THE INFLUENCE OF THE PRESENCE OF IRON IN HIGHLY ALKALINE POLYALUMINIUM CHLORIDES ON THE EFFECTIVENESS OF PRECURSORS OF DISINFECTION BY-PRODUCTS REMOVAL

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Abstract

The mechanism of coagulation with highly alkaline polyaluminium chlorides is well understood, but there is a lack of information on the effect of the presence of iron in these coagulants on the efficiency of purifying water with increased contents of natural organic matters among which humic substances are precursors of disinfection by-products. The dissolved forms of organic substances are the most problematic with regard to water treatment because major concern is the formation of disinfection by-products resulting from reactions between dissolved organic matter fractions and disinfectants. The aim of this study was to evaluate the effectiveness of precursors of disinfection by-products removal using highly alkaline polyaluminium chlorides that had different alkalinity and iron content. In the water after the coagulation process a value of SUVA254 was calculated because this indicator correlates well with dissolved organic matter reactivity and disinfection by-products. The analysis of the obtained results showed that the effectiveness of dissolved organic matter removal was determined by the formation of colored iron-organic complexes.

Keywords: highly alkaline polyaluminium chlorides, organic substances, fulvic acids, iron-organic complexes, protective colloids

1. INTRODUCTION

Natural organic matter in dissolved, colloidal, and particulate forms is ubiquitous in surface water and groundwater. The dissolved and colloidal forms are the most problematic and undesirable types of natural organic matter with regard to water treatment and supply. A major concern for water utilities is the formation of disinfection by-products resulting from reactions between dissolved organic matter fractions and chlorine or other disinfectants/oxidants. Therefore, dissolved organic matter must be...
assessed to effectively predicts its removal from water as well as predict the potential for disinfection by-products formation during treatment. Dissolved organic carbon (DOC), ultraviolet absorbance and specific ultraviolet absorbance (SUVA$_{254}$) are commonly used for this assessment. SUVA is the ratio of ultraviolet light absorbance of wavelength usually 254 nm to the concentration of DOC in the water. Lowering the SUVA$_{254}$ value is associated with a decrease in the share of reactive DOC forms, which results in a lower risk of creating by-products of oxidation. SUVA$_{254} \leq 2 \text{ m}^2/\text{gC}$ values indicate the presence of low molecular weight hydrophilic substances and it is assumed that the criterion of safe water production has been met [1]. Depending on the type and content of organic substances, as well as the pH and the oxidation-reduction potential in the natural waters, iron compounds, along with organic ligands including humic substances, may form iron-organic complexes characterised by various degrees of solubility and thus hinder the removal of both organic matter and iron compounds during water treatment [2-4]. Humic substances are divided in three groups according to their size, properties and solubility: humic acids, fulvic acids and humins. The group of humic substances with a good aqueous solubility that is fulvic acids is of big interest regarding iron transport and complexation. This group consists of rather small molecules with a molecular mass of around 0.5-2 kDa and relatively high oxygen content [5]. Several researchers suggest various mechanisms of binding iron by the humic acids. Formation of chelate complexes with the humic acids in natural waters occurs as a result of an exchange reaction between hydrogen ions of carboxyl and phenol groups of the humic acids and iron cations [6, 7]. According to other authors [8-13], one of the reasons behind iron being stabilised by organic substances in the natural waters may be the formation of so-called protective colloids of a hydrophilic nature, which are created as a result of the adsorption of organic substances on the surface of iron (III) hydroxide. It was moreover confirmed that the constant durability of the iron-organic complex increases along with an increase in pH, which is most likely caused by the growing dissociation of functional groups –COOH and –OH [9]. One of the recommended methods to remove iron-organic complexes from water is the use of a coagulation process [14-20]. When added to water, aluminum and iron coagulants yield hydrolysis products that destabilise the organic material present in the raw water. The destabilisation mechanisms most often quoted in the literature include charge neutralization, enmeshment, and adsorption. Charge neutralization preferentially applies at