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The properties of NOM particles removed from water in ultrafiltration, ion exchange and integrated processes

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ABSTRACT

Natural organic matter (NOM) is a complex mixture of organic compounds consisting of various elemental compositions and chemical structures. The different NOM fractions exhibit different properties in terms of treatability. This research focused on identification of NOM fractions removed from water in ion exchange, ultrafiltration and ion exchange/ultrafiltration integrated processes. Analysis based on fractionation with the use of XAD resins and membrane techniques as well as elemental analysis of organic matter was performed. Obtained results showed that the application of integrated processes allowed for a joint effect of low molecular weight compound removal by ion exchange processes with high molecular weight particle separation by ultrafiltration. Fractional analysis demonstrated a poor separation of hydrophilic fractions and effective removal of hydrophobic compounds by ultrafiltration and ion exchange, while integrated processes effectively removed both hydrophobic and charged hydrophilic NOM fractions. Elemental analysis showed a dominance of fulvic acids in the examined solution.

Keywords: Natural organic matter; Ultrafiltration; Polymeric membranes; Fractionation; Elemental analysis

1. Introduction

Natural organic matter (NOM) is commonly found in virtually every natural water source as well as in soils and sediments. NOM is described as a complex mixture of compounds originating from the decomposition of vegetal and animal remains. The composition of NOM depends mainly on environmental conditions and the age of the original material [1]. Compounds of relatively low molecular weight (e.g. proteins, amino acids) as well as humic substances (humin, fulvic and humin acids) are found to be the main components of NOM [2,3].

NOM influences the properties of water and their concentration should be controlled in water intended for human consumption. During water treatment, several processes are used in order to remove these substances from water. The most popular are coagulation and adsorption; however, nowadays for this purpose, ion exchange and membrane separation are increasingly being used. As already mentioned, NOM is a complex mixture of organic compounds consisting of various elemental compositions and chemical structures. The different NOM fractions exhibit different

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properties in terms of treatability. The efficiency of NOM separation in various processes, as a rule, is determined on the basis of the change in total organic carbon (TOC) or dissolved organic carbon (DOC), colour intensity or UV absorbance at 254 nm. TOC (DOC) concentration is the most reliable method for determining the total amount of NOM, UV adsorption at 254 nm monitors the amount of NOM fractions containing aromatic structures in their molecules, while the colour of water is related to the presence of large fractions of NOM. However, for more detailed knowledge of the properties of matter removed in particular water treatment processes, more advanced techniques should be used.

One of the basic NOM analysis methods is the elemental analysis, which allows the determination of NOM elemental composition [3]. The main stage of this method is analysis of sample combustion results that leads into percentile distribution of coal, nitrogen, sulphur and hydrogen in a sample. On these grounds, O/C, H/C and C/N ratios are calculated and used to identify organic substances of varying origin, changes in structure are monitored and the approximate molecular formula is estimated. Unfortunately, considering chemical complexity, NOM elemental analysis results are limited only to a general view of their structure and origin. The correct choice of analysis parameters as well as their consistent application is essential in order to obtain adequate molecular weight distribution results with this method. It was observed that changes in the pH, concentration and ion strength of a solution may cause conformation modifications of examined compounds, and consequently give different distribution results for the same samples [4].

Comprehensive research on NOM structure and properties requires its isolation from the water matrix. Isolation comprises three stages: condensation, purification and fractionation. The most commonly applied NOM condensation and isolation methods are XAD resin adsorption, diethylaminoethyl cellulose (DEAE-C) adsorption, vacuum evaporation, precipitation, extraction, freezing, ultrafiltration, etc. [5–8]. Isolation procedures are applied in order to acquire NOM in unaltered form as found in environment. Unfortunately, each of the mentioned isolation methods leads to changes in the isolated substance structure [9]. Besides, classification of organic matter depends on the applied method and chemical conditions used in the isolation procedure. Nowadays, the widely used procedure of NOM isolation into fractions of different hydrophilic and hydrophobic character is based on column chromatography on non-ionic XAD resins (or their analogues). This method separates NOM into four fractions: very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilic compounds (CHA) and neutral hydrophilic substances (NEU) [10–12]. The XAD fractionation method has been modified many times, but nowadays, the procedure described by Chow et al. [13] is most commonly employed. With this procedure, it is possible to fractionate NOM in a relatively short time with the use of a small sample volume.

