Anion exchange pretreatment for the removal of natural organic matter from humic rich water

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ABSTRACT

The treatment of humic rich water using anion exchange, coagulation and PAC-adsorption was studied, both independently and in sequence in that order. The commercial aluminium-based coagulant PAX-16, powdered activated carbon W35 and the magnetic ion exchange resin (MIEX®) were used in the study. The source of humic substances was natural water (25.0 g C/m³ as DOC) flowing out from the Great Batorow Peat-Bog (Lower Silesia, Poland). In addition to DOC, color, UV254 absorbance, specific UV absorbance (SUVA254), turbidity, pH and alkalinity were also analyzed. Regardless of the applied technology, in the phase of raw water treatment extraordinary solutions were necessary to treat the humic rich water – a high coagulant (13.1 g Al/m³) or PAC (>200 mg/dm³) dose or a low bed volume (200 BVs) in the case of anion exchange. MIEX®DOC pretreatment had a very positive influence on the course and effects of coagulation resulting in a higher coagulant efficiency for removing organic compounds. In this respect, MIEX®DOC pretreatment allowed the application of a required coagulant dose four times lower compared to the coagulation of raw water. In testing the sequence of processes (MIEX®DOC – coagulation – PAC-adsorption), coagulation was the main process responsible for reducing the SUVA254 value. The improvement in water quality after PAC-adsorption was not significant, although the process removed DOC fractions that could not be removed by coagulation. Each of the applied methods played a role in the treatment of humic rich water and the nearly complete removal of NOM was achieved (in the sequence of processes) under relatively rational operating conditions for the treatment techniques.

Key words | adsorption, coagulation, ion exchange, MIEX® resin, natural organic matter

INTRODUCTION

Natural waters constitute complex systems characterized by variability in their physico-chemical composition and diversity of substances, both anthropogenic and natural. Natural organic matter (NOM) is a heterogeneous mixture of complex organic materials including humic substances, proteins, lipids, etc. (Thurman 1985). Although NOM represents no direct human health hazard, it is necessary to achieve high removal rates from drinking water. This is because NOM strongly affects water treatment processes, e.g. by reducing the efficiency of activated carbon or causing membrane fouling problems. In addition, there is a risk that disinfection by-products (DBP) will form due to the presence of NOM. Recently, many intensive studies have been conducted on new and effective methods of organic matter removal (Morran et al. 2004; Cornelissen et al. 2008; Treguer et al. 2010; Drikas et al. 2011).

An interesting alternative to conventional water treatment methods is the application of a magnetic ion exchange resin (MIEX®) developed for the purpose of removing dissolved compounds from drinking water sources, especially ultraviolet adsorbing and acidic fractions of dissolved organic carbon (DOC) over a wide molecular weight range (Bourke et al. 1999; Neale & Schaefer 2009). MIEX® is a strong base anion exchange resin with magnetic properties which differentiate it from...
other ion exchange resins available on the market. Unlike conventional ion exchange processes, MIEX® is utilized in a continuous mode and does not require pretreatment for suspended matter removal. The MIEX® process (MIEX®DOC) can be successfully used as a polishing step at the end of the water treatment chain, but in practice it is used most often as a pretreatment step followed by powdered or granular activated carbon (PAC/GAC) adsorption (Fabris et al. 2007, 2008) and coagulation prior to micro- or ultrafiltration (Son et al. 2005; Kabsch-Korbutowicz et al. 2006) or even combined with PAC-adsorption (Humbert et al. 2008; Adamski & Majewska-Nowak 2010).

Each of these mentioned processes is able to remove NOM from water; however, a large amount of NOM significantly limits the rational application of these particular methods. In the case of coagulation, its application is limited by increasing alkalinity of the treated water while PAC-adsorption is limited by the dose of the absorbent which cannot be regenerated. In contrast, the MIEX®DOC process is not subject to these disadvantages, i.e. it is not limited by the alkalinity of the water and even rapidly exhausted resin can be regenerated at relatively low cost. However, the use of the MIEX®DOC process requires resin loading within rational limits. Furthermore, the high selectivity of strong base resins for highly charged organic ions enables these ions to be effectively removed at very low input concentrations, typically <15 g C/m³ (Slunjski et al. 2000). When the application of single methods encounters limitations, the solution may be to implement a sequence of treatment steps in order to allow their rational use.

