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CHARACTERISTICS OF NATURAL ORGANIC MATTER REMOVED FROM WATER ALONG WITH ITS TREATMENT

The object of this study was to examine the nature of natural organic matter (NOM) removed on each stage of water treatment train used in the “Mokry Dwór” Wrocław Water Treatment Plant (WTP) and to compare obtained results with water treatment efficiencies achieved with the use of membrane ultrafiltration, ion-exchange and UF/ion-exchange integrated processes. In the experiments fractional analysis with the use of polymeric resins (DAX-8, XAD-4 and IRA-958) was used. Obtained results have shown that most (56%) of the raw water NOM was found in fraction characterized by presence of humic and fulvic acids (VHA and SHA fractions). VHA fraction made the most of DOC removed in examined water treatment train and coagulation was mainly responsible for this effect. Integrated process consisting of MIEX[®]DOC ion exchange and PES 10 kDa ultrafiltration turned out to be very effective at high molecular weight hydrophobic compounds removal from water being much less efficient with hydrophilic compounds.

1. INTRODUCTION

Natural organic matter (NOM) is present in all natural water sources in varying concentration. It is described as complex mixture of compounds of vast property diversity, originating from natural decomposition of vegetable and animal remains. Composition of NOM strongly depends on environmental conditions under which it has been formed [1]. Amongst main NOM constituents low molecular weight components such as hydrophilic acids, proteins, amino acids as well as macromolecular compounds like humic and fulvic acids are worth mentioning [2]. They form 3 fractions: hydrophobic, hydrophilic and transphilic ones [3].

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NOM presence in water being treated is undesirable due to many reasons. The most serious issue results from mutagenic and carcinogenic halogenated hydrocarbons creation during chlorination [4, 5]. Moreover, humic substances react during ozonation, introducing into water biodegradable low and high molecular weight compounds supporting further microbial growth in the distribution system [6]. The NOM presence in treated water could also hinder coagulation process by stabilization of dispersed and colloidal particles thus increasing coagulant demand and water treatment cost [7, 8]. Additionally, during adsorption on activated carbon, NOM competes with compounds harmful to humans such as pesticides, reducing removal efficiency of the latter [9]. NOM is also responsible for water color. It could also precipitate in water distribution system worsening the quality of drinking water and, as a consequence, enforcing whole system cleaning. Because of these reasons, NOM should be removed from water so as to provide meeting standards of drinking water. To reach this goal, a number of technological processes are used in water treatment systems where coagulation, adsorption and chemical oxidation are the most elementary techniques of NOM removal [1]. Increasing use of low pressure membrane filtration (microfiltration – MF and ultrafiltration – UF) employed separately or as an integrated with other treatment processes (e.g., ion exchange) could be recently observed. Integrated processes have numerous advantages over independent membrane filtration such as increased NOM removal efficiency, extended membrane lifetime and reduced membrane fouling [10].

Decreasing NOM content in water requires extensive study on NOM nature as well as developing efficient removal techniques. Dividing NOM substances present in water into fractions that could be submitted to further analysis is an important issue in these efforts. One of the commonly applied methods of fractionation elaborated by Leenheer and Huffman [11] and Malcolm and MacCarthy [12] utilizes adsorption on nonionic macroporous synthetic resins. Original method was modified many times over the years and nowadays, procedure developed by Chow et al. [13] employing XAD resins is most commonly applied. Predominantly Supelite DAX-8, Amberlite XAD-4 and Amberlite IRA-958 or other having similar properties polymeric adsorbents are used. This procedure divides dissolved NOM into 4 groups [14]:

- very hydrophobic acids (VHA) adsorbing onto DAX-8 resin,
- slightly hydrophobic acids (SHA) adsorbing onto XAD-4 resin,
- hydrophilic charged compounds (CHA) adsorbing onto IRA-958,
- hydrophilic neutral compounds (NEU) not absorbing onto any of the aforementioned resins.

Application of this procedure allows NOM fractionation in a comparatively short time using relatively small sample volume.

Taking into account considerations mentioned above, it was advisable to undertake the effort to identify NOM removed on each stage of WTP process train as well as in membrane ultrafiltration, ion exchange with the use of MIEX resin and integrated water treatment systems joining ion exchange and ultrafiltration.