NOM isolation and fractionation is also possible with the use of membrane processes. In contrast to the previously described method, compounds are classified into fractions based on their molecular weight [14,15].

Taking these considerations into account, it was advisable to undertake the characteristics of NOM removed in ion exchange, ultrafiltration and ion exchange/ultrafiltration integrated processes with the use of XAD resins and membrane techniques. Besides, in order to determine the NOM elemental composition of organic substances removed in particular processes, elemental analysis was carried out.

2. Materials and methods

The experiments were carried out on water taken from a humic acid-rich stream flowing from a peat bog in the Stołowe Mountains (Poland) (sampling point: 50°27′29.97″ N; 16°23′16.87″ E). The colour intensity of the feed solution was 203.3 g Pt/m^3, UV 254 nm absorbance was 1.61 cm^{-1} and DOC concentration was equal to 33.7 g C/m^{-3}.

The ion exchange tests were run with the use of MIEX®DOC anion exchange resin at a 5 cm^3/dm^3 dose. The model 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.

The ultrafiltration experiments were done with the use of ceramic ZrO_2/TiO_2 membrane made by Tami Industries. The membrane molecular weight cut-off (MWCO) value was 50 kDa. The membrane transport and separation properties were examined using the cross-flow J.A.M. INOX PRODUKT laboratory installation with transmembrane pressure (TMP) equal to 0.3 MPa and 1.9 m/s of linear flux velocity.

The integrated process comprised of following individual processes: raw water was at first subject to ion exchange followed by sedimentation with a final ultrafiltration of the supernatant sample.

The organic matter concentration in raw and treated samples was evaluated by measuring the DOC concentration, UV absorbance at 254 nm and colour intensity.

NOM types present in raw water and treated in ion exchange, ultrafiltration and integrated processes were examined on the basis of organic carbon content in samples subjected to fractioning on Supelite DAX-8 [16], Amberlite XAD-4 [17] and Amberlite IRA-958 [18] resins. The use of these resins made it possible to fractionate natural organic substances into four groups:

(1) VHA adsorbed by the DAX-8 resin,
(2) SHA adsorbed by the XAD-4 resin,
(3) CHA adsorbed by the IRA-958 resin,
(4) NEU not adsorbed by any of these resins.

CHA is a mixture of proteins, amino acids and anionic polysaccharides, whereas the NEU are ascribed to low molecular weight carbohydrates, aldehydes, ketones and alcohols. The VHA and SHA however are attributed to higher MW humic and fulvic acids [13].

Fractionation of NOM using polymeric adsorbents was performed in three columns (Fig. 1). Fifteen cubic meter of fresh, pre-cleaned resin was placed into columns as a suspension. Five hundred cubic meter of examined solution was acidified before fractionation to pH 2 with the use of 0.1 N HCl. The volumetric flux value during fractionation was equal to 3 cm^3/min (0.2 of bed volume). 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 a IRA-958 column. For each column, an initial 30 cm^3 of permeate was rejected, and 100 cm^3 was collected for DOC measurement.

The amount of VHA, SHA, CHA and NEU fractions (c_{VHA}, c_{SHA}, c_{CHA}, c_{NEU}, respectively) was calculated using the following equations:

$$c_{\mathrm{VHA}} = c_{\mathrm{r}} - c_{\mathrm{DAX-8}}, \quad \mathrm{g\ C/m^{-3}}$$

$$c_{\mathrm{SHA}} = c_{\mathrm{DAX-8}} - c_{\mathrm{XAD-4}}, \quad \mathrm{g\ C/m^{-3}}$$

