1. INTRODUCTION

Surface waters are characterized by a great variability in composition over the course of the year, and additionally the type and amount of contaminants in surface waters is dependent on the region of the world and types of industries present near the water uptake [1-3]. Due to this, tailoring the process to local conditions, or optimization, is so important. The interest in this process has not waned throughout several decades, which results from its use for both water treatment for human consumption and industrial use, as well as being used for sewage treatment. Due to the need for increasing the effectiveness of this process, substances aiding flocculation and/or sedimentation are commonly used, among them polyelectrolytes [4, 5], bentonite [6] and activated silica. Significant changes over the years have also included the types of coagulants used. At first, iron and aluminum salts, mainly chlorides and sulfates, were used for coagulation [7, 8]. A significant change was the introduction of pre-hydrolyzed coagulants to the market [9, 10], which presently make up a large group of products offered by suppliers, differing mainly in degree of pre-hydrolization and the additives that aid
This group is subject to research that shows higher increase in efficiency of dissolved organic carbon (DOC) removal with increase in the pre-hydrolyze level [11]. Pre-hydrolyzed coagulants are more effective in a larger range of water pH in comparison to non pre-hydrolized coagulants [12]. During coagulation by pre-hydrolyzed coagulants efficiency of water colour decrease is higher than that of non pre-hydrlozed coagulant, indicating that the necessary doses of pre-hydrolyzed reagents are lower [13]. Guminska [14] presented that the pre-hydrolyzed coagulants are more useful for mountain water treatment (which is characterized by lower water temperatures).

The most recent coagulant modifications [15] concern joining coagulation mechanisms with ion transfer [15]. This allows for an improved removal of low molecular mass organic substances, which were not effectively removed with conventional coagulants. In order to aid coagulation, ion exchange resins or powderzed activated carbon are also used, as they not only improve effectiveness, but also widen the size ranges of molecules that are removed [16, 17]. These substances are used before flocculation or sedimentation.

Such modifications most often result in increased process costs, which in the case of sewage treatment or water treatment for industrial use is necessary due to the specific quality requirements for such water. However, from the point of view of residential customers, it is important to purchase good quality water for the lowest price possible. Therefore, the overarching goal of water utilities is producing water satisfying the requirements for drinking water at the lowest possible process costs.

The aim of this study was an evaluation of the effectiveness of currently used coagulants at the water treatment plant as compared to others available on the market, as well as the choice of coagulant/coagulants which will enable a sufficient organic substance removal effectiveness for drinking water while maintaining low process costs.

## 2. MATERIALS AND METHODS

The study was conducted with the use of surface water (Olawa river) uptake by a water treatment plant ("Mokry Dwór" in Wrocław) with a throughput of about 60 000 m³/day, supplying drinking water. 10 aluminum coagulants available on the market were used in this study (Table 1), chosen due to their varied properties (degree of pre-hydrolization, aluminum content and presence of additives) and their price.

The optimal coagulation process consisted of the least expensive treatment along with the most effective coagulant and lowest dosage.

The studies were performed in two stages. In the first stage, the effectiveness in removing organic substances for all analyzed coagulants was evaluated at dosage ranges of 1.0 to 6.0 gAl/m³. For the second stage, four coagulants having the highest removal

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**Table 1. Characteristics of used coagulants**

