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OPTIMIZING COAGULANT CHOICE
FOR TREATMENT TECHNOLOGY OF SURFACE WATER
FOR HUMAN CONSUMPTION

The results of optimizing the coagulant choice for surface water treatment for human consumption have been presented. This optimization included not only elimination of organic matter from water with low contamination levels but also determining the cost of the process. Ten coagulants differing in aluminum content and in preliminary hydrolysis have been examined. The costs were calculated for four most effective coagulants.

1. INTRODUCTION

Coagulation is a process commonly used in water treatment, especially for surface water. This process aims to effectively remove organic matter [1, 2] especially precursors of oxidation and disinfection by-products [3–5], whose creation potential is related to absorption values at 254 nm (UV_{254}) [6]. Due to a very large variability in surface water composition over the course of the year and different contamination levels dependent on water source location, it is important to optimally choose coagulant type and dosage. Such optimization is difficult due to the presence of a large number of coagulants on the market. Świderska-Bróż and Rak [7] and Lee et al. [8] have shown that prehydrolyzed coagulants are less sensitive to changes in temperature and pH of the input water than classic ones. Lin et al. [9] suggest however that the effectiveness of coagulation mainly depends on the type and structure of organic matters present in waters, and to a much lesser degree on pH and temperature.

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Due to many factors influencing the effectiveness of the coagulation process, the choice of the optimal coagulant should be performed for a specific water source, and the results require verification in a yearly cycle, which would reflect changes in water composition [10]. It is also important to determine optimal dosage ensuring acceptable removal of organic matter. Unfortunately during the choice of the coagulant, most often the process costs are not taken into account. They include not only its price, but also the cost of possible pH correction, which depends on the consumption of natural water alkalinity during hydrolysis of the coagulant .

Studies of the influence of coagulant basicity on the effectiveness of coagulation and the consumption of natural water alkalinity in the process [11] have shown that an increase in water aggressiveness was nearly proportional to the degree of preliminary hydrolysis. This was the reason for these studies, whose aim was confirming the correctness of the choice of the coagulant in real-life conditions as well as determining the possibility of maintaining process stability with constant or reduced costs.

2. METHODS AND OBJECT OF THE STUDY

The studies were conducted for 10 aluminum coagulants (C1–C10) available on the market, which varied in the degree of hydrolysis and aluminum content (Table 1).

T a b l e 1

Characterization of the coagulants studied

Coagulant	Al^{3+} content [wt. %]	Cl^- content [wt. %]	Basicity[a]	pH	Density at 20 °C [g/dm³]	Price [\$/kg Al]	Addition
C1	8.2±0.2	19±2.0	37±5	1.0	1330	2.40	–
C2	12.5±0.3	8.5±1	85±5	3.5	1340	4.27	–
C3	5.3±0.3	13.0±2	70±5	2.5	1210	4.00	Na^+
C4	4.2±0.2	–	–	–2.4	1310	3.05	–
C5	5.0±0.2	11.5±1	70±10	2.5	1220		Na^+, SO_4^{2-}
C6	8.5±0.3	5.5±0.5	85±5	4.0	1220		Al/Cl > 1.6
C7	10.5±0.5	6.0±0.5	85±5	4.0	1280		
C8	12.0±0.5	6.5±0.5	85±5	4.2	1290		–
C9	9.0±0.5	5.0±0.5	85±5	3.8	1220		SO_4^{2-} 0.8±0.5
C10	9.0±0.5	5.5±0.5	75±5	4.2	1200		

[a]Level of coagulant hydrolysis.

Raw water was used (Table 2) that supplied a surface water treatment plant, with the optimization being performed for the benefit of this plant.

The studies were performed in two stages. In the first stage, the effectiveness organic matter removal was determined for all the analyzed coagulants at doses from 1.0 to 6.0 g Al/m^3. The second stage was performed for four coagulants having the greatest effectiveness in removing organic matter and varying in degrees of preliminary hydrolysis. The tests in the second stage of the study were performed in a narrower dosage range, chosen individually for each coagulant, concentrating around the optimal dose determined in the first stage. Its aim was achieving maximal organic matter removal with the most precise determination of the required coagulant doses, in order to optimize the costs required for reaching the desired effect. Water samples in amounts sufficient for performing the both stages were stored at 5 °C.