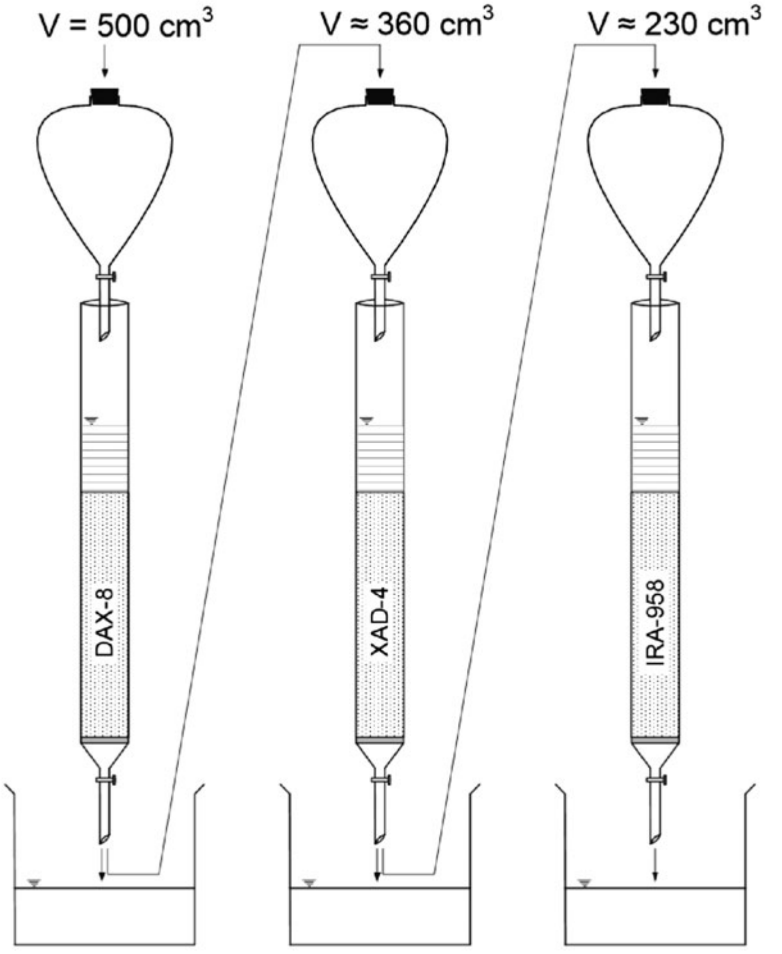

Fig. 1. NOM fractionation schema.

$$c_{\mathrm{CHA}} = c_{\mathrm{XAD-4}} - c_{\mathrm{IRA-958}}, \quad \mathrm{g\ C/m^{-3}}$$

$$c_{\mathrm{NEU}} = c_{\mathrm{IRA-958}}, \quad \mathrm{g\ C/m^{-3}}$$

where c_r—DOC concentration in the examined solution, g C/m^{-3}, $c_{\mathrm{DAX\text{-}8}}$—DOC concentration in the solution after filtration through a DAX-8 resin bed, g C/m^{-3}, $c_{\mathrm{XAD\text{-}4}}$—DOC concentration in the solution after filtration through DAX-8 and XAD-4 resin beds, g C/m^{-3}, and $c_{\mathrm{IRA\text{-}958}}$—DOC concentration in the solution after filtration through DAX-8, XAD-4 and IRA-958 resin beds, g C/m^{-3}.

NOM fractionation by molecular weight was carried out on raw water filtered through a 0.45 μm filter, and on treated water after individual ion exchange, ultrafiltration and integrated processes. Fractionation was carried out with the use of regenerated cellulose ultrafiltration membranes with the following MWCO values: 1, 5 and 10 kDa (Microdyn Nadir). The procedure of fractionation with the use of membranes is depicted in Fig. 2.

NOM distribution was determined on the basis of DOC concentrations in each permeate, thus enabling the calculation of each of the four fractions share in the examined samples:

(1) retained by 1 kDa membrane (later referred to as “<1 kDa”),
(2) retained by 5 kDa membrane, but not retained by 1 kDa membrane (“1–5 kDa”),
(3) retained by 10 kDa membrane but not retained by 5 kDa membrane (“5–10 kDa”; together with a “1–5 kDa” fraction later referred to as “1–10 kDa”),
(4) not retained by 10 kDa membrane (“>10 kDa”).

