

MARIA ŚWIDERSKA-BRÓŹ*, MARTA RAK*

EFFECT OF THE TYPE OF ALUMINIUM COAGULANT AND WATER pH ON THE DESTABILIZATION OF COLLOIDS

The study was conducted on a laboratory scale with the aim to examine how the type and dose of the aluminium coagulant as well as water pH influence the extent of colloid destabilization. The samples used for the purpose of the study contained water from the River Odra, with a natural or an adjusted pH, and were treated with aluminium sulphate (alum) or prehydrolyzed polyaluminium chlorides. The results obtained have revealed that polyaluminium chlorides are more efficient neutralizers of the negative electrokinetic potential of the colloids than alum. As a consequence, the substitution of alum by polyaluminium chlorides reduced the required concentration (g Al/m^3) of water-soluble aluminium hydrolysis products which provided a comparable decrease in the absolute value of the ζ potential. The efficiency of polyaluminium chlorides was found to increase with their basicity and with the polymerization of the products of aluminium prehydrolysis. A major factor contributing to the value of the negative ζ potential of the colloids and to the extent of their destabilization was the concentration of H^+ ions. The decrease in the pH value was concomitant with the decrease in the absolute value of the ζ potential of the colloids that were present in the river water and with the increase in the extent of their destabilization by the coagulants examined. The effect of H^+ ion concentration (in the water being treated) on the destabilization of colloids was the strongest with the alum coagulant and decreased with the increasing basicity of the polyaluminium chlorides tested.

1. INTRODUCTION

The extent to which the colloids in the water being treated are destabilized makes a notable contribution to the efficiency of their removal by coagulation. The stability of the colloids is expressed by the value of the electrokinetic (ζ) potential, which describes the decrease of the potential in the diffusion layer of the colloidal particles. The colloids that are present in the water generally display a negative ζ potential. Their destabilization entails primarily the application of aluminium and Fe(III) salts, since the Al(III) and Fe(III) cations, as well as the products of their hydrolysis, which

* Institute of Environmental Protection Engineering, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland. E-mail: maria.swiderska-broz@pwr.wroc.pl, Marta.Rak@wp.pl

have positive electric charges, account for the neutralization of the negatively charged colloidal particles [6]. According to the Schulz-Hardy law, the efficiency of destabilization increases with the increase in the valency of the ions that neutralize the charges of the colloids.

Among the major factors that contribute to the compression of the diffusion layer of the colloids (i.e. to the decrease in the absolute value of the ζ potential) are the type and dose of the coagulant applied and pH of the water being treated. The pH value is not only a decisive contributor to the form in which the colloidal pollutants occur in the water and to the sign and value of their electric charges, but also substantially influences the form of occurrence as well as the sign and value of the electrical charges of the products generated during hydrolysis of the cations of the coagulants used. When the concentration of the OH^- ions in the water increases due to the adsorption of these anions on the surfaces of the colloidal particles (in the case of organic colloids also due to their enhanced dissociation), the negative charges of the colloids increase, whereas the positive charges of the ionic aluminium forms responsible for the destabilization of the colloids decrease [1]–[3], [9]. As a consequence, the alum coagulant doses that are to provide the required decrease in the negative ζ potential have to be increased when the pH rises. When use is made of non-prehydrolyzed aluminium coagulants, and such is aluminium sulphate, amongst the speciations of aluminium that neutralize the negative charge of the colloids are primarily the following species: aluminium monomers (Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$) and polymers of the general formula $\text{Al}_n(\text{OH})_y^{(3n-y)+}$. The valency of these aluminium forms increases with the increase of the H^+ concentration in the water being treated. It is essential to note, however, that among the products of the uncontrolled and fast hydrolysis of aluminium which occurs in the water dominant are (in quantitative terms) such monomers that may undergo polymerization only under conditions of extended hydrolysis time (1 to 7 s) [4].