acidic pH, while sweep-flocculation and adsorption are commonly referred to in pH-coagulant concentration domains where abundant precipitation of metal hydroxide is expected [21]. In recent years, pre-hydrolysed coagulants, such as polyaluminium chlorides have become increasingly popular which have a lot of advantages over monomeric forms Al salts, such as wider working pH range, lower sensitivity to water temperature and lower residual aluminium concentrations. Coagulants of low alkalinity are characterised by alkalinity below 40%, average alkalinity (from 40 to about 70%) and highly alkaline (from about 80%). Controlled initial hydrolysis of aluminium salts occurring during the production of polyaluminium chloride causes that they contain more polymerised aluminium forms with a high positive charge than those generated during rapid and uncontrolled hydrolysis of aluminium sulphate (VI) [22, 23]. The alkalinity of polyaluminium chloride is determined by the quotient of the number of moles OH$^-$ to Al$^{3+}$ in a coagulant, referred to as the alkalinity ratio (r), which is approached as a coagulant polymerisation degree measure. The polymer $[\text{Al}_{13}\text{O}_{42}\text{(OH)}_{24}]^{19+}$ called the Al$_{13}$ polymer is the most efficient of aluminium polymers in destabilizing negative colloids [24-28]. Various modifiers in small amounts can be added to polyaluminium chlorides in small amounts of up to 5%, e.g., sulfates or silicate in order to increase the effectiveness of flocculation and the sedimentation of flocules [29, 30]. Polyaluminium chlorides can also be modified with iron ions, which, over recent years [20]. The results of the research presented by the author in previous publications [9, 31] showed that iron coagulants provide less efficiency in removing iron and organic substances from water than aluminium coagulants, due to the possibility of creating additional colloidal and dissolved iron-organic complex between organic substances present in
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The treated water and iron ions introduced with the coagulant. In the publications [32-34] it was also shown that the formation of iron-organic complex is favoured by the increase of the dissociation degree of organic substances as a result of the increase in pH to a value of approx. 8, at which also H⁺ ions from hydroxyl groups (-OH) are dissociated. In the author's study [35], it was also shown that the use of highly alkaline polyaluminum chlorides containing iron admixtures in their composition reduced the water treatment efficiency of the entire process system at the water treatment plant. Therefore, the goal of the present study was to try to determine and explain whether the presence of iron ions in high-basic polyaluminum chlorides and pH of approx. 8 during the coagulation process may reduce the removal efficiency of precursors of disinfection by-products, due to the possibility of creating colloidal and / or dissolved iron-organic complexes. As an optimized dissolved organic matter coagulation is a key to better drinking water treatment because of formation of disinfection by-products, the interaction behaviour between organic compounds and coagulant species should be better understood [21].

2. MATERIALS AND METHODS

2.1. Water used to coagulation

The subject of the study was a mixture of surface water and groundwater from Quaternary formations. The groundwater after aeration in forced airflow cascades was mixed with surface water at a volume ratio of 1:3. Raw water being a mixture of groundwater after aeration and surface water was characterised by an increased total iron content from 0.976 to 1.013 ± 0.100 mgFe/L, iron(II) from 0.136 to 0.139 ± 0.100 and iron(III) from 0.840 to 0.874 ± 0.100 mg Fe/L and increased turbidity from 11.00 to 12.30 ± 0.10 NTU, with the intensity of colour at wavelengths of 340 and 410 nm being from 24 to 26 ± 1 mgPt/L and from 29 to 31 ± 1 mgPt/L respectively, a pH of 8.10 ± 0.10 and electro-kinetic potential (ζ) −14.70 ± 0.01 mV. TOC reached values from 8.048 to 8.215 ± 0.001 mgC/L, DOC from 7.085 to 7.143 ± 0.001 mgC/L, and UV254 and UV272 absorption from 19.000 to 19.157 ± 0.001 m−1 and from 15.340 to 15.527 ± 0.001 m−1, which indicates that organic substances containing aromatic rings, which are characterised by a high potential of forming oxidation or disinfection by-products, were present among the dissolved substances in the purified water. In raw water the particle diameter was in the range of 190 to 459 ± 1 nm. The calculated SUVA254 value was of 2.680 ± 0.001 m2/gC, which in turn signifies that both hydrophilic as well as hydrophobic substances, as well as small and large-particle organic compounds, were present in the water, with a dominance of non-humic, hydrophilic substances of low molecular weights [36, 37].