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Aluminum(Al⁺³)</th>
<th>Chlorides (Cl⁻)</th>
<th>Alkalinity *</th>
<th>pH</th>
<th>Density, 20°C</th>
<th>Price</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1; PAX16</td>
<td>8.2 ±0.2</td>
<td>19 ±2.0</td>
<td>37 ±5</td>
<td>1.0</td>
<td>1330</td>
<td>8.65</td>
<td>_</td>
</tr>
<tr>
<td>C2; PAX XL19H</td>
<td>12.5 ±0.3</td>
<td>8.5 ±1</td>
<td>85 ±5</td>
<td>3.5</td>
<td>1340</td>
<td>15.20</td>
<td>_</td>
</tr>
<tr>
<td>C3; PAX XL3</td>
<td>5.3 ±0.3</td>
<td>13.0 ±2</td>
<td>70 ±5</td>
<td>2.5</td>
<td>1210</td>
<td>14.28</td>
<td>Na⁺ ions</td>
</tr>
<tr>
<td>C4; ALS</td>
<td>4.2 ±0.2</td>
<td>-</td>
<td>-</td>
<td>2.4</td>
<td>1310</td>
<td>10.86</td>
<td>_</td>
</tr>
<tr>
<td>C5; PAX XL10</td>
<td>5.0 ±0.2</td>
<td>11.5 ±1</td>
<td>70 ±10</td>
<td>2.5</td>
<td>1220</td>
<td>15.20</td>
<td>Na⁺, SO₄²⁻</td>
</tr>
<tr>
<td>C6; PAX 19F</td>
<td>8.5 ±0.3</td>
<td>5.5 ±0.5</td>
<td>85 ±5</td>
<td>4.0</td>
<td>1220</td>
<td></td>
<td>Al/Cl min. 1.6</td>
</tr>
<tr>
<td>C7; PAX 1910</td>
<td>10.5 ±0.5</td>
<td>6.0 ±0.5</td>
<td>85 ±5</td>
<td>4.0</td>
<td>1280</td>
<td></td>
<td>_</td>
</tr>
<tr>
<td>C8; FLOKOR 1,2A</td>
<td>12.0 ±0.5</td>
<td>6.5 ±0.5</td>
<td>85 ±5</td>
<td>4.2</td>
<td>1290</td>
<td></td>
<td>_</td>
</tr>
<tr>
<td>C9; FLOKOR 1ASW</td>
<td>9.0 ±0.5</td>
<td>5.0 ±0.5</td>
<td>85 ±5</td>
<td>3.8</td>
<td>1220</td>
<td>37.80</td>
<td>SO₄²⁻:0.8 0.5%</td>
</tr>
<tr>
<td>C10; FLOKOR 1.5A</td>
<td>9.0 ±0.5</td>
<td>5.5 ±0.5</td>
<td>75 ±5</td>
<td>4.2</td>
<td>1200</td>
<td></td>
<td>_</td>
</tr>
</tbody>
</table>

*corresponds to degree of coagulant pre-hydrolization
effectiveness and varied degree of pre-hydrolysis were chosen. Tests in the second stage of the study were performed in a narrower range of dosages, concentrated around the optimal dosage value for each coagulant as determined in the first stage. This had as its aim ensuring large organic substance removal effectiveness while precisely determining the optimum coagulant dosage and therefore limiting the costs necessary to obtain the required effectiveness.

The coagulation process was performed on surface water taken in amounts sufficient to perform both study stages. This water was stored at a fixed temperature of 5°C, which allowed for a comparison of the performance of the studied coagulants at unfavorable temperatures.

The coagulation process was performed in a jar test with the use of two six-station coagulators. Rapid mixing was performed for two minutes at a mixing speed of 120 rpm, while flocculation lasted 20 minutes at a mixing speed of 20 rpm. Before analysis, the samples underwent a two-hour thermostatic (+5°C) sedimentation, which allowed for a joint evaluation of coagulation and sedimentation effectiveness. The tests were repeated twice with varying raw water composition. The water used for the first stage was taken during spring whereas the investigation within the second stage was conducted during summer. The greatest difference, except for temperature, concerned raw water turbidity, which during the second test was significantly greater.

The tests were performed at the same temperature of water undergoing coagulation and sedimentation, which allowed for a comparison of effectiveness of the different coagulants.

In all water samples before and after coagulation, the pH values, water alkalinity (Alk), color (C), turbidity (Tr) and UV$_{254}$ absorbance were measured. Dissolved Organic Carbon (DOC) was also measured, along with the post-coagulation residual aluminum concentrations.

Based on the ultraviolet absorbance and the dissolved organic carbon concentration, the specific ultraviolet absorbance indicator (SUVA$_{254}$) was calculated, which reflects, among others, the susceptibility of organic substances to be removed in the coagulation process.

All the water quality indicators were evaluated per methods used in the water quality monitoring laboratory at the treatment plant, and therefore in accordance with legal requirements in Poland. Shimadzu total organic carbon analyzer (TOC-L), Shimadzu UV spectrophotometer (UV 1800), turbidimeter Hach 2100 AN and pH meter Hach HQ40d were used for analysis.

The coagulant choice optimization concerned the resulting organic substance removal effectivenesses (measured as color, UV$_{254}$ absorbance and DOC concentration), and for chosen coagulants, also costs of purchase and pH correction connected with the increase in water acidity after the coagulation process.

3. RESULTS AND DISCUSSION

Tests concerning coagulation process optimization were performed twice, and the results after the first test will be published in a paper [18], in which the subsequent steps in coagulant choice and effectiveness evaluation are described. The repetition of the test allowed for a verification of the results and an evaluation of the effect of water composition on the process optimization and the type of chosen coagulant.

