



Integrated removal of selected hard-to-degrade pollutants on the example of petroleum compounds

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ABSTRACT

Reverse osmosis (RO) and nanofiltration (NF) are effective technologies for removing organic compounds from water. Most research focuses on the removal of organic compounds from water already treated. However, evaluating their removal from groundwater is necessary because coexisting ions affect treatment efficiency. In the case of inorganic compounds, the water's pH, concentration, and membrane charge are the main factors affecting the electrostatic repulsion between the ionic compounds and the charged membrane. This study aims to present the efficiency of removing the studied compounds with NF/RO from groundwater and the physicochemical and chemical processes involved in the removal. As a result of the research, it is found that the hydraulic performance of the membrane, especially for RO, is stable; the efficiency of benzene, ethylbenzene, toluene, and o-, m-, p-xylene removal throughout the research process is at 86% for RO and about 65% for NF.

Keywords: Water; Membranes; Nanofiltration; Reverse osmosis; Petroleum Hydrocarbons

1. Introduction

The occurrence of petroleum-derived compounds in surface and groundwater is considered a significant environmental health hazard; these compounds are difficult or biochemically undegradable.

Contamination by benzene, ethylbenzene, toluene, and o-, m-, p-xylene (BTEX) compounds is associated, among other things, with the fuels used, in which they are found in high concentrations, such as in gasoline or related products such as diesel fuel, lubricating oil and heating oil. The properties of BTEX compounds and their use have meant that they are now used in many environments. This poses a threat to the environment as well as to public health. All of these compounds belong to the group with carcinogenic effects. Effective removal of these compounds has always been a severe challenge for drinking water production [1,2].

Long-term monitoring studies of surface and groundwater for aromatic hydrocarbons (benzene, ethylbenzene, toluene, and isomers of xylene) and aliphatic *n*-alkanes from C₁₂ to C₃₄ in the Podlaskie Voivodeship have shown that concentrations of these pollutants range from a few ng/dm³ to a few tens of µg/L, depending on the type of compound or group affiliation. The highest level of BTEX in Poland was shown in groundwater on air force bases and was 11,245.58 µg/L [1–5].

BTEX removal was carried out in unit processes and hybrid systems. Stripping, reverse osmosis, and volumetric coagulation were used for unitary processes, while two configurations of stripping - reverse osmosis and volumetric coagulation - reverse osmosis were used for hybrid systems. The presented studies showed a significant degree of removal of petroleum group compounds and influenced the intensity of adsorption on the membrane

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surface; however, the hydraulic performance of the membrane significantly decreased throughout the process. The above fact prompted the improvement and development of new unconventional and highly efficient systems for their effective removal [2–4].

Pressurised membrane processes, mainly reverse osmosis (RO) and nanofiltration (NF) are being considered as potential methods for removing organic micropollutants from water [1]. The reverse osmosis process is observed to remove more low-molecular-weight organic compounds. Still, the addition of the nanofiltration process allows for comprehensive water purification in terms of efficiency and quality. This process is a clear alternative to conventional water treatment methods. It is a combined method of removing excessive water hardness, natural organic matter, micropollutants, viruses and bacteria, nitrates, and metals [2–6].

Several previous studies have demonstrated the excellent ability of NF/RO to remove a wide range of volatile organic compounds, including trihalomethanes, organochlorine compounds, and other low-molecular-weight compounds such as trichloroethylene [5–9]. These studies also revealed significant complexity associated with the separation processes (functional group interactions, electrostatic repulsion, membrane pore size).

