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PAC COAGULANTS IN PULP AND PAPER WASTEWATER TREATMENT

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Key words: pulp and paper wastewater, coagulation, PACs.

Abstract

The coagulation/flocculation is a major process in the wastewater treatment. A study was conducted to compare the efficiency of two polymeric PAC coagulants (PAC, PAX 61) and two monomeric coagulants, $Al_2(SO_4)_3$ and $AlCl_3$, in pulp and paper wastewater treatment. PAC and PAX 61 showed the advantage over the traditionally used $Al_2(SO_4)_3$ and $AlCl_3$ in the removal of basic wastewater pollutants. The use of the optimum dose of 10.3 mg Al/dm^3 with PAC ensured over 90% removal of turbidity, color and around 50% COD reduction. A similar effect was obtained after the use of an around 50% higher PAX 61 dose.

KOAGULANTY TYPU PAC W OCZYSZCZANIU ŚCIEKÓW CELULOZOWO-PAPIERNICZYCH

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Słowa kluczowe: ścieki celulozowo-papiernicze, koagulacja, PAC.

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Abstract

Koagulacja/flokulacja jest głównym procesem w oczyszczaniu ścieków. Przeprowadzono badania porównania skuteczności działania dwóch polimerycznych koagulantów typu PAC (PAC, PAX 61) oraz dwóch koagulantów monomerycznych – $Al_2(SO_4)_3$ i $AlCl_3$ – w procesie oczyszczania ścieków celulozowo-papierniczych. PAC i PAX 61 wykazywały przewagę nad tradycyjnie stosowanymi $Al_2(SO_4)_3$ i $AlCl_3$ w usuwaniu podstawowych zanieczyszczeń ścieków. Zastosowanie optymalnej dawki 10,3 mg Al dm^{-3} z PAC zapewniało ponad 90-procentowe usunięcie mętności, barwy i ok. 50% obniżenie ChZT. Podobny efekt uzyskano po zastosowaniu ok. 50-procentowej wyższej dawki PAX 61.

Introduction

Industrial wastewater forms as a result of water consumption during raw material processing to industrial and consumer products. Progress and development lead to an increased amount of wastewater, often environmentally noxious due to their high pollutant load. The pulp and paper industry is distinguished by a high water consumption. Pulp and paper wastewater is characterized by a high content of fine and very fine wood fibers. The mean pollutant values corresponding to the production of 1 t paper are around 20 kg suspended solids, 18 kg settling suspended solids and 50 kg dissolved components. The waste liquor formed during the cellulose production process contains nearly 80% organic substances (these are mostly lignosulfonic acid compounds and lower amounts of sugars and resin) and 20% inorganic substances. Consequently, the formed wastewater is characterized by a high value of the COD and BOD indices. Pulp and paper wastewater reaching water bodies causes significant oxygen content reduction in them, along with water foaming, color and turbidity changes and sometimes even fish death or migration. Easily-decomposable compounds with high concentration contained in this wastewater favor the growth of wastewater fungi and secondary water body silting.

The increasingly used prepolymerised PAC coagulants show a much higher efficiency than conventional coagulants, such as $Al_2(SO_4)_3$ or $AlCl_3$ (PERNITZKY, EDZWALD 2006). The high effectiveness of PAC coagulants (ZOUBOLIS, TZOUPANOS 2010) is due to the presence in the coagulation system of aluminum poliyhydroxycations Al_{13}, which form in aqueous solutions as a result of rapid dilution and hydrolysis. High availability of flocs on an extensive surface with high load density causes increased pollutant adsorption.

The distinguishing feature of PAC coagulants is their alkalinity. It expresses the degree of hydrolysis, which is represented as the molar ratio

R = [OH]/[Al]. During pre-hydrolysis of Al-based coagulants, a number of soluble aluminum forms develop in the solution: Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_3$, $Al(OH)^{4-}$ monomers, $Al_2(OH)_2{}^{4+}$ oligomers, $Al_3(H)_4{}^{5+}$, $Al_{12}AlO_4(OH)_{24}{}^{7+}$ (Al_{13}) and even larger Al_{30} polymers (BOTTERO et al. 1980, PERNITZKY, EDZWALD 2006, WU et al. 2007). EXALL et al. (2003) proved that the $Al_2(SO_4)_3$ solution contains only monomeric Al forms (Al_1), while the occurrence of both Al_1 monomers, Al_2 dimers, oligomers and Al_{13} polymers was observed in solutions of prepolymerised PAC coagulants. Increasing PAC dilution (0.01 mol dm^{-3}) favors an increase in Al_{13} content in a solution with a reduced monomeric forms. In diluted solutions (0.01 mol dm^{-3}), a four times higher amount of polymeric forms of aluminum was observed than in solutions with higher concentration (0.05 mol dm^{-3}).