3.1. Raw water quality

For this study, surface water was used, which is characterized by a variation in composition throughout the year. This variability corresponds to the properties of the raw water used in the two tests of the study (Tab. 2), where the clearest difference is in the water turbidity indicator.

It must be noted that suspended particles (test II) present in turbid water may act as additional masses [19] in floc, resulting in an increase in sedimentation effectiveness. Simultaneously, a greater turbidity may yield an increase in required coagulant dosage, which corresponds to an increase in process cost.

The water samples taken for this study also differed in the organic substance content as measured in DOC concentration. The varied organic substance structure is attested by a comparison of DOC concentrations and UV$_{254}$ values. Water used for the first test was characterized by a greater content of refractive substances measured as UV$_{254}$, which are more susceptible to removal by coagulation [15, 20]. On the other hand, water from the second test had a greater concentration of organic substances of a low molecular mass, which are less susceptible to removal by coagulation. The different structure and susceptibility to removal by coagulation between the waters used for the two tests is shown also by SUVA values, which were 2.43 m$^{2}$/g C and 1.89 m$^{2}$/g C for the two
raw waters. In both cases, these are values testifying to a low susceptibility to removal by coagulation [21–23]. This testifies to the great importance of coagulant choice and its dosage. Despite a small difference in water pH of waters used for this test, the value of this parameter may have an effect on process effectiveness. This is connected to the pH range at which each coagulant is the most effective (manufacturer’s data).

The different amounts and types of coagulant present in water undergoing coagulation allowed for a verification of the results of first study.

3.2. Organic substance removal effectivenesses (TI, TII)

Due to the varied properties of the coagulants used, their effectiveness ranges also varied and were dependent on parameter type and its value in raw water. The greatest difference in effectiveness concerned turbidity, whose values in raw water differed the most (Fig. 1). For all coagulants a greater effectiveness was found in the second test at the same dosages. Simultaneously, the turbidity removal effectiveness in the second test depended on the coagulant dosage to a much smaller degree, which is testified by the small ranges of the resulting effectiveness.

Despite a large effectiveness in reducing turbidity in the more contaminated water (test II), the value of this parameter post-coagulation exceeded the allowable values for drinking water. On the other and, at low turbidity values in raw water the use of large coagulant dosages allowed for a reduction in the parameter to below 1 NTU. This means that in the case of uptaking highly turbid water, a filtration process is necessary.
Due to the use of the coagulation process for removing organic substances from surface waters, the choice of optimum coagulant is determined by post-process DOC concentrations. The effectiveness in removing organic substances in subsequent tests were different, and the individual coagulants allowed different levels of elimination of these substances. Unfortunately, it was not always possible to find an unambiguous relationship between an increase in coagulant dosage and the increase in DOC removal and the decrease in UV$_{254}$ absorbance. Despite a larger organic substance content in the second test (DOC$_{I}$ < DOC$_{II}$), greater effectiveness in removing DOC was obtained in the first test for most coagulants (Fig. 2). Coagulants C8-C10 were the exception, since for both tests a similar effectiveness was found, which indicated a smaller sensitivity to raw water quality.

The greater effectiveness in removing organic substances in the first test results from the presence of substances more susceptible to removal, which is attested by the greater value of SUVA$_{254}$ in raw water used for this test (Tab. 2). This result confirms the fact that SUVA$_{254}$ values accurately characterize the coagulative potential of organic substances. At the same time it was found that the group of coagulants having similar properties (C8-C10) exhibit a lower sensitivity to changes in raw water quality, which, at high water contamination levels, may not allow a reduction in DOC concentrations to values allowed for drinking water.

Consequently, there was a greater reduction in concentrations of organic substances adsorbing UV light and lower ranges of specific absorbance found in water after coagulation during the second test and a greater reduction in this parameter in the first test.

The effective elimination of organic substances (DOC) is decided therefore by a larger amount of refractive substances present, which is confirmed by the relationship found between the effectiveness of reduction of these parameters (Fig. 3). Such a relationship was found regardless of the raw water contamination level, and may be useful in forecasting organic substance removal effectivenesses based on a simple UV$_{254}$ measurement, and not a DOC concentration analysis. For each water type such a relationship should be determined independently due to the differing characteristics of the organic substances in water.

The relationships were determined as linear regressions with coefficient of correlation R = 0.788 and R = 0.632 for test I and test II respectively.