At the pH of natural water and at sufficient alkalinity, the hydrolysis of aluminium cations to $\text{Al}(\text{OH})_3$ practically occurs immediately upon alum addition. Although the precipitating $\text{Al}(\text{OH})_{3(s)}$ has a positive surface charge at a pH between 5.5 and 7.6, its destabilizing force with respect to the negatively charged colloids is noticeably weaker than that of Al^{3+} or that of its positively charged hydroxycomplexes. The precipitating $\text{Al}(\text{OH})_{3(s)}$ acts not only as an adsorbent, but also as a factor that coprecipitates the pollutants being removed from the water. In the light of the foregoing, an efficient destabilization of the negatively charged colloids will only be achieved when the reaction of the cationic aluminium speciations with the colloidal particles occurs prior to the process of $\text{Al}(\text{OH})_3$ precipitation. Such conditions are fulfilled when the pH of the water being treated is lower than 6.0, which can practically be obtained by acidifying the water prior to coagulation or by applying increased alum doses. Regretfully, such technological approach has the disadvantage of increasing the corrosive behaviour of the water. This problem can be

minimized by substituting alum by prehydrolyzed aluminium coagulants, e.g. polyaluminium chlorides. The solutions of these coagulants contain not only aluminium monomers but also polymerized hydroxycomplexes of aluminium with high positive charges (ranging from 3 to 12) as well as $[Al_{13}O_4(OH)_{24}]^{7+}$, by some investigators referred to as polymer Al_{13} [9]. EDZWALD et al. [5], [13] make it clear that among the aluminium polymers Al_{13} is the most effective destabilizer of negatively charged colloids. Upon its addition to the water being treated, the polycationic products of aluminium prehydrolysis are hydrolyzed to $Al(OH)_3$ at a remarkably slower rate as compared with the aluminium that is present in the alum. And what is more, they preserve their dissolved and polymerized (“primary”) form over a wider range of the pH as compared to aluminium sulphate when used as a coagulant [11], [12]. The properties of the polyaluminium chlorides mentioned above seem to substantiate their higher propensity for destabilizing negative colloids in comparison with the non-prehydrolyzed aluminium coagulants. The verification of the hypothesis was the objective of this study.

2. METHODS AND SCOPE OF THE STUDY

The aim of the experimental study was to establish how the type and dose of the aluminium coagulant (D_c , g Al/m³) as well as the pH of the water being treated influence the extent of destabilization of the colloids that are present in the Odra River water. The tests were conducted with aluminium sulphate (ALS, alum) and prehydrolyzed polyaluminium chlorides marketed under the brand names of PAC, PAX-18, PAX-XL3 and PAX-XL61. Their basicity are compiled in table 1.

Table 1

Basicity of the polyaluminium chlorides tested [7]

Type of coagulant	PAC	PAX-18	PAX-XL3	PAX-XL61
Basicity (%)	35	41 ± 3	70 ± 5	70 ± 10

In order to determine the effect of the pH on the ζ potential value, the tests were performed both at a natural and an adjusted pH of the water. The samples were alkalinized with an aqueous NaOH solution and acidified with the water solutions of hydrochloric acid (tests involving polyaluminium chlorides) or sulphuric acid (ALS-entailing tests). Electrokinetic potential values of the colloids were measured in raw water samples as well as in the samples subjected to three-minute rapid mixing (at 200 rpm) with a defined coagulant dose. Relevant measurements were conducted by the electrophoretic light diffusion method, using the Malvern Zetameter 2000, with 12 replications for each sample. The raw water samples contained colloids displaying a negative electrokinetic potential (ζ_0) whose values varied from -15.3 mV to -19.1 mV.

For the interpretation of the results obtained, the differences in the negative electrokinetic potential values of the colloids prior to (ζ_0) and after their interaction (ζ) with the monomers and polymers of aluminium were expressed as $|\Delta\zeta|$.

The efficiency of the colloid destabilization (η) was calculated according to the formula:

$$\eta = (|\Delta\zeta| / |\zeta_0|) \cdot 100\%.$$

3. DISCUSSION OF RESULTS

3.1. EFFECT OF COAGULANT TYPE AND COAGULANT DOSE

When added to the water of a natural pH (8.02), the coagulants tested produced a diverse extent of colloid particle destabilization. As was expected, the extent of destabilization increased with the increase in the coagulant dose (which varied from 2.27 to 5.31 g Al/m³) and in basicity (figure 1).

