Revista de Chimie
https://revistadechimie.ro
https://doi.org/10.37358/Rev. Chim.1949

New Materials Synthesized by Sulfuric Acid Attack Over Power Plant Fly Ash

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Abstract: *In the current work, the preparation of a complex wastewater coagulant based on polymeric sulfates of aluminum/iron from fly ash is presented. The performance of the coagulation–flocculation process is mostly influenced by the coagulant type, which enhances the aggregation of particles and leads to formation of fast-settling flocs by charge neutralization or chain-bridging mechanisms. Within the preparation process, the reaction temperature was controlled at 80°C and 90°C for 4 h, the synthesized materials being characterized through different techniques (SEM, EDAX, FTIR, and XRD) and further used as coagulants for real wastewater treatment. As a novelty of this study, it can be mentioned that there were analyzed the possibilities of capitalization of Romanian fly ash collected from Iasi area and its transformation into complex based on aluminum - iron sulfates. Fly ash containing different concentrations of* Fe_2O_3 *and* Al_2O_3 *was successfully used in producing complex coagulants by reacting with 10% technical sulfuric acid solution. The produced complex coagulants contain both polymeric ferric sulfate (PFS) and polymeric aluminum sulfate (PAS) (demonstrated by complex characterization) and proved to be effective in wastewater treatment. These sustainable materials exhibited a good performance in coagulation–flocculation process (e.g. it was obtained a TSS removal efficiency of 84% at the coagulant dosage of 60 mg/L).*

Keywords*: acid attack, fly ash, polymeric aluminum sulfate, polymeric ferric sulfate*

1. Introduction

Coagulation process is a simple and economic wastewater treatment technology, recommended for domestic and industrial wastewater, in the primary purification treatment [1, 2]. In general, both coagulation and flocculation are used in the treatment process [3].

After addition of the coagulant, the aggregation of the microscopic suspensions of colloidal particles occurs, which induces the loss of stability of the colloids in the water [4]. The aggregation of colloidal particles results in the formation of flocs [5]. The flocculation process determines the agglomeration of small flocs that lead to improvement of decantation and separation processes. These processes are used simultaneously as coagulation-flocculation (CF) process. The process depends on particles surface, stability, dosage and coagulant type.

The population growth and industrialization result in large quantities of wastewaters that have to be treated in order to prevent the degradation of various ecosystems, or to be reused in the same process [6-10]. In the last years, many studies on improving the performance of the CF process have been performed [11-14]. The coagulation–flocculation process is mostly used for treatment of wastewater from textile industry, municipal sewage, oily wastewater, paper industry wastewater etc.

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Ferrous and ferric salts such as sulfate or chloride - ($Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $FeCl_3$ - are examples of inorganic coagulants, while polymeric compounds such as polyelectrolytes are examples of flocculation agents [15]. Since the potential toxicity of residual aluminum over human health was already demonstrated, new types of coagulants were recommended – namely inorganic polymers such as poly-ferric chloride and poly-ferric sulfate [16, 17]. Pre-polymerized sulfates were formed during the synthesis process, which proved to be more effective than the conventional inorganic salts.

On the other hand, adsorption can be used in tandem with coagulation–flocculation process in order to reduce heavy metals, color and organic compounds from wastewaters resulted from textile, electroplating, dyes and paper industry, as well as municipal sewage or micro-polluted water etc. [17-19].

The complex macromolecules flocculants neutralize the particles and decrease the surface potential. However, the high dosage of flocculants can determine the charge reversal of colloidal particles and leads to a stable colloid. The selection of the most suitable polyelectrolyte for a real wastewater depends on the particle type and the pollutants found in the wastewater. The influence of type, respectively the dosage of flocculant and coagulant should be investigated at laboratory scale, especially for real wastewaters, pilot plant studies being necessary before implementation of new materials. The residual turbidity can be measured as a function of different parameters, such as flocculant/coagulant dosage, mixing rate, *p*H, and temperature etc., using an inexpensive jar tests in a laboratory scale set up. Separation of aggregated particles after flocculation process is done by sedimentation based on particle sizes, shapes, and densities, the supernatant being analyzed [20].