The amount of removed organic substances that absorb UV light was connected with the degree of color intensity reduction, which is confirmed by the linear correlation found for results of both tests:

\[ \eta_{UV_{254}} = 1.15 \times \eta_{B} - 0.31 \] (linear regression, R=0.75).

A comparison of the individual coagulant effectivenesses in removing organic substance removal showed that coagulant C1, which was effective in the first test, did not ensure a sufficient level of organic substance removal in the second test. A much greater removal effectiveness was found for coagulants C8, C9 and C10. In this group of coagulants, the greatest effectiveness was exhibited by coagulant C9, which was chosen for the second stage of the study instead of coagulant C1.

Eventually, coagulants C1, C2, C3 and C4 were chosen for the second stage of the study in the first test, while in the second test coagulants C2, C3, C4 and C9
were chosen. This coagulant choice was decided by not only the post-coagulation water composition, but also differences in degree of pre-hydrolysis and the fact that two of them (C3 and C4) were already currently used at the water treatment plant.

It is also significant that in the range of the analyzed organic substance concentrations in raw water, the optimal dosages for all studied coagulants were in the range of 2.0-3.5 g Al/m³, and differences between them decided the process costs.

3.3. Coagulant choice according to effectiveness and cost criteria

A comparison of coagulant effectivenesses for coagulants chosen for the second test was performed for a narrower dosage range. For a comparison of coagulant usefulness, a unit effectiveness (%/g Al/m³) was calculated, with the results shown in Table 3.

A consequence of smaller organic substance removal effectivenesses in the second study was lower unit effectivenesses (Fig. 4) No unambiguous correlation was found for changes in unit effectiveness and coagulant dosage. This lack of correlation may be caused by the differing properties of the individual coagulants.

For all three coagulants that were studied in both tests, the same order of organic substance removal effectiveness was found: C2>C4>C3. The effectiveness of coagulant C1 was the smallest for that found in the first test, while for C9 the greatest effectiveness was found in the second test. In the final optimization, coagulants C1 and C9 were not taken into account due to their usefulness only in narrow water composition ranges, which would require the use of many coagulants throughout the year. This is not favorable economically as it is connected with additional maintenance tasks such as system flushing, frequent coagulant choice test, imprecise coagulant switching dates etc.

Among organic substances, large molecular mass refractive substances were most effectively removed, as is testified by the almost twofold greater reduction

### Table 3.
Ranges of unit effectivenesses

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>First test</th>
<th>Second test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C1</td>
<td>C2</td>
</tr>
<tr>
<td>C</td>
<td>%/g Al/m³</td>
<td>6.6-10.8</td>
<td>10.1-17.8</td>
</tr>
<tr>
<td>Tr</td>
<td>%/g Al/m³</td>
<td>25.4-31.9</td>
<td>14.6-43.9</td>
</tr>
<tr>
<td>DOC</td>
<td>%/g Al/m³</td>
<td>2.4-6.1</td>
<td>6.7-8.7</td>
</tr>
<tr>
<td>UV&lt;sub&gt;254&lt;/sub&gt;</td>
<td>%/g Al/m³</td>
<td>5.4-8.8</td>
<td>9.8-15.3</td>
</tr>
</tbody>
</table>

Figure 4.
Unit organic substance removal efficiency in the second stage of the study (doses test I: 1.8; 2.3; 2.7; 3.0; 3.5; 4.5 g Al/m³; test II: 2.5; 3.0; 3.3; 3.6; 3.9; 4.5 g Al/m³)
in UV$_{254}$ than DOC. The orders of effectiveness in removing DOC as well as UV$_{254}$ were the same in both tests, which confirms the dominating influence of the large molecular mass DOC fraction.

A narrower dosage range allowed for determining the optimal coagulant dosage, i.e. the minimum dosage at which a satisfactory water quality is obtained. These dosages were different in the two tests for individual coagulants, which was a consequence of the differing water composition. The optimal dosages for coagulants C2, C3 and C4 were, respectively, 2.19 g Al/m$^3$; 3.0 g Al/m$^3$ and 2.7 g Al/m$^3$ in the first test and 3.0 g Al/m$^3$; 3.0 g Al/m$^3$ and 3.6 g Al/m$^3$ for the second test.

