Environment Protection Engineering

Vol. 27 2001 No. 3–4

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ON THE ADVANTAGES OF USING PREHYDROLYSED ALUMINIUM COAGULANTS

The advantages of applying polyaluminium chlorides (i.e. prehydrolysed aluminium coagulants differing in basicity) are specified. Experiments were carried out on riverine water samples (from the Odra and its tributary, the Oława) which varied in temperature and pollution level. Polyaluminium chlorides yielded a greater destabilisation of colloids and their efficiency in the removal of water pollutants was higher compared with conventional aluminium sulphate coagulant. They were also of greater utility than aluminium sulphate because of a lower residual aluminium concentration and a smaller increase in water corrosivity. The increase in the basicity of the prehydrolysed coagulants exerted a favourable influence on their efficiency and allowed reduction of their doses.

SYMBOLS AND NOTATION

Al_r – concentration of residual aluminium, g Al/m^3,
Col_r – residual colour, g Pt/m^3,
G – velocity gradient, s^{-1},
T_r – residual turbidity, g SiO$_2$/m^3,
N – number of samples,
TOC – total organic carbon,
pH_a – adjusted pH,
pH_n – natural pH,
COC – colloidal organic carbon,
DOC – dissolved organic carbon,
COD_p – permanganate oxygen demand, g O$_2$/m^3,
COD_{pr} – residual permanganate oxygen demand, g O$_2$/m^3,
M – total alkalinity, val/m^3,
η_M – efficiency of turbidity removal, %,
η_{Col} – efficiency of coloured matter removal, %,
η_{CODp} – efficiency of permanganate oxygen demand removal, %,
η_{TOC} – efficiency of total organic carbon removal, %,
η_{COC} – efficiency of colloidal organic carbon removal, %,
η_{DOC} – efficiency of dissolved organic carbon removal, %.

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1. INTRODUCTION

Coagulation has been successfully applied to water treatment for over a century. In spite of this, many environmental scientists and engineers have directed their attention to the problem of how to upgrade the efficiency of the process. Their interests have focused not only on the separation of natural colloid pollutants, but also on the removal of anthropogenic dissolved organic fractions and pathogenic microorganisms which are highly resistant to disinfection, e.g. *Giardia lamblia* or *Cryptosporidium parvum* [1], [2]. A major objective of some investigations is to minimise the undesired effects of the process, i.e. to reduce residual cation concentrations and the increased corrosivity of the water after coagulation.

One of the various methods for the enhancement of the coagulation process is the use of highly efficient coagulants, such as the prehydrolised polyaluminium chlorides reported in the literature. Their usefulness should be attributed to the increased basicity (compared to that of the conventional alum coagulant), as well as to the fact that among the products of prehydrolysis of the aluminium salts (during production of the coagulant) there are more polymeric forms with highly positive charges in the polyaluminium chloride solution than among the products of hydrolysis of non-prehydrolysed coagulants which have been dosed at natural pH [3], [4], [5].

The objective of the study reported in this paper was to compare the utility of alum and polyaluminium chlorides (differing in their basicities) in the treatment of riverine water collected from the Odra and one of its tributaries, the Oława.

2. METHODS AND MATERIAL

Volume coagulation was carried out by the jar test method at natural or adjusted pH. Rapid (200 rpm; $G = 220\ \mathrm{s}^{-1}$) and slow (30 rpm; $G = 20\ \mathrm{s}^{-1}$) mixing took 3 and 30 minutes, respectively. After coagulation, the samples were subjected to 1-hour sedimentation. Physicochemical parameters of non-treated and treated (by coagulation and sedimentation) water were determined according to Polish standards. TOC, COC and DOC concentrations were measured by thermal method (using a TOC 5050 analyser made by Shimadzu), DOC content being established in water samples after their filtration through 0.45 μm pore diameter Teflon filters. Water samples subjected to filtration through 1.2 μm pore diameter Teflon membranes were made use of to establish the sum of COC and DOC and thereafter to calculate COC as a difference between the concentration sum (COC+DOC) and DOC. Zeta potential was measured using a Zetasizer 2000 made by Malvern. Variations in increased corrosivity of the water were analysed in terms of Langelier saturation index (LSI), Ryznar (saturation) index (RSI) and coefficient of corrosivity (I):

$$I = (CO_{2\,\text{aggressive}})^2/(CO_{2\,\text{bound}} + CO_{2\,\text{aggressive}}).$$

