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EFFICIENCY OF ALUM AND PREHYDROLYZED POLYALUMINIUM CHLORIDES AS COAGULATING AGENTS: A COMPARATIVE STUDY

The experiments were carried out with alum and five prehydrolyzed polyaluminium chlorides as coagulants, which differed in basicity. The aim of our experiments was to compare the following parameters: the removal efficiencies of the aforementioned coagulants for colour, turbidity and organic substances, as well as the residual concentrations of aluminium in the treated samples. Coagulation was performed on riverine water samples (collected from the Odra and its tributary the Oława), which differed in temperature and pollution levels. Polyaluminium chlorides were found to be more efficient coagulants than alum, and their performance increased with their basicity. The prehydrolyzed coagulants were less sensitive to pH variations and low temperature (5 to 12 °C) of the water to be treated. Their application allowed the required dose to be decreased, but the treatment effect was comparable with that of the alum coagulant, and the residual aluminium concentration was lower than that obtained with alum.

1. INTRODUCTION

The effectiveness of the coagulation process contributes significantly to the performance and operating costs, as well as to the nature of subsequent unit processes which are part of the water treatment train. Of various factors that affect the coagulation performance, the most important is the nature of the coagulant. As it may be inferred from the literature [1], [2], the effectiveness of the process can be improved when use is made of prehydrolyzed coagulants. In the solutions of prehydrolyzed coagulants, polymeric species with high positive charges occur more frequently among the hydrolysis products than in the solutions of non-prehydrolyzed coagulants, which are added to the raw water at a natural pH [3], [4]. Although prehydrolyzed and non-prehydrolyzed coagulants follow the same mechanism of removal, the neutralization of charged colloids and dissolved pollutants, as well as bridging processes [5] have a great contribution to the removal of pollutants in the coagulation process which involves prehydrolyzed coagulants (and these in-

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cludes polyaluminium chlorides). Furthermore it is believed that better effectiveness of prehydrolyzed coagulants should be attributed to the larger size of the hydrolysis products, which increases the probability of their collision with the colloids [6]–[8].

The objective of the study reported in the present paper was to compare the performance of two coagulating agents, alum and polyaluminium chlorides, which differed in basicity and, hence, in the degree of prehydrolization.

2. MATERIAL AND METHODS

Experiments were carried out with riverine water samples (collected from the Odra and its tributary, the Oława), which differed in temperature and pollution levels. Coagulation was performed by the jar test method with 3-minute rapid mixing ($G = 220\ s^{-1}$) and 30-minute slow mixing ($G = 20\ s^{-1}$). Then the samples were allowed to sediment for one an hour. The efficiency of alum (ALS) and five polyaluminium chlorides (PACls) was established during water treatment at natural (pH_n) and adjusted pH (pH_a) (table 1).

Table 1

Type and basicity of the coagulants tested

Type of coagulant	ALS	PACls				
		PAC	PAX-18	PAX-XL3	PAX-XL60	PAX-XL61
Basicity (r), %	0	35	41±3.0	70±5.0	70±10.0	85±10.0

The treatment efficiency of the coagulants chosen was tested for the removal of colour, turbidity, permanganate COD (COD_p) and total organic carbon (TOC). The effect of coagulant type on residual aluminium concentration in treated water (Al_r) was analyzed. The treatment effects obtained with or without pH adjustment, coagulation and sedimentation will be referred to as 'coagulation efficiency'. Coagulant doses are expressed in g Al/m^3, and the value of the coefficient of coagulant utilization (CCU_X) has been calculated as the ratio of the amount of pollutants (Δx) to the coagulant dose applied (D_c). In the adopted criterion for coagulation efficiency, the decrease in the colour intensity (Col), the turbidity (Tur), COD_p, and the aluminium concentration to the values of ≤ 15 g Pt/m^3, ≤ 1 g SiO_2/m^3, ≤ 5 g O_2/m^3, and ≤ 0.2 g Al/m^3, respectively, are taken into account.