An Amicon 8,400 (Millipore) lab-scale set-up was used for NOM fractionation. The TMP used was 0.1 MPa.

In order to ascertain the elemental composition of humin and fulvic acids that make up NOM, elemental analysis yielding the content of carbon (C), nitrogen (N), sulphur (S) and hydrogen (H) was performed with the use of a Thermo Scientific FLASH 2000 analyzer. Oxygen content (O) was calculated based on equation:

$$\mathrm{O} = 100\% - (\mathrm{C} + \mathrm{H} + \mathrm{N} + \mathrm{S}),\ \% \tag{1}$$

On the basis of these values, O/C, H/C and C/N atomic ratios have been calculated.

3. Results

On the basis of results obtained in the integrated process tests, it can be concluded that the final water quality was mostly influenced by the joint effect of ion exchange and sieving by the membrane. Comparison of DOC, UV 254 nm absorbance and colour removal from water by individual processes and integrated processes is shown in Fig. 3. For example, while DOC removal rates in membrane filtration and ion exchange amounted to 75 and 72%, respectively, the integrated process upgraded this value to 90%. The observed effect confirms a high efficiency of the ion exchange/ultrafiltration integrated process in NOM removal from water.

All parameters typically used for characterization of water treatment efficiency do not inform about the nature and chemical properties of removed substances. This is why fractionation of NOM particles is very important. It may give some information about the mechanisms of organic substance removal, and in particular, the examined processes. On the basis of ion exchange fractionation results (Fig. 4), it can be stated that in the examined solution VHA and SHA fractions, characteristic for humic and fulvic acids, make up 54% of NOM content. Five percentage of NOM was found to be a CHA fraction and 41% was a NEU fraction, consisting of low molecular weight hydrophilic, neutral charge compounds. The NEU fraction includes short-chain aliphatic amines, alcohols, aldehydes, esters, ketones, short-chain aliphatic amides, polyfunctional alcohols, carbohydrates, cyclic amides and polysaccharides [19]. It is usually the predominating one in natural waters. As a result of ultrafiltration with the use of 50 kDa membrane, the VHA, SHA, CHA and NEU content is removed by 88, 82, 77 and

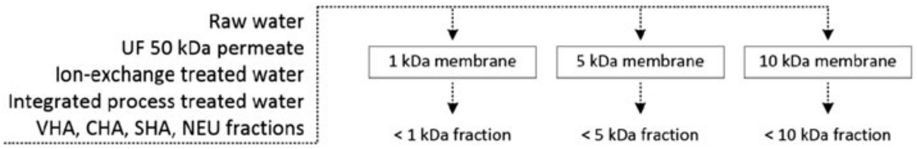

Fig. 2. NOM fractionation by molecular weight.

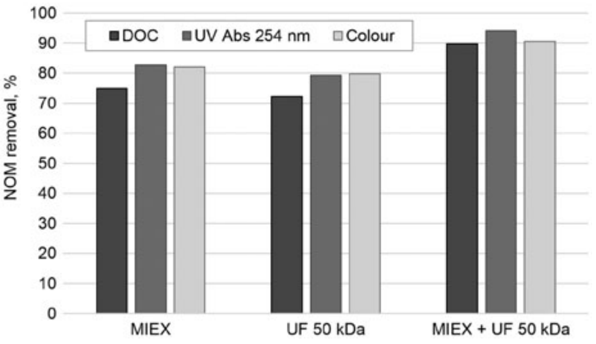

Fig. 3. Comparison of DOC, UV 254 absorbance and colour removal in individual ion exchange, membrane filtration and integrated processes.