For the coagulation, a jar test system was used with two six-station coagulators. Rapid mixing was performed for 2 min with a mixer speed of 120 rpm, the flocculation lasted 20 minutes and was performed at 20 rpm. Before analyses, the samples were subjected to a 2 h thermostatic (5 °C) sedimentation process, which allowed a joint evaluation of the effectiveness of coagulation and sedimentation. The effectiveness of the used coagulants was tested in similar non optimal temperatures.

For all the water samples, pH, general water alkalinity (Alk), color, turbidity (Tr) and UV_{254} absorbance were measured. Dissolved organic carbon concentration (DOC) was also determined, and for samples after coagulation, the residual aluminum content was measured and the specific UV absorbance (SUVA) was calculated. All water quality indicators were determined according to the Polish standards. Every test was conducted once, the analysis was done according to the procedure of an accredited laboratory. The optimization of the coagulant choice concerned the effectiveness of removing organic matter (measured as color intensity, UV_{254} absorbance and DOC), and for chosen coagulants, also costs of purchase and pH correction connected with the increase in water acidity after the coagulation process. The water quality was considered sufficient if it met the requirements for drinking water [12].

That aim of this study was to preliminarily determine the usefulness of coagulants used at the treatment plant, comparing their effectiveness with others available on the market and evaluating the possibility of increasing or maintaining the effectiveness of organic matter removal with simultaneous maintaining or reducing current costs. These studies, due to the large variability of surface water, had a preliminary character and require several repetitions at different water source contamination levels.

3. RESULTS AND DISCUSSION

Studies of coagulation choice optimization were performed during a period of low water contamination (Table 2), which resulted in low organic matter removal effective-

ness [13]. This is why the results that have been obtained require verification with different contamination levels and temperatures of the water source. The ranges of water quality indicators of post-coagulation water and raw water are presented in Table 2.

Table 2

Ranges of fresh and treated water quality parameters

	pH	Alkalinity [eq/m³]	Turbidity [NTU]	Color [g Pt/m³]	UV$_{254}$ absorbance [m^{-1}]	DOC [g C/m³]	Al (residual) [g Al/m³]	SUVA [m²/g]
RW	8.09	3.14	5.1	8.9	9.49	3.9	–	2.46
Stage I[b]								
C1	7.74–8.06	2.69–3.04	0.79–3.45	5.1–7.9	5.58–8.06	2.74–3.58	0.24–0.47	2.03–2.25
C2	7.98–8.10	3.00–3.02	2.09–4.48	5.8–7.8	5.82–7.95	2.53–3.28	<0.04[a]	1.97–2.42
C3	7.45–8.09	2.91–3.00	1.30–4.55	5.0–7.7	6.25–8.40	2.70–3.44	0.16–0.45	2.17–2.58
C4	7.38–7.91	2.87–3.06	1.07–6.10	4.6–6.3	5.62–7.95	2.7–3.44	0.25–0.49	2.08–2.31
C5	7.86–8.16	2.87–3.06	0.92–3.86	4.6–8.4	5.67–8.75	2.96–4.06	<0.04–0.14	1.91–2.98
C6	8.12–8.21	2.93–3.05	0.81–2.52	4.9–8.4	6.01–8.64	2.74–5.88	<0.04[a]	1.03–2.59
C7	8.11–8.25	3.08–3.02	0.88–3.5	5.0–8.1	5.49–8.16	3.10–3.99	<0.04[a]	2.03–2.51
C8	7.84–8.25	2.94–3.03	1.96–3.31	6.4–8.7	6.23–8.49	3.10–3.99	<0.04[a]	1.93–2.17
C9	8.12–8.22	2.91–3.09	0.63–4.04	5.2–8.1	5.68–7.96	2.75–3.60	<0.04[a]	1.96–2.11
C10	8.11–8.22	2.93–3.14	2.24–3.44	5.4–7.2	5.68–7.63	2.97–3.61	<0.04[a]	1.91–2.11
Stage II[c]								
C1	7.71–7.76	2.81–3.00	0.67–1.99	6.0–7.9	6.64–7.95	3.08–3.72	0.28–0.30	2.14–2.35
C2	8.00–8.14	3.02–3.10	0.87–2.57	5.5–6.9	6.10–6.92	2.96–3.27	<0.04[a]	2.06–2.21
C3	7.87–7.97	2.81–2.98	0.52–1.96	5.0–7.7	6.19–7.93	2.91–3.40	0.23–0.28	2.12–2.41
C4	7.45–7.78	2.58–2.91	0.90–2.08	4.8–5.4	6.12–6.75	2.96–3.18	0.23–0.30	2.07–2.17

[a]0.04 g Al/m³ is the detection level.
[b]Doses of coagulants used 1.0–6.0 g Al/m³.
[c]Doses of the coagulant depended on its type, generally they ranged between 2.0 and 4.5 g Al/m³.