2.2. Experimental procedure of coagulation

In the research of the effectiveness of jar test in water treatment was determined. The tests were carried out by a 1 L six-place paddle stirrer (Flocculator Kemira 2000, Sweden). Coagulation was carried out in water samples of 1 L through 1 min. fast mixing at a speed of 250 rpm and 25 min. flocculation with an intensity of mixing of 30 rpm. The coagulants used were prehydrolysed polyaluminium chlorides with the trade names PAXHP908, PAXXL1911 and PAXXL10 that had different alkalinity (85, 85 and 70%) and iron content (< 0.01, 0.7 and < 0.01%) (Table 1). The doses of coagulants were expressed in mg Al/L and varying from 1 to 5 mg Al/L. After coagulation the samples were subject to sedimentation process for 1 hour. Polyaluminium chlorides were used as coagulants, produced by KEMIPOL company in Police (Poland). The characteristics of the coagulants are shown in Table 1.
Table 1. Selected properties of the tested coagulants and the degree of polymerisation of the coagulants according to the conventional ferronometry [38, 39]

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Type of coagulant</th>
<th>PAXXL10</th>
<th>PAXXL1911</th>
<th>PAXHP908</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity ratio, [OH⁻]/[Al³⁺]</td>
<td></td>
<td>2.1</td>
<td>2.55</td>
<td>2.55</td>
</tr>
<tr>
<td>Alkalinity (Z), %</td>
<td></td>
<td>70</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>AP³⁺, %</td>
<td></td>
<td>5</td>
<td>11.5</td>
<td>11.5</td>
</tr>
<tr>
<td>Fe₉₀₄, %</td>
<td></td>
<td>&lt; 0.01</td>
<td>0.7</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Monomeric Al species (Al₁), %</td>
<td></td>
<td>22.4</td>
<td>14.2</td>
<td>14.3</td>
</tr>
<tr>
<td>Polymerised Al species (Al₂), %</td>
<td></td>
<td>29.0</td>
<td>40.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Colloidal Al species (Al₃), %</td>
<td></td>
<td>48.6</td>
<td>45.8</td>
<td>45.7</td>
</tr>
</tbody>
</table>

2.3. Analytical methods

The physical-chemical composition of both the raw water as well as treated water was determined according to the International Standard methods. The organic substances were determined by measuring total (TOC) and dissolved organic carbon (DOC) concentration, color (absorbance of 410 and 320 nm wavelength), and absorbance at 254 and 272 nm. TOC (DOC) concentration is the most reliable method for determining the total amount of NOM, UV absorption at 254 nm monitors the amount of NOM fractions containing aromatic structures in their molecules. This measurement is also used as an indicator of the potential for the formation of disinfection by-products. Absorbance at λ = 272 nm is also used for this purpose [37]. The TOC and DOC were measured using the thermal method and a Shimadzu TOC analyser (Shimadzu Corporation, Kyoto, Japan). DOC was analysed by the TOC analyser after filtration through 0.45 µm pore diameter membranes. UV absorbance at 254 nm (UV₂⁵₄) and at 272 nm (UV₂₇₂) was measured by a UV-VIS spectrophotometer Agilent Cary 60 (Agilent Technologies, Inc. Santa Clara, CA, USA) using a quartz cell with a 1 cm path length after filtration through a 0.45 µm membrane. DOC and UV₂⁵₄ are used in the calculation of the specific UV absorbance (SUVA₂⁵₄).