3. RESULTS

3.1. TURBIDITY

In the majority of experiments, turbidity was removed with the highest efficiency (over 90%). The removal efficiency for the pollutants which contributed to turbidity

increased with their initial concentrations (in the raw water) and was only slightly dependent on the type of the coagulant used. However, PACls were found to be more effective than ALS, especially over the lower range of coagulant doses (figure 1) and during water treatment at low temperature (figure 2).

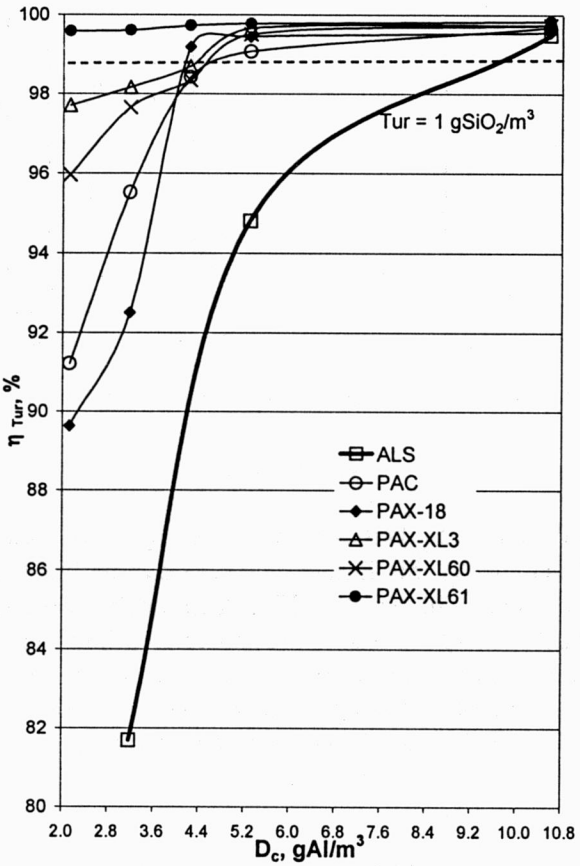

Fig. 1. Efficiency of turbidity removal (η_{Tur}) versus coagulant dose and coagulant type

The number of water samples of turbidity higher than 1 g SiO_2/m^3 after PACl (specifically after PAX-XL61) coagulation was smaller than after ALS coagulation (table 2).

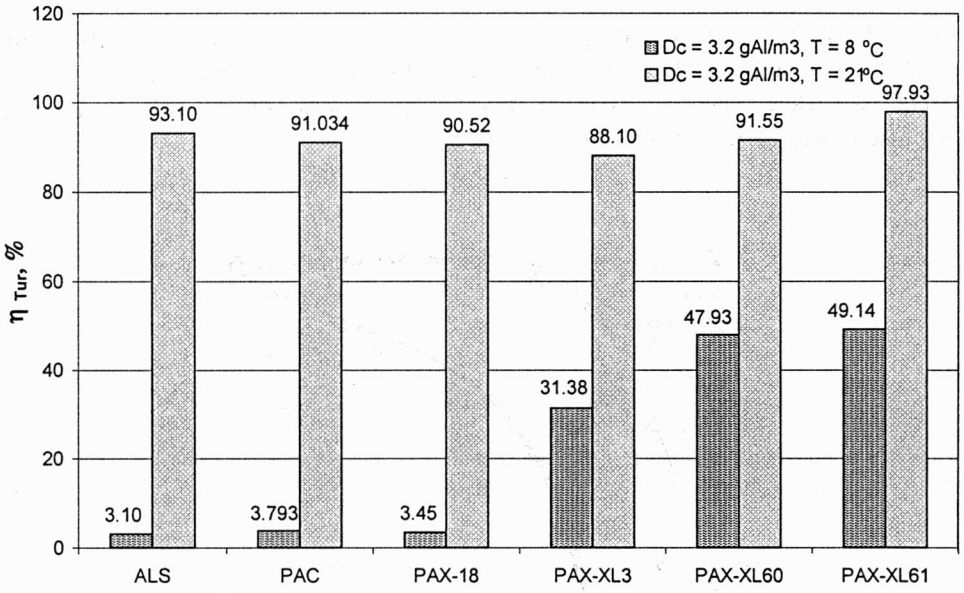

Fig. 2. Efficiency of turbidity removal (η_{Tur}) versus temperature, coagulant dose and coagulant type

