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STUDY CONCERNING PERFORMANCES OF TWO TYPES OF PREHYDROLYZED POLYMER IN COMPARISON WITH ALUMINUM SULPHATE AS A COAGULANT FOR WASTE WATER

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ABSTRACT. The main environmental problems of pulp and paper production are water consumption, pollutant fillings of effluents (biogenic and refractory organic compounds, suspended solids, colloids, toxic inorganic compounds). This industry is obliged to minimize its impacts on the aquatic environment and at the same time, due to huge water consumption, must adopt strategies for sustainable use of water resources, in the context of ensuring European requirements for integrated pollution prevention and control and implementation of the Framework Directive of water.

The original experimental research refers to the improvement of the efficiency of conventional physicochemical treatment of residual effluents from the pulp and paper industry by using new prehydrolysed coagulation-flocculating agents. This stage is preliminary to the advanced effluent treatment stage, for its recirculation in the technological process.

Correlating these structures with the efficiencies obtained in coagulation, it is noted that the low coagulant doses of PAC-1 and PAC-2 compared to SA, are due to the existence of more active polymeric species of ${Al_{13}}^{7+}$ or ${Al_{30}}^{18+}$, with higher load and molecular weight than in the case of aluminium monomeric species formed in the use of aluminium sulphate.

There are high efficiencies for removing turbidity between 98-99% as well as organic loading of about 70% for the three coagulants studied (SA, PAC-1, PAC-2), but for the same efficiencies the doses of SA were double or even triple those required for PAC-1 and PAC-2.

Key words: *pollutants, water treatment, flocculation coagulation*

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INTRODUCTION

The pulp and paper industry are large consumers of high-quality water and involve two stages of manufacture: that of pulp and paper so the resulting effluents have different pollutants. Paper industry consumes large amounts of water (about 250-300 m^3/t of paper produced) and generates almost an equal amount of wastewater having biochemical oxygen demand (BOD), chemical oxygen demand (COD), turbidity and colour [1-3]. The pulp and paper industry are one of the industries that is obliged to reduce their impact on the aquatic environment and at the same time to develop and adopt sustainable strategies for the use of water resources; in the context of ensuring European requirements for integrated pollution prevention and control and implementation of the Framework Directive of water [3-7].

Although several treatment methods are in use in large mills, including physicochemical and biological, small mills suffer from the unavailability of proper treatment systems due to financial constraints [8-9].

Thus, one of the possibilities to improve the conventional treatment processes is to improve the efficiency of conventional physicochemical treatment (because this type of treatment is intended for several types of pollutants, such as: biogenic and refractory organic compounds, solid in suspension and colloids), by using new coagulation or flocculating agents; or by modifications made to the coagulation-flocculation process in order to increase the global purification efficiencies [1], [10-16]. Coagulation using alum, poly aluminium chloride (PAC-1) and (PAC-2) have been studied extensively [17-19]. Poly aluminium chloride has been used by many investigators in the treatment of oil-water emulsions, however, the use of PAC for the removal of soluble and colloidal organics from pulp and paper mill effluents has been scarcely studied [20-23].

PAC, which is an inorganic polymer, has been found to exhibit improved performance over other coagulants in terms of removal of turbidity, organic load, etc. PAC treatment requires smaller dosage leading to generation of smaller sludge volume than that obtained with other coagulants. The use of synthetic polymers poly aluminium chloride (PAC) for the removal of COD and turbidity from wastewater has been investigated by many research workers [24-25].

The primary goal of this study was to derive experimental data for the removal of COD and turbidity from the acid wastewaters, of the small agri-based pulp and paper mill by means of the coagulant (PAC), (SA). The specific objectives of this study were to examine the removal of COD and turbidity from wastewater of agri-based pulp and paper mills. The study also focused on the single stage wastewater treatment using PAC-1, PAC-2 and SA [14-15].