\[ \text{SUVA}_{254} = \frac{\text{UV}_{254}}{\text{DOC}} \left( \text{m}^{-1}\text{gC} \right) \]  

where SUVA is specific UV absorbance at 254 nm (m⁻¹) and DOC is dissolved organic carbon (gC/m³) [37]. Colour was indicated in accordance with ISO 7887-Method C [40], using a spectrophotometer Agilent Cary 60. Quartz cuvette with a path length of light 5 cm was used. It was determined after filtration of the water sample through a membrane filter of pore size 0.45 µm. The iron and aluminum concentration was determined with the atomic emission spectroscopy (ISP-OES, 5300DV, Perkin Elmer Company, Waltham, Massachusetts US). The total iron and iron (II) concentrations were determined also with the Dr 3900 HACH Lange (HACH Lange, CO, USA) spectrophotometer using the 1,10 phenanthroline method. As a reducing agent of ferric ions to the ferrous ions, hydroxylamine hydrochloride was used. The amount of iron (III) was calculated as the difference between the total iron and iron (II) concentrations. The pH of the raw water and the purified water was determined with a WTW Multi Line P4 with a combination pH electrode with temperature corrections. Turbidity was measured using the Turbidimeter 2100N, Hach Company, Loveland, Kolorado, USA. The Al species distribution in the PACls (PAXXL10, PAXXL1911, PAXHP908) samples was analysed by Ferron complexation timed spectrophotometry [39] Al³⁺ reacts with Ferron reagent (Sigma-Aldrich, St. Louis, MO, USA) to form an Al-Ferron complex at pH = 5, λ = 370 nm. An Agilent Cary 60 (Santa Clara, California, USA) spectrophotometer was used to measure the Al-Ferron kinetics. Based on the kinetic
difference of reactions between Ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonylic acid) with different hydrolysed species, hydrolysed Al species can be divided into three types: monomeric Al species (Al\(_a\)) (instantaneous reaction: 0 to 1 min), medium polymerised Al species (Al\(_b\)) (reaction within 120 min), and species of colloidal (Al\(_c\)) (no reaction in 120 min). The results are shown in Table 1. Measurement of the electro-kinetic potential \(\zeta\) was made in water samples using the Zetasizer Nano Analyser (Malvern Panalytical Company, Cambridge, UK), which calculates the Zeta potential by determining the electrophoretic mobility of the particles using the laser technique of speed measurement based on the Doppler effect. In the water, the particle size was also measured using the Zetasizer Nano Analyser. The Zetasizer Nano Analyser measures particle size using the dynamic light scattering (DLS, dynamic light scattering) process, also known as photon correlation spectroscopy (PCS, photon correlation spectroscopy), which measures Brown’s motion and calculates particle size on this basis. The intensity of the fluctuation of the scattered laser light that the particles are illuminated by was analysed. Water samples following the coagulation process using PAXXL10, PAXXL1911 and PAXHP908 were filtered through a filter 0.45 µm in diameter. Humic substances were extracted from the colloids isolated from water following the PAXXL10, PAXHP908 and PAXXL1911 coagulation process according to the methodology developed by Aiken et al. [41], using different solubilities in acids and alkalis for individual fractions of humic substances. Humic substances were analyzed using infrared (IR) spectroscopy using an FTIR Thermo Scientific Nicollet iS50 spectrometer (Waltham, MA, USA) operating in the NIR-, MID-, and FAR-IR ranges using the KBr compensation tablet technique.