2. MATERIALS AND METHODS

Feed solutions. Experiments were conducted using river water samples taken from the Oława River fed by the tributary Nysa Kłodzka River (Poland). Both river waters, joint by the Michałów channel system, are taken by the “Mokry Dwór” Wrocław WTP. The treatment plant produces daily 60 000 m³ of water, but designed capacity is twice that value. The treatment processes include coagulation, sedimentation, filtration, ozonation, activated carbon adsorption and chlorination. Water samples used in this experiment were collected after selected consecutive treatment processes. Scheme of the water treatment process train applied in the “Mokry Dwór” Wrocław WTP is shown in Fig. 1. Water samples were taken on intake, after sedimentation, after sand filtration, after sorption and on plant outlet.

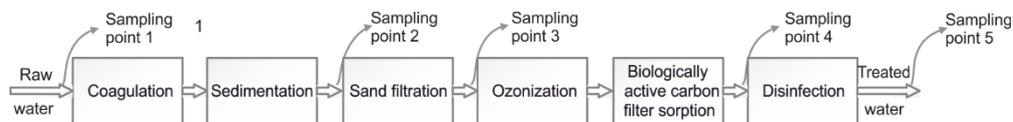


Fig. 1. Water treatment process train applied in the “Mokry Dwór” Wrocław WTP

Ion exchange process. The efficiency of NOM removal in the ion-exchange process was investigated using MIEX[®] (Orica Watercare), polyacrylic, macroporous, strong base anion exchange resin. Resin characteristics can be found in literature [15–17]. In these tests the water taken after sedimentation from the “Mokry Dwór” WTP was fed with proper amount of resin. Experiments with the use of MIEX[®] resin were conducted at a 5 cm³/dm³ and 10 cm³/dm³ doses. The solution with resin was placed on a mechanical stirrer and mixed for 20 min at 135 rpm. The sample was then left for sedimentation for 30 min.

Ultrafiltration process. Ultrafiltration Microdyne-Nadir flat-sheet membranes made of polyethersulfone (PES) and regenerated cellulose (C) were used. A cut-off of the membranes amounted to 5 and 10 kDa. A tubular ceramic membrane of 15 kDa supplied by Tami Ind. made of zirconium-titanium oxides was used as well. PES and C membrane filtration was carried out on a dead-end bench-scale installation [18] under 0.3 MPa transmembrane pressure. Ceramic membrane ultrafiltration tests were performed on a cross-flow lab-scale unit [18] under 0.3 MPa transmembrane pressure and 1.9 m/s of linear velocity. As a feed solution for all ultrafiltration tests water taken after sedimentation process from the “Mokry Dwór” WTP treatment train was used.

Integrated ion exchange – ultrafiltration process. Ion-exchange ultrafiltration process was conducted with the use of MIEX[®] resin (10 cm³/dm³ dose). Decanted solution

was then ultrafiltered with the use of ceramic 15 kDa or polymeric PES 10 kDa membranes. Process conditions for ion exchange and ultrafiltration were identical to the mentioned above.

Fractionation of NOM. Fractionation techniques based on non-ionic and ionic resins made it possible to obtain four different fractions of the NOM. In order to determine NOM type removed from water on each water treatment stage, three following polymeric adsorbents were used: Supelite DAX-8 (Supelco), Amberlite XAD-4 and IRA-958 (Rohm and Haas). Adsorbent characteristics provided by the manufacturers can be found in [19–21].

Fractionation of NOM using polymeric adsorbents was performed in 3 columns, each containing 15 cm³ of fresh, pre-cleaned DAX-8, XAD-4 or IRA-958 resin as a suspension. 500 cm³ of examined solution was acidified before fractionation to pH 2 with the use of 0.1 M HCl. The volumetric flux during fractionation was kept at 3 cm³/min (0.2 BV/min). Acidified solution was infiltrated through DAX-8 and XAD-4 resin columns consecutively. XAD-4 column permeate was alkalized using NaOH to pH 8, then infiltrated through an IRA-958 column. For each column, initial 30 cm³ of permeate were rejected, and 100 cm³ were collected for DOC measurement.