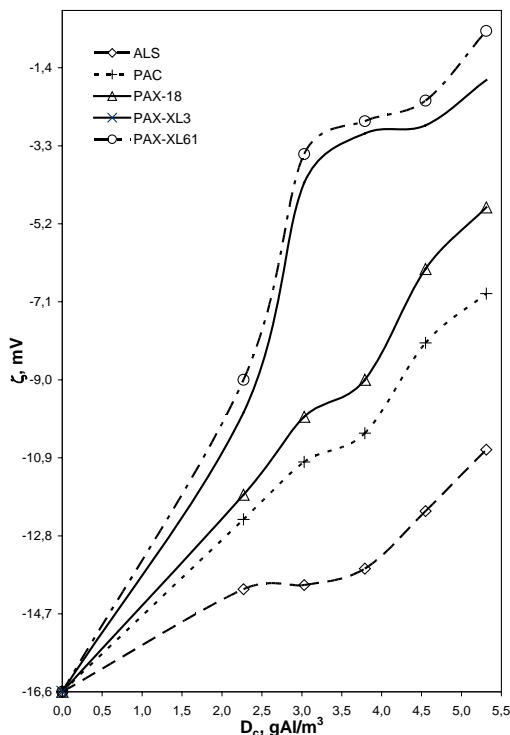


Fig. 1. Effect of coagulant type and coagulant dose on the electrokinetic potential value

The most distinct decrease in the negative electrokinetic potential value was achieved with PAX-XL61 and PAX-XL3, whereas ALS was found to be least efficient

in decreasing this value. As a consequence, the coagulant doses that provided comparable destabilization of the colloids decreased with the increasing basicity of the reagents used. The lowest dose (2.27 g Al/m^3) of the two coagulants with the highest basicity (PAX-XL61 and PAX-XL3) accounted for a higher extent of colloid destabilization as compared to the dose of the coagulants with moderate basicity (PAC or PAX-18), which was approximately 1.5 times as high, and to the ALS dose, which was more than twice as high.

The enhanced capacity of the prehydrolyzed coagulants for destabilizing negatively charged colloids as well as the significance of their basicity in this respect are also reflected in the mean values of the decrease in the ζ potential by $D_c = 1 \text{ g Al/m}^3$ (table 2).

Table 2

Mean values of $|\Delta\zeta|/D_c$, $\text{mV/g Al}\cdot\text{m}^{-3}$

Type of coagulant	ALS	PAC	PAX-18	PAX-XL3	PAX-XL61
$ \Delta\zeta /D_c$	0.966	1.802	2.198	3.287	3.507

The same pattern was observed in other water samples displaying a similar pH (7.82 to 7.98) and differing in the concentrations of pollutants, where the electrokinetic potential of the colloids varied between -17.5 and -18.8 mV (figure 2).

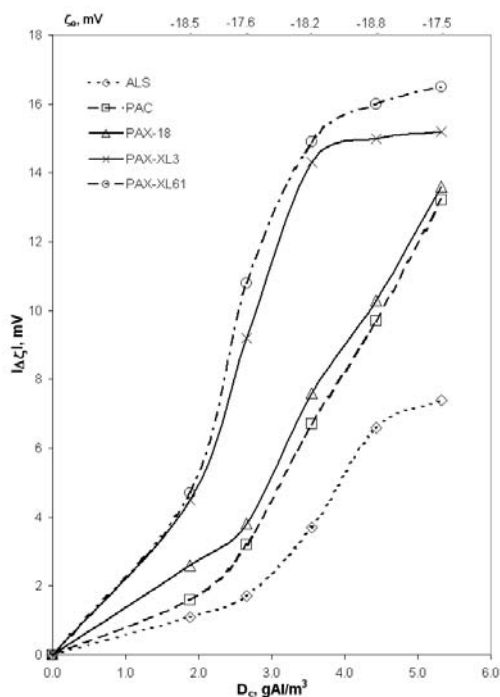


Fig. 2. Effect of coagulant dose and type on the decrease in the negative electrokinetic potential of the colloids