RESULTS AND DISCUSSION

Characterization of PAC-1 and PAC-2 coagulants

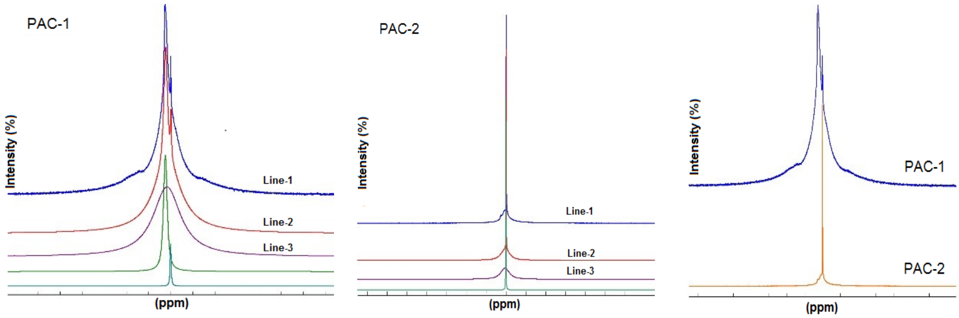
Basic aluminum polychloride is an acidic product in liquid form, commercial products (called PAC-1 and PAC-2, produced in Hungary), were used with the following characteristics:

Table 1. Physicochemical properties of basic aluminum polychloride PAC-1 and PAC-2

No.	Parameter	PAC-1	PAC-2
1.	Concentration, (g Al/L)	127.00	63.96
2.	pH (concentrate)	3.8 ± 0,3	2.60
3.	Density, (kg/dm3)	1.27 ± 0.02	1.30 ± 0.03
4.	Viscosity, (mPas)	<10	-
5.	Basic, (%)	83.0	65.0
6.	Al content, (%)	10.0	5.20
7.	Chloride composition,(%)	8.0	12.50
8.	Content Al_{13}^{7+}	80.94 %	5.19 %
9.	Content Al_{30}^{18+}, or other species	19.06	94.81 %

Basic aluminum polychloride (PAC) is a polymer that can be prepared "in situ", even before use or delivered in concentrated solution, and less often in powder form. The preparation "in situ" is done by neutralizing the aluminum chloride with a base. The commercial product, known in Europe as PAC, WAC, Saptoclar, is of two categories: with or without aluminum sulphate, having as chemical formulas $Al_n(OH)_m(SO_4)_k Cl_{3n-m-2k}$ or $Al_n(OH)_m Cl_{3n-m}$ [22-25]

Figure 1 shows the spectra obtained in the NMR analysis of basic aluminum polychlorides PAC-1 and PAC-2, for the structural characterization of coagulants prehydrolyzed by Al_{13}^{7+} and Al_{30}^{18+} species. [27]



PAC-1 PAC-2 PAC-1 and PAC-2

Figure 1. NMR spectra of basic aluminum polychloride PAC-1, PAC-2
The data obtained by NMR analysis of basic aluminum polychloride are presented in table 4.

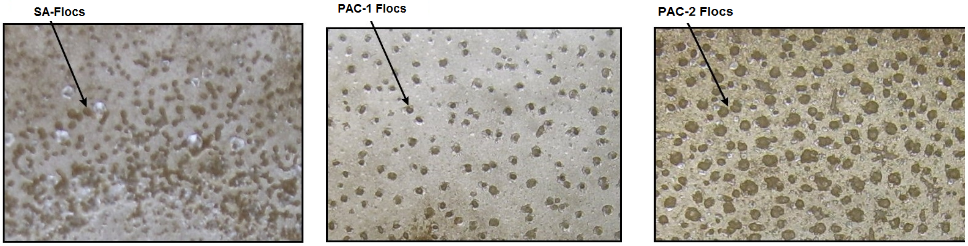
Table 2. The values obtained in the NMR analysis of the basic polychlorides PAC-1 and PAC-2.

	PAC-1			PAC-2		
	Line-1	**Line-2**	**Line-3**	**Line-1**	**Line-2**	**Line-3**
Amplitude (u.a.)	14675.73	24525.92	9229,20	28609.23	0.00	522231.90
Position (ppm)	6.19	9.18	-0.40	1.73	0.00	-0.05
Width (ppm)	60.27	8.00	2.00	20.92	0.00	0.45
Intensity (%)	30.30	50.64	19.06	5.19	0.00	94.81

From the NMR spectrum it results that the majority species in PAC-1 is Al_{13}^{7+} in proportion of 80.94%, and in PAC-2 Al_{30}^{18+} in proportion of 94.81%.