The amounts of VHA, SHA, CHA and NEU fractions in g C/m³ were calculated as follows:

$$[\text{VHA}] = [\text{DOC}]_{\text{raw sample}} - [\text{DOC}]_{\text{DAX-8}}$$

$$[\text{SHA}] = [\text{DOC}]_{\text{DAX-8}} - [\text{DOC}]_{\text{XAD-4}}$$

$$[\text{CHA}] = [\text{DOC}]_{\text{XAD-4}} - [\text{DOC}]_{\text{IRA-985}}$$

$$[\text{NEU}] = [\text{DOC}]_{\text{IRA-985}}$$

where: [DOC]_{raw sample} – DOC concentration in the examined solution, [DOC]_{DAX-8} – DOC concentration in the solution after filtration through a DAX 8 resin bed, [DOC]_{XAD-4} – DOC concentration in the solution after filtration through DAX 8 and XAD-4 resin beds, [DOC]_{IRA-985} – DOC concentration in the solution after filtration through DAX-8, XAD-4 and IRA-958 resin beds.

For fractionation the following samples were used: water samples taken from Mokry Dwór WTP (cf. Fig. 1) and water taken after sedimentation from the WTP and purified in: MIEX[®] DOC ion exchange, membrane ultrafiltration, and ion-exchange (ultrafiltration integrated process).

Analytical methods. NOM in all samples was determined by measuring colour, absorbance at 254 nm (HITACHI U-1900), total (TOC) and dissolved organic carbon (DOC) concentration (HACH IL550 TOC-TN).

3. RESULTS

3.1. FRACTIONATION OF NOM REMOVED ON EACH STAGE OF WTP PROCESS TRAIN

In Table 1, water quality parameters in water samples taken from the treatment train are given. It could be noticed that coagulation and sedimentation are responsible for removing most of the DOC from the raw water.

Table 1

Properties of WTP water samples from Mokry Dwór

| Solution | Sampling point | DOC [g C/m ³] | Colour [g Pt/m ³] | Absorbance [cm ⁻¹] | Turbidity [NTU] | pH | SUVA ^a [dm ³ ·mg ⁻¹ ·m ⁻¹] |
|----------|-----------------------|---------------------------|-------------------------------|--------------------------------|-----------------|-----|---|
| 1 | WTP intake | 7.21 | 8.32 | 0.102 | 4.98 | 7.9 | 1.41 |
| 2 | after sedimentation | 4.32 | 5.10 | 0.068 | 1.06 | 7.5 | 1.57 |
| 3 | after sand filtration | 3.48 | 4.52 | 0.059 | <0.5 | 7.5 | 1.69 |
| 4 | after sorption | 3.02 | 1.87 | 0.035 | <0.5 | 7.5 | 1.16 |
| 5 | WTP outlet | 2.88 | 1.58 | 0.029 | <0.5 | 7.7 | 1.00 |

The DOC level has been decreased during these processes by 2.98 g C/m³, while during the remaining ones, following coagulation and sedimentation only by 1.44 g C/m³ altogether (Fig. 2). The efficiency of DOC removal amounted to 40.1%, 51.7%, 58.1%, and 60.1% for samples taken after sedimentation, filtration, adsorption, and from WTP outlet, respectively. The efficiency of colour removal in these samples amounted to 38.7%, 45.7%, 77.5%, and 81%, respectively.

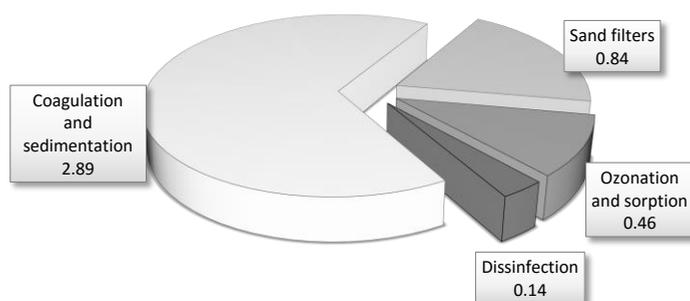


Fig. 2. DOC removal [g C/m³] on each process train in the “Mokry Dwór” Wrocław WTP

The specific UV absorbance (SUVA) of raw water is generally low (<2 dm³·mg⁻¹·m⁻¹) indicating low aromatic content of NOM in the water samples [22, 23]. Notable, there was a decrease in the SUVA values through the water treatment train which indicated a decrease in the aromatic component of NOM in the water samples.