Table 1

Major physicochemical parameters of the water investigated

Sampling site	pH	Alkalinity [val/m^3]	Turbidity [g SiO_2/m^3]	Colour [g Pt/m^3]	COD$_P$ [g O_2/m^3]	TOC [g C/m^3]	DOC [g C/m^3]	Al$_r$ [g Al/m^3]	Temperature [°C]
The Odra	6.74–8.41	1.55–2.55	6.86–184.0	23.33–260.5	5.2–11.9	5.88–13.6	3.529–7.898	0–0.168	21
The Oława	7.10–7.77	2.70–3.25	5.43–15.1	24.99–53.66	4.1–6.1	6.05–8.71	2.799–4.124	0–0.023	5–21

The samples of riverine water (collected from the Odra and its tributary, the Oława) used in the experiments differed in pollution level (table 1). Coagulants (alum (ALS) and five polyaluminium chlorides differing in basicity) were dosed in the form of aqueous solutions of a known aluminium concentration, and their efficiencies were compared. All coagulant doses (D_c) are expressed in g Al/m^3. Relevant data are listed in table 2.

Table 2

Type and basicity of the aluminium coagulants tested [6], [7]

Type of coagulant	ALS	Polyaluminium chlorides				
		PAC	PAX-18	PAX-XL3	PAX-XL60	PAX-XL61
Basicity [%]	0	35	41±3.0	70±5.0	70±10.0	85±10.0

3. DISCUSSION OF RESULTS

3.1. DESTABILISATION OF COLLOIDS

All of the polyaluminium chlorides tested ensure a more efficient destabilisation of colloids than did ALS (figure 1).

The curves in figure 1 prove that the increase in the basicity of the coagulants and the high positive charge account for the decrease of the dose required which provides a certain reduction of the absolute zeta potential value. As a result, the ALS dose required to achieve a comparable destabilisation of the colloids was noticeably larger than the doses of polyaluminium chlorides required. This favourable effect resulting from the increased basicity of the prehydrolysed coagulants was observed in the entire investigated range of water pH (figure 2).

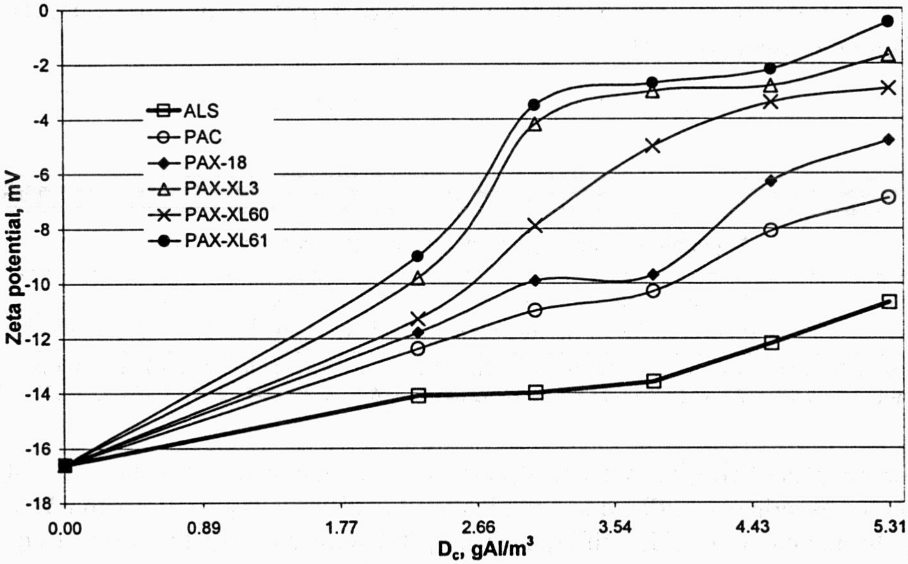

Fig. 1. Effect of coagulant type and coagulant dose on the zeta potential value

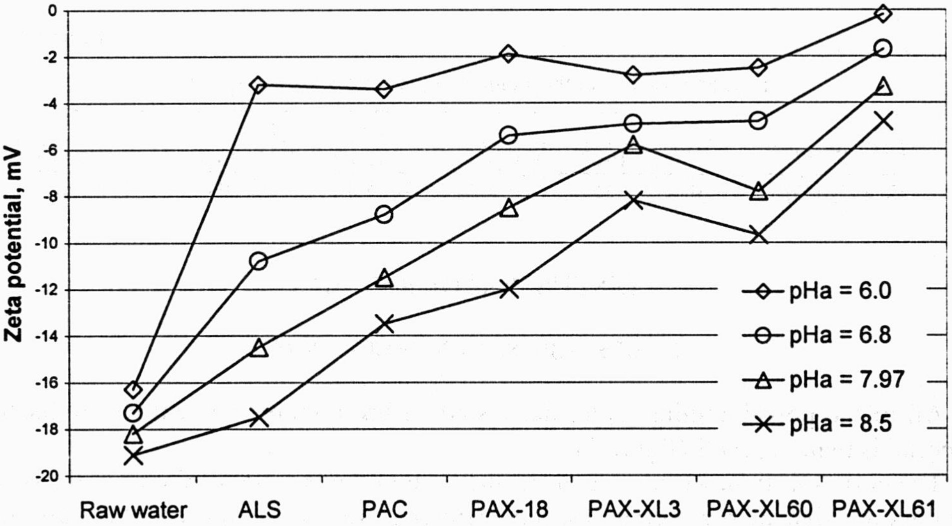

Fig. 2. Effect of coagulant type and adjusted pH (pH_a) on the zeta potential value