Correlating these structures with the coagulation efficiencies, it is noted that the low coagulant doses of PAC-1 and PAC-2 compared to SA, are due to the existence of more active polymeric species (Al_{13}^{7+} sau Al_{30}^{18+}) of or with higher molecular weight and weight than in the case of species. monomeric aluminum formed in the use of aluminum sulfate. [27-29]

In figure 2 are presented the images for the resulting flocs from type 1 coagulation of synthesis water SET 1 for the three coagulants: A) SA, B) PAC-1, C) PAC-2.



A) B) C)

Figure 2. Behavior of aluminium base coagulants (SA, PAC-1, PAC-2 for type 1 water treatment

Prepolymerised forms of $Al_{13}{}^{7+}$ şi $Al_{30}{}^{18+}$ from PAC-1 and PAC-2, are stable and present opportunities for adsorption on negative colloidal particles and neutralization of negative charges.

Coagulation experiments were performed at pH-7, which is the optimal pH for which it has a slightly higher neutralizing capacity than Al_{30} . Instead, Al_{30} can form more stable and larger flakes than Al_{13} [26-29].

Characterization of synthetic waters

Table 3 shows the characteristics of synthetic waters studied and prepared in the laboratory compared to the characteristics of real wastewater from the pulp and paper industry.

Table 3. Values of the characteristic parameters of synthetic waters shared with the characteristics of real wastewater from the pulp and paper industry.

No	Parameters	SET-1				SET-2				AR
		1	2	3	4	1	2	3	4	
1.	pH	4.12	4.12	4.08	4.11	4.14	4.14	4.26	4.16	6.73
2.	T°(NTU)	260	290	280	300	230	210	230	229	1180
3.	S.S. (mg/L)	400	400	400	400	250	250	250	250	3600
4	Salts content: NaCl (mg/L)	1000	250	1000	250	1000	250	1000	250	350
	Na_2SO_4 (mg/L)	1000	250	250	1000	1000	250	250	1000	524
5.	CCO-Cr (mgO_2/L)	1000	1000	1000	1000	700	700	700	700	2285

Two types of synthetic waters characterized by organic loading of 1000 mg O_2/L and 700 mg O_2/L were studied, with solid suspensions of 400 mg/L and 250 mg/L. The waters were prepared to establish the optimal doses of coagulant SA, PAC-1, PAC-2, and for the database which represents a model for the application of the coagulation process in the case of real waters from the pulp and paper industry.

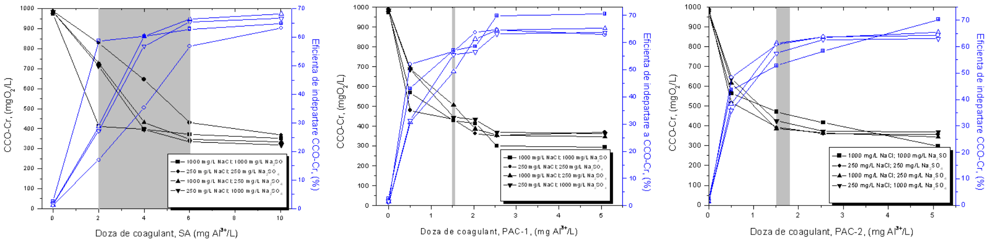
For SET-1 water the pH values were between 4.08 - 4.12, turbidity 260 - 300 (NTU); suspended matter 400 mg/L, organic load 1000 mg O_2/L CCO-Cr. The content of inorganic salts was between 250 - 1000 mg/L Na_2SO_4, and in the case of NaCl the values were in the range of 500 - 2000 mg/L.

In the case of SET-2 synthetic water, the content of suspended matter was lower, 250 mg/L. The values of the turbidity parameter ranged from 210 - 230 NTU. Also the organic matter load was lower than 700 mgO_2/L CCO-Cr, and the inorganic salt content was similar to the waters of SET-1.