3. RESULTS AND DISCUSSION

Analysis of the research results obtained showed that the pH of water after coagulation with the PAXXL1911 coagulant (Z = 85%, Fe = 0.7%) ranged from 7.86 to 8.00 ± 0.10, with the PAXHP908 (Z = 85%, Fe < 0.01%) ranged from 7.85 to 8.00 ± 0.10, and in water following PAXXL10 coagulation (Z = 70%, Fe < 0.01%), from 7.50 to 7.70 ± 0.10 for doses from 1 to 5 mgAl/L. The effectiveness of organic substances removal from water was also determined by coagulation method depending on the type and dose of the tested aluminium coagulant. Analysis of the obtained results of the research presented in Figure 1 showed that the effectiveness of the tested coagulants in removing TOC, DOC, \(\text{UV}_{254}\) and \(\text{UV}_{272}\) decreased in accordance with the following series:

\[
\text{PAXHP908} > \text{PAXXL10} > \text{PAXXL1911}.
\]

![Fig. 1. The effect of the type and dose of a coagulant on the efficiency of removing TOC (a), DOC (b), UV\(_{254}\)(c) and UV\(_{272}\)(d)]](image-url)
The highest efficiency of TOC (from 17.35 to 35.20%) and DOC (from 8.44 to 31.40%) removal from water was provided by the coagulant PAXHP908 characterised by an alkalinity of 85%, and PAXXL10 with an alkalinity of 70% showed a slightly lower efficiency: TOC from 11.70 to 34.02% and DOC from 6.08 to 29.14% (Fig.1a and 1b). The PAXHP908 coagulant was also the most effective in the removal of UV\textsubscript{254} from 24.32 to 50.53% and UV\textsubscript{272} from 26.79 to 51.76% (Fig.1d and 1c). The least effective coagulant in TOC (from 10.88 to 32.59%), DOC (from 3.00 to 25.94%), UV\textsubscript{254} (from 6.68 to 30.53%) and UV\textsubscript{272} (from 10.37 to 33.93%) removal was PAXXL1911 characterised by an alkalinity of 85% and containing iron in its composition. The analysis of the obtained test results also showed that in the range of applied doses of tested coagulants DOC fractions characterised by a high content of aromatic rings (UV\textsubscript{254} and UV\textsubscript{272} - Fig 1d and 1c) were effectively eliminated, and thus a large potential for creating by-products of disinfection. It is believed that a higher reduction in the UV absorbance value of 254 and 272 with respect to the reduction of DOC (Fig.1) means that aromatic substances are removed more effectively during coagulation, than other organic matter fractions [2-4].

The turbidity and concentration of iron was also determined in the water after the coagulation process. Analysis of the obtained test results showed that, as in the case of organic matter removal, the coagulant PAXHP908, with an alkalinity of 85% and no iron in its composition, was the most effective in removing turbidity (from 79.11 to 91.22%) and iron (from 82.63 to 95.16 %), while the coagulant PAXXL1911 characterised by an alkalinity of 85% and containing iron in its composition was the least effective (turbidity: from 66.15 to 81.00 %, iron: from 68.24 to 77.15 % ) (Fig.2). In the case of polyaluminium chlorides (PAXHP908 and PAXXL1911) with an alkalinity of 85% for the highest dose tested of 5 mgAl/L, there was a slight reduction iron and turbidity removal efficiency (Fig.2). In water after coagulation with the least effective coagulant PAXXL1911, the concentrations of iron, total organic carbon and turbidity were respectively: from 0.223 to 0.306 ± 0.100 mgFe/L, from 5.425 to 7.172 ± 0.100 mgC/L and turbidity from 1.85 to 3.30 ± 0.10 NTU. The effectiveness of the coagulation process with the tested coagulants was also evaluated by measuring the electro-kinetic potential ζ, which determines the stability of the colloidal system. According to literature reports [30, 42, 43] with the increase in the absolute value of the potential ζ, the stability of colloids increases. The measured value of the raw water electro-kinetic potential was -14.70 ± 0.01 mV. Analysis of the dependences presented in Figure 3 showed that the highest degree of destabilisation of the electro-kinetic potential, which varied between -9.00 and -3.80 ± 0.01 mV, was obtained in samples of water during coagulation with
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polyaluminium chloride PAXHP908 over the entire range of tested doses from 1 to 5 mg Al/L. The lowest degree of destabilisation of the electro-kinetic potential, which varied between -10.78 and -7.18 ± 0.01 mV, was obtained in samples of water during coagulation with polyaluminium chloride PAXXL1911 characterised by an alkalinity of 85% and containing iron in its composition over the entire range of tested doses from 1 to 5 mg Al/L. The zeta potential for post-coagulation water samples was lower than that found for raw water.