Coagulation in the optimal dosage range yielded a decrease in water alkalinity, with the magnitude of these changes being inversely proportional to the degree of coagulant pre-hydrolization, which means that this reduction was significant only for coagulant C4 (non-pre-hydrolyzed coagulant). Consequently there was a presence of aggressive carbon dioxide in water samples after coagulation with this coagulant. These concentrations for the two tests amounted to 0.0-3.0 g CO$_2$/m$^3$ and 0.5-2.0 g CO$_2$/m$^3$ and increased with increasing coagulant dosage. This means that a pH correction connected with the necessity of binding aggressive carbon dioxide concerned only this coagulant and only in test I. Due to this, costs of a potential alkalizing agent (sodium hydroxide) were calculated only for this coagulant.

The choice of optimal coagulant included the evaluation of not only removal effectiveness but also the costs of utilizing a given coagulant (Tab. 4). For all studied coagulants, removal effectivenesses that ensured the required water quality were obtained. The highest unit effectiveness was found for coagulant C2, yet the costs of using this coagulant may influence the choice of a different coagulant as the optimal one.

In the case of optimal coagulant choice based only on economic criteria, coagulant C4 should be chosen. However, it should be noted that this is not a pre-hydrolyzed coagulant and along with increasing coagulant dosages (decrease in raw water quality) it will be necessary to bind aggressive carbon dioxide in amounts far surpassing those taken into account in this analysis, which increases process cost and may point to a choice of a pre-hydrolyzed coagulant as the optimal one. Such a coagulant does not require binding of aggressive carbon dioxide in a wide dosage range. On the other hand, in the case of maximizing organic substance removal, C2 is the one that should be chosen.

The decision should also take into account the water treatment plant throughput. In the case of treating large amounts of water, even small differences in cost generate significant increases in total operating costs, assuming a fixed coagulant price.

### 4. CONCLUSIONS

1. The raw water contamination level influenced the effectiveness of the individual coagulants, and therefore influenced the optimal dosage for each coagulant.

2. The efficiency of DOC removal 4.64–25.4% in test I and 8.1–20.4% in test II depended on coagulants type and its dosage. The observed higher efficiency in test I is probably related to a higher SUVA value in raw water.

3. In both tests, a great efficiency of raw water treatment was found for the same coagulant or coagulants of similar characteristics. Optimal doses in test I were between 2.19–3.00 g Al/m$^3$, in test II 3.00–3.60 g Al/m$^3$.

4. The non pre-hydrolyzed coagulant was the most effective independent quality of water before coagulation.

### Table 4.
**Comparison of effectiveness and coagulation process cost for chosen coagulants (at optimal dosages; red color marks greatest values)**

<table>
<thead>
<tr>
<th>coagulant</th>
<th>C, %/g Al/m$^3$</th>
<th>DOC, %/g Al/m$^3$</th>
<th>UV254, %/g Al/m$^3$</th>
<th>M, %/g Al/m$^3$</th>
<th>Cost, PLN/1000m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TI</td>
<td>TII</td>
<td>TI</td>
<td>TII</td>
<td>TI</td>
</tr>
<tr>
<td>C1</td>
<td>9.0</td>
<td>-</td>
<td>3.2</td>
<td>-</td>
<td>7.3</td>
</tr>
<tr>
<td>C2</td>
<td>17.3</td>
<td>8.2</td>
<td>8.7</td>
<td>4.7</td>
<td>14.1</td>
</tr>
<tr>
<td>C3</td>
<td>8.0</td>
<td>8.1</td>
<td>4.4</td>
<td>3.0</td>
<td>6.5</td>
</tr>
<tr>
<td>C4</td>
<td>14.2</td>
<td>8.8</td>
<td>7.4</td>
<td>3.5</td>
<td>9.7</td>
</tr>
<tr>
<td>C9</td>
<td>-</td>
<td>7.5</td>
<td>-</td>
<td>4.0</td>
<td>-</td>
</tr>
</tbody>
</table>

*Cost takes into account binding of aggressive carbon dioxide.
5. Correct pH of water was necessary only after using non-prehydrolyzed coagulant and only in high doses.
6. The efficiency of DOC removal did not correlate with the level of pre-hydrolyzed coagulant.
7. Coagulant choice optimization for surface water treatment should be repeated at extreme raw water compositions
8. The final coagulant choice should be determined by the overall process goal, i.e. the need to maximize organic substance removal or cost reduction, i.e. obtaining water just meeting the requirements.
9. Due to small differences in unit treatment process costs, the final coagulant choice should take into account the water treatment plant throughput.

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REFERENCES