Even the smallest difference in the efficiency of destabilisation caused by ALS and that ensured by other coagulants at $pH_a = 6.0$ should be attributed to the fact that at this H^+ ion concentration the hydrolysis of ALS yields a larger amount of polycation products than at higher pH values.

3.2. EFFICIENCIES OF THE REMOVAL OF POLLUTANTS

Of the pollutants investigated, those producing water turbidity were removed with the highest efficiency. Thus, at a water temperature equal to, or higher than 20 °C, the efficiency of pollutant removal exceeded 90% in the majority of the samples. Although the type of the coagulant used did not greatly affect the turbidity removal, ALS was less effective than the prehydrolysed polyaluminium chlorides. As the basicity of polyaluminium chlorides increased, the number of samples with turbidity greater than 1 g SiO_2/m^3 decreased. The increased efficiency of prehydrolysed coagulants was particularly distinct in the lower range of the doses applied (figure 3).

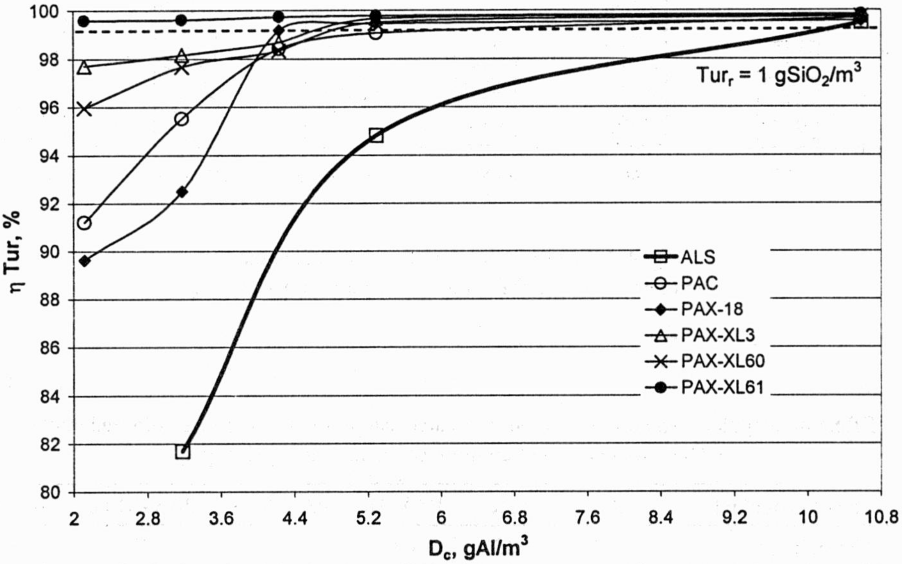

Fig. 3. Effect of coagulant type and dose on the efficiency of turbidity removal

The removal of coloured matter and organic substances proceeded according to a similar pattern, but in such a case the coagulant basicity was found to be more pronounced than for the removal of turbidity. Hence, ALS was the least useful and PAX-XL61 (characterised by the highest basicity) was the most effective coagulant. This finding was corroborated by the values of the coefficient of coagulant utilisation for colour removal (CCU_c), i.e. by the ratio of coloured matter reduction to the amount of aluminium utilised in the course of the process, as well as by the number of the samples treated wich were characterised by an excessive content of coloured matter. Relevant data are plotted in figure 3 and listed in table 3.