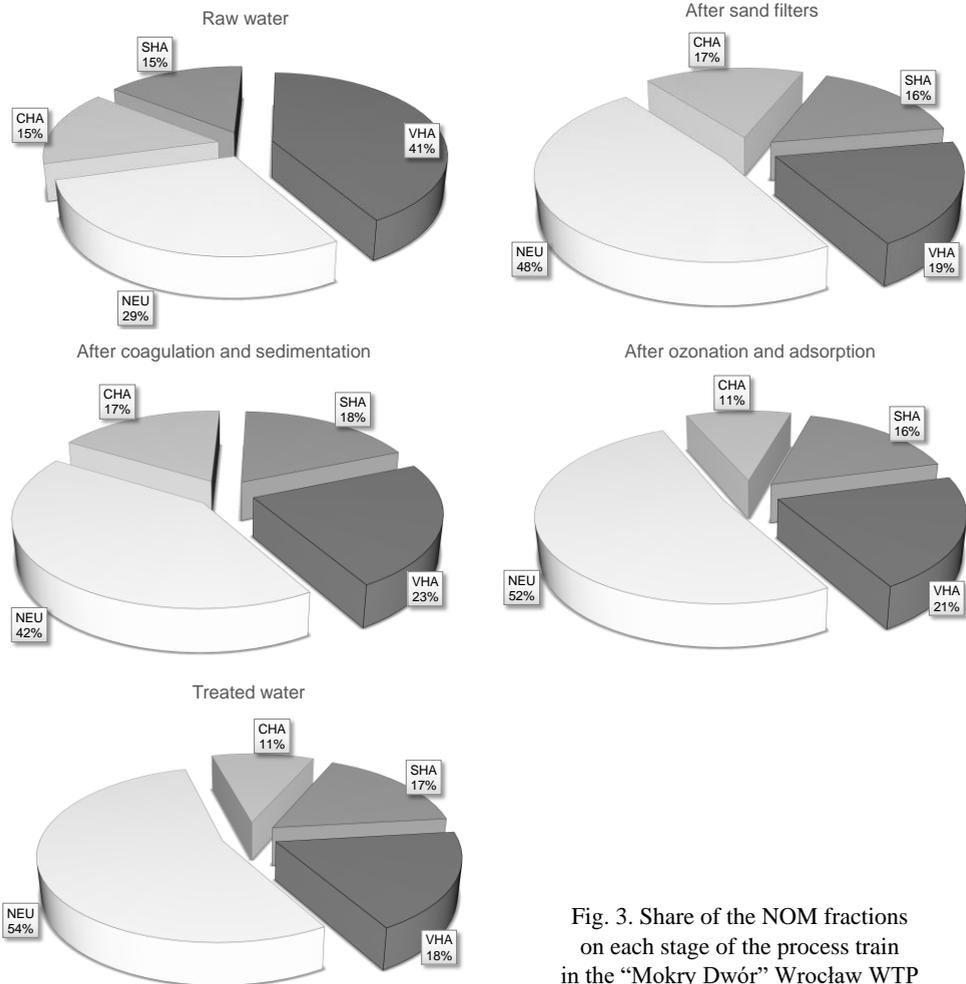


Fig. 3. Share of the NOM fractions on each stage of the process train in the “Mokry Dwór” Wrocław WTP

Based on the fractionation results (Fig. 3), it was observed that NOM present in solution 1 (WTP intake) is dominated by VHA and SHA fractions (56%) typical of humic and fulvic acids [24]. The share of the CHA fraction was 15% while that of the NEU fraction that is known for containing electrically inert hydrophilic compounds of low molecular weight [24] made up 29% of NOM. NOM should be removed during water treatment up to such level to meet drinking water quality standards. To achieve this goal, various processes are employed in the WTP process train. The most commonly applied and basic methods are: coagulation, activated carbon adsorption and chemical oxidation. The efficiency of particular treatment processes in various NOM fractions removal differs.