If for the commercial coagulant, the dosage and mechanism are known, the investigations are focused on the synthesis of new coagulants able to improve the coagulation–flocculation process for wastewater treatment. These new materials must be low cost, but to have the advantage of improving the coagulation–flocculation process, such as inorganic and composite coagulants.

The capitalization of waste, particularly power plant waste, has a great importance in waste management, saving resources and ensuring the environmental protection. Many studies are focused on capitalization of power plant waste as filler, in construction and building materials, in low cost adsorbent manufacture, etc. [21- 26]. Also, there are better methods that consist in extraction of iron and aluminum and their capitalization [27-29].

Low cost coagulants, obtained from fly ash have been proposed for application in water treatment plant, as a result of their efficiency comparative with that of commercial coagulants. The main method for preparing new coagulants from fly ash involves its treatment with acid solution, especially sulfuric acid, which results in compound with high CF efficiency. Gao et al. [30] have studied a composite coagulant, polymeric aluminum-silicate chloride, revealing that this improved the efficiency of particles aggregation, the result being superior compared to those obtained when hydroxylated poly aluminum-chloride was used. Sun et al. [31] investigated the performance of poly-ferric-aluminum-silicate-sulfate synthesized from fly ash.

In this paper, new coagulants consisting in mixtures of polymeric ferric sulfate (PFS) and polymeric aluminum sulfate (PAS) in the presence of SiO_2 have been synthesized by acid treatment of fly ash collected from a thermal power plant in the city of Iasi. The chemical and the morphological characterization of these sustainable materials were performed using Fourier transformed infrared (FT-IR) spectrophotometer, X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The synthesized materials were investigated for treatment of real wastewaters resulted from a fertilizer plant. The influence of type and dosage were investigated for the determination of flocculation efficiency of the obtained materials compared with commercial materials.

2. Materials and methods

2.1. Description of water sources

Wastewater samples were collected from an industrial ammonia plant, the uptake site being located at 5 km away from the plant. Samples were collected in the period 1–30 August 2019 and the parameters are presented in Table 1.

Table 1. Real wastewaters characteristics

Parameters	Values	u.m
Temperature	24.1 ± 0.05	°C
Total dissolved solids	140-180	mg/ L
Conductivity	300-1100	μS/cm
Ammonia	2-1700	ppm
Nitrate	0-8	mg/L
Nitrite	0-0.2	mg/L
pH	7.0 -8.22	
SiO_2^{-}	0-25	mg/L
SO_4^{2-}	0-25	ppm
Total hardness	60-93	mg/L in $CaCO_3$

The tests that were performed with the real wastewaters from ammonia plant revealed that the initial TSS was between 140 and180 mg/L, depending on the period of sampling. A very large dispersion of conductivity has been observed, with values in the range of 300 - 1100 μS/cm, these results being in accordance with those reported for other plants [32].

2.2. Preparation of coagulant from fly ash

Fly ash (FA) - an inorganic waste produced by burning of pulverized coal in a thermal power plant (CET Holboca Iasi)- was used in this study. The main characteristics of FA are: the color is gray to black (depending on carbon unburned), particles sizes are between 0.01 and 100 μm; the shape of particles is spherical, specific surface is between 4800 and 200 g/m^2 and the density is between 2400 and 2550 kg/m^3 [33]. For the beginning, the fly ash was characterized, the results revealing the following composition: SiO_2 – 58.82%; Al_2O_3 –17.08%; Fe_2O_3 – 8.98%; CaO-8.31%; MgO-1.09 %; SO_3 –1.538%, in accordance with the previously published papers [33, 34].

The ratio of fly ash to the sulfuric acid solution was based on the stoichiometry of reactions between the iron and aluminum oxides. A quantity of 200 g of fly ash and 500 mL of 10% sulfuric acid solution was added in reactor, as shown in Figure 1.