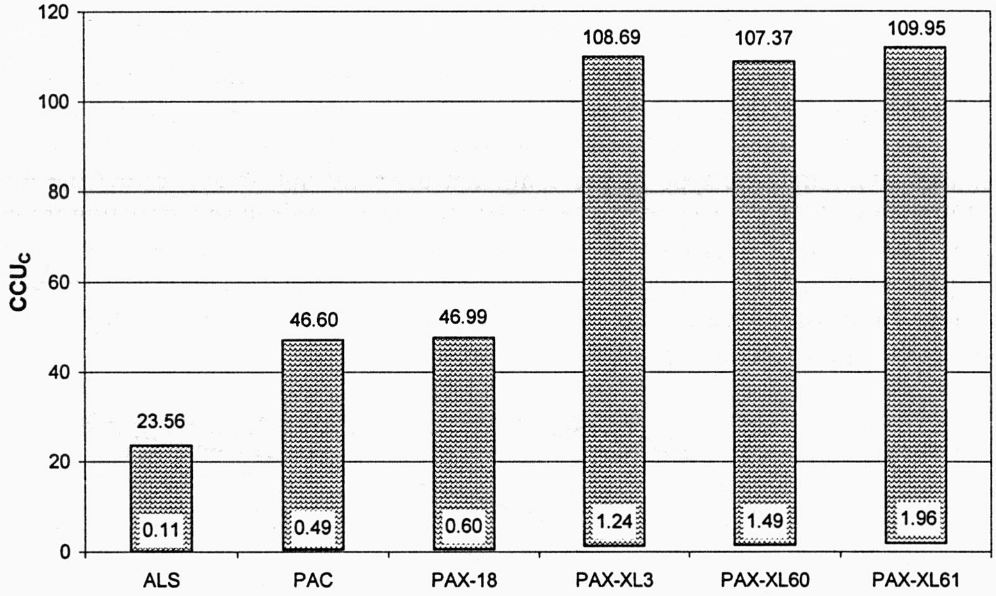

Fig. 4. Effect of basicity of aluminium coagulants on their utilisation for coloured matter removal (CCU$_c$)

Table 3

Effect of coagulant type on the number of treated samples with excessive coloured matter, COD$_p$ and residual aluminium concentrations (pH$_a$ = pH$_n$)

Type of coagulant	ALS	PAC	PAX-18	PAX-XL3	PAX-XL60	PAX-XL61
Basicity [%]	0	35	41	70	70	85
Col$_r$ > 15 g Pt/m^3 (N = 382)	21	15	12	9	11	3
COD$_p$ > 5 g O$_2$/m^3 (N = 382)	17	12	4	1	2	0
Al$_r$ > 0.2 g Al/m^3 (N = 317)	32	28	26	10	10	2

The presence of aluminium polycations in the solutions of prehydrolysed coagulants enhanced their efficiency in removing organic pollutants expressed as COD$_p$ (table 3, figure 5) and TOC (figure 6a). It was advantageous that polyaluminium chlorides were far more effective than ALS in removing dissolved organic fractions, as evidenced by the plots of figure 6b and by the efficiency ranges listed in table 4 for all the water samples investigated. Owing to the increased efficiency of polyaluminium chlorides it was possible to reduce (compared to ALS) the required dose which provided a comparable removal of organic pollutants (table 5).

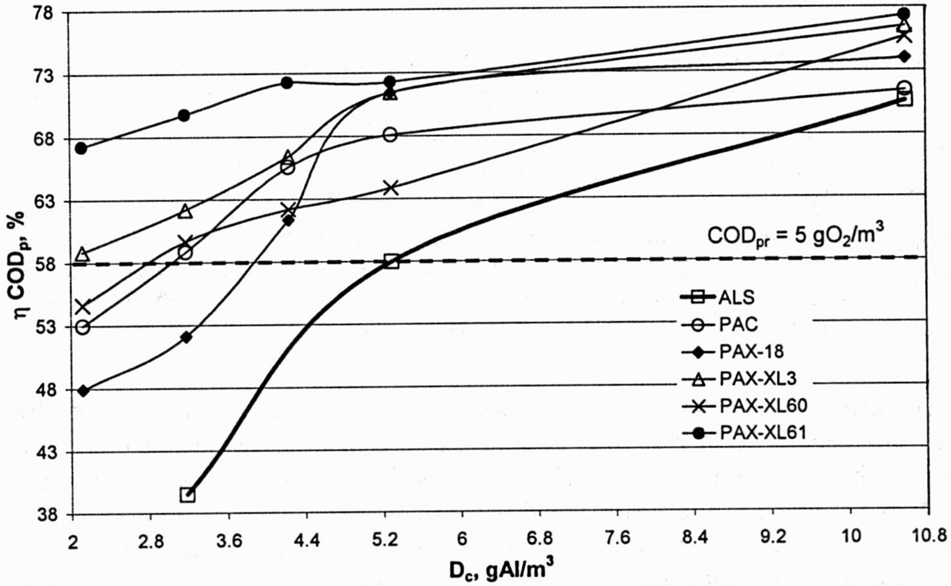

Fig. 5. Effect of coagulant dose and coagulant type on the efficiency of COD$_p$ removal