The aim of the study was to compare the efficiency of two polymeric coagulants PAC and PAX and of two monomeric coagulants $Al_2(SO_4)_3$ and $AlCl_3$ in removing the various pollutants of pulp and paper wastewater. This work sought to determine the effect of the dose and type of coagulant on the degree of wastewater treatment.

Materials and Methods

Pulp and paper wastewater from a pulp and paper plant in Ostrołęka were studied. Two-polymeric coagulants of the PAC type: PAC (51,6 gAl^{3+}/l), PAX 61 (107 gAl^{3+}/l)) and two monomeric coagulants $Al_2(SO_4)_3$ (9,1% as Al) i $AlCl_3$ (33,5 gAl^{3+}/l) were used. Chemical coagulation was conducted using the standard jar test method: rapid stirring (400 rpm) – 1 min., slow stirring (30 rpm) – 15 min. and 15 min. of sedimentation. The wastewater from a pulp and paper plant "Intercell" in Ostrołęka was tested. The raw wastewater was corrected to the pH = 5, using 0.1 m HCl. The determination of the particular parameters was performed using HACH 2000. The determinations of the particular parameters were performed using the following methods: turbidity was determined with the absorption method, color was determined with the platinum-cobalt method, COD was determined with the spectrophotometric method. The study was performed on a laboratory scale, using a 20-stand system for CAF (Computerised Automated Flocculation) testing.

Results and Discussion

Pulp and paper wastewater constitute a group of industrial wastes which are particularly cumbersome and difficult to treat. The purpose of the process of chemical coagulation of pulp and paper wastewater is to maximally remove the pollutants responsible for COD, turbidity, suspended solids and color. The wastewater from a pulp and paper plant "Intercell" in Ostrołęka was tested. The raw wastewater was corrected to the pH = 5, using 0.1 m HCl.

In Table 1, the values of the parameters illustrating the degree of treatment of the studied pulp and paper wastewater are summarized. The use of PAC in amounts from 10 mg Al dm^{-3} to about 40 mg Al dm^{-3} of wastewater enabled over 92–97% turbidity reduction, about 49–54% removal of the pollutants according to the COD scale, and 92–97% reduction in the content of substances responsible for the color of the coagulated wastewater.

Table 1

The results of pulp and paper wastewater coagulation using PAC

PAC dose [mg Al dm^{-3}]	Turbidity	COD	Suspended solids	Color
	[mg dm^{-3}]			
0.0	860	1754	680	4680
10.3	67	894	31	354
15.2	52	866	25	272
20.6	31	836	20	191
25.3	30	830	18	173
30.1	28	825	15	152
35.2	26	820	13	136
41.3	24	816	11	124

Analyzing the data summarized in the Table 1, it is possible to conclude that from the economical point of view, already the lowest of the applied doses of PAC, being 10.3 mg Al dm^{-3} of wastewater, seems to be optimal, as it ensures an over 90% removal of turbidity, suspended solids, color and an approximately 50% COD reduction. An increase in the dose of PAC above 10 mg Al dm^{-3} results in an undesirable pH reduction. Although the chemical coagulation of wastewater using PAC is effective at pH = 4.8 (BOTTERO et al. 1989) and even lower, under such conditions the solubility of the primary product of coagulation, i.e. $Al(OH)_3$ increases (STUMM, MORGAN 1970), which may result in an undesirable increase in the content of Al^{3+} ions and other ions containing Al (the so-called Al-rest) in the treated wastewater. According to BOTTERO and BERSILLON (1989)

depending on the pH, a wide range of PAC hydrolysis products are formed, with different charges and structures, which consequently has an effect on colloid sorption. In solutions with pH < 5.5–6, the coagulation-flocculation process happens through neutralization of the acid groups of organic pollutants, which results in their precipitation. At pH > 6.5 the treatment is performed by adsorption on a very developed surface of sorbent. According to RAKOTONARIVO et al. (1988), the optimal conditions of the aggregation process for polymer forms of Al_{13} are created by pH < 5. Under conditions of higher pH = 7–7.5, the concentration of Al_{13} polycations is too high and the sorption of surface pollutants is much more difficult. However, coagulation pH in the range of 6.0–7.0 are most common as it gives the best removal via a combination of mechanisms. Nevertheless, the experiments reported here are carried out much lower coagulation-pH resulted due to natural reduction of pH due to hydrolysis of aluminum ions. The intention was to avoid the use of pH adjusting chemicals which complicates the operations in practice.