The contents of NOM fractions present in water at each stage of treatment differ significantly from that of raw water. Decrease of dominant VHA fraction (41% in raw water, 21% in treated water) in favor of NEU (29% and 50%, respectively) is noteworthy. Application of coagulation influenced mostly VHA fraction (70% of removed DOC, Fig. 4) while other fractions were removed from water to much less extent.

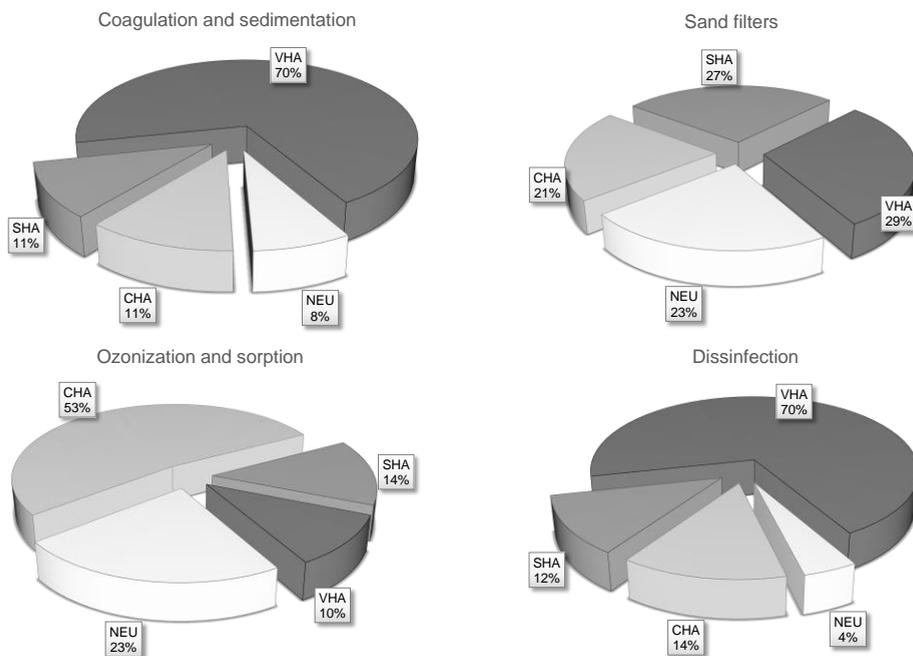


Fig. 4. Share of NOM fractions in TOC being removed from water on each process train in the “Mokry Dwór” Wrocław WTP

Chemical oxidation is frequently applied in water treatment technology. The “Mokry Dwór” Wrocław WTP uses ozone as an oxidizing agent. Ozone partially degrades NOM by breaking the bonds of the NOM structure and convert organic carbon to easily adsorbing and biodegradable. Ozonation of natural waters containing NOM causes ozonation by-product formation. Due to this issue, activated carbon adsorption is recommended as an immediate step after oxidation, especially in the form of biologically active carbon filtering that ensures adsorption as well as biodegradation of oxidation by-product. Ozonation and adsorption conducted at pH typical of natural waters results in removal of DOC (by 6%), colour intensity (by 32%) and in decrease of absorbance at 254 nm (by 24%, Fig. 5). The CHA fraction made 53% of DOC removed during ozonation and adsorption while NEU, SHA and VHA fractions made 23%, 14% and 10%, respectively. It is clearly visible that in these processes, preferentially charged hydrophilic compounds were removed.