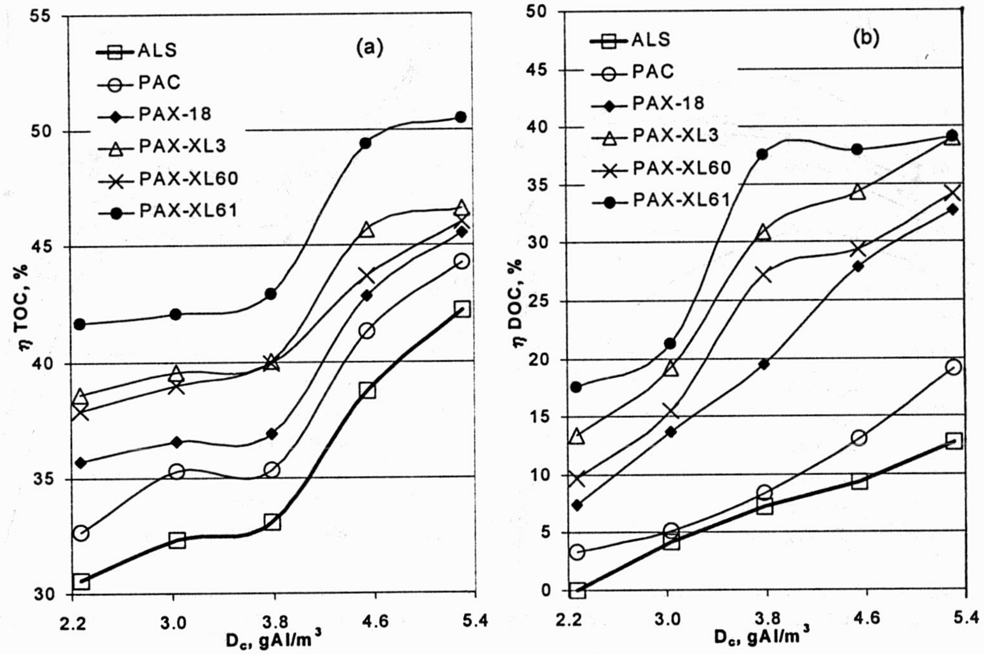

Fig. 6. Effect of coagulant dose and coagulant type on the removal efficiency of TOC (a) and DOC (b) (for the Odra river water)

Table 4

Efficiency of the coagulants in removing coloured matter and organic pollutants at natural pH

Removal efficiency [%]	Type of coagulant					
	ALS	PAC	PAX-18	PAX-XL3	PAX-XL60	PAX-XL61
η_{Col}	1.24–95.80	5.68–97.52	7.44–97.64	15.65–99.18	18.29–99.36	24.65–99.62
η_{CODp}	1.22–70.59	2.44–71.43	3.66–73.95	6.66–76.47	7.32–75.63	8.54–77.31
η_{TOC}	2.19–55.11	8.27–55.72	11.14–57.03	16.64–59.21	18.25–59.85	27.86–59.95
η_{COC}	48.51–96.35	64.48–100.0	74.45–100.0	77.97–100.0	85.27–100.0	91.34–100.0
η_{DOC}	0–23.37	0–34.95	0–33.34	5.16–38.98	4.85–35.45	14.12–42.73

The efficiency of the polyaluminium chlorides was only slightly affected by pH variations (figure 7). Aluminium chloride-based coagulants were found to be more efficient than ALS, especially at pH > 8.0. This finding suggests their advantage over the ALS coagulant in the treatment of water of high pH; there is no need of pH adjustment to the acid reaction prior to the coagulation process, which brings about an increased corrosivity of water.