In the first stage of the study, a reduction in all analyzed water quality indicators was found regardless of the coagulant and dose used. It must be stressed that the observed changes in color were small since raw water itself was characterized by a low color intensity, significantly lower than that considered to be acceptable – 15 g Pt/m³ The color intensity after coagulation, in the case of coagulants C2, C6, C7, increase in the highest dose (Fig. 1). In this case, the maximum dose was exceed. However, for the remaining coagulants, the color intensity decreased upon increasing the dose of the coagulant.

This means that for most coagulants, using large doses, larger than those considered to be economical, did not yield the maximum color removal effectiveness. At the same time, with respect to refractive substance removal, which is measured by UV$_{254}$ absorbance [2, 4], none of the doses used for all (except C2) coagulants were sufficient for

reaching the maximum effectiveness (Fig. 2). However, at doses larger than 3 g Al/m^3 the increases in effectiveness decreased visibly, while the costs of reaching such effectiveness could not necessarily be justifiable.
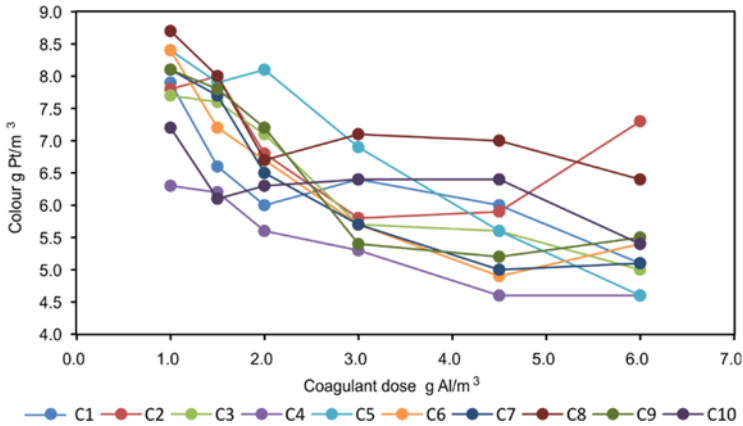

Fig. 1. Water color after the coagulation
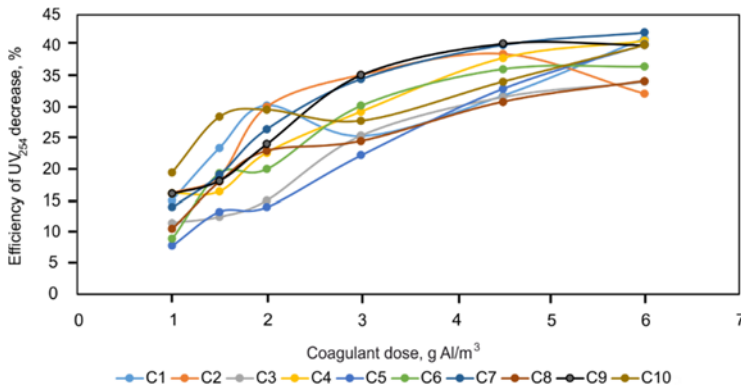depending on the dose and type of the coagulant

Fig. 2. Efficiency of UV$_{254}$ absorbance decrease during the coagulation process
depending on the dose and type of the coagulant