In this experimental series, PAX-XL61 and PAX-XL3 were also found to be the most efficient destabilizers of negatively charged colloids. The higher efficiency of polyaluminium chlorides than that of alum is attributable to the fact that the solutions of PAX-XL61 and PAX-XL3 contain (in addition to aluminium monomers) large quantities of polycationic products generated during prehydrolysis of aluminium, which effectively neutralize the negative charges of the colloids. What is more, when the basicity of polyaluminium chlorides increases, the concentration of the hydrolyzing aluminium in the water being treated decreases, and there is a concomitant rise in the polymerization ($r = [\text{OH}/\text{Al}^{3+}]$) of the aluminium speciations with a positive charge, which facilitates their adsorption on the surfaces of the destabilized colloids. As a result, the doses of the coagulants tested that provided a comparable destabilization of the colloids decreased in the following order: ALS > PAC > PAX-18 > PAX-XL3 > PAX-XL61.

3.2. EFFECT OF pH

Apart from the type and dosage of the coagulants used, there was another decisive factor, pH of the water, that affected not only the electrokinetic potential values of the colloids, but also the extent of their destabilization by the coagulants tested. The increase in the H^+ ion concentration brought about the decrease in the absolute value of the electrokinetic potential, while the alkalization of the water produced exactly the opposite phenomenon, as can be inferred from the data in table 3.

Table 3

Effect of the pH of the water on the electrokinetic potential of colloids

pH	6.0	7.0	8.0*	9.0
ζ mV	-10.3	-13.6	-15.3	-15.9

* Non-adjusted pH.

Seemingly, the decrease observed in the negative electrokinetic potential is attributable to the adsorption of H^+ ions onto the surfaces of the colloids. And this implies that the reduction in the stability of the colloidal system due to the acidification of the water prior to coagulation will reduce the demand for the coagulant to a defined extent. This assumption has been corroborated by the plots in figure 3.

The decrease in the pH from 7.98 to 6.0 made it possible to reduce the coagulant dose from 6.2 to 3.54 g Al/m³ and thus provide a comparable extent of colloid destabilization. When dosed in the quantity of 6.2 g Al/m³ into the water of a non-adjusted pH (pH = 7.98), the PAX-XL61 coagulant accounted for the change in the sign of the electrokinetic potential from the negative ($\zeta_0 = -16.1$ mV) to the positive one ($\zeta = +0.5$ mV).

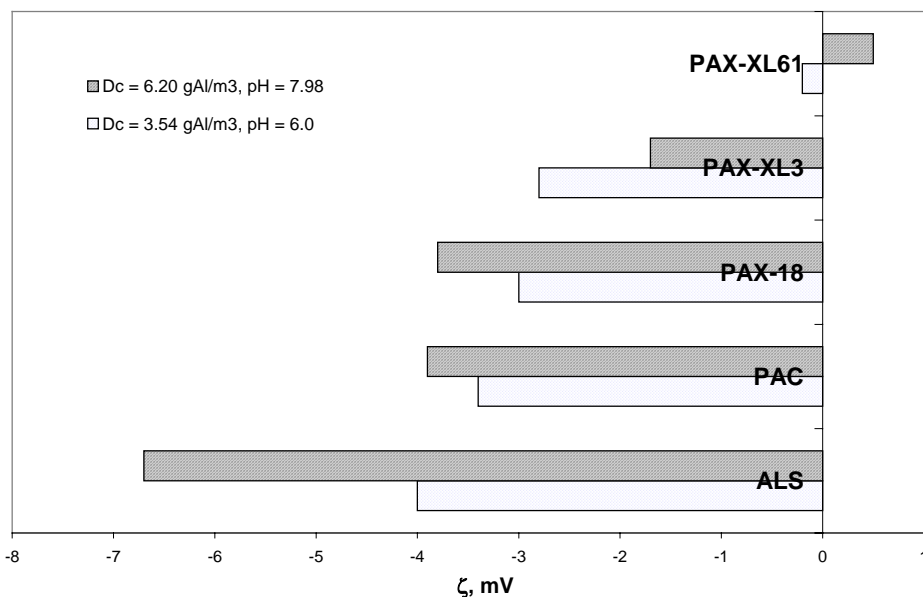


Fig. 3. Comparison of the electrokinetic potential values obtained upon destabilization of the colloids by the aluminium coagulants tested ($\zeta_0 = -16.1$ mV)