Table 4. Characteristics of synthetic and real water samples obtained when applying the optimal doses of classic and prehydrolyzed coagulants based on aluminum.

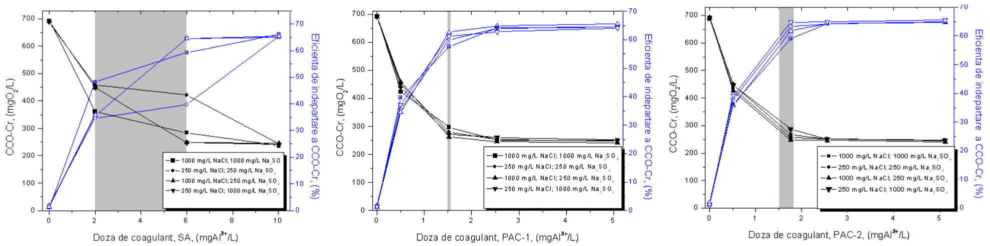
No.	Coagu-lant	Water type	Coagulant dose (mg Al/L)	Treated waters					
				SET-1		SET-2		AR	
				T (NTU)	CCO-Cr mgO_2/L	T (NTU)	CCO-Cr mgO_2/L	T (NTU)	CCO-Cr mgO_2/L
1.	**SA**	1	2.00	9.55	412.20	8.50	362.18	-	-
		2	6.00	5.50	405.00	8.25	421.54	-	-
		3.	6.00	6.60	396.80	6.64	247.87	-	
		4.	6.00	6.75	431.20	7.45	247.80	-	-
		AR	10.02	-	-	-	-	180.0	394.40
2.	**PAC-1**	1.	1.52	7.80	428.90	9.26	297.15	-	-
		2.	1.52	9.50	433.50	8.45	279.93	-	-
		3.	1.52	8.20	400.30	8.45	271.32	-	-
		4.	1.52	7.55	385.30	9.75	261.52	-	-
		AR	12.70	-	-	-	-	285.0	374.28
3.	**PAC-2**	1.	1.76	5.35	416.70	7.90	286.58	-	-
		2.	1.51	6.80	392.30	7.40	256.83	-	-
		3.	1.76	9.85	387.00	7.40	267.54	-	-
		4.	1.76	9.45	425.00	6.35	246.61	-	-
		AR	10.08	-	-	-	-	145.0	366.97

Figures 3 and 4 show the results of applying the Jar-Test method for each type of water using coagulation agents used: aluminum sulfate (SA); basic aluminum polychloride type 1 (PAC-1) and basic aluminum polychloride type 2 (PAC-2).



a) b) c)

Figure 3. Variation of organic charge for SET-1 of synthetic water, when establishing the optimal coagulant doses (a - SA, b - PAC-1, c - PAC-2)



a) b) c)

Figure 4. Variation of organic charge for SET-2 of synthetic waters, when establishing the optimal coagulant doses (a - SA, b - PAC-1, c - PAC-2)

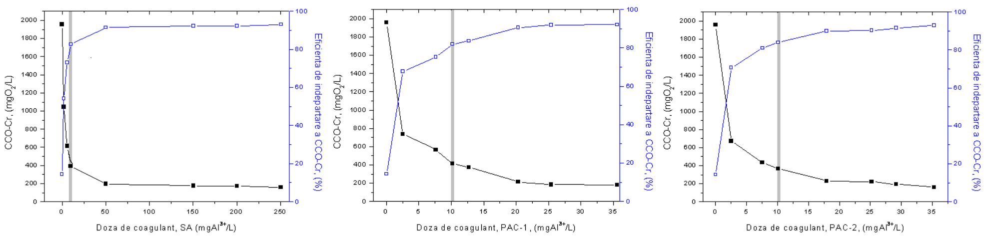
Optimal coagulant doses were established for residual turbidity less than or equal to 10 NTU and organic load expressed by the CCO-Cr parameter less than or equal to 500 mg O_2/L according to NTPA 002.

According to the graphical representation of Figure 2, the optimal doses of SA coagulant used to remove organic matter and turbidity was 2.0 mg Al/L for type 1 water from SET-1 and SET-2 synthetic water. At this dose the turbidity was between 9.55 - 8.50 NTU and the organic load was in the range of 412.20 - 362.18 mg O_2/L.