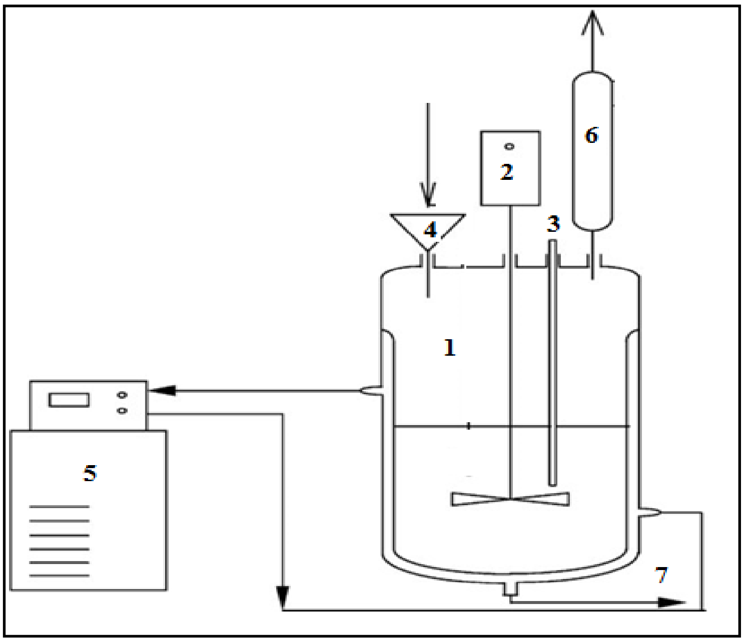

Figure 1. Experimental plant used for producing complex coagulant from fly ash. (1) reactor heating unit; (2) mechanical stirrer; (3) thermometer, (4) funnel (sulfur acid feeding), (5) thermostat; (6) condenser; (7) complex coagulant evacuation

The reaction temperature was controlled at 80°C and 90°C for 4 h and the resulted slurry was cooled and filtered. The materials obtained were dried at 50°C for 24 h.

New synthesized materials were characterized by: X-ray diffraction, using a X'Pert PRO MRD X-ray diffractometer; SEM/EDAX was determined with Quanta 3D - AL99/D8229); FTIR spectra, was carried out using FTIR spectrophotometer model Nicolet in transmittance mode, with a resolution of 4 cm^{-1} in the 4000–400 cm^{-1} range.

2.3 Coagulation flocculation experiments (jar tests)

For coagulation were used different materials:

- coagulant 71221, a liquid blend of organic polymer and inorganic coagulant based on aluminum. The 71221 coagulant, supplied by Nalco, is recommended to coagulate suspended solids and organic matter with application in industrial water clarification, primary and secondary effluent clarification, oily wastewater clarification, but it is not approved for use in potable water treatment (https://aniq.org.mx/Pqta/pdf/ULTRION%20(LIT).pdf).
- Aluminum sulfate, supplied as Nalco 7530, available in the solid form, with the composition: $Al_2(SO_4)_3\ 18H_2O$.

Preparation of flocculants has been achieved by complying Nalco recommendations: 0.5% solutions was prepared by adding 1 g of product to 199 g of water and mixing for 30 minutes. Coagulants with the convenient solution strength were subjected to dosing with the syringe (1.0-10%).

- The complex coagulant produced was used to test the removal capacity of total suspended solid (TSS) in a real wastewater from ammonia plants, its performance being tested using a JAR Tester. Four beakers of 500 mL were used for this purpose, one of them constituting the blank. In each beaker were added the desired amounts of coagulant with a syringe. The coagulant was weighed carefully in order to ensure a pre-established concentration (2-12 ppm) in the wastewater sample. The samples have been stirred at 130 rpm for 10 min, in order to maintain a homogeneous TSS distribution. Further, stirring speed was reduced to 20-40 ppm for 15 minutes, simulating the plant slow mix conditions. The results of coagulation occurring in all of the beakers have been compared with those from control beaker (blank). Settling rate and clarity were determined using a turbidity meter. The turbidity was measured with a Cole Parmer Model 8391-40 turbidity meter. The pH and conductivity were monitoring, with SevenCompact S230 Basic Mettler-Toledo and portable pH-meter.

The complex coagulants produced at 80◦C (C1) and 90◦C (C2) have been characterized and apriority tested for removal of total suspended solid (TSS) from wastewater. On the base of the testing results, the coagulant named as C2 was chosen for the further investigation

The performances have been presented in terms of percentage of pollutant removal from wastewater, (R%) calculated with equation:

$$R(\%) = \Delta T_{SS}/T_i\ 100 \qquad (1)$$

where T_i is the initial total suspended solid before coagulation; ΔT_{SS} is the variation of total suspended solid at a predetermined settling time (t) after the coagulation run.