3.2. COLOUR

Prehydrolysis of alum coagulants had a noticeably favourable effect on the removal of coloured matter. As this influence increased, the number of treated water samples with colour intensity higher than 15 g Pt/m^3 declined (table 2). The presence of polycation products of hydrolysis in the polyaluminium chloride solutions improved their utilization in the removal of colour-producing pollutants (CCU_{Col}). The CCU_{Col} values for prehydrolyzed coagulants (particularly those whose basicity was equal to, or greater than 70%) were distinctly higher than those for ALS (figure 3).

Table 2

Effect of alum coagulant on the number of samples with exceeded turbidity, colour intensity, COD_p and aluminium concentration (number of samples (N); Tur = 359, Col = 359, COD_p = 424 and Al_r = 317)

Index	Number of samples after coagulation					
	ALS	PAC	PAX-18	PAX-XL3	PAX-XL60	PAX-XL61
Tur > 1 g SiO_2/m^3	27	20	20	14	14	8
Col > 15 g Pt/m^3	21	15	12	9	11	3
COD_p > 5 g O_2/m^3	17	12	4	1	2	0
Al_r > 0.2 g Al/m^3	32	28	26	10	10	2

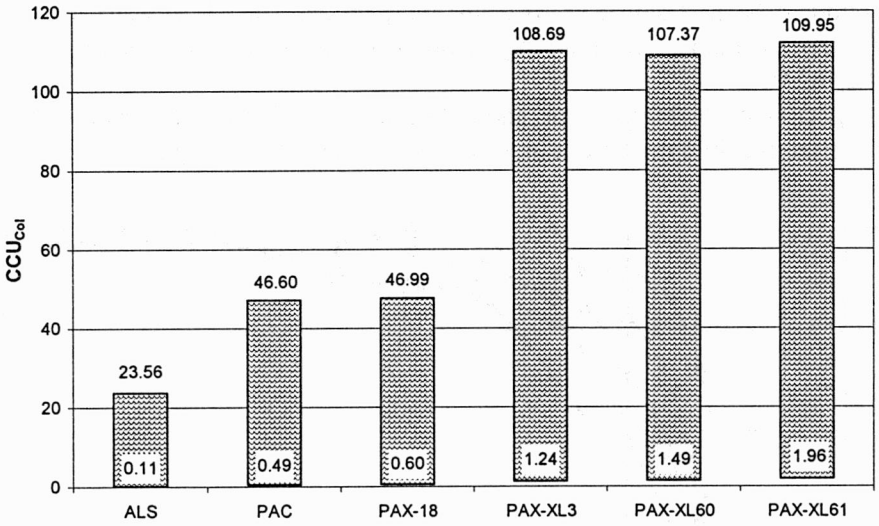

Fig. 3. Effect of basicity on the utilization of aluminium coagulants in coloured matter removal

Owing to the increased efficiency of the PACls it was possible to reduce their dose by about 30% without deteriorating the efficiency of colour removal, which was comparable to the efficiency obtained due to applying the alum coagulant. Prehydrolyzed coagulants were