The efficiency of the process of removing petroleum group compounds benzene, ethylbenzene, toluene, and o-, m-, p-xylene (BTEX) from groundwater is not based only on the size exclusion of the molecule but also on the interaction of organic and inorganic compounds on the membrane charge. For trace organic compounds, electrostatic interactions between the charged solute and the negatively charged membrane surface may also play a key role [7–10]. In addition, it has been shown that hydrophobic compounds can adsorb on membrane surfaces and then diffuse through RO and especially NF membranes, resulting in lower efficiencies than expected based on sieve mechanisms alone. Hydrophobicity is considered an essential factor affecting removal [8–14]. Most studies focus on the removal of organic compounds from water already treated. However, it is necessary to evaluate their removal from groundwater or surface water because coexisting ions in the groundwater affect the removal efficiency of organic compounds. In the case of inorganic compounds, the water's pH, concentration, and membrane charge are the main factors affecting the electrostatic repulsion between the ionic compounds and the charged membrane [5–8]. The variety of chemical and

physical properties of these substances has necessitated the development of methods that will eliminate or negate the pollution caused by a particular group of hydrocarbons in the most efficient way possible. Research related to BTEX removal has focused on combining classical and membrane methods.

This study aims to present the effectiveness of BTEX removal from groundwater using the NF/RO membrane system and to investigate the physicochemical and chemical processes occurring during removal. The article's authors dealt with a new solution using an integrated membrane system to treat groundwater from BTEX.

2. Research methodology

2.1. Technological research

The experiments were conducted semi-technically using commercial NF/RO membranes, namely NF-1812 and RO-1812-75 from KeenSen (China). The system was operated in a cross-flow arrangement with a spiral module membrane (Table 1).

The research in the integrated system consisted of treating water using the NF/RO process (Table 2).

The structure of BTEX compounds (Table 3) is very similar; despite this, they show differences in physicochemical properties. Under normal conditions, they are colourless liquids with a sweet odour, but their most important characteristics include high volatility and poor solubility in water.

For the study, an integrated system was used: nanofiltration-reverse osmosis. During the tests, the transport-separation properties of the membranes at both stages of filtration (NF and RO) were determined based on the value


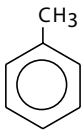
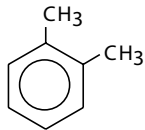
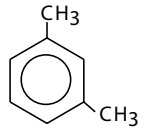

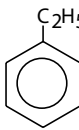
Table 2
Process parameters using reverse osmosis and nanofiltration

Nanofiltration		
Transmembrane pressure (MPa)	0.9	1.15
Total concentration of BTEX in the feed (µg/L)	3,148	
Reverse osmosis		
Transmembrane pressure (MPa)	1.3	1.5
Total concentration of BTEX in the feed (µg/L)	1,183	

Table 1
Specifications parameters of the nanofiltration and reverse osmosis process

	NF 1812	RO 1812-75
Active membrane surface	0.46 m ²	0.39 m ²
Membrane material	Polyamide (PA)	Polyamide (PA)
Molecular weight cut-off (Da)	200	100
Na ⁺ rejection (%)	86.5%	98.7%
Concentrate flow rate	1.75 L/h at 30% recovery (conversion)	5.5 L/h at 50% recovery (conversion)
Permeate flow rate	5.5 L/h at 60% recovery (conversion)	5.5 L/h at 60% recovery (conversion)
Flow rate	284 L/d	284 L/d
Transmembrane pressure	1.0 MPa	1.5 MPa

Table 3
Summary of physiochemical BTEX data [3]

Physical property	Benzene	Toluene	o-Xylene	m-Xylene	p-Xylene	Ethylbenzene
Structure						
Molecular weight (g/mol)	78	92	106	106	106	106
Dipole moment at 20°C (D)	0.00	0.36	0.45	0.37	0.00	0.35
Acetanol-water partition coefficient at 20°C (logK _{ow})	2.13	2.69	2.77	3.15	3.15	3.20
Constant by Henry's law at 25°C (kPa m/mol)-3-	0.55	0.67	0.50	0.70	0.71	0.80

of the permeate volume flux and the calculation of the concentration retention factor of the tested compounds from the oil group.

$$R = \left(1 - \frac{C_p}{C_f} \right) \times 100\% \quad (1)$$

where C_p and C_f are the permeate and the feed concentrations, respectively.

The first step was the removal of BTEX and ions contained in the water (calcium, manganese chlorides, and iron by nanofiltration (Table 4) - the treated water after nanofiltration was fed into a reverse osmosis system.

