The effectiveness of organic matter removal in unit processes of the technological groundwater treatment system

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Abstract. The study evaluated the content of hydrophobic and hydrophilic organic substances in water subjected to purification in the technological system: coagulation, filtration on anthracite-sand deposits and biofiltration on granular activated carbons. The estimation of the removal efficiency of individual NOM fractions was made on the basis of fractionation method using polymeric resins (DAX-8, XAD-4 and IRA-958). The obtained results allowed to state that the applied water treatment system is effective in removing organic matter and its effectiveness in relation to individual parameters was: 55% for total organic carbon (TOC), 49% for dissolved organic carbon (DOC), 80% for particulate organic carbon (POC), 68% for UV absorbance, 83% for permanganate value and 100% for colour. In the intaken groundwater, the value of the hydrophobic fraction was 84%. The dominant fraction was very hydrophobic acid (VHA), whose content was 4.87 mg C/L (65% DOC). On the grounds of the information on the content of the NOM fraction in the intaken waters, the effectiveness of their removal in the unit processes of the technological system cannot be unequivocally determined. The content of NOM fractions established on the basis of the fractionation procedure and the SUVA parameter does not give explicit results. Further research should be carried out in this respect.

1 Introduction

One of the basic problems of water treatment technology is to obtain a product with a quality that guarantees not only edibility, but also chemical and biological stability. One of the main parameters determining the stability of treated water is the content of organic matter (NOM) [1, 2]. The occurrence of NOM in the intaken waters for potable use contributes not only to the deterioration of organoleptic properties of water, the reduction of the efficiency of unit treatment processes, but also is responsible for secondary water pollution in distribution systems [3, 4]. In addition, the presence of NOM can lead to an increase in the amount of dangerous oxidation/disinfection products that have mutagenic

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and carcinogenic properties [5–7]. Water treatment systems should ensure the greatest possible elimination of organic compounds, therefore it is necessary to thoroughly understand the properties of organic matter in water. Taking into account the restrictive requirements as well as the continuous increase pollution of the intaken water, stable water production is not an easy task [8, 9].

Natural organic matter (NOM) is defined as a mixture of complex organic compounds that are commonly found in the aquatic environment [10]. The NOM chemical structure for most organic compounds is difficult to identify, but it is possible to group them due to their hydrophobic and hydrophilic properties. One of the basic methods allowing to characterize NOM is the fractionation method using polymeric resins. This procedure allows to estimate the content of fractions such as: (1) very hydrophobic acids (VHA), (2) slightly hydrophobic acids (SHA), (3) hydrophilic charged compounds (CHA) and (4) hydrophilic neutral compounds (NEU) [11–13].

The aim of the research was to find the relationship between the kind of the organic compounds fraction and the effectiveness of their removal in the unit processes of the technological water treatment system. The work presents a detailed analysis of NOM properties including their division into hydrophobic and hydrophilic compounds.

2 Methodology

2.1 The subject of study

The study was carried out on groundwater, rich in organic compounds, intaken from a quaternary aquifer with a depth of about 15 m bgl. The technological water treatment system included the following processes: aeration, coagulation, sedimentation, filtration on anthracite-sand deposits and biofiltration on granular activated carbon type WG-12 [Fig. 1]. The study determined the effectiveness of the technological system in removal individual NOM fractions based on changes in selected parameters: (I) total organic carbon (TOC), (II) dissolved organic carbon (DOC), (III) particulate organic carbon (POC) (using a TOC Sievers 5310 C analyzer; PN - EN 1484: 1999), (III) permanganate value (by the $KMnO_4$ method, PN - EN ISO 8467: 2001), (IV) colour (using a Merck spectrophotometer): PN - EN ISO 7887: 2012) and (IV) UV absorbance (using a Merck spectrophotometer).

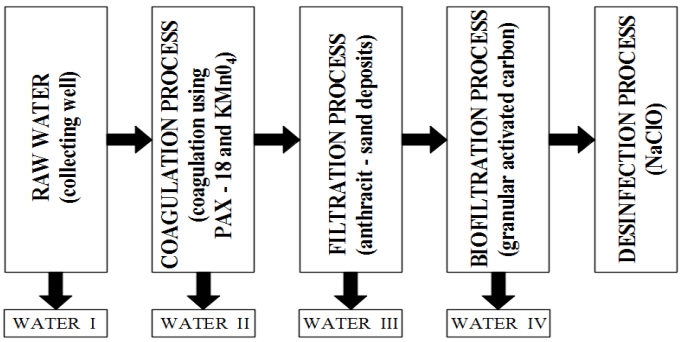


Fig. 1. Technological water treatment system.