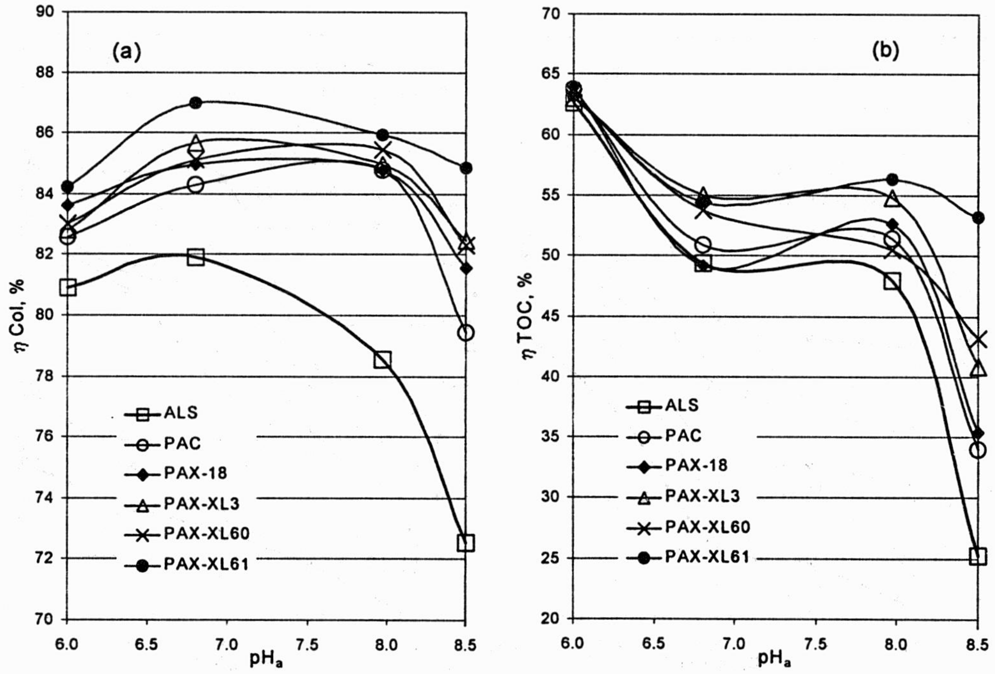

Fig. 7. Effect of pH adjustment and coagulant type on the removal efficiency

Table 5

Required coagulant doses (D_{rc}) providing a comparable removal of organic pollutants ($pH_a = pH_n$)

Type of coagulant	D_{rc} (g Al/m^3)			
	COD_p	TOC	COC	DOC
ALS	5.31	5.31	5.31	5.31
PAC	$4.55 < D_{rc} < 5.31$	$4.55 < D_{rc} < 5.31$	$4.55 < D_{rc} < 5.31$	$3.79 < D_{rc} < 4.55$
PAX-18	$D_{rc} = 4.55$	$3.79 < D_{rc} < 4.55$	$3.79 < D_{rc} < 4.55$	$2.27 < D_{rc} < 3.03$
PAX-XL3	$3.79 < D_{rc} < 4.55$	$3.79 < D_{rc} < 4.55$	$3.03 < D_{rc} < 3.79$	$D_{rc} < 2.27$
PAX-XL60	$3.79 < D_{rc} < 4.55$	$3.79 < D_{rc} < 4.55$	$3.03 < D_{rc} < 3.79$	$2.27 < D_{rc} < 3.03$
PAX-XL61	$3.79 < D_{rc} < 4.55$	$3.03 < D_{rc} < 3.79$	$2.27 < D_{rc} < 3.03$	$D_{rc} < 2.27$

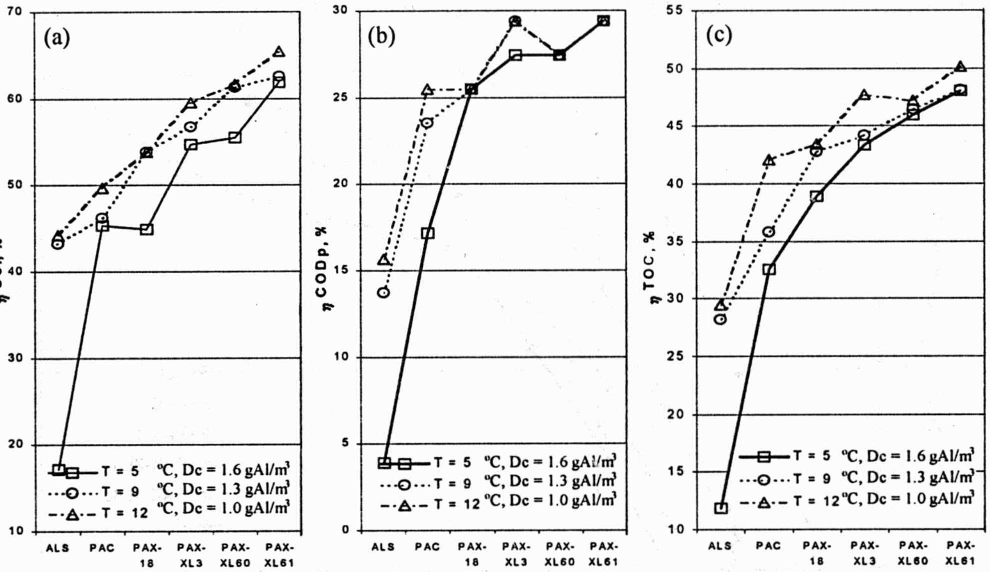

Fig. 8. Effect of temperature, coagulant type and coagulant dose on the efficiency of removal of coloured matter (a), COD_p (b) and TOC (c)

The prehydrolysed coagulants were also more effective than the ALS coagulant when the water under treatment had a temperature of 5 to 12 °C (figure 8). The adverse effect of low temperature on the efficiency of coloured matter and TOC removal generally diminished as the basicity of the coagulant rose (table 6).