For waters of type 2, 3, 4, from SET-1 and SET-2, respectively, the optimal dose of coagulant was 6 mg Al/ L when treated waters with turbidity between 5.50 - 8.25 NTU were obtained and the loading organic was in the range of 247.80 - 431.20 mg O_2/L (below the level allowed by NTPA 002).

When using the PAC-1 coagulant, figure 2b, the optimal doses of coagulant for the removal of organic matter and turbidity was 1.52 mg Al/L for all types of water from both SET-1 and SET-2. At this dose the turbidity was between 7.55 and 9.75 and the organic load was in the range of 433.50 - 261.52 mg O_2/L.

In the case of PAC-2 coagulant, figure 2c, for type 1, 3, 4, waters from SET-1 and SET-2, respectively, the optimal dose of coagulant was 1.76 mg Al/L, when water treated with turbidity was between 5.35 - 9.85 NTU, and the organic load was in the range of 246.61 - 425.00 mg O_2/L. Also in the case of type 2, SET-1 and SET-2 water, the optimal dose of coagulant was 1.51 mg Al/L. At this dose the turbidity was between 6.80 - 7.40 NTU and the organic load was in the range of 256.83 - 392.30 mg O_2/L.



a) b) c)

Figure 5. Variation of organic load for wastewater from the pulp and paper industry, in determining the optimal coagulant doses (a - SA, b - PAC-1, c - PAC-2)

According to the graphical representation, figure 5-a), the optimal dose of SA coagulant used for the removal of organic matter and turbidity was 10.02 mg Al/L for wastewater from the pulp and paper industry.

When using the basic aluminum polychloride coagulant PAC-1, figure 5-b), the optimal dose in removing organic load and turbidity was 10.16 mg Al/L. In the case of the basic aluminum polychloride coagulant, PAC-2, figure-5c), the optimal dose established in removing the turbidity and the organic load was 10.08 mg Al/L.

CONCLUSIONS

Wastewater from the pulp and paper processing industry is water with variable organic and inorganic loading.

The technological process of purification of these waters has the basic coagulation-flocculation operation.

In order to optimize the coagulation operation, a model was developed based on a database based on 8 types of synthetic waters prepared in the laboratory. The agent used in the technological process is a classic coagulating agent aluminum sulphate SA and two types of prehydrolyzed coagulants. PAC-1 with ${Al_{13}}^{7+}$ species content of 80.94% and ${Al_{30}}^{18+}$ or other species of 19.06%. PAC-2 prepolymerized agent with ${Al_{13}}^{7+}$ species content of 5.19% and ${Al_{30}}^{18+}$ species or other species of 94.81% requires lower doses by up to 25% compared to aluminum sulfate.

A successful and important method for improving the efficiency of inorganic coagulants is the partial hydrolysis of the respective salts with the formation of optimal polymeric species.

The efficiency of two prepolymerized coagulants (prehydrolyzed), based on aluminum called basic aluminum polychloride PAC-1 and PAC-2, was compared with the classical coagulant aluminum sulphate (SA).

In order to evaluate the performances attributed to the prepolymerized metal coagulants compared to the conventional ones, characterization analyzes of the materials and structure of the polymeric species contained in the two types of basic aluminum polychloride studied PAC-1 and PAC-2 were performed. From the NMR spectrum it results that the majority species in PAC-1 is ${Al_{13}}^{7+}$ in proportion of 80.94%, and in PAC-2 ${Al_{30}}^{18+}$ in proportion of 94.81%.

Correlating these structures with the coagulation efficiencies, it is noted that the low coagulant doses of PAC-1 and PAC-2 compared to SA, are due to the existence of more active polymeric species of or with higher molecular weight and weight than in the case of species. monomeric aluminum formed in the use of aluminum sulfate.

EXPERIMENTAL PART

Reagents used:

Aluminum sulphate (SA), • $18H_2O$.

Commercially produced aluminum sulphate (SA) was used to prepare the coagulant solution. The solution prepared by the coagulant had a concentration of 309.00 g/L and a density of 1.277 g/L [14], [16-25].