59%, respectively. It can be deduced that membrane filtration mainly separated hydrophobic, high molecular weight compounds and was not as effective with the NEU fraction. On the other hand, MIEX® resin preferentially separates VHA, SHA and CHA, but NEU content is not so intensively lowered in ion exchange processes. Water treated in ion exchange/ultrafiltration integrated processes was also analysed for fraction content. The joint effect of both processes allowed a significant removal of VHA, SHA and CHA. The removal of charged compounds can be attributed to ion exchange playing an influential role in the water treatment process. The NEU fraction was always the dominant fraction and did not show a

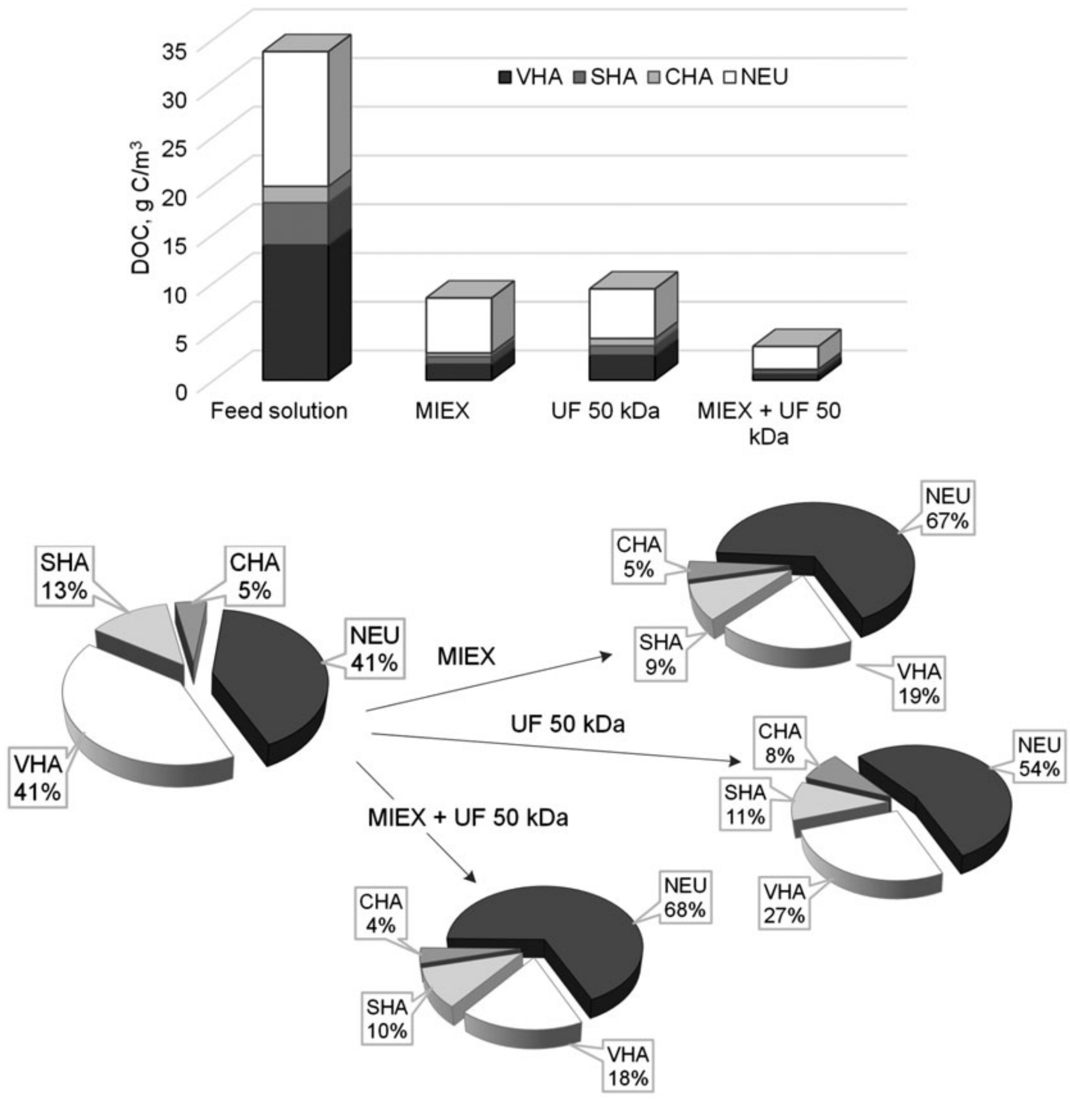

Fig. 4. The amount of each NOM fractions present in the feed solution and water treated in ion exchange, ultrafiltration and integrated processes.