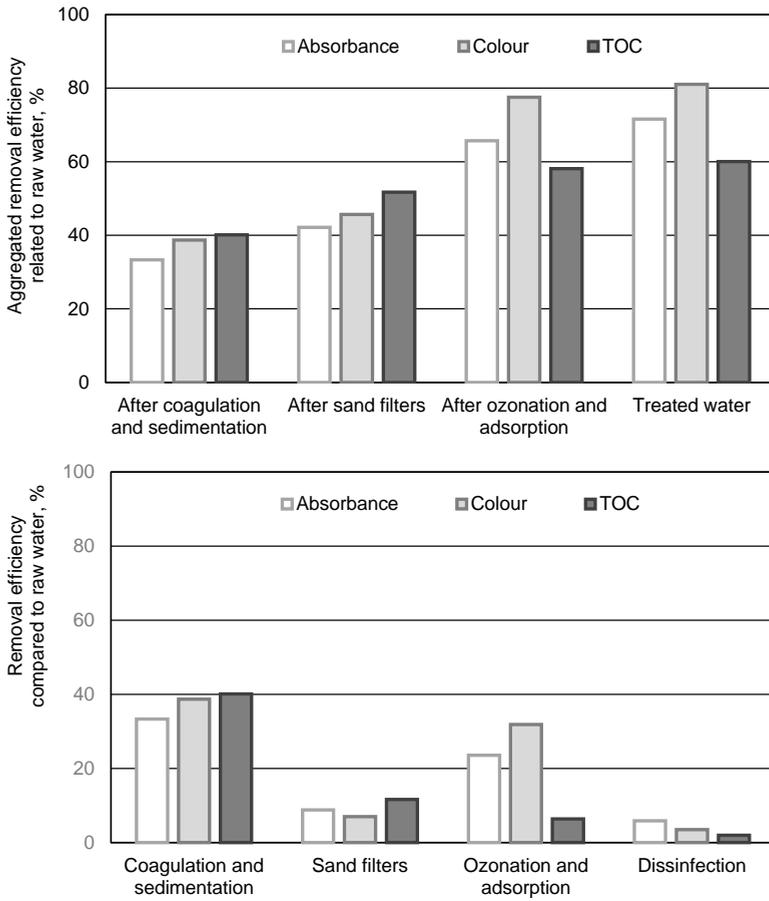


Fig. 5. Efficiency of NOM removal (aggregated and attributed to each stage of WTP process train)

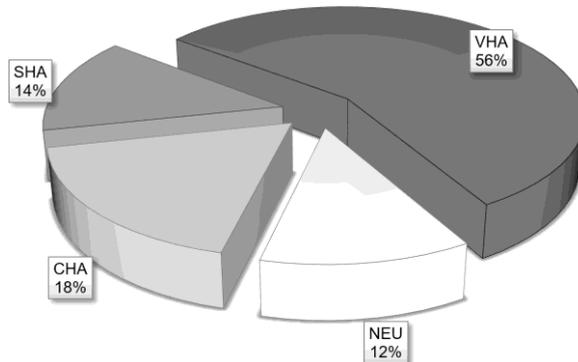


Fig. 6. Composition of NOM removed in the "Mokry Dwór" Wrocław WTP when compared to raw water

VHA constituted most of NOM removed in the “Mokry Dwór” Wrocław WTP (56%, Fig. 6). Coagulation and sedimentation is responsible for removing most of NOM (as well as VHA). Entire WTP process train removes 90% of DOC, 66% and 57% of CHA and SHA fractions are removed, respectively, while NEU fraction content decreased only by 23% when compared to raw water (Fig. 7).

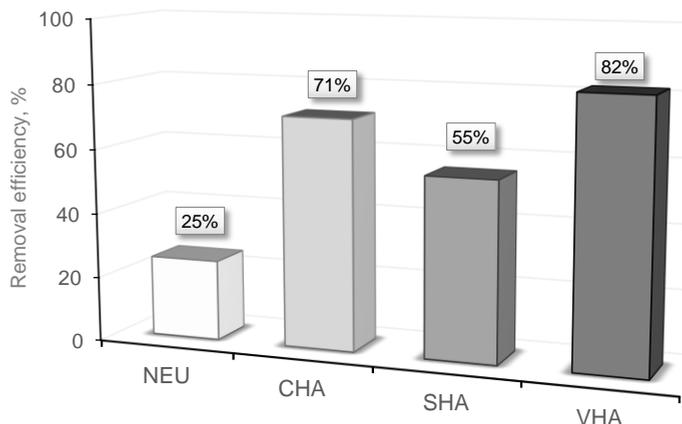


Fig. 7. NOM fraction removal efficiency in the “Mokry Dwór” Wrocław WTP

3.2. INFLUENCE OF ADDITIONAL PROCESS APPLICATION ON NOM FRACTIONS

Integrated processes being combinations of membrane filtration and physical, chemical or biological treatment are recently more and more often used in WTPs. The purpose of utilizing integrated process is to improve NOM removal, prolong membrane lifetime and reduce fouling. Coagulation and ion exchange are most frequently coupled with membrane filtration for natural water treatment. In subsequent studies, we examined the effectiveness of NOM removal with the use of ion exchange, ultrafiltration, and integrated ion exchange/ultrafiltration processes, from water pretreated in coagulation and sedimentation. The properties of water samples treated in various investigated processes are presented in Table 2.

