ complex generation [9]. The interaction between iron and silica is mainly dictated by the pH and silica concentration [10]. Preparation of polyferric-silicate coagulants using both techniques, starting from $FeCl_3$ and $FeSO_4$, respectively, has been reported [5, 11].

The aim of this paper is to establish the working parameters for the obtaining of stable and effective Fe-based prehydrolyzed coagulants through simple techniques and to perform preliminary tests on their coagulation and separation ability.
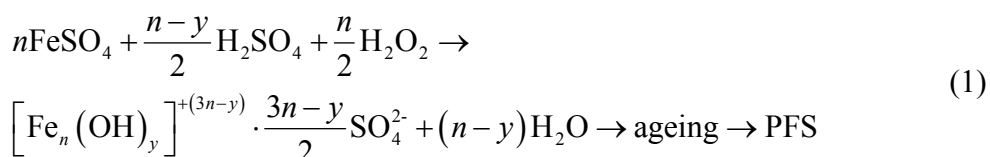

MATERIALS AND METHODS

Materials

All reagents were analytical grade chemicals: ferrous sulfate heptahydrate $FeSO_4 \cdot 7H_2O$ 98%; sulfuric acid H_2SO 98 %; sodium silicate $Na_2Si_3O_7$ with 27 % SiO_2, 10 % NaOH and d = 1.39 g/mL; hydrogen peroxide H_2O_2 30 % (wt/v); kaolin. All the other required reagents were of synthesis grade. All solutions were prepared with deionized water, excepting the kaolin suspension, for which tape water was used.

Preparation of PFS coagulants

The general oxidation – basification process can be written according to Eq. (1):

$$n\text{FeSO}_4 + \frac{n-y}{2}\text{H}_2\text{SO}_4 + \frac{n}{2}\text{H}_2\text{O}_2 \rightarrow$$

$$\left[\text{Fe}_n\left(\text{OH}\right)_y\right]^{+(3n-y)} \cdot \frac{3n-y}{2}\text{SO}_4^{2-} + \left(n-y\right)\text{H}_2\text{O} \rightarrow \text{ageing} \rightarrow \text{PFS} \tag{1}$$

Starting solutions of $FeSO_4$ were prepared by dissolving ferrous sulfate heptahydrate $FeSO_4 \cdot 7H_2O$ 98% in deionized water, previously acidulated with H_2SO_4 98 % in such amounts that the satisfaction degree of the maximum stoichiometric requirement (St.Req.) ranges between 0 % and 100 % (see Table 2). The required H_2SO_4 quantities were calculated from Eq. (1), taking $n = 1$ and $y = 0$.

The mixture was heated at 55-60 ºC under moderate stirring for complete dissolution, than cooled down to 40-42 ºC. The concentration of Fe(II) in the starting solutions was limited by the solubility limit of copperas at 40 ºC. The hydrogen peroxide was slowly injected in the reaction mass with a rate of 0.5 mL/min., under vigorous magnetic stirring. In order to provide complete oxidation, the $FeSO_4 : H_2O_2$ molar ratio was kept at 1:1, which corresponds to 200% of the St.Req. The starting temperature was 40 ºC and carefully kept below 50 ºC, as the reaction is strongly exothermic. After complete H_2O_2 addition, the reaction mass was mixed at 50 ºC for more 30 min and during cooling down, until no gas bubble was noticed in the reaction mass. One duplicate of sample 6 was subjected to supplemental heating at 70 ºC in order to promote accelerated ageing, and than cooled down to room temperature.

Preparation of PFSiS coagulants

Silicate was diluted with water to a water/WG mass ratio = 4:1 and added dropwise to the Fe(II) solutions under vigorous mixing at 40-45 ºC, so that the $FeSO_4/SiO_2$ molar ratio = 10:1. The resulting mixture must be perfectly limpid and fluid, which indicates no PSA gelation. Subsequent oxidation/basification procedure was identical to those described above. Replicates of starting samples 3, 5, 7, 8 and 9 (see Table 2) were used for the preparation of PFSiS coagulants.