Regardless of the analyzed indicator and coagulant type, doses in the range of 1.0–2.0 g Al/m^3 were not sufficient for ensuring effective removal of organic matter. Also, in this doses range the greatest changes in the effectiveness of color removal and absorbance decrease were found (Figs. 1, 2). At the same time, an increase in the coagulant doses from 4.5 g Al/m^3 to 6.0 g Al/m^3 did not yield significant reduction in color intensity and UV$_{254}$ absorbance. Consequently, doses in the ranges of 3.0–4.5 g Al/m^3 were found to be beneficial, for which the effectiveness of DOC removal was in the range of 14.0–35.3% (Fig. 3).
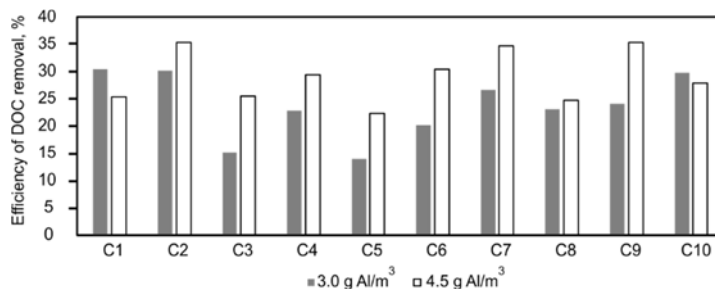
Fig. 3. Efficiency of dissolved organic carbon removal
during coagulation with optimal doses

The efficiency of organic mater removal during coagulation depends on the value of SUVA which in raw water was equal to 2.43 m^2/g C. It means that NOM in raw water is non susceptible removing to coagulation [14] and explains low efficiency removal of DOC and UV_{254} absorbance.

The efficiency of turbidity removal for the optimal dosage fell within the range of 40.4–87.6% and was proportional to DOC removal which is expressed by a linear correlation between the DOC and turbidity

$$\eta DOC = 0.2208 \eta Tr + 7.535$$

where η is the efficiency of removal, %.

The presented results may seem to be hard to read, since they simultaneously show results from experiments with many coagulants. However, the observed tendencies are coincident, and by evaluating the boundary values, an apparent differentiation in the effectiveness of the evaluated coagulants can be seen. For example, at a dose of 2.0 g Al/m^3, the reduction of UV_{254} absorbance was in the range of 14–30%, depending on the coagulant used (Fig. 2).

For all coagulants (except for C4, which is not a pre-hydrolyzed coagulant) it was found that for doses higher than 2.0 g Al/m^3, the reduction in water alkalinity was inversely proportional to the degree of hydrolysis of the coagulant used (for 4.5 g Al/m^3):

$$\Delta Alk = -0.0048 Alk_0 + 0.55$$

where: ΔAlk is the decrease of alkalinity during coagulation, Alk_0 coagulant alkalinity (both in eq/m^3), $n = 9$, $p > 99.0\%$.

A coagulant hydrolyzes in water, which causes a decrease in water alkalinity. Pre-hydrolyzed coagulants hydrolyze in water to a much smaller degree. At a large degree of pre-hydrolysis the effect of decreasing water alkalinity can only be observed at large coagulant doses. The efficiency removal of DOC did not depend on the coagulant degree of hydrolysis.

Consequently, with an increase in the degree of coagulant hydrolysis, water natural alkalinity decreases, and therefore the corrosion level in water increases to a much lower degree. The quantities of the reagent used for correction of pH and to reestablish the carbonate–calcium equilibrium decrease. An increase in water aggressiveness causes an increase in coagulation costs, which should be also taken into account.

Due to their outstanding effectiveness in organic matter removal, coagulants C1 and C2 were chosen for the second stage of the study. The coagulants C3 and C4 were qualified for second stage too. The C2 coagulant was also efficient (like C6–C10) for generating low residual aluminum content in the treated water (Table 2). On the other hand, the C1 coagulant had a very good effectiveness at small doses, attractive price (Table 1) and was also the only representative of moderately pre-hydrolyzed coagulants. The coagulant C4 was qualified for the second stage due to its hydrolytic character and attractive price, while the coagulant C3 was the currently used coagulant.