For chemical analysis, water samples were taken after NF and RO. The process took 4 h; permeate and feed samples 0.5 mL (two replicates) were taken every 1 h.

The assumed recovery rate was between 60% and 70%. Before the tests, membrane stabilisation was performed by filtering distilled water until a stable stream was obtained. The distilled water was then replaced with BTEX-dosed groundwater. After the actual tests, the membrane was rewashed with distilled water. The change in transport properties of the membrane after operation on groundwater was thus determined. The efficiency of the water filtration process was evaluated based on transport and separation properties.

2.2. Analytical method

The temperature, turbidity, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS), and redox (water quality parameters) were measured using HQ2200, portable multimeter to measure pH, conductivity, TDS, salinity, dissolved oxygen (DO) and redox potential (ORP), iron, manganese, and calcium were determined according to the current test methodology.

Determinations of petroleum hydrocarbons (BTEX) in water were made using a gas chromatograph coupled with a Varian 4000 mass spectrometer (USA). For the determination of BTEX, 500 mL of the test water was used. The device was equipped with a column VF-5MB with parameters

Table 4
Groundwater used in the study

Turbidity (NTU)	0.5
Dissolved oxygen (mg/L)	1.78
Electrical conductivity (μS/cm)	1,800
Total dissolved solids (g/L)	1.49
pH	6.6
Redox (mV)	-107
Calcium (mg-Ca/L)	82.4
Manganese (mg-Mn/L)	0.1
Iron (mg-Fe/L)	0.7

30 m × 0.25 mm × 0.25 mm. The stationary phase comprised polydimethylsiloxane with a 5% share of phenol groups. The isolation was performed at room temperature, equal to 20°C ± 2°C, on a magnetic stirrer at a rotational speed of about 800 rpm using 50 mL of dichloromethane. After separating the aqueous and organic layers, the eluate was transferred to volumetric flasks and then dried with anhydrous sodium sulfate (Na₂SO₄). The concentrated extract was subjected to separation and detection on a GC-MS instrument. The carrier gas used was helium with purity of 6.0 [1,12,14]. The temperature program was as follows: 40°C (5 min) to 130°C (0 min), with increments of 10°C/min to 300°C, the temperature of the transfer line 230°C, ion source temperature 180°C [1,12,14]. Details of the method are presented in [3]. Quantitative analysis was performed using the calibration curve method.

3. Results and discussion

The studies conducted on removing BTEX from groundwater (Tables 5 and 6) in the NF/RO integrated system are a continuation of earlier studies where the NF unit process was used to remove BTEX-model water treatment (distilled water with BTEX-s). The results presented in the paper are the average of three replicates.

Tests in NF/RO water treatment differed in efficiency in removing inorganic ions depending on the BTEX content of

the water. The retention factor decreased by about 2% for all parameters compared to groundwater not contaminated with BTEX. Studies have shown that removing sodium ions, calcium, chloride, and sulfate ions increases with increasing pH for RO and NF membranes [5,6,11,13–15].

Table 6 shows the applied initial concentrations of total BTEX and those obtained after each successive hour of the ongoing process. The results obtained for NF for groundwater are, on average, about 6% lower than for BTEX model

water treatment (distilled water with BTEX-s). The retention rate was highest for distilled water at the beginning of the process. The RO process achieves a BTEX removal efficiency of 86%.

The retention factor in RO for individual compounds in the BTEX group of Fig. 2 ranges from 81% for ethylbenzene to more than 91% for benzene in the RO process. The retention factor for all compounds in this group was about 20% lower in the nanofiltration process compared to RO.