2.1 The fractionation of NOM

The studies were carried out according to the fractionation method described in the work [11]. The fractionation procedure involved the sorption of organic compounds present in water on three polymeric resins type: Supelite DAX-8, Amberlite XAD-4 and Amberlite IRA-958. The technique used enabled the separation of organic matter into four fractions:
(I) very hydrophobic acids VHA - adsorbed by DAX-8 resin,
(II) slightly hydrophobic acids SHA - adsorbed by XAD-4 resin,
(III) hydrophilic charged compounds CHA - adsorbed by IRA-958,
(IV) hydrophilic neutral compounds NEU that are not retained on any from used resins.

Before performing the analysis, the resins were prepared according to the procedure described in the work [14]. The method of performing the fractionation of NOM is detailed in figure 2.

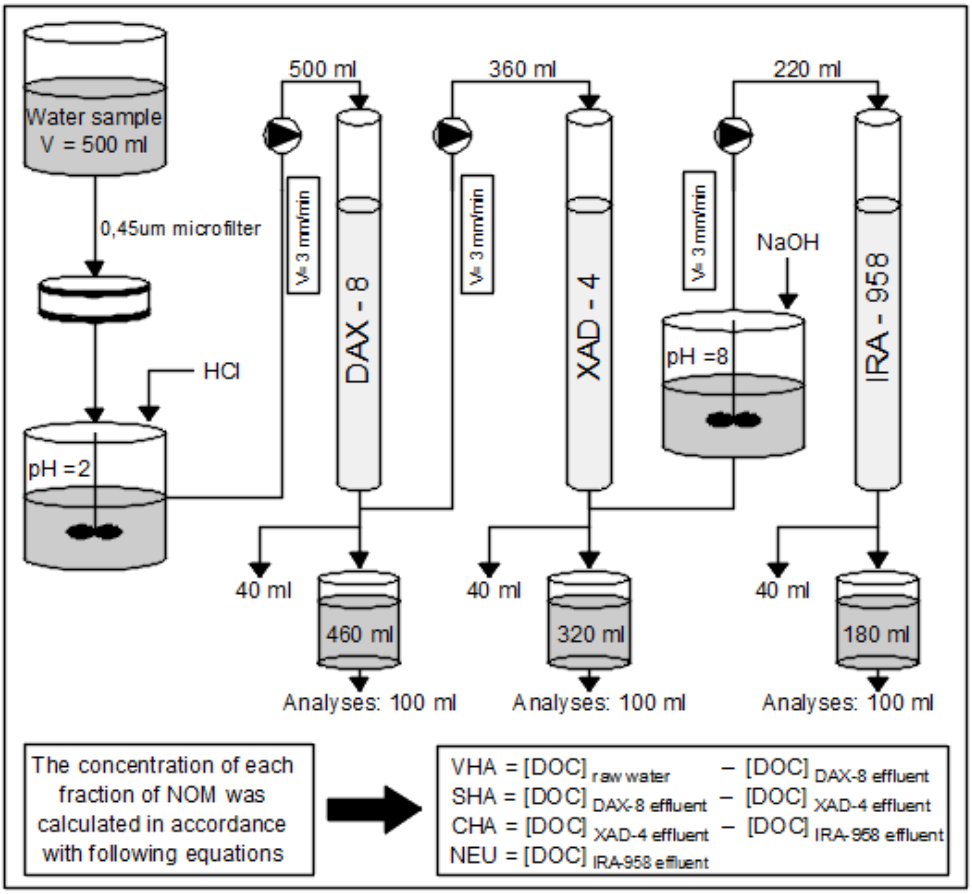


Fig. 2. The fractionation of natural organic matter on polymeric resins [12, 13].