![Diagram showing the effect of the type and dose of a coagulant on the change in zeta potential](image)

**Fig. 3.** The effect of the type and dose of a coagulant on the change in zeta potential

In drinking water treatment, the main motivation for studying dissolved organic matter stems from its role as precursor of carcinogenic chlorination by-products during the disinfection stage therefore, a value of SUVA$_{254}$ was calculated in the water after the coagulation process. SUVA$_{254}$ provides insight into the nature of the dissolved organic matters. By combining both DOC and UV$_{254}$ into a single parameter, SUVA$_{254}$ provides a quantitative measure of aromatic content per unit concentration of organic carbon [1]. Figure 4a shows changes in the SUVA$_{254}$ value in water during the coagulation process depending on the type and dose of the coagulant tested.

![Diagram showing the effect of the type and dose of a coagulant on the change in particle size distribution](image)

**Fig. 4.** The effect of the type and dose of a coagulant on the change in SUVA$_{254}$ (a) and on the change in particle size distribution (b)
The lowest SUVA\textsubscript{254} values from 2.199 to 1.918 m\textsuperscript{2}/gC respectively for doses of 1 to 5 mg Al/L were found in water after coagulation with PAXHP908 and the criterion of safe water production was met only after the highest doses of 4 and 5 mg Al/L (SUVA\textsubscript{254} ≤ 2). According to the technological guidelines regarding the risk of creating by-products of oxidation and disinfection, there is no need for coagulation for SUVA\textsubscript{254} ≤ 2, and it is assumed that the criterion of safe water production has been met [42]. The SUVA\textsubscript{254} values in water after coagulation with PAXXL10 ranged from 2.399 to 2.285 m\textsuperscript{2}/gC, in water after coagulation with PAXXL1911 ranged from 2.591 to 2.526, and for any of the doses tested was not fulfilled the production of safe water. Based on the calculated values of SUVA\textsubscript{254} and literature [36, 37], it can be concluded that in water after coagulation with PAXXL1911 and PAXXL10 both hydrophilic and hydrophobic as well as small and large organic compounds were present, and in water after coagulation with PAXHP908 for doses from 4 to 5 mg Al/L there were hydrophilic, low molecular weight non-humus substances (SUVA\textsubscript{254} ≤ 2 m\textsuperscript{2}/gC). According to many authors [1, 19, 35, 37] SUVA\textsubscript{254} correlates well with dissolved organic matters reactivity and disinfection by products formation. Aromatic structures are important components of dissolved organic matters with respect to disinfection by products formation because they are believed to constitute the primary sites attacked by Cl\textsubscript{2} or other oxidants, which suggests that SUVA\textsubscript{254} is valuable characterization parameter for the assessment of dissolved organic matters reactivity. Strong correlations have been reported between SUVA and disinfection by products formation.