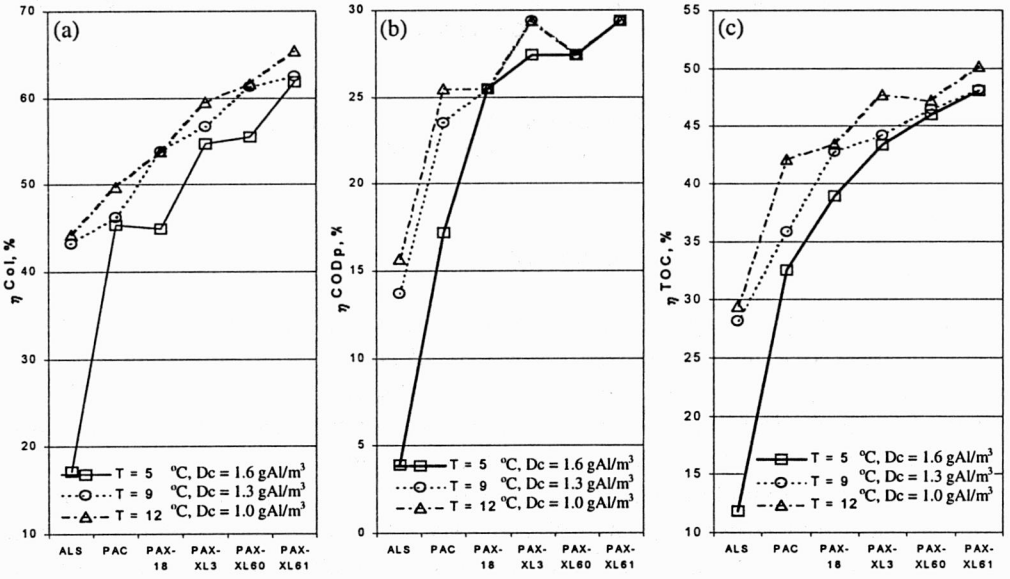

Fig. 4. Effect of temperature, coagulant type and coagulant dose on the removal of colour (a), COD_P (b) and TOC (c)

also found to be less sensitive to water temperature variations than ALS, so they became more effective in removing coloured matter from water of lower temperature (figure 4).

Irrespective of the temperature and pollution level of raw water, ALS was noticeably less effective than the PACls investigated (see the plots in figure 5).

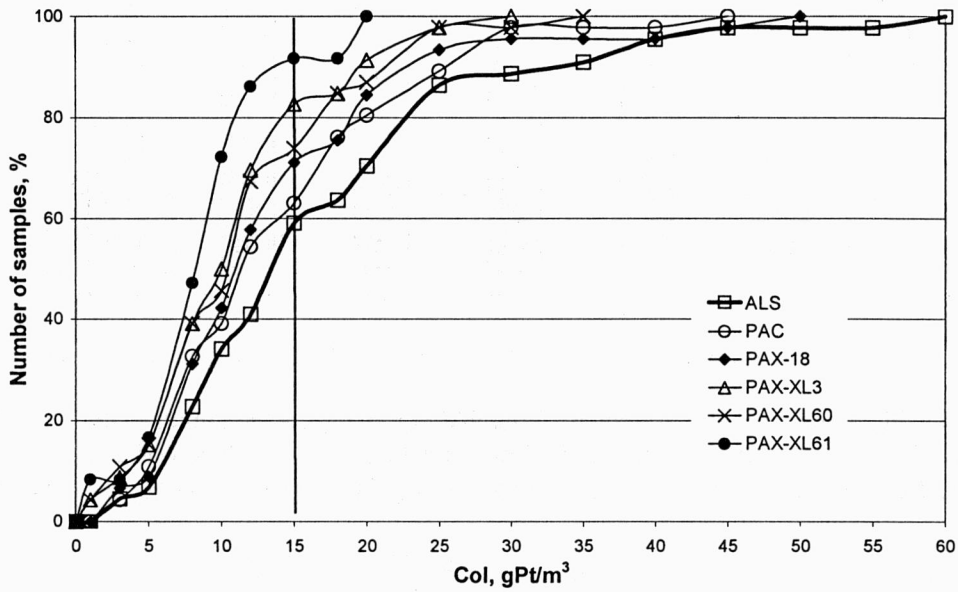

Fig. 5. Frequency of coloured matter occurrence in treated water (N = 144)

3.3. ORGANIC POLLUTANTS

The efficiency of organic matter removal increased with the increasing dose of each of the coagulants tested. Like in the case of colour removal, PACls were found to be more effective than ALS in decreasing COD_p and TOC. The favourable influence of the prehydrolysis products was particularly distinct when the coagulant doses and the temperature of the water to be treated were low (figure 4), i.e., under conditions of decreased yield of aluminium ion hydrolysis. The concentration of aluminium ions was the highest in non-prehydrolyzed ALS. The dose, which yielded a comparable efficiency of COD_p and TOC removal, was the highest for ALS, and decreased with the basicity of PACls (figure 6).