The testing was performed using real wastewater from an ammonia plant sampled over a period of 30 days, during 15 August - 15 September 2019. Each experiment was achieved in triplicate, for excluding any errors.

3. Results and discussions

3.1. Characterization of materials

The characteristics of raw materials have been presented in a previous paper [25]. The FTIR spectra for the synthesized materials are presented in Figure 2.

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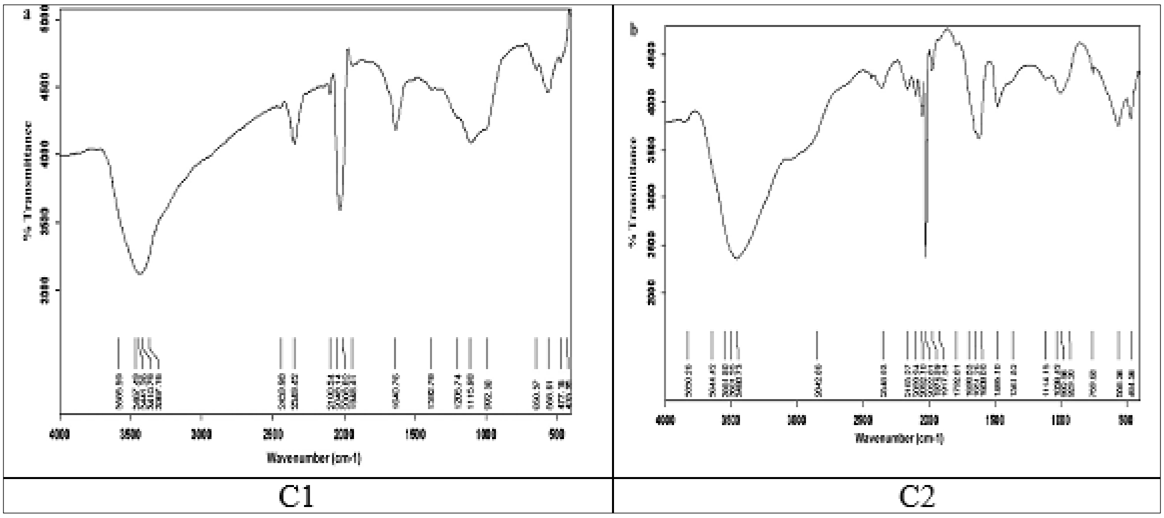


Figure 2. FTIR spectra for coagulant materials

The spectra from Figure 2 shows bands at 570 cm^{-1} and 630 cm^{-1} due to Fe–O stretching of hematite. The band at 468 cm^{-1} is determined from lattice vibration mode of FeO_6. The bands in the range of 3200–3650 cm^{-1} for both coagulants were attributed to the stretching vibration of –OH group. The peaks in the range of 1600–1700 cm^{-1} were assigned to the bending vibration of –OH groups in the water molecule (H–O–H), suggesting that the materials could contain structural and adsorbed water. The characteristic absorption peak for sulfate was evident in the range 900–1200 cm^{-1}, taking into consideration that sulfate structure is tetrahedral, exhibiting symmetrical and anti-symmetrical stretching vibration. The peaks at 1114 and 1115 cm^{-1} were assigned to the SO_4^{2-} stretching vibration. The absorption at 1485 and 2163 cm^{-1} can be assigned to the Al–O–Al bonds stretching [15].

For the identification of the compounds or phases, X-ray powder diffraction was used. Figure 3 shows that the major phase is $Fe_{14}S_{18}O_{75}\cdot xH_2O$.