Table 6

Differences in the treatment efficiency of aluminium coagulants ($\Delta\eta$) used at the water temperature of 21 °C and 8 °C (the Oława river)

$\Delta\eta$	Type of coagulant					
	ALS	PAC	PAX-18	PAX-XL3	PAX-XL60	PAX-XL61
Turbidity	90.0	87.24	87.07	56.72	43.62	48.79
Colour	62.39	56.58	54.34	47.82	43.17	47.06
TOC	36.51	30.94	33.64	30.32	29.69	22.62

3.3. RESIDUAL ALUMINIUM CONCENTRATION (Al_r)

Irrespective of water temperature, the concentration of residual aluminium was lower after coagulation by polyaluminium chlorides than after ALS coagulation and was inversely proportional to the basicity of the reagents tested (table 3, figure 9).

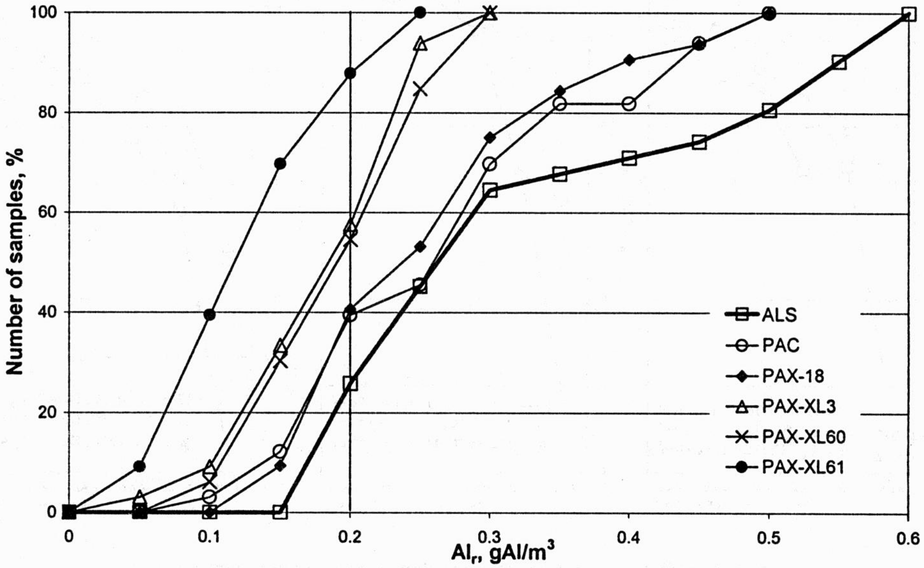

Fig. 9. Frequency of Al_r occurrence in the water samples treated ($N = 195$, $pH_a = pH_n$, $D_k = 2.12–10.56$ g Al/m^3)

Another factor affecting the concentration of Al_r was the pH of the water to be treated; Al_r levels higher than 0.2 g Al/m^3 were measured predominantly in the samples coagulated at pH_a ranging from 8.28 to 8.5. But also in this pH range, the polyaluminium chlorides of the highest basicity (PAX-XL3 and PAX-XL60) were found to be noticeably more efficient than ALS; this applies particularly to PAX-XL61, the only coagulant which yielded Al_r concentrations below 0.2 g Al/m^3 at $pH_a = 8.5$ (figure 10).

The evidenced influence of the coagulant type and water pH on Al_r should be attributed to the presence of polymeric products of prehydrolysation in the aluminium chloride solution; these products remain stable in a wider pH range than do the products of ALS hydrolysis.