Based on results presented in Table 2, it is visible that all investigated processes enhanced the efficiency of NOM removal. Water polishing with the use of MIEEX[®] ion-exchange resin was more effective in removal of organic substances (R_{DOC} 59.5–63.9%) as compared to ultrafiltration membranes (R_{DOC} 50.9–53.9%). Integration of both unit processes resulted in improvement of water quality (R_{DOC} 84.1–86.2%). Moreover, changes of SUVA values suggest that the use of integrated processes decreased to the greatest extent the concentration of aromatic components of NOM.

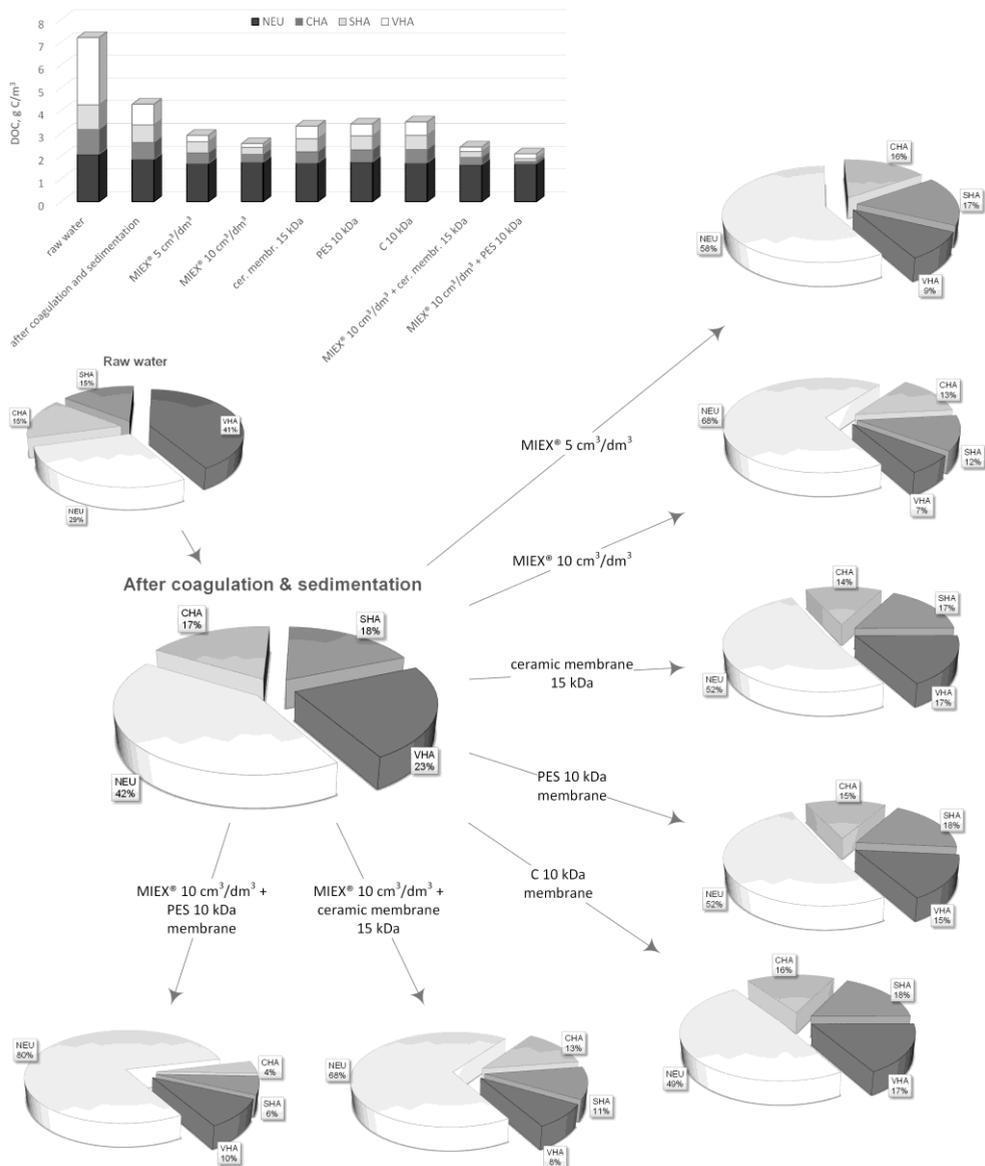


Fig. 8. Share of NOM fraction in solutions treated using various methods

The most effective integrated process in terms of NOM removal measured as decrease in DOC concentration was MIEX[®] DOC ion exchange followed by PES 10 kDa membrane filtration (Fig. 8). Usage of 15 kDa ceramic membrane instead of PES 10 kDa resulted in slightly inferior but still very good efficiency. Ion exchange with the use of 10 cm³/dm³ MIEX[®] resin or integrated process enabled DOC removal below

2.88 g C/m³ which is the DOC concentration in the “Mokry Dwór” Wrocław WTP treated water (2.60, 2.40, and 2.17 g C/m³ for MIEX[®]DOC 10 cm³/dm³, MIEX[®]DOC + 15 kDa ceramic membrane and MIEX[®]DOC + PES 10 kDa, respectively).

Table 2

Water quality parameters for samples treated in various processes
(samples pretreated in coagulation and sedimentation)

| Process | DOC [g/m ³] | Colour [g Pt/m ³] | Absorbance [cm ⁻¹] | SUVA [dm ³ ·mg ⁻¹ ·m ⁻¹] |
|--|----------------------------|----------------------------------|-----------------------------------|---|
| WTP intake | 7.21 | 8.32 | 0.102 | 1.41 |
| After coagulation and sedimentation | 4.32 | 5.10 | 0.068 | 1.57 |
| MIEX [®] DOC, 5 cm ³ /dm ³ | 2.92 | 1.64 | 0.031 | 1.06 |
| MIEX [®] DOC, 10 cm ³ /dm ³ | 2.60 | 1.43 | 0.025 | 0.96 |
| Ceramic membrane 15 kDa | 3.32 | 2.08 | 0.039 | 1.17 |
| Polymeric membrane PES 10 kDa | 3.52 | 2.15 | 0.043 | 1.22 |