The aim of this study was to investigate the efficiency of the anion exchange process (MIEX®DOC) in removing natural organic matter from humic rich water and to evaluate the impact of the magnetic ion exchange resin on coagulation and PAC-adsorption performance. The major sequence of examined processes was MIEX®DOC as a pretreatment stage followed by coagulation and PAC-adsorption; however, in order to assess the influence of MIEX® resin on coagulation and adsorption performance, PAC-adsorption for raw water and coagulation tests following MIEX® treatment were also conducted.

## MATERIALS AND METHODS

### Water source

Experiments were performed using water prepared by mixing natural water (NW) with dechlorinated tap water (TW) at a ratio of 3:2. Then the prepared water was used as the raw water (RW) for the conducted research. The source of humic substances was natural water flowing out from the Great Batorow Peat Bog (Lower Silesia, Poland). Tap water collected in the laboratory was supplied by the drinking water treatment plant (Wroclaw, Poland) treating surface water by infiltration, aeration, rapid filtration, GAC-adsorption and disinfection with chlorine dioxide. The dilution of peat-bog water with tap water was intended to maintain the pH at which the humic substances are present in water in dissolved form, stabilize the pH (NW water had no alkalinity) and decrease color along with the organic matter content. Due to the application of GAC-adsorption, the TW had a very low content of organic matter so that the main source of organic matter was the NW. Table 1 presents the characteristics of natural water, tap water and mixed raw water.

### Analytical methods

Water samples for analyzing the DOC, UV 254 and color were passed through membrane filters with a pore diameter of 0.45 μm. The DOC was measured using a HiPerTOC Thermo Scientific analyzer which applies the UV-persulfate oxidation method. The color and UV absorbance at 254 nm

### Table 1 | Water quality characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Natural water (NW)</th>
<th>Tap water (TW)</th>
<th>Raw water (RW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>g C/m³</td>
<td>37.0</td>
<td>2.0</td>
<td>25.0</td>
</tr>
<tr>
<td>UV at 254 nm</td>
<td>m⁻¹</td>
<td>204.0</td>
<td>4.0</td>
<td>133.0</td>
</tr>
<tr>
<td>Color</td>
<td>g Pt/m³</td>
<td>377.0</td>
<td>4.0</td>
<td>254.0</td>
</tr>
<tr>
<td>SUVA 254</td>
<td>m⁻³/g C-m</td>
<td>5.51</td>
<td>1.85</td>
<td>5.32</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>2.0</td>
<td>0.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Conductivity</td>
<td>μS/cm</td>
<td>57</td>
<td>584</td>
<td>254</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>4.75</td>
<td>8.05</td>
<td>7.06</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>val/m³</td>
<td>0.00</td>
<td>3.10</td>
<td>1.05</td>
</tr>
</tbody>
</table>
were determined spectrophotometrically using a Shimadzu UV–VIS 1240 spectrophotometer with a quartz cuvette light path length of 1 or 3 cm depending on the measurement range. In qualitatively evaluating the amount of organic substances removed, a SUVA \textsubscript{254} (Specific UV Absorbance) parameter was used which is derived from the DOC and UV absorbance (UV\textsubscript{254}/DOC) (Karanfil et al. 2002). Controlling turbidity was above all related to the effects of coagulation and was done with the help of a HACH 2100N IS turbidimeter. Conductivity and pH measurements were taken using a multiparameter WTW Multi 350i device. The alkalinity was determined by titration with methyl orange. All tests were conducted at a temperature of 20 °C.

**Experimental procedures**

This study applied the following sequence of processes for removing organic matter from water: anion exchange–coagulation–adsorption on PAC. In addition, for comparison purposes tests were performed on raw water with coagulation and adsorption. The treated water samples were labeled according to the abbreviations of the treatment processes: C-RW was RW after coagulation, M-RW was RW after the MIEX®DOC process, A-RW was RW after adsorption on PAC, C-M-RW was MIEX®-treated water after coagulation and A-C-M-RW was MIEX®-coagulation treated water after adsorption on PAC.