In the water samples after the coagulation process, the particle size was also measured using the dynamic light scattering process (Fig.4b). Analysis of the obtained test results showed that in the water after the coagulation of PAXHP908 (Z=85\%, Fe<0.01\%), there were particles whose diameter ranged from 3200 to 2596 ± 1 nm for doses from 1 to 5 mg Al/L. In water after coagulation with PAXXL10 (Z=70\%, Fe<0.01\%), the particle diameter was in the range of 3452 to 1468 ± 1 nm, and after coagulation with PAXXL1911 (Z=85\%, Fe=0.7\%) from 3500 to 4708 ± 1 nm. Only in the water samples after coagulation with the coagulant PAXXL1911 characterised by an alkalinity of 85\% and containing iron in its composition did the size of the particles remaining in the treated water increase with increasing dosage from 1 to 5 mgAl/L, and thus with an increase in the amount of iron introduced with the coagulant (Fig.4b). Relationship between iron, iron (III), turbidity, colour and organic substances indices, measured as: TOC, DOC, UV\textsubscript{254} and UV\textsubscript{272} showed strong correlations in water following coagulation with PAXXL1911 (Fig.5). This confirms that colored iron-organic complexes were created in the water during coagulation including protective colloids. The coloured iron-organic complexes formed during PAXXL1911 coagulation most likely exhibited the character of protective colloids, hence leading to the significantly higher turbidity that followed PAXXL1911 coagulation as compared to the turbidity after PAXXL10 and PAXHP908 coagulation which were respectively: from 2.20 to 3.30 ± 0.1 NTU (PAXXL1911), from 1.10 to 2.10 NTU (PAXXL10) and from 1.00 to 1.40 ± 0.1 NTU (PAXHP908).
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According to numerous researchers [11, 31-33, 44], the reasons for the stabilisation of iron by organic substances is the formation of chelate complexes and the formation of so-called protective colloids of a hydrophilic nature. According Kwakye-Awuah et.al [45] the iron ion pollution in groundwater may interact with the dissolved constituents, such as dissolved organic carbon (DOC), present as a humic-like material. These interactions lead to complex formations and to potential solid precipitation. It was moreover confirmed that the constant durability of the iron-organic complex increases along with an increase in pH, which is most likely caused by a growing dissociation of functional –COOH and –OH groups [11, 31-33]. The reason behind the formation of chromatic iron-organic complexes over the course of coagulation with the highly-alkaline PAXXL1911 coagulant may have been the high pH, falling into the range of 7.86 to 8.00 ± 0.10, in which the functional groups of –COOH and –OH organic substances are more reactive in relation to iron ions and have been also the introduction of additional iron ions along with the coagulant, which may have reacted with the organic substance present in the treated water. Rahman et al. [46] proved that iron usually connects with carboxyl groups and that iron’s organic complex compound is large and polydisperse with size of hundreds nanometres. The analysis of the IR spectrum confirmed that fulvic acids, which, in comparison to humic acids, have more carboxyl and aliphatic group vibrations [47-49], were present in colloids isolated from water following the process of coagulation using highly alkaline polyaluminium chloride PAXXL1911 (Z=85%, Fe=0.7%), (Fig. 6).
The IR spectra of humic and fulvic acids are similar. The main difference between the two is that the absorption zone in the wave number range of 1720 cm\(^{-1}\) of fulvic acids is much stronger \[46, 49, 50\]. According Jung et al. \[21\] Fe-hydrolysed species associate with carboxylic groups of humic colloids at pH 8, thus inducing a release of previously complexed calcium ions. At alkaline pH that a reorganization of humic macromolecules from a stretched to a coiled conformation takes place upon interaction with coagulant species.

4. CONCLUSIONS

The conducted research showed that the presence of iron in high-basic polyaluminium chlorides affected the effectiveness of water purification in the coagulation process and particularly the removal of precursors of disinfection by-products. After the polyaluminium chloride coagulation which is characterised by a alkalinity 85% and additionally contains iron in its composition found the highest the value of SUVA\(_{254}\), which ranged from 2.591 to 2.526 m\(^2\)/gC, which means that the criterion of safe water production was not met (SUVA\(_{254}\) ≤ 2 m\(^2\)/gC) due to the presence of precursors of oxidation and disinfection by-products that is organic substances containing aromatic rings. The reason behind the smallest effectiveness of water purification in the coagulation process upon applying high-basic polyaluminium chloride additionally contains iron in its composition was the formation of iron-organic complexes, most likely in the form of protective colloids containing fulvic acids.

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