significant reduction throughout the treatment. There was an overall decrease in the VHA, CHA and SHA fraction amounts during the treatment of water, and therefore an overall decrease in the content of DOC was observed. These results are in accordance with the observations of Vieira et al. [20] who consider NEU fractions as the most difficult to remove.

The results of mass distribution analysis for feed solution, 50 kDa membrane permeate, water treated in MIEX®DOC and in integrated processes can be found in Fig. 5.

Analysis of NOM mass distribution found in the feed solution (Fig. 5) shows that in raw water and in each fraction except NEU, the ">10 kDa" dominates (46% in raw water, 60% in VHA, 49% in SHA, 78% in CHA and only 23% in NEU). On the other hand, particles "<1 kDa" (37% in raw water) are dominant in NEU fractions, while being much less frequent in others (27% in VHA, 32% in SHA, 15% in CHA and 58% in NEU). The mass distribution for hydrophobic fractions (VHA and SHA) was similar and had ">10 kDa" and "<1 kDa" particles dominant over contaminants identified as "1–10 kDa" which were much less frequent. A similar distribution was observed for hydrophilic charged fractions (CHA). NEU fractions were found to be different: nearly 60% of the total DOC was present as "<1 kDa" particles, ca. 20% as "1–10 kDa" and 23% as ">10 kDa".

Fig. 5 also presents the mass distribution of contaminants present in 50 kDa membrane permeate and isolated NOM fractions. Based on the results, it could be inferred that the ">10 kDa" particles share dropped from 46 to 34%, the "1–10 kDa" particle share also dropped from 17 to 8% while "<1 kDa" increased from 31 to 58%. When compared with raw water, ultrafiltration processes did not significantly change the amount of VHA, SHA and CHA fractions. On the other hand, NEU fraction molecular weight distribution changed: the ">10 kDa" and "1–10 kDa" contribution changed from 23 and 12% to 19 and 9%, respectively, while the "<1 kDa" share increased from 50 to 79%.

Molecular weight distribution in water treated in ion exchange with the use of MIEX® resin shows that this process significantly changed the "<1 kDa" molecule share (37–12%). Besides, the "1–5 kDa" and "5–10 kDa" contribution also dropped while ">10 kDa" increased. These observations confirm earlier reports [21,22] about visibly better removal of contaminants with low molecular weight by ion exchange with the use of ion exchange when compared to other water treatment processes. Analysis of NOM fractions in treated water demonstrated that the ">10 kDa" share in VHA and SHA fractions increased to 65 and 75%, respectively, while the CHA contribution was lowered by 10%. Different distribution was observed for NEU fractions that included hydrophilic low molecular weight particles. In comparison to raw water, the "> 10 kDa" fraction share increased significantly from 23 to 88% at the expense of the "<1 kDa" particle contribution that decreased from 58 to 8%. For the "1–10 kDa" fraction, a lesser impact was observed.

Molecular weight distribution of organic contaminants after a MIEX®DOC/ultrafiltration integrated process and its isolated NOM fractions showed that joint membrane filtration and ion exchange did not change