The aluminium-based coagulant (PAX-16) with an Al\textsuperscript{3+} content of 8.2%, density of 1,350 g/dm\textsuperscript{3} and basicity of 37% (Kemipol, Poland) was used in this study. PAX-16 was selected in the preliminary test due to its advantage of reducing the color and DOC from low-alkalinity waters better than e.g. alum. Powdered activated carbon W35 (Norit, the Netherlands) was used in this study. This particular activated carbon was chosen due to its high BET surface area (875 m\textsuperscript{2}/g) and extra fine particle size distribution (d\textsubscript{50} = 15 μm) assuring fast adsorption kinetics. Moreover, PAC W35 is suitable for the removal of dissolved organic matter of both low and high molecular weight. The applied MIEX® resin is a micro size (mean particle diameter < 180 μm), macroporous, strong base ion exchange resin with a magnetic component incorporated into its polymeric structure (Slunjski et al. 2000). The MIEX® resin was specially developed and optimized for the removal of DOC in municipal water treatment. All of these mentioned treatment materials are used for the removal of organic constituents in the production of drinking water.

In order to evaluate the NOM reduction in examined water samples, the following experimental stages were conducted: kinetic jar tests at various MIEX®/PAC doses and contact times, a multiple loading jar test with a selected MIEX® resin dose and contact time as well as standard jar tests for determining the proper coagulant dose and pH for coagulation.

Kinetic tests consisted of mixing the absorbent with water samples for 60 min in the case of the anion exchange resin and for 8 h (RW treatment) or for 4 h (C-M-RW treatment) in the case of PAC. Samples for analysis were collected at intervals determined in the preliminary study without interrupting stirring. The range of the applied MIEX® resin dose was from 2 to 40 cm\textsuperscript{3}/dm\textsuperscript{3}. The applied PAC dose ranged from 5 to 480 mg/dm\textsuperscript{3} for RW and from 5 to 160 mg/dm\textsuperscript{3} for C-M-RW. The multiple loading test simulates the work of the adsorbent under flow conditions. The equivalence of these conditions is assumed based on the bed volumes (BV). The bed volume describes the multiplicity of the volume of treated water in relation to the applied volume of adsorbent. The multiple loading test was performed only for the MIEX®DOC technology and was repeated two times to collect the required volume of water (M-RW) for the subsequent testing. The test parameters (resin dose = 20 cm\textsuperscript{3}/dm\textsuperscript{3}, contact time = 20 min) were chosen on the basis of the results of the kinetic test.

In both jar tests intensive mixing was applied (150 rpm for MIEX® resin, 180 rpm for PAC) ensuring the uniform distribution of adsorbent in the reactors.

Two types of tests were conducted for coagulation: a test for selecting the proper pH and for selecting the proper dose. The first test was performed only for RW while the second for RW and for water after the MIEX® DOC process (M-RW). The value of the pH determined for RW coagulation was also used for the coagulation of M-RW. The pH values obtained from the pH selection test were representative of the rapid mixing stage. The pH selection test for coagulation was conducted in the pH range from 5 to 7.5 and the coagulant dose was constant, equaling the theoretical dose with
regard to the removal of color. An empirical formula which expresses the theoretical dose of coagulant needed for the coagulation step was derived on the basis of numerous experimental data collected over several years: 

\[ D_t = n\sqrt{C}, \]

where \( D_t \) is the theoretical coagulant dose \((g Al_2(SO_4)_3·18H_2O/m^3)\), \( C \) is the color \((g Pt/m^3)\) and \( n \) is the constant \((n = 7-8, \text{ assumed as } n = 7)\).