Table 2

The results of pulp and paper wastewater coagulation using PAX 61

PAX 61 dose [mg Al dm^{-3}]	Turbidity	COD	Suspended solids	Color
	[mg dm^{-3}]			
0.0	860	1754	680	4680
5.0	208	1462	107	1155
10.0	78	1068	32	409
15.0	46	901	24	241
20.0	38	814	16	196
25.0	32	808	13	190
30.0	30	801	11	188
40.0	27	798	9	184

The Table 2 presents experimental data of the coagulation process of pulp and paper wastewater using PAX 61. A satisfactory level of 49% removal of the main pollutants responsible for COD was obtained using 15 mg Al dm^{-3}. This dose also ensured an over 94–96% reduction in the indices of turbidity, suspended solids and color at $pH_f = 4.8$ (pH_f– the final pH), which was attainable for PAC (Table 2) with a dose of 10 mg Al dm^{-3}. An increase in the dose of PAX 61 above 15–20 mg Al dm^{-3} did not result in significant changes in the values of particular parameters in the treated wastewater. Polymeric coagulants lower the pH in a similar way, though PAX 61 has a greater effect on the pH than PAC, which probably results from a lower alkalinity ([OH]/[Al]) of PAX 61, compared to PAC.

Table 3

The results of pulp and paper wastewater coagulation using $Al_2(SO_4)_3$

$Al_2(SO_4)_3$ dose [mg Al dm^{-3}]	Turbidity	COD	Suspended solids	Color
	[mg dm^{-3}]			
0.0	860	1754	680	4680
5.0	266	1492	162	1370
10.0	116	1102	56	626
15.0	68	899	31	346
20.0	64	860	26	336
25.0	62	858	27	320
30.0	58	856	24	306
40.0	55	852	22	290

Table 4

The results of pulp and paper wastewater coagulation using $AlCl_3$

$AlCl_3$ dose [mg Al dm^{-3}]	Turbidity	COD	Suspended solids	Color
	[mg dm^{-3}]			
0.0	860	1754	680	4680
5.4	292	1501	177	1605
10.7	121	1118	54	710
15.2	105	886	41	450
21.4	86	878	29	368
25.3	64	877	25	360
30.2	58	875	24	321
42.9	57	872	23	294

Table 3 and Table 4 present the results of two tests performed at the same time, of the wastewater treatment using $Al_2(SO_4)_3$ and $AlCl_3$. The values of pollution, measured by the COD index gradually increased with an increasing dose of Al. The obtained results indicate that following an addition of 15 mg Al dm^{-3} to wastewater with the pH = 5 there was a 49.5% reduction in the COD level. The use of the above dose produces a better result in removing the color (about 3%) and turbidity (about 4%) using $Al_2(SO_4)_3$, compared to $AlCl_3$. An addition of coagulant results in a reduction in the pH_f value. $AlCl_3$, had the most intensive effect on pH (from 4.7 to 3.8) in a dose from 5.4 to 42.9 mg Al/dm^3. The low value of the final pH = 4.34 could also have an effect on the lower effectiveness of treatment using $AlCl_3$. According to BOTTERO and BERSILLON (1989), sulfate ions, compared to chloride ions, have a greater affinity to the dispersed solid phase of $Al(OH)_3$.

As a result of sudden dilution and hydrolysis, PAC forms active forms of Al_{13} in a solution with very high valency (e.g. + 7) (BOTTERO et al. 1988, RAKOTONARIVO et al. 1985, 1988). The strongly-developed surface of octa-

hedral polycations of Al_{13} enables free access of organic substances to the adsorption interface, which creates the proper conditions for their complexing and adsorption. The characteristic property of aggregates formed in this way is their fractal nature (AXELOS et al. 1985, 1986).

The use of PAC- and PAX-type coagulants, compared to the traditional $Al_2(SO_4)_3$, ensures more effective removal of pollutants, lower "alkalinity consumption", broader range of pH for the optimum of coagulation-flocculation, lower susceptibility to low temperatures and a lower residual of Al in treated wastewater.

In this work, the efficiencies of monomeric and polymeric coagulants in removing particular pollutants were compared. The obtained results indicate much higher effectiveness of PAC, compared to other coagulants. Above 20 mg Al dm^{-3} the difference between the effects of PAC and PAX 61 gradually disappears, particularly in removing turbidity and suspended solids.

Conclusions

1. Polymeric coagulants have a great advantage over monomeric coagulants in removing the basic pollutants in pulp and paper wastewater.
2. The optimum PAC dose is 10.3 mg Al dm^{-3}, which ensures over 90% removal of turbidity, suspended solids and color and an about 50 % COD reduction. A similar effect was ensured by an approximately 50 % higher PAX 61 dose.
3. A similar coagulation efficiency in decreasing the levels of particular pollutants was displayed by the both studied monomeric coagulants, $Al_2(SO_4)_3$ and $AlCl_3$.

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