During the second stage of the study, doses in a narrower range were used, chosen individually for each of the coagulants based on the results of the first stage of the study. Their effectiveness in organic matter removal varied from 4.6 to 25.4% depending on the coagulant type and dose (Fig. 4).
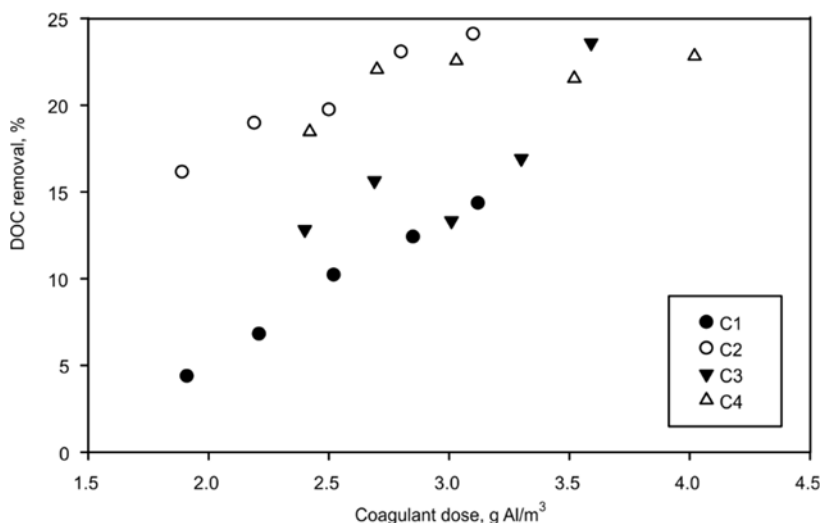

Fig. 4. Dependence of the efficiency of DOC removal on the coagulant doses

A comparison of the effectiveness of the chosen coagulants in terms of DOC content reduction (Fig. 4) showed two groups of coagulants. The C2 and C4 coagulants were already effective at small doses and yielded similar maximum effectiveness. The effectiveness of the coagulant C4 did not increase after reaching the dose of 2.7 g Al/m^3. The effectiveness of coagulant C1 and C3 was lower, and highly dependent on dosages

throughout its entire range. During the second stage, the efficiency of turbidity removal was proportional to DOC removal.

In order to better evaluate the coagulant effectiveness, their specific changes were evaluated represented by DOC removed per 1 g of Al used. They were in the ranges of 0.09–0.24 (C1), 0.26–0.34 (C2), 0.17–0.26 (C3), 0.56–0.94 g C/g Al (C4). Evaluated in this manner, the coagulant C4 was the most effective, and C1 was the least effective.
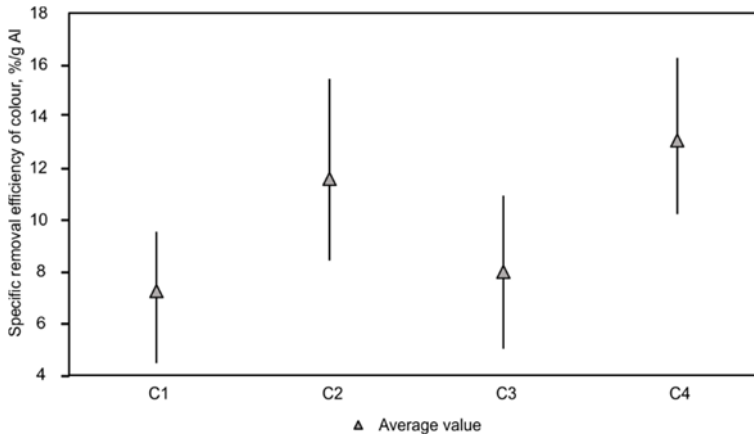
Fig. 5. Ranges and average values of the specific efficiency of color removal

In the organic matter removed, colored substances dominated, therefore, above all, humic acids, as a consequence of which a reduction in color followed the coagulation process (Fig. 5). With respect to removal of these contaminants, the coagulants may also be divided into two groups: C1 with C3 and C2 with C4. Coagulants of the second group are characterized by a large specific removal efficiency of colored contaminants (%/g Al).
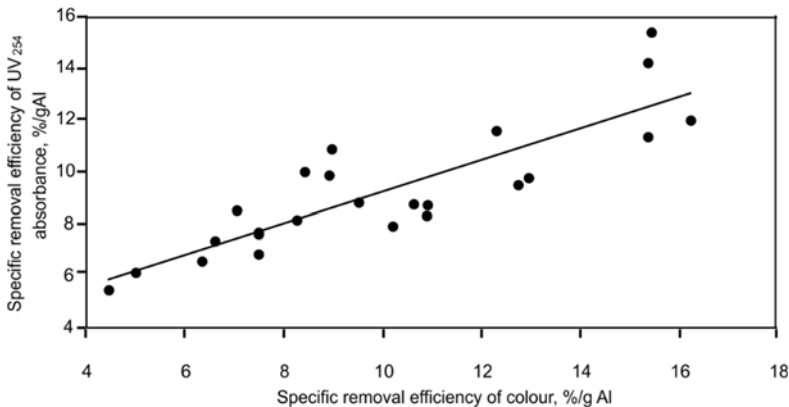
Fig. 6. Relationship between removal efficiency of color and specific UV absorbance

Among the removed colored substances, refractive compounds dominated, which is shown by linear correlation between specific removal efficiency of color and UV_{254} that occurred regardless of coagulant type and dose (Fig. 6).