Due to the low turbidity of raw water, the water color determined the coagulant dose. The dose-selection test was performed at the optimal pH value based on the results of the pH selection test. For pH adjustment 0.1\( \text{HCl} \) and 0.1\( \text{NaOH} \) solutions were used. The optimal coagulant dose determined in the dose selection test for water after the anion exchange process was applied in the coagulation stage in order to obtain post-coagulation water for testing the adsorption on PAC. The following coagulation parameters were applied: intensity of rapid mixing – 170 rpm, time of rapid mixing – 5 min, intensity of flocculation – 30 rpm, time of flocculation – 20 min and time of sedimentation – 60 min. In the case of RW, the coagulant dose ranged from 6.5 to 13.1 mg Al/dm\(^3\) and for M-RW from 1.1 to 9.8 mg Al/dm\(^3\).

**RESULTS**

This study purposely used water with a high content of organic substances \(25.0 \text{ g C/m}^3\) as DOC causing the associated water color \(254.0 \text{ g Pt/m}^3\). In terms of quality, the water was also characterized by a large SUVA\(_{254}\) value \(5.3 \text{ m}^3/\text{g C-m}\) suggesting a significant proportion of hydrophobic as well as aromatic and high molecular weight fractions in the DOC \((\text{Edzwald & Van Benschoten 1990; White et al. 1997})\). These water features are important in the coagulation process – for water with a SUVA\(_{254}\) \(\geq 4.0 \text{ m}^3/\text{g C-m}\), the NOM content determines the course of water coagulation. Together with the selective removal of the hydrophobic fraction of DOC during coagulation, the SUVA\(_{254}\) value is expected to significantly decrease \((\text{Edzwald & Tobiason 1999})\).

Waters with such permanently high organic content are rarely considered as a source of drinking water. More often, such conditions are found periodically demanding the temporary implementation of extraordinary technological solutions to ensure the production of water that meets the specified quality requirements. In theory, all three tested methods of removing NOM from water can be adapted to allow for a changing water composition.

**Raw water treatment**

Of the three RW treatment methods tested, the least efficient was PAC-adsorption \((\text{Figure 1})\). PAC doses below 50 mg/dm\(^3\) did not alter the composition and were not included in the plots. The noticeable effect of improving NOM removal was obtained by changing the dose from 160 to 320 mg/dm\(^3\). With the highest applied dose \((480 \text{ mg/dm}^3)\) it was possible to reduce the value of DOC by about 70%, UV\(_{254}\) by 72% and color by 70%. However, the required dose significantly exceeds the acceptable values for practical applications in which doses in the range of 20–100 mg/dm\(^3\) are considered large \((\text{Montgomery 1985})\). Furthermore, even for the highest applied PAC dose the final values of the water quality parameters were still high \((\text{DOC} = 7.4 \text{ g C/m}^3, \text{color} = 75.0 \text{ g Pt/m}^3, \text{UV}_{254} = 37.0 \text{ m}^{-1})\). PAC adsorption did not have a significant influence on the SUVA\(_{254}\) value which decreased slightly from 5.3 to 5.0 m\(^3\)/g C-m. The equilibrium time of adsorption was about 2 h irrespective of the PAC dose.

The coagulation of water using aluminium compounds requires pH optimization of the process. The hydrogen ion concentration determines the form of organic pollutants as well as the sign and charge of the Al-hydroxy complexes \((\text{Swiderska et al. 2008})\). The results of the pH selection test showed that effective coagulation with the theoretical dose \((D_t = 8.9 \text{ g Al/m}^3)\) required a low pH value, preferably about 5.0 \((\text{Figure 2})\). However, a consequence of this was the nearly complete depletion of the alkalinity \((0.05 \text{ val/m}^3 \text{ remaining})\) leading to a loss in water chemical stability. Taking this into consideration, the pH of the process was maintained at 6.0. At this pH, coagulation effects were worse, but the alkalinity only decreased to the value of 0.45 val/m\(^3\). Not without significance, there was more than a twofold reduction in the amount of acid needed to adjust the pH. Other factors taken into account during optimization of the pH value were as follows: the possibility of a significant turbidity and color decrease using a higher dose of coagulant \((1.5 \text{ times higher than for } \text{pH} = 5, \text{respective})\).
Figure 3) with a higher remaining alkalinity (0.3 val/m³); and the possibility of additional turbidity removal during the filtration process accompanying coagulation.