3 Results and discussion

The groundwater subjected to the treatment processes was characterized by an increased content of organic matter as evidenced by the values of organic carbon, permanganate value, colour and UV absorbance [Tab. 1].

Table. 1 Physicochemical quality of the analyzed waters after the unit processes of the technological water treatment system.

Water	TOC	DOC	POC	Permanganate value	UV absorbance	Colour
	mg C/L			mg O_2/L	UV_{254}	mg Pt/L
1	9.09	7.52	1.52	7.1	22.74	17
2	7.2	6.64	0.56	3.6	20	10
3	6.67	5.9	0.77	2.9	14.7	8
4	4.14	3.84	0.3	1.2	7.26	0

The effectiveness of organic matter removal in the technological water treatment system fluctuated in the range from 48.9% to 100%, depending on the parameter. The effectiveness of the unit processes was varied as shown in Figure 3. The coagulation process to the greatest extent removed organic compounds responsible for the value of permanganate value, colour and particulate organic carbon content. Filtration on anthracite-sand deposits with the highest efficiency eliminated organic substances determining the value of UV absorbance. On the other hand, the process of biofiltration on granular activated carbon deposits contributed to the reduction of all indicators indicating the content of organic matter: colour, UV absorbance, TOC and permanganate value [Fig. 3].

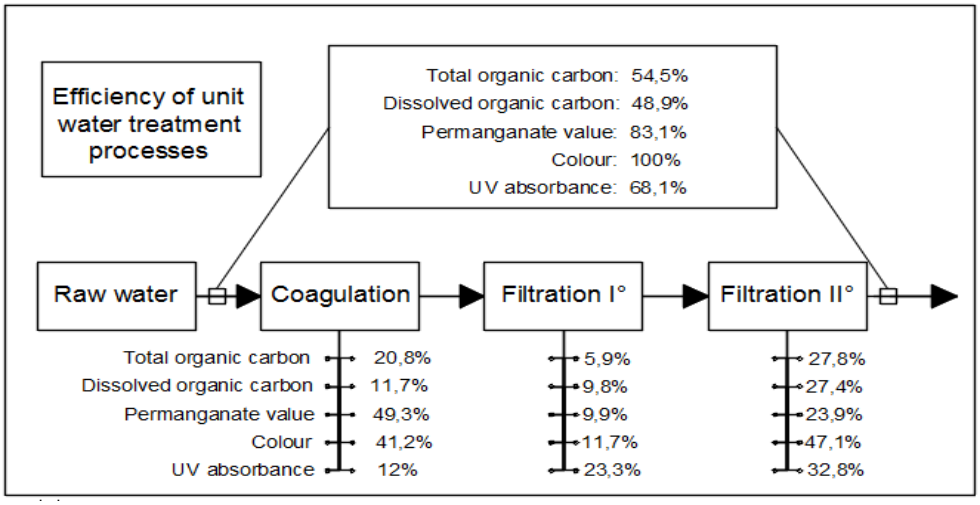


Fig. 3. The effectiveness of organic compounds removal.

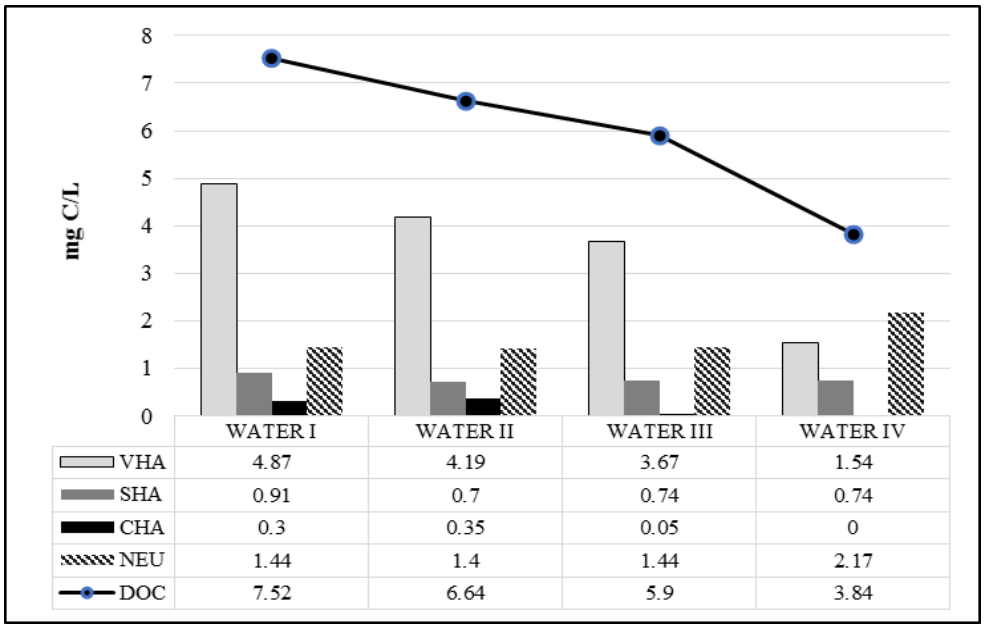
Effective NOM elimination is a problem during water treatment due to the large variety of organic compounds and their specific features.