The increase in H^+ ion concentration not only reduced the absolute value of the ζ_0 potential, but also extended the time of the hydrolysis of Al^{3+} ions to $Al(OH)_3$, and thus provided favourable conditions for the destabilization of the negatively charged colloids by the polycationic forms of aluminium. The beneficial effect of water acidification was particularly distinct when use was made of ALS-containing aluminium cations, whose hydrolysis occurred in the water being treated. In polyaluminium chlorides, the concentration of non-hydrolyzed aluminium is lower than in ALS, which explains why the acidification of the water prior to coagulation exerted a less significant influence on their efficiency in neutralizing the surface charges of the colloids. The effect of water alkalization was quite the reverse. The influence of water alkalization on the efficiency of the coagulants in decreasing the negative values of the electrokinetic potential is depicted by the plots in figures 4 and 5.

The results obtained have revealed that irrespective of the type of the coagulant used, the extent of destabilization over the investigated pH range decreased with the rise in the concentration of OH^- ions which not only increase the ζ_0 value and the extent of hydrolysis of Al^{3+} ions to $Al(OH)_3$, but also provide favourable conditions for the formation of defined quantities of $Al(OH)_4^-$, depending on the pH of the water.

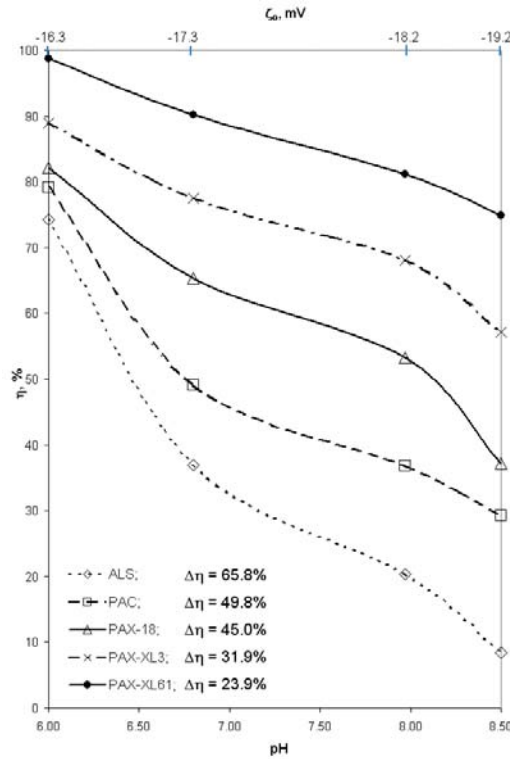


Fig. 4. Effect of pH on the destabilization of colloids (η) with aluminium coagulants ($D_c = 3.54 \text{ g Al/m}^3$; $\zeta_0 = -16.3$ to -19.1 mV , $\Delta\eta = \eta(\text{at pH } 6.0) - \eta(\text{at pH } 8.5)$)

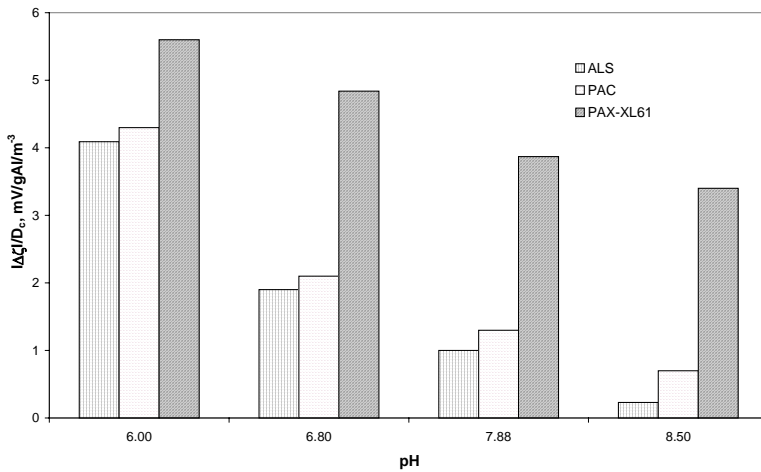


Fig. 5. Effect of pH on the efficiency of coagulants in the destabilization of colloids ($\zeta_0 = -16.9 \text{ mV}$, $D_c = 3.1 \text{ g Al/m}^3$)