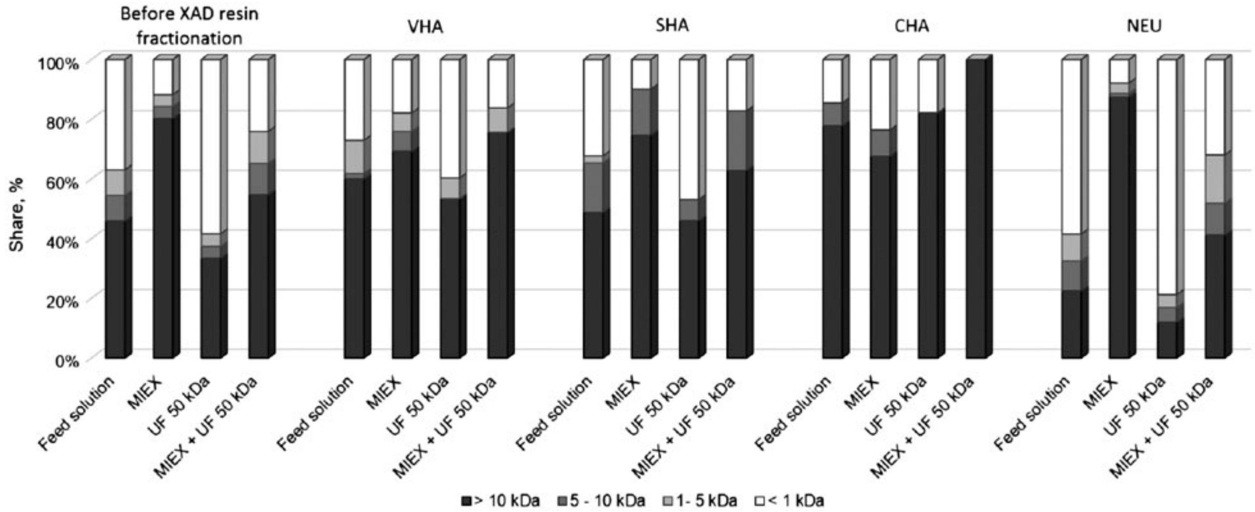

Fig. 5. Molecular weight distribution of NOM in model solution, UF 50 kDa permeate, MIEX®-treated water, integrated process-treated water and its NOM fractions.

Table 1
Elemental composition and atomic ratio of NOM present in raw and treated water and isolated using molecular weight fractionation

		Elemental composition (weight %)					Atomic ratio		
Sample	Fraction	C	H	N	S	O	O/C	H/C	N/C
Feed solution	Total	49.2	4.0	1.8	1.1	43.9	0.67	0.98	0.029
	<1 kDa	51.8	3.5	1.6	0.9	42.2	0.61	0.81	0.025
	1–5 kDa	50.1	3.9	1.9	1.0	43.1	0.65	0.93	0.030
	5–10 kDa	49.8	3.8	1.7	1.0	43.7	0.66	0.92	0.027
UF 50 kDa permeate	Total	45.6	3.7	1.5	0.9	48.3	0.79	0.97	0.026
	<1 kDa	46.5	3.9	1.6	0.8	47.2	0.76	1.01	0.028
	1–5 kDa	45.8	3.6	1.5	1.2	47.9	0.78	0.94	0.026
	5–10 kDa	45.5	3.8	1.5	1.1	48.1	0.79	1.00	0.026
MIEX®DOC-treated solution	Total	47.0	3.9	1.3	1.0	46.8	0.75	1.00	0.022
	<1 kDa	49.9	3.6	1.2	1.0	44.3	0.67	0.87	0.019
	1–5 kDa	47.1	3.9	1.4	1.1	46.5	0.74	0.99	0.024
	5–10 kDa	43.8	4.5	1.1	1.1	49.5	0.85	1.23	0.020
Integrated process-treated solution	Total	45.4	4.2	1.2	1.0	48.2	0.80	1.11	0.021
	<1 kDa	48.5	3.9	1.3	0.9	45.4	0.70	0.96	0.021
	1–5 kDa	46.9	3.6	1.5	1.1	46.9	0.75	0.92	0.026
	5–10 kDa	45.3	4.1	1.1	1.1	48.4	0.80	1.09	0.019