On the basis of the obtained results [Fig. 4] it was found that in the intaken groundwater the predominant group of organic compounds was the fraction of very hydrophobic acids VHA, which content was 4.87 mg C/L (65% DOC). In this group of NOM compounds, mention may be made of humic compounds (i.e. humic, fulvic and humic acids) and high molecular weight carboxylic acids [11]. Literature reports indicate that in water treated for drinking purpose, the content of the hydrophobic fraction may range from 56% to as much as 79% of DOC [3–7, 11]. In the structure of both NOM fractions, fundamental differences are observed. Hydrophobic (allochtonic) compounds are mainly compounds characterized by a phenolic structure with a system of conjugated double bonds, while

hydrophilic (autochthonic) compounds are mainly aliphatic hydrocarbons and nitrogen compounds [15].

The research results allowed to state that in the groundwater the value of the hydrophobic fraction (VHA and SHA) accounted for 84%, but with the highest efficiency only very hydrophobic acids VHA were removed [Fig. 4].

Hydrophilic charged compounds (CHA) were the smallest fraction, their content in water I and II was 0.3–0.35 mg C/L. The reduction of the CHA content was noted only in the filtration and biofiltration processes [Fig. 4]. Slightly hydrophobic acids (SHA) were not removed in the technological system discussed. The fraction of hydrophilic neutral compounds NEU is considered to be the group of substances most difficult to eliminate [14, 15]. After the biofiltration process, its content was even increased [Fig. 4]. The observed phenomenon could be caused by the penetration into the water of the products of the metabolism of microorganisms that form the biological membrane on the surface of the deposits. The compounds included in the NEU fraction include short-chain aliphatic amines, alcohols, aldehydes, esters, ketones, carbohydrates and polysaccharides [16]. In conclusion, the results of the research, the most effective process of DOC removal in the analyzed technological system of groundwater purification was the biofiltration process, which removed 27.4% DOC.



	WATER I	WATER II	WATER III	WATER IV
VHA	4.87	4.19	3.67	1.54
SHA	0.91	0.7	0.74	0.74
CHA	0.3	0.35	0.05	0
NEU	1.44	1.4	1.44	2.17
DOC	7.52	6.64	5.9	3.84

Fig. 4. Change in the content of NOM fraction in unit processes of the technological system.

The research carried out by [11] showed that in the removal of dissolved organic compounds, the most effective was the coagulation process, where the removal of DOC in 40.1% was observed. The biofiltration process removed only 6.3% DOC. Differences can be caused by the type of treated water (surface water, groundwater) and the content of individual NOM fractions. The study analyzed the technological system of surface water treatment, which additionally contained the process of ozonization before the filtration process on activated carbon. The comparison of the effectiveness of DOC removal in both technological systems and differences in the content of NOM fractions in the intaken waters are presented in Tables 2 and 3. It should be noted that after the biofiltration process there

was a small change in DOC content, which may suggest the absence of biological processes on activated carbon deposits.

Table 2. The effectiveness of DOC removal in the technological treatment system of surface and underground water.