The pH value during the dose selection test was kept constant (pH = 6.0) irrespective of the coagulant dose. Satisfactory results were obtained only when the coagulant dose was 13.1 mg Al/dm³ (Figure 3). This value was over 50% greater than the theoretical dose necessary for removing color. Water after coagulation with the dose of 13.1 mg Al/dm³ and 1 h of sedimentation had a pH of 6.15, alkalinity of 0.3 val/m³, turbidity of 0.85 NTU, DOC of 3.5 g C/m³ (86% removal), color of 11 g Pt/m³ (96% removal) and UV254 of 10 m⁻¹ (93% removal). The values of color and DOC were within the acceptable limits (assumed respectively as 15 g Pt/m³ and 5 g C/m³) for drinking water according to Polish and EU regulations.
Coagulation also significantly reduced the SUVA$_{254}$ value to 2.8 m$^3$/g C-m. The only drawback with these coagulation conditions was the extremely high coagulant dose.

In the first stage of investigating the MIEX$^\text{DOC}$ process the kinetic test was performed. The results presented in Figure 4 confirmed the usefulness of this method in removing NOM from the tested water. Even the lowest amount of resin (2 cm$^3$/dm$^3$) enabled the removal of 44% DOC, 36% color and 40% UV$_{254}$. However, in this case the time required to achieve equilibrium was much too long exceeding 60 min. As expected, for higher doses (20–40 cm$^3$/dm$^3$), the relative equilibrium of the process was achieved much faster, i.e. after about 20 min. This readily corresponds to the practical application of the MIEX$^\text{DOC}$ method. Doses in the range of 20–40 cm$^3$/dm$^3$ with a
contact time of 20 min allow for the removal of 84–90% DOC, 80–88% color and 82–89% UV$_{254}$. Similar to the case of PAC-adsorption, significant changes in the SUVA$_{254}$ value were not observed. Despite the lack of a clear regularity in the changes of the SUVA$_{254}$ for the specific doses and contact times, the value of this ratio was always higher after contact with the resin than before.

The preferences of the MIEX®DOC process concerning the removal of the DOC fraction characterized by low and high SUVA$_{254}$ values are not clear (Molczan 2008; Mergen et al. 2009). However, more often it is encountered that the MIEX® resin preferentially removes the DOC fraction having high SUVA$_{254}$ values; thus, the MIEX®DOC process is more efficient in removing DOC from water that has a high SUVA$_{254}$ value (Chow et al. 2002; Boyer & Singer 2005, 2006; Budd et al. 2005; Fonseca et al. 2005; Singer & Bilyk 2002). Similar to past research, an increase in the value of the specific UV absorbance was observed for small resin doses and short contact times (Molczan 2008), i.e. when fresh resin is accompanied by an excess of potential substrate. It was suggested that this could be the result of different ion exchange preferences in which smaller ions with a larger magnitude of charge are more likely to be removed, with the size of the particles playing the dominant role (Croué et al. 1999) whereas large SUVA$_{254}$ values are related to high molecular weight substances (Edzwald & Van Benschoten 1990; White et al. 1997; Edzwald & Tobiason 1999).

The kinetic test results of the MIEX®DOC process demonstrate the potential possibilities of applying this method. Reactors operating in a continuous mode not only contain fresh resin (as in the kinetic tests), but they also contain resin having varying degrees of saturation. For this reason, the practical possibilities of applying this process can only be evaluated by the multiple loading test in which the effects of treatment become worse with increasing bed volume. The MIEX® resin typically works in the range 1,000–2,000 BVs. The multiple loading test was performed twice (the first and second runs are shown in Figure 5) under the conditions determined during the kinetic test: a resin dose of 20 cm$^3$/dm$^3$ and contact time of 20 min. Both the dose and the contact time were typical for the conventional dual stage MIEX®DOC process configuration.