Coagulation tests

A stock suspension of 1g/L kaolin was first prepared, from which 1L samples of 100 mg/L kaolin were obtained.
The coagulation efficiency of the polyferric sulfate, PFS (sample 5), the PFSiS (sample 4.8) and the $FeSO_4$ was assessed. The coagulation tests were performed according to a conventional Jar Test procedure, at: coagulant dosage of 50 mg/L Fe_2O_3, 2 min rapid mixing and 15 min slow mixing, no flocculant added; the suspension *pH* was adjusted to 8 – 8.2, with Na_2CO_3 1N. During settling, supernatant samples were collected at 2.5 cm beneath the liquid surface, at 5, 10, 15, 20, 30 and 40 min respectively, for residual turbidity measurements.

Analysis methods

All the iron basic solutions were characterized in terms of total iron concentration, residual Fe(II) concentration, density, free acidity, time evolution of basicity degree and stability. Ferrous(II) and ferric(III) iron concentrations were determined through the permanganometric and complexometric volumetric methods, respectively. The solutions basicity and free acidity were determined by titration with NaOH in the presence of phenolphtaleine and benzyl-red, respectively following a procedure similar to those used for Cr(III) basic salts and described in [12]. Stability was determined as the period until the ferric hydroxide precipitate was first noticed. Solutions density was measured by the pycnometric method.
The turbidity of kaolin suspensions was measured on a FEK-56M-Y4.1 photocolorimeter/nephelometer, at 440 nm.

RESULTS AND DISCUSSION

Main characteristics of the **PFS** solutions are given in Table 2. Successive oxidation and basification can be directly observed during preparation through the color change: the solution turns from pale green to dark brown in the first stages, which confirms the $Fe_2(SO_4)_3$ formation, and then turns to reddish-brown, which corresponds to the cationic complexes formation. The higher the $H_2SO_4 : FeSO_4$ ratio, the later the color change, which confirms that the acid prevents the intrusion of the OH^- ions in the Fe(III) coordination sphere. Unlike basification by conventional alkali adding, when the hydrogen peroxide is used local precipitation does not occur, which is essential in avoiding rapid mass precipitation. Reaction of a non-acidified $FeSO_4$ solution with the H_2O_2 (sample 1) results in a voluminous, amorphous yellow-reddish $Fe(OH)_3$ precipitate, which can be easily redissolved in strong acids. For sample 2, precipitation was observed after 24 hours. Samples 8 and 9 did not undergo immediate hydrolysis – their basicity degree remained null several weeks under preparation - due to the high acidic protection. Samples 5, 6 and 7 led to stable basic solutions, but only samples 5 and 6 attained a convenient basicity in due time. Sample 10 exhibited an interesting behavior: the basification was speeded up by the higher temperature and finally leaded to an extremely stable solution with convenient basicity, which confirms that the hydrolysis pathway is essentially dependent on the OH/Fe ratio and temperature does not affect the hydrolysis overall scheme [13]. The basicity of the solutions grew from $2.96\% \div 5.26\%$ in the freshly prepared solutions to the final values given in Table 2. The addition of the oxidation agent only initiates a hydrolysis process, the duration of which is in inverse ratio to the solution stability. Initial basicities higher than $20 - 22\%$ initiate a fast, irreversible hydrolysis that results in precipitates. These result are consistent with the four-stage Fe (III) hydrolysis scheme, as proposed by Pykhteev *et al*. [13]: (**1**) hydrolysis to mono and dimeric equilibrium hydroxo complexes (**EHC**); (**2**) reversible, rapid growth to low molecular-weight polymers, containing between 3 and 13 ferric ions, through olation between **EHCs** (**polyFe$_{3-13}$** fraction $[Fe_x (OH)_y]_n^{(3x-y)\,n+}$); (**3**) formation of slowly reacting, medium weight polynuclear products, **polyFe$_{13-33}$**, through irreversible oxolation reactions; **4)** formation of final hydrolysis products, i.e. stable high molecular-weight polymers **polyFe$_{33-101}$** and crystalline precipitates. The pre-hydrolysis degree $Z = [OH^-]/[Fe(III)]$, mainly dictates the molecular-weight distribution between different monomeric and polymeric forms of Fe(III) in solution. Polyferric solutions, mainly consisting of low molecular weight species, *i.e.* **polyFe$_{3-13}$** fraction, exhibit best coagulating properties [4]. Coagulants with commercial value can be obtained from basic solutions with a shelf life of 6 months at least and a basicity of $9 - 14\%$, attained in a short time; samples 5, 6 and 10, corresponding to moderate degrees of acidic protection, meet these requirements.