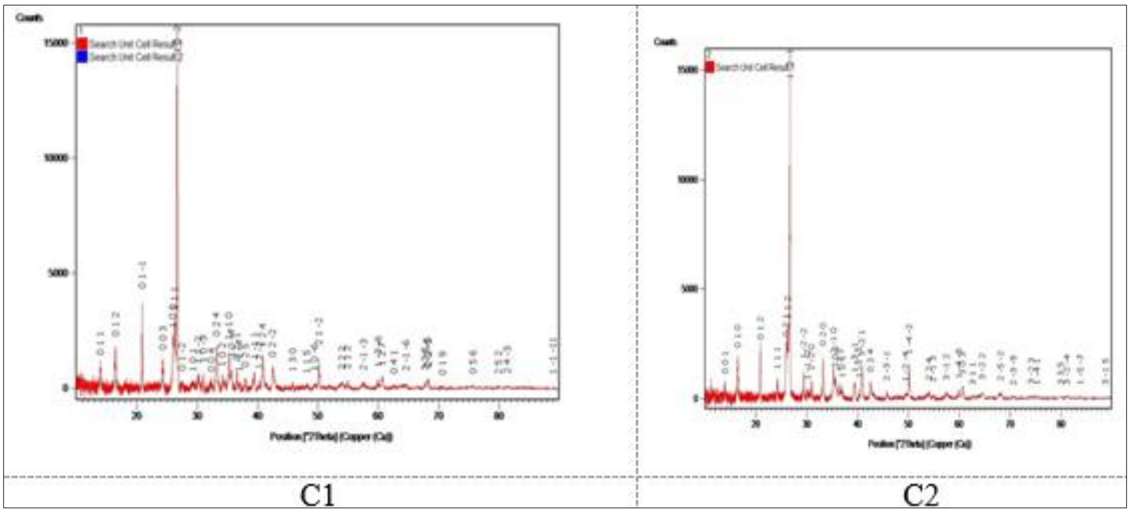
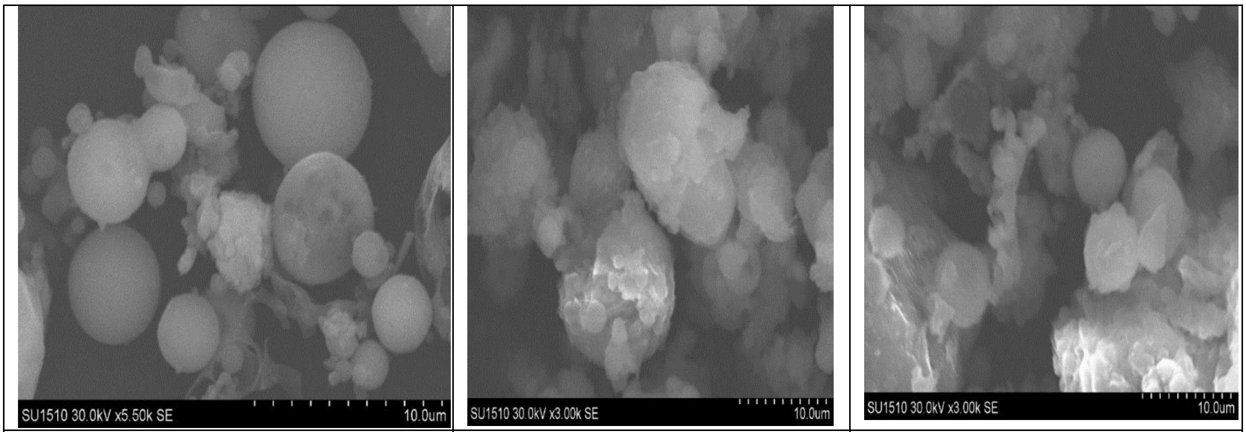


Figure 3 XRD for synthetized materials

The basic iron sulfate salts were nonstoichiometric compounds, whose phase structure did not change considerably in the presence of Al.

The solid coagulant was characterized by SEM (Figure 4). Micrograph of fly ash shown in Figure 4a reveals the fact that the particles of fly ash are smooth, spherical and amorphous, and several aluminum oxides are found alongside silicon and iron oxides. The light spots were identified as being mullite, which has a crystalline structure derived from aluminosilicate minerals. The analysis demonstrated that aluminosilicate particles exhibit complex structures, the silicate and aluminum compounds being bonded together in fly ash mass [35]. The morphology of the synthesized materials, C1 and C2, was influenced by the synthesis conditions. In addition, Figure 4 shows that C2 exhibited more synthesized sulfates, compared with C1, fact that proved the increased influence of the temperature. On the other hand, the sulfates are crystalized with different, in general non-stoichiometric, water molecules.



Fly ash	C1	C2

Figure 4. The micrograph of materials (a) Fly ash, (b) C1, (c) C2

The solid coagulant may be transformed into slurry by heating, due to crystallized water. For improving the stability of the materials, one possibility would be to adjust the basicity or use stabilizing materials. In this research, no other additive was used, since the coagulant exhibited a relative high stability.