| Polymeric membrane C 10 kDa | 3.54 | 2.09 | 0.048 | 1.35 |
| MIEX [®] DOC 10 cm ³ /dm ³ + ceramic 15 kDa | 2.40 | 1.32 | 0.022 | 0.92 |
| MIEX [®] DOC 10 cm ³ /dm ³ + PES 10 kDa | 2.17 | 1.15 | 0.020 | 0.92 |

Irrespective of the examined process, significant change in NOM fraction in treated water compared to water after coagulation and sedimentation could be observed: the share of NEU fraction increased from 42% to 51–80%. It is caused by preferential removal of hydrophobic, high molecular weight compounds (decrease of VHA content by 33–49%) and low efficiency of elimination of hydrophilic fraction (NEU by 9–19%).

4. SUMMARY

Meeting constantly growing drinking water quality standards requires efficient NOM removal during treatment process. These compounds contain hydrophilic and hydrophobic, charged or electrically inert fractions. NOM removal efficiency improvement makes it important to identify compounds present in treated water. Experiments carried out on surface water from water intake at the “Mokry Dwór” Wrocław WTP have shown that VHA and SHA fractions known for presence of humic and fulvic acids made up 56% of DOC (remaining CHA and NEU made up 15% and 29%, respectively). It has been shown that 56% of DOC removed in WTP process train was in the form of VHA fraction, and was eliminated from solution mostly during coagulation. It was observed that the improvement of water quality, i.e. enhancement of NOM separation might be obtained with the application of ion exchange or ultrafiltration processes as well as integrated processes combining both listed previously. Obtained results indicated that, among examined integrated processes, most efficient in terms of NOM removal was MIEX[®]DOC ion exchange followed by PES 10 kDa or 15 kDa ceramic

membrane ultrafiltration. Application of these processes enabled the removal of preferential hydrophobic high molecular weight compounds with simultaneous elimination of inferior hydrophilic fraction.

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