The residual Fe(II) concentration did not exceed 0.4 g/L (which is equivalent to less than 0.1%) for any of the basic solutions. Free acidity was determined on samples 5, 6 and 10 and the obtained values were of: 1.12 %, 1.55 % and 1.78 %, respectively, which fall into the accepted range of $0.5 \div 2$ %.

Table 2. *Characteristics of the PFS solutions obtained through the one-step procedure*

Sample	% of H_2SO_4 St.Req.	$\dfrac{FeSO_4}{H_2SO_4}$ molar ratio	Fe^{3+} [g/L]	Fe^{3+} [%] w/w	ρ [g/cm^3]	Stability (Shelf life)	Basicity, %			
							7 days	14 days	21 days	1 year
1	0	-	-	-	-	Instant precipitation	-	-	-	-
2	10	20:1	-	-	-	Precipitation after 24 hrs	-	-	-	-
3	20	10:1	110.71	8.05	1.37	1 month	20.19	23.16	22.57	-
4	30	6.67:1	107.86	7.99	1.35	2 months	12.58	16.58	16.58	-
5	40	5:1	110.56	8.95	1.23	6 months	13.2	13.2	13.2	-
6	50	4:1	108.54	8.82	1.23	1 year	8.87	8.87	8.87	-
7	60	3.33:1	108.54	9.08	1.19	> 2 years	2.96	2.96	2.96	11.45
8	80	2.5:1	111.25	8.86	1.25	> 2 years	0	0	0	7.50
9	100	2.03:1	106.10	8.44	1.25	> 2 years	0	0	0	6.60
10*	60	3.33:1	132.96	9.29	1.43	> 2 years	14.2	10.73	10.8	13.8

* With supplemental heating at 70 ºC for 30 min

The obtaining of the **PFSiS** solutions, whose characteristics are given in Table 3, is more difficult through the proposed copolymerization technique, as the stability of such products implies neither precipitation of Fe(III), nor gelation of PSA.

Table 3. *Characteristics of the PFSiS solutions*

Sample*	% of H_2SO_4 St.Req	$\dfrac{FeSO_4}{H_2SO_4}$ molar ratio	$\dfrac{FeSO_4}{SiO_2}$ molar ratio	Fe^{3+} [g/L]	Fe^{3+} [%] w/w	ρ [g/cm^3]	pH	Stability (Shelf life)	Basicity, %	
									7 days	14 days
1.3	20	10:1	10:1	-	-	-	-	Strong precipitation after 3 days	-	-
2.5	40	5:1	10:1	-	-	-	-	Weak precipitation after 5 days	-	-
3.7	60	3.33:1	10:1	97.18	7.71	1.26	≅1.8	Weak precipitation after 2 weeks	22.74	22.87
4.8	80	2.5:1	10:1	93.9	7.34	1.28	≅1.6	Stable after 6 months	13.18	13.21
5.9	100	2.03:1	10:1	102.1	8.04	1.27	≅1.0	Gelation after 6 weeks; no precipitation	0	0

* The first figure indicates the experience number and the second one indicates the corresponding sample from the one-step procedure experiment, for which the **H_2SO_4 St.Req.** was replicated