Table 5
Treatment of groundwater in an integrated system without and with BTEX

	Turbidity (NTU)	Dissolved oxygen (mg/L)	Electrical conductivity (µS/cm)	Total dissolved solids (g/L)	pH	Redox (mV)	Calcium (mg·Ca/L)	Manganese (mg·Mn/L)	Iron (mg·Fe/L)
	0.5	1.78	1,800	1.49	6.6	-107	82.4	0.1	0.7
R (%)	100	99	99	99			99	99	98
R (%) + BTEX	98	96	96	93			96	94	96

Table 6
Removal of BTEX from distilled water by NF and from groundwater by NF and RO process

	Model water (NF)		Groundwater	
			NF	RO
Duration of the process (h)	Σ BTEX concentration (µg/L)/R (%)			
Raw samples	647	3,148		1,259
1.0	135 (79%)	724 (67%)		165 (86%)
2.	204 (68%)	818 (64%)		165 (86%)
3.0	201 (68%)	818 (64%)		165 (86%)
4.0		1259 (60%)		165 (86%)

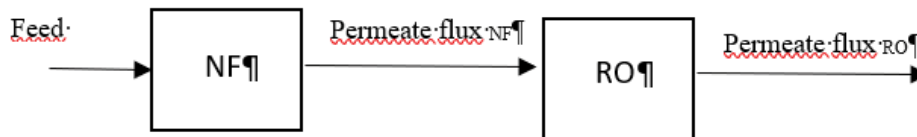


Fig. 1. Scheme of the membrane installation (Source: own elaboration).

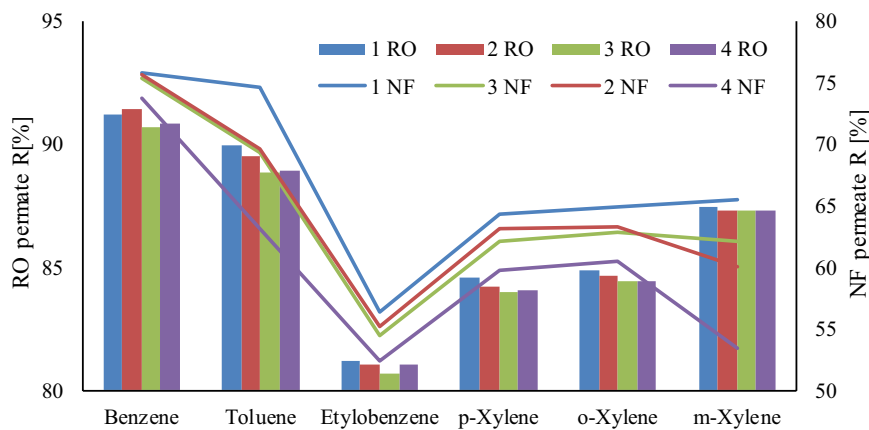


Fig. 2. Efficiency of BTEX removal from groundwater.

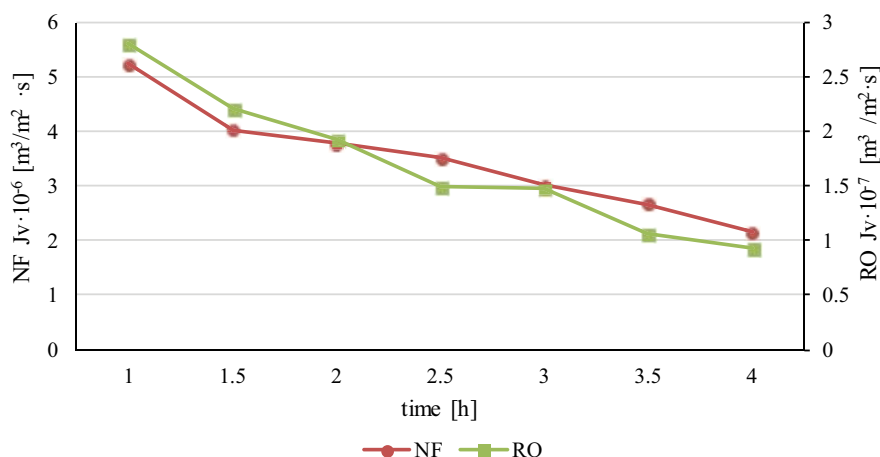


Fig. 3. Hydraulic performance of the membrane in NF and RO.