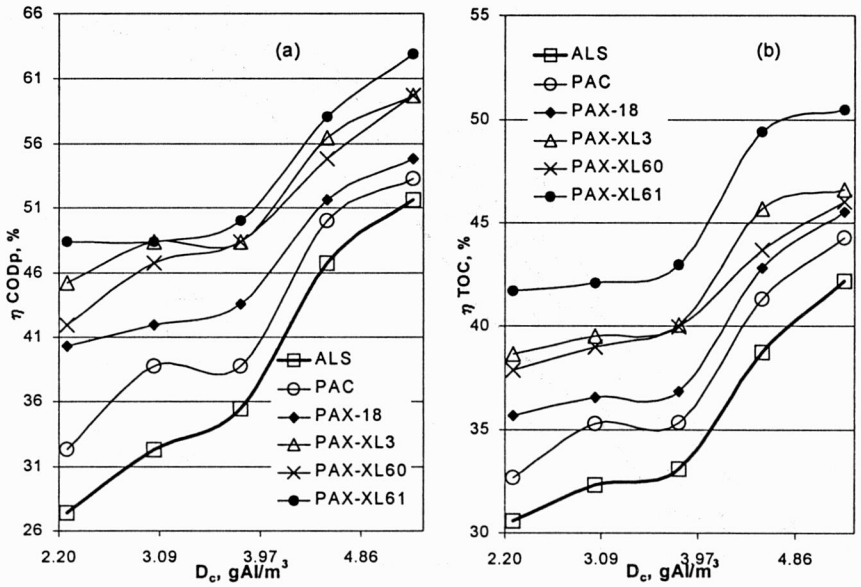

Fig. 6. Effect of coagulant type and coagulant dose on the removal of COD_p (a) and TOC(b)

The higher performance of PACls compared to ALS is evidenced by the cumulative curves of COD_p and TOC in figure 7 and figure 8, respectively.

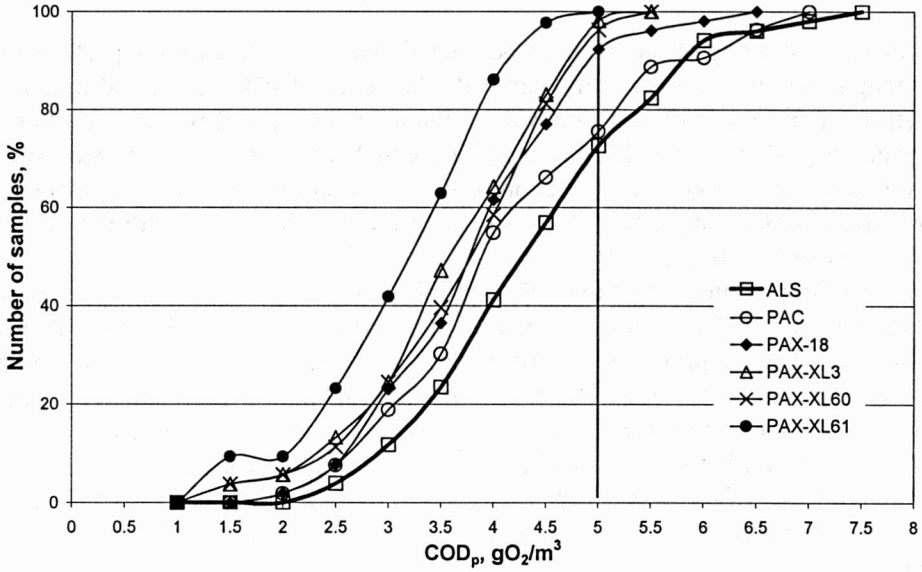

Fig. 7. Effect of coagulant type on the frequency of the admissible COD_p value being exceeded (pH_n, $N = 305$)