These requirements can be met through careful control of H_2SO_4 and silicate concentrations, so that: (1) the resulting basicity is lower than 20% in order to prevent uncontrolled hydrolysis and (2) the SiO_2 content is lower than 3% and the *pH* is between 1.5 and 2, in order to avoid advanced polymerization of the silicic acid. If the $FeSO_4 : SiO_2$ molar ratio is maintained to a reasonable value of 10:1, stable **PFSiS** coagulants can be obtained through the proposed procedure over a narrow range of the

$FeSO_4$: H_2SO_4 molar ratio, placed around 2.5:1 (see sample 4.8). Higher $FeSO_4$: H_2SO_4 molar ratios determine iron precipitation because part of the sulfuric acid is consumed by the silicate, while high H_2SO_4 concentration results in gelation, due to low pH values. The residual Fe(II) concentration is around 0.32 g/L, which indicates advanced oxidation yields.

The coagulation tests emphasized the superior efficiency of pre-hydrolyzed coagulants over the conventional one. While the $FeSO_4$ acted as a poor coagulant (the turbidity decreased with only 43% in the absence of a flocculation agent), the percent decrease of turbidity achieved by **PFS** and **PFSiS** is 77.5% and 82%, respectively (Figure 1).
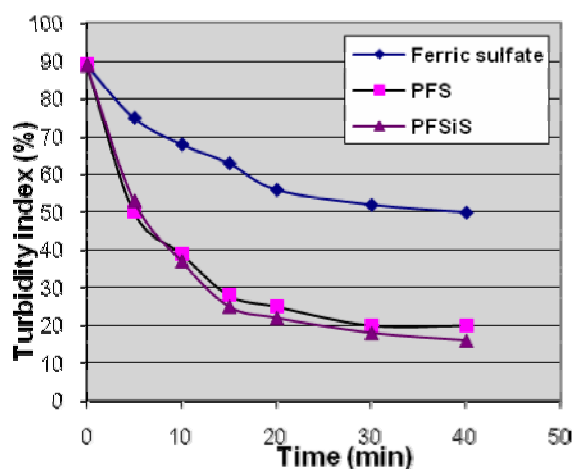

Figure 1. Coagulating efficiency of conventional and improved coagulants

The **PFS** and **PFSiS** separation efficiency are close, but one must take into consideration that the metal-silicate coagulants are intended to put together the coagulation effect of the positively charged Fe(III) hydrolitic species and the aggregation effect of the polysilicic acid. Taking into consideration that the PSA lowers the zeta potential of the ferric oxycations and weakens the charge neutralization effect, an optimal Fe/Si ratio must be established at which both effects show optimal values.

CONCLUSIONS

Hydrolysis of Fe(III) salts follows a complex hydrolysis scheme, in which uncontrolled olification /oxolification reactions take place; unlike other hydrolyzable metals, the molar ratio between the hydroxyl ions and the ferric ion, cannot stoichiometrically control the basicity of the basic solution.

Stable **PFS** solutions can be prepared through a one -step procedure, in which the oxidizing agent performs both the oxidation and the partial hydrolysis; no catalysts needed, no supplemental ions introduced in the reaction mass. The $FeSO_4$: H_2SO_4 molar ratio is the main factor controlling the process, but temperature, addition rate of the oxidation -basification agent and mixing regime must also be taken in account.

The partial hydrolysis must result mainly in olation products with low and medium molecular mass, which are active in the coagulation treatment and avoid large oxolation

species, which are much more amenable to precipitation and exhibit poor coagulating efficiency. Ferric poly-silicate coagulants can be prepared through a simple copolymerization technique, provided the $FeSO_4$: H_2SO_4 and $FeSO_4$: SiO_2 are simultaneously carefully controlled.

The modified coagulants have similar clarifying performances on the tested suspension and further work on actual waters or wastewaters is needed in order to ascertain superior coagulating behavior of **PFSiS** over **PFS.**

Stable and effective coagulants can be obtained through a simple technology, as a way to give added value to cheap, nontoxic raw materials such as water glass or to recycle cheap and abundant industrial by-products from other industries, like ferrous sulfate, sulfur dioxide and sulfuric acid.

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