Ethylbenzene was also the least removed here, from 52% to 56%. It is probably because the removal efficiency of petroleum hydrocarbons in membrane processes is also affected by the molecule's spatial configuration, the molecule's radius, and the molecule's average size [1,15–23]. These parameters sometimes determine the separation properties to a greater extent than the molar mass alone [1,15,18,19]. Similar efficiency was obtained in studies [1,3,15] of removing isomers from the BTEX group (trimethylbenzene, tetrabutylbenzene, *m* = *p* xylene, and ethylbenzene) by nanofiltration on distilled water [1,12,14–17]. In tests on distilled water, a higher retention rate of total BTEXs was obtained, which could be influenced by the other aromatic hydrocarbons, *o*-xylene, toluene, and benzene.

Ongoing studies in the NF/RO integrated system for groundwater with high concentrations of petroleum hydrocarbons have shown that the decrease in permeate flux (Fig. 3) is less steep than the unitary reverse osmosis process [1,14,16]. The permeate flux in nanofiltration has a higher value, forming from 5.23 to $2.15 \cdot 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$. In the RO process, the volumetric permeate flux was much lower than NF. It systematically decreased and formed from 2.8 to $0.93 \cdot 10^{-7} \text{ m}^3/\text{m}^2 \cdot \text{s}$.

Studies have shown that the retention factor of both inorganic and organic compounds and flux for RO and NF membranes significantly affect hydrodynamic operating parameters such as water recovery (ratio of total permeate volume to initial feed volume). Solute concentration also affects transport through RO and NF membranes because membrane charge becomes more negative as solution pH increases and solute concentration decreases [1,5,7–9].

On the efficiency of entrapment in NF on distilled water and underground water, observing the data obtained, it was noted that the size of the solute or the shape and polarity or hydrophobicity and the pore size and charge of the membrane had an influence [25–28].

In their study, Quintanilla et al. [24] proved that pure NF-90 membrane removed almost all neutral hydrophobic compounds (95%–98%). It was mainly due to the molecular size exclusion of the chemical compound. High retention rates were obtained after the RO step (>99% for macrolides, pharmaceuticals, cholesterol, and disinfection by-products,

95% for diclofenac, and >93% removal of sulfonamides [10,12,25–30]. Removal of triclosan by RO membranes was almost 100% because the molecular width of this compound was more significant than the estimated average effective membrane pore size [11]. When RO (virgin XLE) was used, a high retention rate (90%–100%) was achieved for the removal of six pharmaceuticals and personal care products, and the dominant mechanism was molecular size exclusion [7,9,12,28–31]. The octanol-water partition coefficient ($\log K_{ow}$) is essential (Table 3). Solutes with greater width, length, and $\log K_{ow}$ will be expected to have higher retention for most membranes used. In contrast, ethylbenzene has the highest $\log K_{ow}$ and removed the least in the study [5,7,8,32]. This assessment requires further research to recognise its removal mechanism or the influence of existing inorganic ions in the water on this process (Table 6). In addition, some mechanisms contribute to removing this compound (e.g., repulsion size exclusion) and adsorption on the membrane. Adsorption adversely affects the retention factor because some compounds can dissolve in the membrane's active layers, diffuse through the polymer, and eventually desorb on the permeate side [22,30–32].

4. Conclusions

The research conducted allows us to draw the following conclusions:

- Nanofiltration and reverse osmosis is an effective method for removing petroleum hydrocarbons from groundwater.
- When NF/RO treats groundwater without monoaromatic hydrocarbons, higher retention rates for inorganic compounds are achieved.
- When evaluating the effectiveness of NF/RO when removing petroleum compounds from groundwater, the effect of other compounds present in the water must be considered.
- Recognising the mechanism of ethylbenzene removal from groundwater requires further research.
- Inorganic and organic matter in the water can modify the membrane surface and cause fouling and treatment efficiency.

- To achieve consistent and high performance of the membranes and extend their life (prevention), filtration or coagulation should be particularly important at higher organic content in water.

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