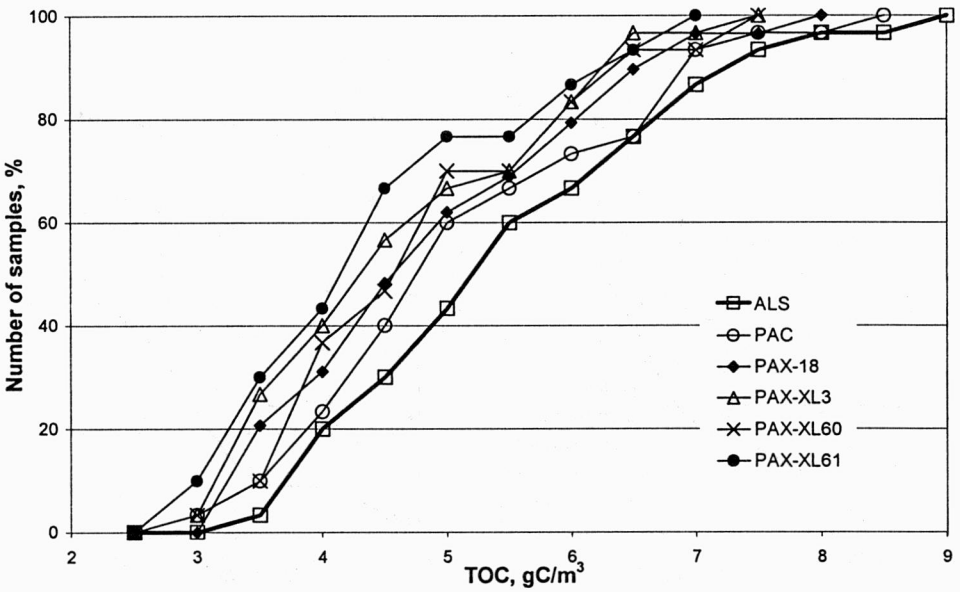

Fig. 8. Cumulative curves of residual TOC for the aluminium coagulants investigated (pH_n, $N = 179$)

3.4. EFFECT OF pH

Acidity or alkalinity of the water to be treated had poor effect on the performance of the coagulants used for turbidity removal. The level of pH_a was found to exert a much stronger influence on the removal of coloured matter and organic substances, which were degraded most efficiently at pH_a ranging between 6.0 and 6.8, irrespective of the coagulant type used. Acid reaction of water favourably affected coagulant efficiency, especially that of ALS, and this favourable effect decreased with the increase in the basicity of PACls (figure 9).

These findings indicate that the polyaluminium products of prehydrolysis, which are present in the PACl solutions, remain stable within a wider pH range than do the positively charged products of ALS hydrolysis, which form in the environment of high H^+ ion concentrations. Hence, in order to achieve a performance of ALS comparable to that of the prehydrolyzed coagulants, which are dosed at pH_n, it is necessary to adjust pH to the value below 7 prior to coagulation, thus enhancing the corrosive tendency of the water to be treated. Alkaline reaction has to be blamed for decreasing the performance of all coagulants investigated, especially that of ALS (figure 10).