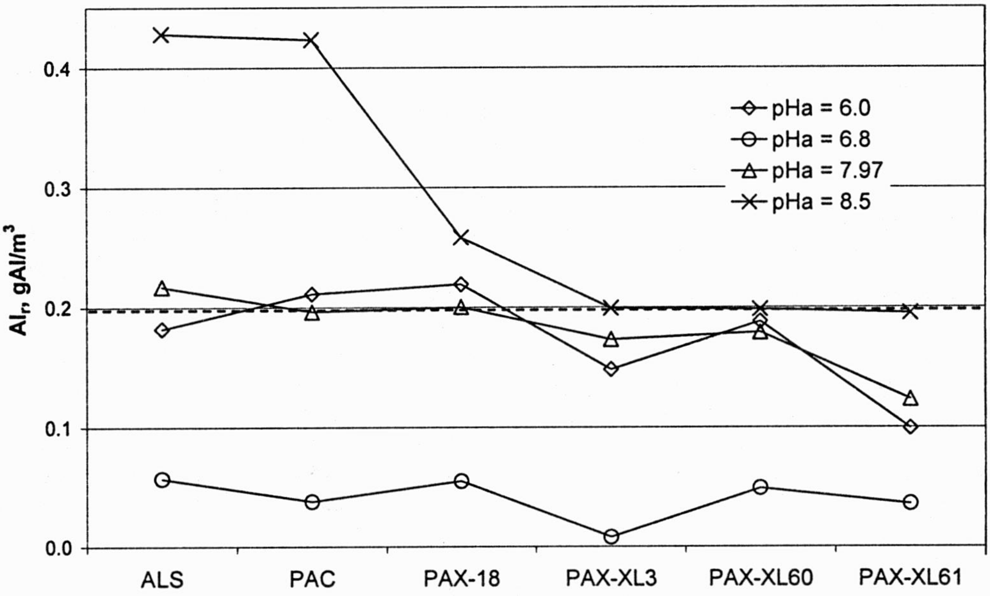

Fig. 10. Effect of coagulant type and pH adjustment on Al_r

3.4. RISE IN CORROSIVITY

The type and consequently the basicity of the coagulants exerted a decisive influence on the corrosivity of the water under treatment. As the efficiency of prehydrolysis of coagulants increased, the acidity of the water samples decreased which was also reflected by alkalinity (table 7). As a result, in the whole investigated

Table 7

Effect of coagulant type on ΔpH and decrease in alkalinity ΔM ($M^* = 3.05$ val/m^3)

Type of coagulant	ALS	PAC	PAX-18	PAX-XL3	PAX-XL60	PAX-XL61
Δ pH	0.26–1.37	0.17–1.18	0.12–1.04	0.04–0.83	0.03–0.85	0.00–0.83
$\Delta M/D_c$ [val/g Al]	0.136–0.142	0.094–0.102	0.082–0.092	0.037–0.054	0.044–0.056	0.019–0.032

* Raw water alkalinity.

range of coagulant doses and pH, polyaluminium chlorides enhanced (to a smaller degree than ALS) the corrosivity of the water, which increased with the increasing dose of all the coagulants tested and was inversely proportional to their basicity. The most corrosive and the least corrosive were the samples coagulated by ALS and PAX-XL61, respectively. Relevant data have been gathered in table 8.

Table 8

Effect of coagulant type on the per cent of water samples (after coagulation) of a defined corrosivity ($N = 218$)

Corrosivity	Corrosivity index	Per cent of water samples after coagulation					
		ALS	PAC	PAX-18	PAX-XL3	PAX-XL60	PAX-XL61
Non-corrosive	I	21.43	28.57	30.77	50.00	42.86	77.78
	LSI	0.0	0.0	2.86	5.56	8.33	18.52
	RSI	0.0	0.0	0.0	0.0	0.0	0.0
Low or moderately corrosive	I	28.57	35.72	30.77	50.00	35.71	22.22
	LSI	82.35	88.89	88.57	88.89	88.89	81.48
	RSI	17.76	24.44	20.29	34.33	33.33	44.44
Highly corrosive	I	50.00	35.71	38.46	0.0	21.43	0.0
	LSI	17.65	11.11	8.57	5.55	2.78	0.0
	RSI	82.24	75.56	79.71	65.67	66.67	55.56

4. CONCLUSIONS

1. Prehydrolysed aluminium coagulants yielded a greater destabilisation of colloids, and their efficiencies in the removal of polluting species, particularly coloured matter and organic substances, were higher compared to aluminium sulphate.

2. The efficiency of polyaluminium chlorides increased with their basicity and to a smaller degree depended on temperature and pH than the efficiency of aluminium sulphate.

3. Smaller doses (g Al/m^3) of prehydrolysed coagulants brought about the removal of efficiency comparable to that of aluminium sulphate.

4. Polyaluminium chlorides, especially those displaying a high basicity (≥ 70%), were found to be of greater utility than aluminium sulphate, because their application yielded a lower concentration of residual aluminium and a smaller rise in the corrosivity of the water.

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ZALETY WSTĘPNIE ZHYDROLIZOWANYCH KOAGULANTÓW GLINOWYCH

Omówiono zalety wstępnie zhydrolizowanych koagulantów glinowych o różnej alkaliczności, tzw. chlorków poliglinu. Badano próbki wody z Odry i Oławy różniące się temperaturą i poziomem zanieczyszczenia. Chlorki poliglinu zapewniły większą destabilizację koloidów oraz efektywniejsze usuwanie zanieczyszczeń niż tradycyjnie stosowany siarczan glinu. Okazały się też bardziej przydatne z uwagi na mniejsze stężenie glinu pozostałego i intensyfikację korozyjności oczyszczanych wód. Stwierdzono zarówno dodatni wpływ zwiększającej się alkaliczności koagulantów wstępnie zhydrolizowanych na ich efektywność, jak i zmniejszenie wymaganej dawki koagulantu.