3.2. Coagulation-flocculation efficiency

The synthesized materials containing both polymeric ferric sulfate and polymeric aluminum sulfate proved to be effective in real wastewater treatment.

A preliminary and simple gravity separation (42 min., based on the industrial background) was performed in the laboratory in order to reduce the number of great particles from wastewater. Subsequently, approximately 300 L of clarified wastewater was refrigerated at 2°C in order to inhibit biological activity.

The experiments were conducted at *p*H range of 6.98–8.22, without any correction. The new materials were compared with conventional aluminum sulfates. The effect of flocculants type was also investigated for individual materials or mixture of them as shown in Table 2.

The obtained results are presented in Table 2 and Figures 5-8.

Table 2. Experimental results

				71221					
Dosage (mL)	**ppm**	**pH**	**m**	**λ μS/cm**	**T_{SS}**	**t_i ^{0}C**	**t_f ^{0}C**	**ΔT_{SS}**	**R, %**
0.7	2	7.35	92	572	25	1.8	9.3	127	84
0.8	4	7.19	91	555	24	1.8	9.7	128	84
0.85	6	7.19	90	545	22	1.9	7.9	130	86
0.9	8	7.17	92	543	24	1.9	7.8	128	84
1	10	7.15	89	542	21	2.2	7	131	86
1.1	12	7.15	89	541	24	2.2	7	128	84
				$Al_2(SO_4)_3$					

0.7	0.6	7.09	75	529	20	2.1	7.7	132	87
0.9	0.7	6.98	60	527	18	2.1	8.5	134	88
71221 + $Al_2(SO_4)_3$									
$Al_2(SO_4)_3$	**71221**	**pH**	**m**	**λ**	**T_{SS}**	**t_i ^0C**	**t_f ^0C**	**ΔT_{SS}**	**R, %**
0.6	4	6.98	73	548	8	1.8	9.3	144	95
0.6	8	6.96	68	530	8	1.8	9.7	144	95
0.6	10	6.86	69	530	9	1.9	7.9	143	94
0.7	12	6.7	70	527	10	1.9	7.8	142	93
71221 + synthesized material									
C2, mg/L	**71221**	**pH**	**m**	**λ**	**T_{SS}**	**t_i ^0C**	**t_f ^0C**	**ΔT_{SS}**	**R, %**
20	4	6.98	73	548	8	1.8	9.3	141	93
30	8	6.96	68	530	8	1.8	9.7	143	94
40	10	6.86	69	530	9	1.9	7.9	141	93
50	12	6.7	70	527	10	1.9	7.8	140	92
Wastewater initial		8.22	93	570	180	1.8			
After 42 min.		8.19	91	564	152	6.7			

The analysis of data was done in order to evaluate the TSS removal efficiency of synthesized material compared with commercial coagulants. Regarding the decrease in T_{SS}, the settling for 42 min, alone, reduced the initial T_{SS} with 15.5%.

The T_{SS} removal efficiency was unsatisfactory, even at high dosages, in the case of both 71221 and aluminium sulfate. On the contrary, the removal efficiency of T_{SS} in the case of the mixture of 0.6 ppm $Al_2(SO_4)_3$ and 4 ppm 71221coagulant reached a value equal to 95%. In general, the data indicate that the T_{SS} removal efficiency increased from 84% to over 92 % by using the both coagulants.

By replacing aluminium sulfate with synthesized material of different dosage, in the range 20-50 mg/L, the T_{SS} removal efficiency reached a value of 94%, superior to that obtained only with 71221, but smaller than in the case when 71221+Al was used (Figure 5). Figure 3 shows that T_{SS} removal efficiency slightly increases with the increase in flocculant dose. Other important conclusion was that no substantial improvement was observed when the flocculant dose increased (Figure 6).