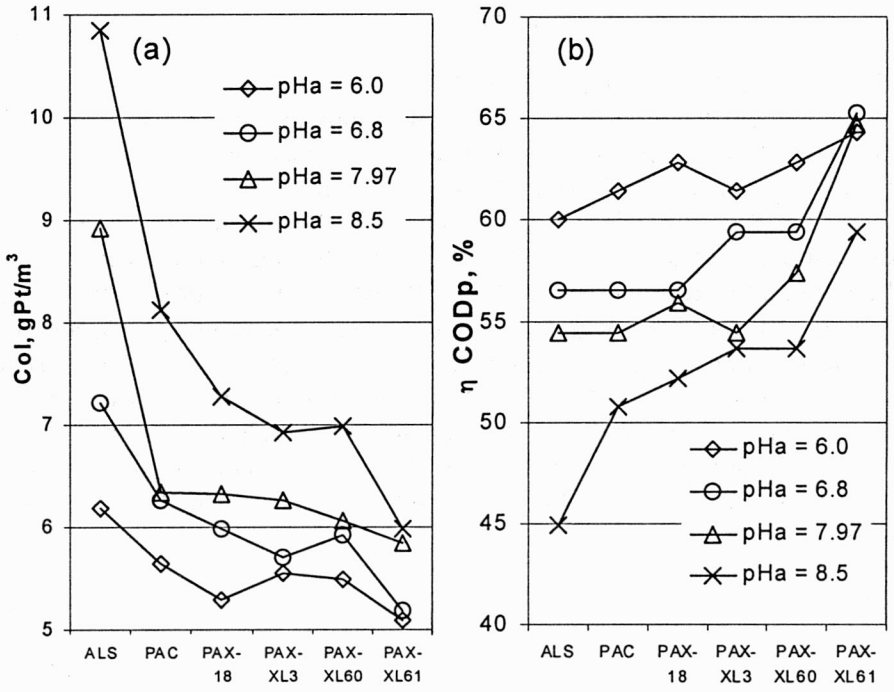

Fig. 9. Effect of pH and coagulant type on residual colour (a) and efficiency of COD_p removal (b)

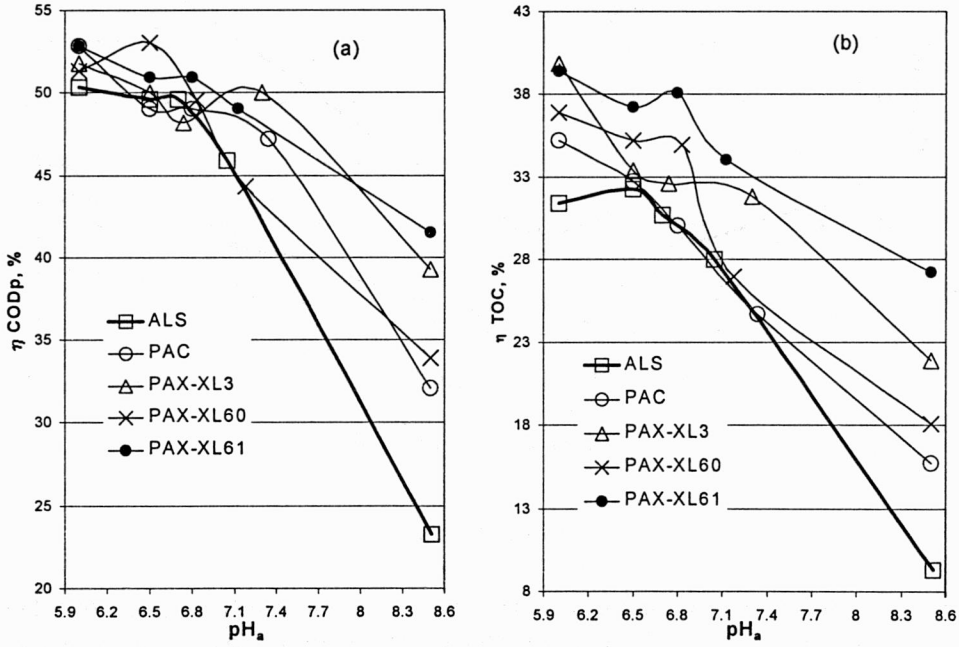

Fig. 10. Effect of pH_a on the removal efficiency of the coagulants for COD_p (a) and TOC (b)