Applying a typical dose in water with an unusually high NOM content resulted in the rapid depletion of resin capacity and significantly reduced the number of possible bed volumes to apply (Figure 5). In the range of the applied bed volumes (50–600 BVs), the values of the water quality parameters increased as follows: from 4.2 to 16.8 g C/m$^3$ (83–33% DOC removal), 56–184 g Pt/m$^3$ (78–28% removal of color) and 26–90 m$^{-1}$ (81–32% UV$_{254}$ removal). The value of specific UV absorbance decreased from about 6.1 m$^3$/g C-m (for 50 BVs) to 5.4 m$^3$/g C-m (for 600 BVs), but this value remained higher than for raw water (5.3 m$^3$/g C-m). The fresh resin had a greater affinity for removing the DOC fraction with a relatively small SUVA$_{254}$ value while progressive resin saturation resulted in the resin affinity shifting to the fraction characterized by higher SUVA$_{254}$ values. During the treatment of water using the MIEX®DOC method, changes in pH and alkalinity were not observed; only a slight increase in conductivity occurred due to the release of chloride ions.

Similar to PAC-adsorption and coagulation, treating humic rich water with the MIEX®DOC process requires the use of extraordinary solutions and in this case bed volumes had to be used below their typical range. The ultimate decision about whether to select the MIEX®DOC process as pretreatment before subsequent water treatment steps depends on the following observed factors:

- in contrast to coagulation, the MIEX®DOC process did not change the chemical properties of water (in particular the pH and alkalinity) and it was not necessary to adjust the pH;
- the application of this method is associated with resin consumption, although in contrast to coagulation and PAC-adsorption, the material is not lost; it can be regenerated and reused. Only the regeneration agent (NaCl) is used up, but its cost is relatively low.

**Coagulation of MIEX® treated water**

As in the case of coagulation of raw water, the pH value during the dose-selection test was kept constant (pH = 6.0), irrespective of the coagulant dose. MIEX® treated water was obtained by mixing samples after the multiple loading test in the range of 50–400 BVs. The quality of prepared water (DOC = 9.9 g C/m$^3$, color = 123 g Pt/m$^3$,
$UV_{254} = 57 \text{ m}^{-1}$ and $SUVA_{254} = 5.75 \text{ m}^{3}/\text{g C-m}$ was equivalent to water treated with a resin dose of $20 \text{ cm}^{3}/\text{dm}^{3}$, contact time of 20 min and 200 BVs. As expected, the turbidity of water after the MIEX®DOC process (8.0 NTU) was higher than that of raw water (1.6 NTU). The increase of turbidity was typical and can be explained by the presence of residual resin in the water (Singer & Bilyk 2002). Satisfactory results of coagulation (i.e. DOC < 5 g C/m$^3$, color < 15 g Pt/m$^3$, turbidity < 1 NTU) were recorded at a coagulant dose of 3.3 g Al/m$^3$ although the value of the theoretical dose for water with the color of 123 g Pt/m$^3$ was about 6.5 g Al/m$^3$. C-M-RW had 0.4 NTU (95% removal of turbidity), 1.5 g C/m$^3$ (85% removal of DOC), 3 g Pt/m$^3$ (97% removal of color) and 3 m$^{-1}$ (95% removal of $UV_{254}$) (Figure 6). This shows that the amount of coagulant used for coagulation of MIEX® treated water was four times lower compared with the dose required for coagulation of
RW and two times lower than the calculated theoretical dose for M-RW. The alkalinity of the coagulated water (C-M-RW) decreased to 0.3 val/m³ and the pH value was 6.5. It is important to note that coagulation was the main process responsible for the reduction in the value of the specific UV absorbance. The MIEX®DOC pretreatment step increased the SUVA254 in relation to RW (from 5.3 to 5.75 m³/g C-m) while both the coagulation of MIEX® treated water and coagulation of raw water caused a decrease in the SUVA254 value to 1.85 and 2.8 m³/g C-m, respectively.

The positive impact of MIEX®DOC pretreatment on the course and effects of coagulation has been observed by other investigators (Bolto et al. 2002; Drikas et al. 2002, 2003; Singer & Bilyk 2002; Fearing et al. 2004; Boyer & Singer 2005, 2006; Humbert et al. 2005; Kitis et al. 2007). They reported a significant reduction in the applied coagulant dose which was accompanied by minor changes in the pH of water samples (Singer & Bilyk 2002). In addition, it was noted that coagulants and ion exchangers remove different NOM compounds and thus NOM removal can be significantly increased by combining these methods (Bolto et al. 2002).