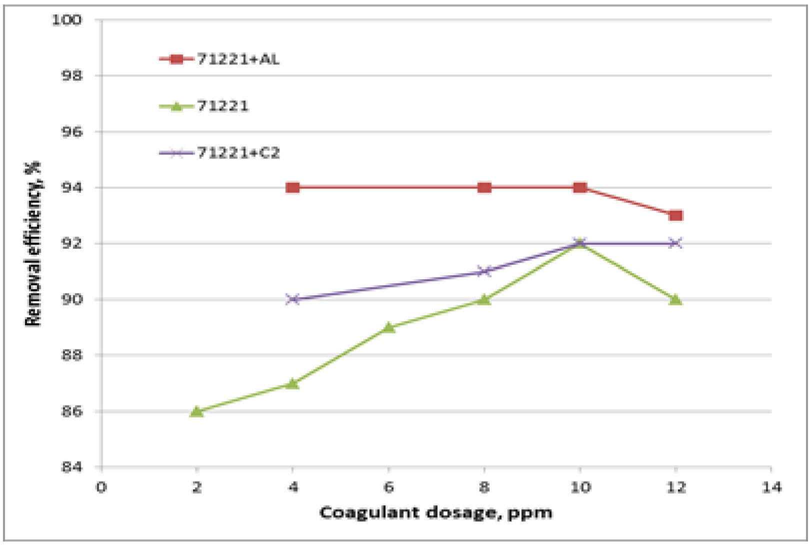


Figure 5. Removal efficiency at T_{SS}-142, conductivity – 337 µS/cm

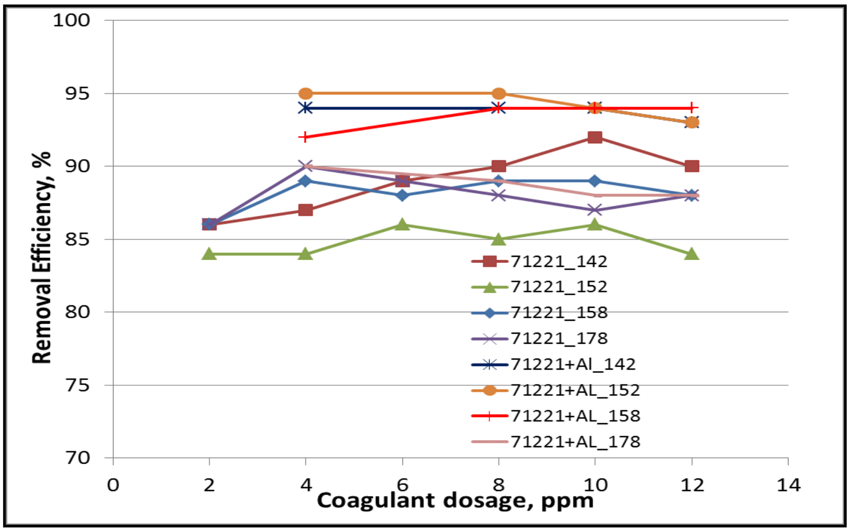


Figure 6. Influence of T_{SS} initial value over removal efficiency

Comparing the experimental data over the whole interval of time, it can be highlights that in the case of commercial coagulant 71211, a removal efficiency of maximum 92% was reached. Al2(SO4)3 determines an efficiency of maximum 88 %, whereas very good results are obtained for the mixture 71211 + Al, when efficiency is equal to 93 %. In the case of synthesized coagulant, efficiency exhibited values in the range 92-95 %.

The experimental also revealed that the removal efficiency depended on TSS initial value. In all tested period the T_{SS} exhibited values between 140-180 mg/L. The removal efficiency versus T_{SS} initial value is presented in Figure 7. From this figure it can be noted that that removal efficiency decreases with the increasing of T_{SS} initial value at the same dosage of coagulant, while increasing of dosage did not result in the increase of efficiency.