The undesired effect of the rise in the pH from 7.88 to 8.50 was weaker in the case of polyaluminium chlorides than alum. The increase in the concentration of H^+ ions upgraded the efficiency of alum to the greatest extent and the efficiency of the polyaluminium chloride PAX-XL61 to the smallest one (figure 5). As can be inferred from the foregoing, the cationic products of the prehydrolysis of aluminium (which are present in the solutions of polyaluminium chlorides) remain stable over a wider pH range and more efficiently neutralize the surface charges of the negative colloids as compared to the aluminium hydrolysis products that form in the water being treated.

4. CONCLUSIONS

The analysis of the results obtained allows the following conclusions to be drawn:

1. Polyaluminium chlorides were more efficient in destabilizing negative colloids as compared to aluminium sulphate, and the efficiency of each coagulant tested increased with the increase in its dosage.

2. The concentration of H^+ ions had a decisive effect on the value of the negative electrokinetic potential and on the destabilization of the colloids.

3. Regardless of the type of the coagulant applied, the acidification of the water prior to its treatment by coagulation enhanced the neutralization of the negative surface charges of the colloids and thus reduced the required coagulant dose. The alkalinization of the water produced a reverse effect.

4. The efficiency of polyaluminium chlorides in reducing the absolute value of the electrokinetic potential increased with the increase in their basicity.

LITERATURE

- [1] BUSTAMANTE H.A. et al., *Interaction between Cryptosporidium oocysts and water treatment coagulants*, Wat. Res., 2001, Vol. 35, 13, 3179.
- [2] CHENG W.P., CHI F.H., *A study of coagulation mechanisms of polyferric sulfate reacting with humic acid using a fluorescence-quenching method*, Wat. Res., 2002, Vol. 36, 11, 4583.
- [3] CHOI K.V., DEMPSEY B.A., *In-line coagulation with low-pressure membrane filtration*, Wat. Res., 2004, Vol. 38, 4271.
- [4] DENNET K.E. et al., *Coagulation: its effect on organic matter*, JAWWA, 1996, 4, 136.
- [5] EDZWALD J.K. et al., *Polyaluminium coagulants for drinking water*, Chemical Water and Wastewater Treatment, Springer-Verlag, 2000, 3.
- [6] EIKEBROKK B. et al., *NOM characteristics and treatability by coagulation: Comparison of Norwegian and Australian waters*, Chemical Water and Wastewater Treatment, IWA Publishing, 2007, 207.
- [7] Informacje katalogowe o koagulantach, Kemipol sp. z o.o., Police.
- [8] JIANG J.Q., GRAHAM N.J.D., *Evaluation of poly-alumino-iron sulphate (PAFS) as a coagulant for water treatment*, Chemical Water and Wastewater Treatment, Springer-Verlag, 1998, 15.
- [9] SØGAARD E.G., *Production of the coagulation agent PAX-14. Contents of polyaluminium chloride compounds*, Chemical Water and Wastewater Treatment, IWA Publishing, 2002, 3.

- [10] TANG H.X., LUAN Z.K., *The differences of behaviour and coagulating mechanism between inorganic polymer flocculants and traditional coagulants*, Chemical Water and Wastewater Treatment, Springer-Verlag, 1996, 83.
- [11] TANG H.X., LUAN Z.K., *Differences in coagulation efficiencies between PACl and PAlCl*, JAWWA, 2003, 1, 79–85.
- [12] TANG H.X. et al., *Optimization of the concepts for poly-aluminium species*, Chemical Water and Wastewater Treatment, IWA Publishing, 2004, 139.
- [13] Van BENSCHOTEN J.E., EDZWALD J.K., *Chemical aspects of coagulation using aluminum salts – I. Hydrolytic reactions of alum and polyaluminum chloride*, Wat. Res., 1990, 12, 1519.