PAC-adsorption of MIEX®-coagulation treated water

Parameters of the MIEX®-coagulation treated water (turbidity = 0.5 NTU, DOC = 1.7 g C/m³, color = 9 g Pt/m³, UV254 = 5 m⁻¹ and SUVA254 = 5.0 m³/g C-m) used for PAC-adsorption (Figure 7) differ from those described in the previous section (Figure 6). This is because the coagulation was conducted separately and at a larger scale resulting in slightly worse water quality. However, the values of determined parameters remained within the limits of water intended for human consumption. In both
cases the efficiency of the anion exchange and coagulation processes was high enough so that the water did not require further treatment. However, it was found that some fractions of NOM remaining in MIEX®-coagulation treated water can be removed by PAC-adsorption. Even the lowest applied PAC dose (5 mg/dm³) caused a significant reduction in the color (50%), UV₂₅₄ (34%) and SUVA₂₅₄ (26%) while only 11% DOC removal was observed (Figure 7). Increasing the PAC dose resulted in the enhancement of the process efficiency; however, no significant change in NOM removal was observed when the PAC dose was ≥80 mg/dm³. This was found to be consistent with previous results (Szlachta & Adamski 2009).

With a sufficiently large quantity of applied adsorbent (80–160 mg/dm³), it was possible to reduce the value of DOC to 0.2 g C/m³ (removal of 88%), color to 0.4 g Pt/m³ (96%), UV₂₅₄ to 0.25 m⁻¹ (95%) and SUVA₂₅₄ to 1.25 m³/g C-m (58%). The time required for achieving adsorption equilibrium was about 60 min, independent of the PAC dose.

The improvement in water quality following PAC-adsorption was not significant; however, the process removed the DOC fractions that could not be removed through coagulation, irrespective of the applied coagulant dose. In particular, there was a further reduction in the SUVA₂₅₄ value.

The summary of the final results (Figure 8) presents the treatment effects of the unit processes applied separately and in sequence under conditions that could be applied in practice (which differed from the best possible results obtained in this study). In this regard, the following limitations were considered: for PAC-adsorption the dose was...
no greater than 100 mg/dm³ while the contact time did not exceed 2 h; for coagulation a minimum alkalinity of coagulated water was maintained (≥0.2 val/m³ – with the pH of coagulation equaling 6.0, this term was satisfied for each coagulant dose); and in applying the MIEX®DOC process as a preliminary treatment step at least one of the two parameters (dose, bed volume) had a typical value, assumed as 20 cm³/dm³ and 200 BVs for the dose and bed volume, respectively.

**CONCLUSIONS**

Regardless of the applied technology, in the phase of raw water treatment extraordinary solutions were necessary to treat humic rich water (25 g C/m³ as DOC). This implies the use of an especially high coagulant or PAC dose or unusually low bed volume in the case of the MIEX®DOC process. A significant improvement in water quality was achieved by applying coagulation or MIEX®DOC while PAC-adsorption was less effective. In addition, MIEX®DOC pretreatment had a very positive influence on the course and performance of coagulation. Specifically, a higher coagulant efficiency for removing organic compounds was attained as demonstrated by the application of a required coagulant dose four times lower compared to the coagulation of raw water.

In testing the following sequence of processes: MIEX®DOC – coagulation – PAC-adsorption, coagulation was the main treatment technique responsible for the reduction in the SUVA₂₅₄ value. The improvement in water quality after PAC-adsorption was not significant, although the process removed DOC fractions that could not be removed through coagulation over the entire range of the applied coagulant dose. The final values for DOC, color and UV₂₅₄ indicated that there was only a trace of NOM (0.2 g C/m³ as DOC) present in the PAC-treated water. It was also observed that PAC-adsorption achieved a further significant reduction in the specific UV absorbance value.

It has been demonstrated that each of the applied processes played a role in the treatment of humic rich water leading to the almost complete removal of NOM under relatively rational operating conditions.

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