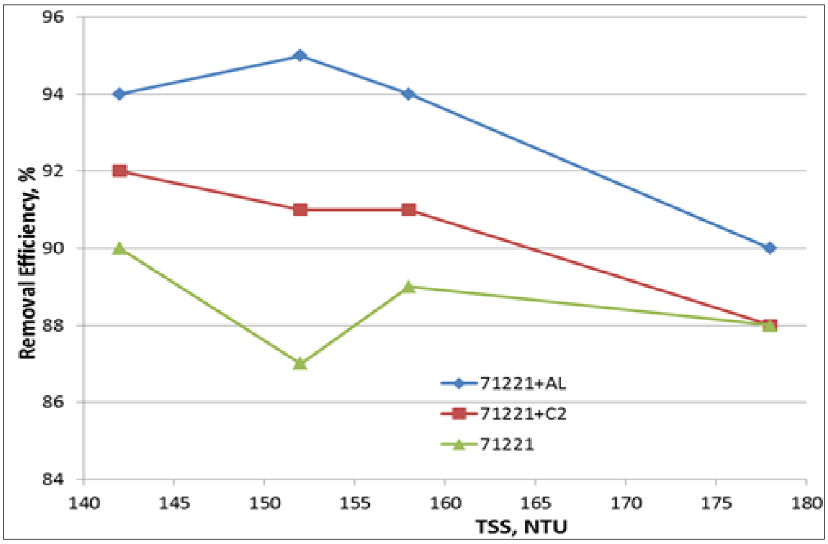


Figure 7. Influence of TSS over removal efficiency,
at 8 ppm 71221 and 60 mg/L coagulants

It should be mentioned that it was not possible to test more values for TSS, taking into account that all experiments were performed with real wastewater. At close values (142 and 152 mg/L) no significant influence was observed. However, the experimental data led to other significant observation. The conductivities ranged between 300-400 μS/cm had no influence on the TSS removal efficiencies, while at conductivities higher than 500 μS/cm, a decrease in the efficiency to maximum 89 % was observed.

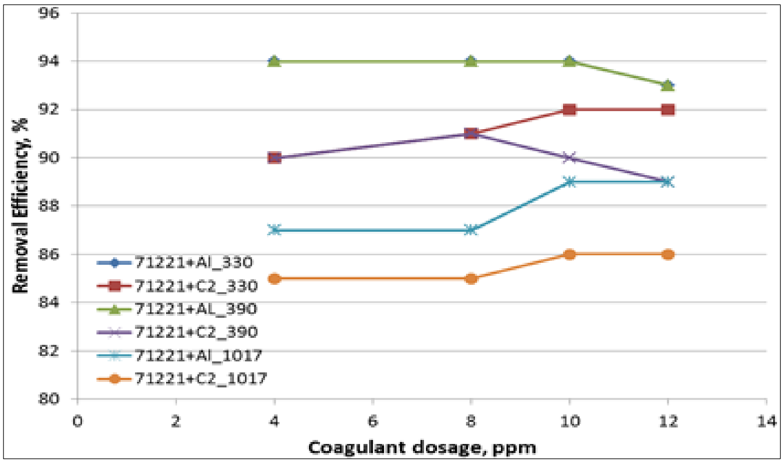


Figure 8. Influence of initial conductivity over removal efficiency

As a general observation, the mixture aluminium sulfate + 71221 provided better results; the removal efficiencies were over 88% for all real wastewater tested.

The synthesized materials combined with 71221 Nalco coagulant exhibited very good removal efficiency, allowing an advanced capitalization of fly ash modified by sulfuric acid attack.

In the synthetized materials from fly ash can be found inactive silicates and aluminosilicates that cannot be extracted. The waste resulted from the coagulation process could be used in manufacture of new building materials.

4. Conclusions

In this paper, the synthesis and characteristics of new materials obtained by acid attack of fly ash were investigated. The experimental results led to the following conclusions:

1. FT-IR analysis indicated that some chemical bonds, such as H–OH, Fe–OH, Al–OH, O-Fe-O, Fe-O-Al, Al-SO42−, present in the synthesized materials, are responsible for the efficiency of the new coagulants.

2. XRD patterns shown that the major phase structures are non-stoichiometric iron sulfate salt, but the presence of aluminum leads to formation of complex compounds as sulfo-aluminate-ferric crystals.

3. SEM images show that the synthesized materials have a compact network structure, more favorable to coagulation process, since they allow the aggregation of flocs;

4. CF experiments show that the best flocculation was obtained for 0.6 ppm $Al_2(SO_4)_3$ and 4 ppm 71221, when TSS removal efficiency was of 95%.

5. The mixture of aluminum sulfate and 71221 provided better results in CF processes; the removal efficiencies were over 88% for all real wastewater tested.

6. The synthesized materials combined with 71221 Nalco coagulant exhibited very good removal efficiency, allowing an advanced capitalization of acid modified fly ash.

Preliminary researches demonstrated the possibility to transform the fly ash into a complex coagulant, containing polymeric sulfates of aluminum and iron that can be used for wastewater treatment.

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Manuscript received: 02.06.2020