3.5. RESIDUAL ALUMINIUM (Al_r)

In the assessment of aluminium coagulant performance not only the removal efficiencies for particular pollutants should be taken into account, but also residual aluminium concentrations. The experimental results evidenced clearly that after the use of prehydrolyzed coagulants the concentration of Al_r in the treated water samples was lower than after the use of alum coagulant (table 2). Apart from the type and dose of the coagulant used, it was also the pH_a of the water that accounted for the concentration of Al_r; excess concentrations, i.e. those greater than 0.2 g Al/m^3, persisted in the water samples of $pH_a \geq 8.3$ which favoured formation of water-soluble aluminates. However, also within this pH range, the concentrations of Al_r were noticeably lower in the samples treated with prehydrolyzed coagulants (figure 11). This finding should be attributed, on one hand, to the greater stability of the prehydrolysis products (compared to that of the products formed in the water under treatment) and, on the other hand, to the amount of non-prehydrolyzed aluminium, which in PACls was smaller than in ALS.

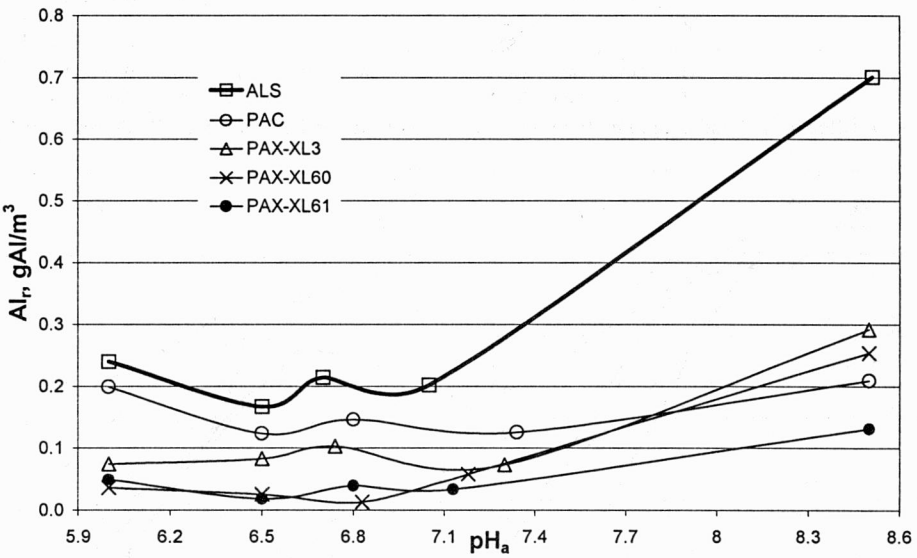

Fig. 11. Effect of pH_a on Al_r

4. CONCLUSIONS

• The polyaluminium chlorides investigated were more effective as coagulating agents than alum, and the difference in effectiveness between these species increased with the increasing degree of prehydrolysis.

• The performance of prehydrolyzed coagulants was less dependent on the pH and temperature of the water to be treated than the performance of alum.

• Substitution of alum for polyaluminium chlorides (mainly of a basicity equal to, or greater than 70%) allowed an approximately 30% reduction of the coagulant dose (g Al/m^3) giving a comparable treatment effect.

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SKUTECZNOŚĆ KOAGULANTÓW WSTĘPNIE ZHYDROLIZOWANYCH I SIARCZANU GLINU – BADANIA PORÓWNAWCZE

Porównano przydatność siarczanu glinu oraz 5 chlorków poliglinu o różnej alkaliczności do usuwania zarówno zanieczyszczeń, jak i stężenia glinu pozostałego w wodzie po koagulacji. Przedmiotem badań były naturalne wody Odry i Oławy różniące się temperaturą i poziomem zanieczyszczenia. Wyniki badań wykazały, że chlorki poliglinu były bardziej przydatne niż siarczan glinu, a ich skuteczność zwiększała się wraz ze wzrostem alkaliczności. Koagulanty wstępnie zhydrolizowane były ponadto mniej wrażliwe na zmianę odczynu i niską temperaturę oczyszczanej wody, a ich zastosowanie sprawiło, że stężenie glinu pozostałego w wodzie było mniejsze, a zmniejszona dawka zapewniała porównywalny efekt oczyszczania wody jak ten uzyskany po zastosowaniu siarczanu glinu.