Basic aluminum polychloride.

Two commercial products called PAC-1 and PAC-2, produced in Hungary, were used [30-32]. The concentrations of basic aluminum polychloride (PAC-1; PAC-2) used in experimental coagulation studies were 1:100 compared to the concentration of SA.

Sodium hydroxide (NaOH).

In the preparation of the sodium hydroxide solution used to correct the pH of the water, 98.0% pure NaOH of the CHEMAPOL type, produced in the Czech Republic, was used.

Bentonite, potassium acid phthalate, sodium chloride and sodium sulfate.

Used in the preparation of wastewater, similar to those in the pulp and paper industry.

Potassium acid phthalate, 99.5-100% purity, RENAL type, produced in Hungary.

The bentonite used was in powder form, from the Aghireş quarry, Cluj county, (Aghireş bentonite).

Anhydrous sodium sulphate of 99.0% purity of the MERCK type, produced in Germany.

Anhydrous sodium chloride (NaCl), 99.0-100% purity, MERCK type, produced in Germany.

METHODS

The “Jar-test” method was used to determine the optimum coagulation conditions. The doses of coagulation reagents were added in samples of 250 ml wastewater, which were fast stirred for 3 minutes, with a speed of 160-170 (rotations/minute), then slow stirred for 15 minutes with a speed of 40-45 (rotations/minute) and placed for sedimentation for 30 minutes. From the supernatant were taken samples of treated water to determine the following parameters: turbidity, organic load expressed by the chemical oxygen demand (COD-Cr). For the coagulation experiments an agitating device of type FC6S VELP (SCIENTIPICA) was used. To determine the turbidity a HACH 2100 turbidimeter was used. Water turbidity was expressed in NTU [22,23].

COD parameter was determined in accordance with SR ISO 6060-96, and suspended solids in accordance with STAS 6953-81 [33-35]

Clorides (Cl^- mg/L) was determined in accordance with STAS 8663-70; and sulfates (SO^-_4 mg/L) in accordance with STAS 8601-70 [36-37]

The pH was determined using an electronic "INOLAB" pH meter with an electrode of the "SenTix41 Electrode" type [33]

NMR analysis of basic aluminum polychlorides (PAC-1; PAC-2) was performed with the "Bruker Spectrometer NMR 400 Avance" with a central field of 9.4 Tezla for the structural characterization of coagulants prehydrolyzed by Al13 and Al30 species.

Preparation of synthetic waters

Two sets of synthetic waters (SET-1, SET-2) were prepared, each comprising four types of water, different from each other by adding organic, inorganic and turbidity matter; experimental studies of the coagulation process were performed on synthetic waters having the characteristics presented in table 5. In the preparation of synthetic waters, the composition of "real" wastewater resulting from the manufacture of pulp and paper was taken into account.

Table 5. Domains of variation of the initial characteristic parameters of the synthetic wastewater, subjected to the coagulation process.

Parameter	CCO-Cr (mgO_2/L)	s.s. (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)
Range of concentration variation	400-1000 (K acid phthalate); $C_8H_5O_4K$	150-400 (bentonite from Aghireş)	250-1000 (NaCl)	250-1000 (Na_2SO_4)

The studied wastewater was taken from a pulp and paper processing plant.

Table 6. Values of characteristic parameters, wastewater from the pulp and paper industry subjected to the coagulation process.

Parameter	pH	CCO-Cr (mgO_2/L)	s.s. (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)
Values for initial concentration	6.73	2285.00	3600	350	525

Table 6 shows the values of some characteristic parameters: organic charge expressed by CCO-Cr, solid suspensions, turbidity, chlorides and sulfates. Wastewater from the pulp and paper industry showed great variations in its composition. The composition of the water includes: very high organic load, high turbidity, a very large amount of suspended solids, the presence of dyes (a pink color), mineral substances (sodium sulfate, sodium chloride, etc.).

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35 Suspended solids in accordance with STAS 6953-81;
36 Chlorides (Cl^- mg/L) was determined in accordance with STAS 8663-70;
37 Sulfates (SO^-_4 mg/L) in accordance with STAS 8601-70.