The reduction of water alkalinity that was found regardless of coagulant type and dosage was proportional to the coagulant alkalinity. Thus the reduction of water alkalinity decreased according to the series C4 > C3 > C1 > C2. The decrease in alkalinity caused by the coagulant hydrolysis caused an increase in carbon dioxide content, which was proportional to the reduction in alkalinity. Only for the coagulant C4, the increase in concentration of carbon dioxide was large enough for its binding to occur. In this case, the maximum aggressive carbon dioxide concentration amounted to 3.0 g CO_2/m^3, and its binding required a dose of 1.9 g CaO/m^3 or equivalent amount of alkalizing medium.

T a b l e 3

Comparison of specific removal efficiency
of water quality parameters and coagulant cost

Parameter	Coagulant			
	C1	C2	C3	C4
Dose, g Al/m^3	2.50	2.52	3.01	3.03
ηC, %/g Al	4.5	9.0	6.3	13.0
ηAlk, %/g Al	27.7	24.2	23.5	23.5
ηUV_{254}, %/g Al	5.4	10.8	6.6	9.7
ηDOC, %/g Al	4.0	7.9	4.4	7.5
ηTr, %/g Al	27.7	24.2	23.5	23.5
Cost, $/1000 m^3$	5.62	11.25	11.25	8.43[a]

[a]The price included the cost of pH correction.

A comparison of the specific coagulation efficiency (for optimal coagulant doses) (Table 3) again pointed to the following coagulant groups: C1 with C3 and C2 with C4. In the second group once more a larger organic matter removal effectiveness was found, and therefore the optimal coagulant choice from this group was warranted by the unit process cost. Despite the use of large dose of coagulant C4 and the necessity of chemical binding of aggressive carbon dioxide, the coagulation cost of this non-pre-hydrolyzed coagulant was found to be smaller than that for coagulant C2 of a similar efficiency (Table 3).

The comparative analysis of the cost and effectiveness for low input water contamination levels showed the utility of a simple and low cost without the need for increasing costs by purchasing expensive reagents. This means that with a change of input water quality during the course of the year and the increase in the required doses of all studied coagulants, there may be a variation in the effectiveness in removing organic matter and

costs, among which the cost of pH correction in the case of coagulant C4 makes up more than 30% of the total cost (the optimal dose coagulant cost was 5.06 $/1000 m^3 and the cost of sodium hydroxide was 3.37 $/1000 m^3). In this case pH correction was necessary to obtain the carbon–calcium balance.

In the study, one product from a group of ten coagulants has been selected, fulfilling both the organic matter removal criteria being economically reasonable. The change of coagulant from C3 to C4 that took place shortly after this study yielded the expected results. The periodic variation in the content and properties of the input water cause that this choice is not final and should be verified in order to select of coagulant of the greatest utility.

4. CONCLUSIONS

- The degree of reduction in organic matter content did not depend on the degree of preliminary coagulant hydrolysis, which influences the water corrosivity, since with an increase in preliminary coagulant hydrolysis the amount of carbon dioxide formed decreases.
- The increase in water corrosivity is directly proportional to increase in coagulant dose and inversely proportional to the alkalinity of the coagulant used.
- Each of the studied coagulants resulted in removal of organic matter measured as the reduction in DOC, color or UV$_{254}$ absorbance, yet their effectiveness in this respect varied.
- The coagulants chosen for the second stage of the study ensured a large reduction in water quality indicators connected with contamination by organic matter.
- In the range of doses studied, only the non-pre-hydrolyzed coagulants caused large enough increase in water acidity to require the use of chemical carbon dioxide binding.
- The paired coagulants used in stage II were similar in terms of effectiveness of organic matter removal.
- Due to the lowest cost and good effectiveness, at the contamination levels studied, the most effective coagulant was found to be coagulant not pre-hydrolyzed.

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