	Groundwater		Surface water [11]	
	DOC [mg C/L]	Reduction [%]	DOC [mg C/L]	Reduction [%]
Raw water	7.52	-	7.21	-
Coagulation	6.64	11.7	4.32	40.1
Filtration	5.9	9.8	3.48	11.7
Biofiltration	3.84	27.4	3.02*	6.3
The technological system	-	48.9	-	58,1

***** The biofiltration process preceded by the ozonization process.

Table 3. The percentage of NOM fraction in intaken groundwater and surface water.

Frction	The content of the NOM fraction in the intaken waters [%]	
	Groundwater	Surface water [11]
VHA	65	41
SHA	19	15
CHA	4	15
NEU	12	29

The effectiveness of the coagulation process in removal DOC from groundwater has been confirmed in the paper [17]. The removal efficiency of the VHA, SHA and CHA fractions was 61%, 30% and 21%, respectively. The content of the NEU fraction did not change, which confirms the difficulty in removal this group of organic compounds. In the intaken water, the dominant fraction was VHA, representing 70% DOC.

In study [14], the highest efficiency of DOC removal was recorded in the process of counter current dissolved air flotation and filtration. In the analyzed water, in contrast to the above-mentioned examples, the hydrophilic fraction (64% DOC) prevailed, and the most numerous group of compounds in this case were hydrophilic neutral compounds (57% DOC).

In order to quickly analyze the properties of NOM, a specific UV absorbance is used (SUVA = UV_{254nm}/DOC). SUVA > 4 $L \cdot mg^{-1} \cdot m^{-1}$ suggests that in the water are contained organic compounds with strong hydrophobic properties (mainly high molecular weight humic compounds), whereas SUVA < 2 $L \cdot mg^{-1} \cdot m^{-1}$ dominated by hydrophilic substances (low molecular weight non-humic compounds). In the intaken water SUVA reaches the value of 3 $L \cdot mg^{-1} \cdot m^{-1}$, which indicates the presence of both hydrophobic and hydrophilic substances (the fractionation method confirms the presence of both fractions but the dominant was a hydrophobic fraction - 84%). In subsequent processes of the technological system, the value of this parameter was successively reduced and after the biofiltration process on granular activated carbon, it finally obtained 1.9 L·mg-1·m-1. This indicates that in the water should be present only hydrophilic substances (according to the fractionation procedure in water IV, the content of the hydrophobic fraction decreased, but still accounted for 51%).

The SUVA parameter is also used as an indicator for determining the water susceptibility to removing organic compounds in the coagulation process. It is assumed that in waters for which SUVA ≥ 4 $L \cdot mg^{-1} \cdot m^{-1}$ the effectiveness of this process can reach up to 80%, whereas SUVA ≤ 3 $L \cdot mg^{-1} \cdot m^{-1}$ usually does not exceed 30% [18]. The effectiveness of the coagulation process in removal the dissolved organic carbon fraction in groundwater was 18%. However it should be noted that during coagulation 63% suspended organic carbon was removed. The content of NOM hydrophilic and hydrophobic fractions determined on the basis of the fractionation procedure and the SUVA parameter does not give unambiguous results. Further research should be carried out in this respect.

3 Conclusions

1. The water treatment system consisting of the coagulation, filtration on sand-anthracite deposits and biofiltration on granular activated carbon is effective in removial organic matter. The NOM elimination efficiency was: 55% for total organic carbon (TOC), 49% for dissolved organic carbon (DOC), 80% for particulate organic carbon (POC), 68% for UV absorbance, 83% for permanganate value and 100% for colour.
2. In the intaken groundwater the value of the hydrophobic fraction was 84%, the remaining part of the organic matter is a hydrophilic fraction. In the groundwater, the dominant fraction was very hydrophobic acids (VHA), the content of which was 4.87 mg C/L (65% DOC).
3. During unit water treatment processes, VHA was the most efficiently removed group of organic compounds, which was 68% lower reaching the value of 1.54 mg C/L after the biofiltration process. The content of SHA during water treatment was not reduced, and removal of the CHA fraction occurred only in the filtration processes. The removal of the NEU fraction was not observed, and after the biofiltration process an increase in its content was noted.
4. Among the analyzed unit processes, the most effective process for removal hydrophobic fractions was the biofiltration process on granular activated carbon.
5. The design of a water treatment system requires complex technological research, and the NOM fractionation method may be only an auxiliary method in determining technology. However, further research in this area should be carried out.

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