the permeate composition significantly, i.e. the ">1 kDa" particles share changed from 46 to 55%, ">10 kDa" particles from 37 to 24%, while for "1–5 kDa" and "5–10 kDa" particle contributions were modified even less. Analysis of the molecular weight distribution of VHA NOM fractions showed ">10 kDa" growth in the VHA fraction that reached the maximum observed value amongst all the examined solutions (76%). Particles with lower molecular weight were barely detected ("1–5 kDa": 8%, "<1 kDa": 16%) or even eliminated completely ("5–10 kDa"). SHA fraction analysis indicated the complete removal of "1–5 kDa" particles, a slight increase of the "5–10 kDa" share and substantial changes in ">10 kDa" and "<1 kDa" contributions (increase and decrease respectively). The CHA fraction was dominated by ">10 kDa" particles. It can be noticed that the integrated process outcome is an accumulated effect of both ion exchange and membrane filtration.

In order to perform more profound analysis of properties of NOM particles removed in analysed processes, elemental analysis of organic substances in feed solution and in water after treatment in particular processes was carried out.

Table 1 contains the C, H, N, O and S weight share in organic matter and, derived from them, O/C, H/C, N/C atomic ratios which are useful for the purpose of creating structure formulas or formula weights and identification of types of humic substances [23].

The weight share of C in raw water (49.2%) suggests that fulvic acids make up the majority of organic matter. It is probably connected with the early stage of vegetable remains humification (decomposition is characterized by a loss of C in the form of CO_2). The humification process is induced by microbes and soil micro fauna, enzymes contained in plant tissue remains and atmospheric factors. Prolonged cooperation of these elements causes conversion of tannins, lignins, pectins, proteins and polysaccharides from deceased cells into macromolecular organic acids containing nitrogen [24,25]. Nitrogen content (below 2% of mass) seems to confirm that fulvic acids dominate over humic acids in the examined solution: according to [26], humic acids contain twice as much nitrogen as fulvic acids.

The O/C atomic ratio is known as an indicator of carbohydrate and carboxylic acid content in organic matter [27,28]. A higher O/C ratio points to a considerable contribution of O-alkyl, methoxy, carboxyl and carbonyl groups. Literature data suggest [26] that the O/C atomic ratio is typically higher for fulvic acids (0.65–0.99) than for humic acids (0.42–0.65), thus the ratio obtained for raw water (0.67) confirms earlier findings. The H/C atomic ratio shows the maturity level of humic substances: a greater H/C ratio translates into a greater condensed or substituted aromatic ring content [29]. The H/C ratio for organic matter found in the model solution (0.98) indicates that for each carbon atom there is one atom of hydrogen. A value far from one would have suggested a high non-humic contaminant content. The C/N ratio is known as the humic substances origin indicator in the natural environment [30]. The low value obtained for raw water (0.029) indicates that NOM found is a product of lignin decomposition and got through to the water by soil infiltration. No significant differences between raw water and NOM fractions were observed. It may result from a relatively narrow range of isolation ("1–10 kDa") as well as similar atomic ratios in humic compounds of various molecular weights.

Elemental analysis of organic matter found in ultrafiltration permeate, in water after ion exchange and water treated in integrated processes showed that in all examined samples the O/C and H/C atomic ratio increases while N/C decreases, which suggests that the fulvic acid share is even higher than in raw water. Neither substantial deviations of the atomic ratio nor weight share in NOM fractions separated from treated waters were found (similarly to raw water).

4. Conclusions

The conducted experiments have shown that water treatment in ion exchange/ultrafiltration integrated processes allows for a much more effective NOM removal than achieved in independent processes alone. On the basis of results obtained during fractionation with the use of XAD resins, it can be stated that both ion exchange and ultrafiltration separate first all the hydrophobic NOM fractions, while not being able to effectively remove hydrophilic ones. The integrated process application significantly improves the separation efficiency of hydrophobic and charged hydrophilic fractions. Research conducted on NOM mass fractionation has shown that ultrafiltration separates ">10 kDa" compounds very effectively, while ion exchange is efficient in the case of separation of small particles. Elemental analysis indicated the dominance of fulvic acids in NOM present in the examined solution. Their presence might be explained by soil infiltration of lignin decomposition products.

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