



Organic micro-contaminants removed from water in the nanofiltration process – preliminary research results

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ABSTRACT

Pressure membrane processes such as nanofiltration (NF) play an important role in purifying water, from which not only inorganic substances but also petroleum-derived organic compounds can be removed. The study evaluated the removal of petroleum hydrocarbons from water using nanofiltration. The work was carried out applying a spiral module equipped with a commercial NF-212 membrane. Model water was used for the study. Determinations of studied petroleum aliphatic hydrocarbons from C7 to C33 and monoaromatic hydrocarbons were performed on a gas chromatograph coupled with a mass spectrometer. Quantitative analysis was performed using the calibration curve method. During the process, the retention factor, volumetric flow of deionized water (J_w), both before and after the process and volumetric flow of model water permeate were calculated, and the relative membrane permeability value for the deionized water stream α_w and the relative membrane permeability for the model water stream α_v was calculated.

Keywords: Water; Nanofiltration; *n*-alkanes; Benzene; Toluene; Ethylbenzene; Xylene

1. Introduction

The occurrence and fate of petroleum hydrocarbons in surface and groundwater have been identified as a significant environmental health concern [1,2]. It would be fair to say that there is full agreement between the scientific community and water authorities to minimize petroleum hydrocarbons, however, the majority of these contaminants in the environment are still poorly understood, and are a topic of growing interest from both research and regulatory perspectives. Benzene, toluene, ethylbenzene, and xylene (BTEX) compounds are common water resource and potable water pollutants that are often left undetected and untreated by municipal treatment systems in spite of the negative repercussions associated with their ingestion. The US EPA has classified these pollutants as priority pollutants, yet they are persistently present in a variety of water resources [1–3]. In the last decade, nanofiltration

(NF) and reverse osmosis (RO) have been proposed as attractive technologies for the removal of organic trace contaminants including volatile organic compounds from the aquatic environment [2–4]. The study by Agenson et al. [5] and Fujioka et al. [6] showed the excellent ability of NF/RO to remove a wide range of volatile organic compounds including trihalomethanes, organochloric compounds, petroleum hydrocarbons, and other low molecular weight compounds such as toluene and trichloroethylene [7]. These studies have also revealed a substantial degree of complexity associated with the separation processes involved. As a result, various parameters such as membrane properties, solution chemistry, and physicochemical properties of the volatile organic compounds can significantly affect the removal efficiency of these components by NF/RO membranes [5–7]. Among membrane methods, the ultrafiltration, nanofiltration, and reverse osmosis processes are mainly used to remove petroleum micro-contaminants

[1–7]. Complex technological systems including purification of water from petroleum products entail high costs, therefore new and cheaper technological solutions using integrated membrane systems are still sought [2,6–9]. A number of studies were conducted regarding the treatment of underground water on a pilot scale and the effectiveness of nanofiltration itself as well as nanofiltration combined with classic methods was assessed, which resulted in high efficiency of the system [10–13]. In the scientific literature, however, there are few studies devoted to research on the removal of petroleum hydrocarbons from water by means of nanofiltration. There are no systems developed that include effective removal of petroleum derivatives, including monoaromatic and aliphatic hydrocarbons. The purpose of the research was to determine the possibility of removing petroleum hydrocarbons during the nanofiltration process.

2. Methods

2.1. Subject of study

The process of removing petroleum contaminants was carried out by means of nanofiltration (NF) in a continuous system with partial recirculation of the concentrate applying a small NF station (Fig. 1). The studies were carried out using the NF-212 polyamide membrane supplied by KEEN SEN (China) with molecular weight cut-off (MWCO) 450 Da and spiral-wound configuration module, operating in a cross-flow filtration mode. Parameters of the nanofiltration process:

Membrane surface	0.56 m ² ,
Volume permeate flux	3.67 × 10 ⁻⁵ m ³ /m ² s,
Trans-membrane pressure	2.0 MPa.

Tested sample has consisted of distilled water with the addition of a fuel mixture. The mixture was petrol and diesel oil in the ratio of 1:3. The ratio of fuel mixing resulted from the quantity and type of fuels sold on the domestic market in 2010–2012 [2]. The sample was made in the proportion of 0.3 mL of the fuel mixture (diesel oil, gasoline) per 1 L of distilled water. To obtain a homogeneous mixture, the fuel mix sample was emulsified with water using an ultrasonic homogenizer. There were 10 L of mixture per membrane module at one time. Prior to the commencement of the basic research, the nanofiltration membrane was conditioned by passing deionized water to stabilize the volume permeate stream. Duration of the test for a single series and at a given pressure was 3.5 h. The test system was also rinsed to observe the effect of petroleum substances on the hydraulic performance of the membrane. Samples were collected during the ongoing process at 5 min intervals. Such a sampling pattern enabled observation of the separation process and assessment of its efficiency from the initial to the final phase. One of the purposes of such sampling was also to observe the adverse phenomena that occur in the case of membrane techniques, like among others “scaling,” “fouling,” and any other irregularities. Aliphatic hydrocarbons (*n*-alkanes), total BTEX, trimethylbenzenes, ethylbenzene, *m*-xylene, and tetrabutylbenzene were determined in the purified water. In the article, instead of systematic, simplified names for particular C₁₂–C₃₃ hydrocarbons were used.

2.2. Analytical methodology

Determinations of petroleum hydrocarbons (*n*-alkanes, BTEX) in water were made using gas chromatography coupled with VARIAN 4000 mass spectrometer. For the determination of BTEX and *n*-alkanes, 500 mL of the test water was used. The isolation process was carried out 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 separation of the aqueous and organic layers, the eluate was transferred to volumetric flasks and then dried with anhydrous sodium sulfate (Na₂SO₄). Concentrated extract was subjected to separation and detection on a GC-MS instrument. The carrier gas used was helium with a purity of 6.0. Aliphatic hydrocarbons were extracted from water applying liquid–liquid method using hexane [1,12,14]. Details of the method are presented in Piekutin [2]. Quantitative analysis was performed using the calibration curve method.

3. Results and discussion

Studies on the BTEX removal (Table 1) from model water in the nanofiltration process showed that they were removed with efficiency from 51% to 79% during the 3.5 h process. The highest effect was obtained in the 1st hour of treatment, and then the retention factor decreased by 2.5 h of the process reaching 51%. After rinsing the system, the retention factor increased by 13%.

Studies on removal of monoaromatic hydrocarbons expressed as Σ BTEX from model water in the nanofiltration process showed that they were removed with a yield of 51%–79% in a 3.5 h process. The greatest effect was obtained in the 1st hour of treatment, and then the retention rate decreased in 2.5 h process, reaching 51%. The mechanism of micropollutants transport in the initial filtration period is associated with the phenomenon of compound adsorption on the membrane surface [1,2]. Then, due to saturation of the membrane surface charge, the compound retention decreases, and the transport mechanism depended on the phenomenon of dissolution and diffusion. The increase in efficiency could have been related to the membrane rinsing process which was carried out after 2.5 h of system operation (Fig. 4) thereby restoring the membranes efficiency.

Table 1
Removal of BTEX in the nanofiltration process

Duration of the nanofiltration process (h)	R (%)	Σ BTEX concentration (µg/L)
Raw sample	%	647.73
1	79	135.39
1.5	67	217.36
2	67	214.68
2.5	51	327.44
3.0	59	267.42
3.5	64	238.67

R, Retention coefficient.

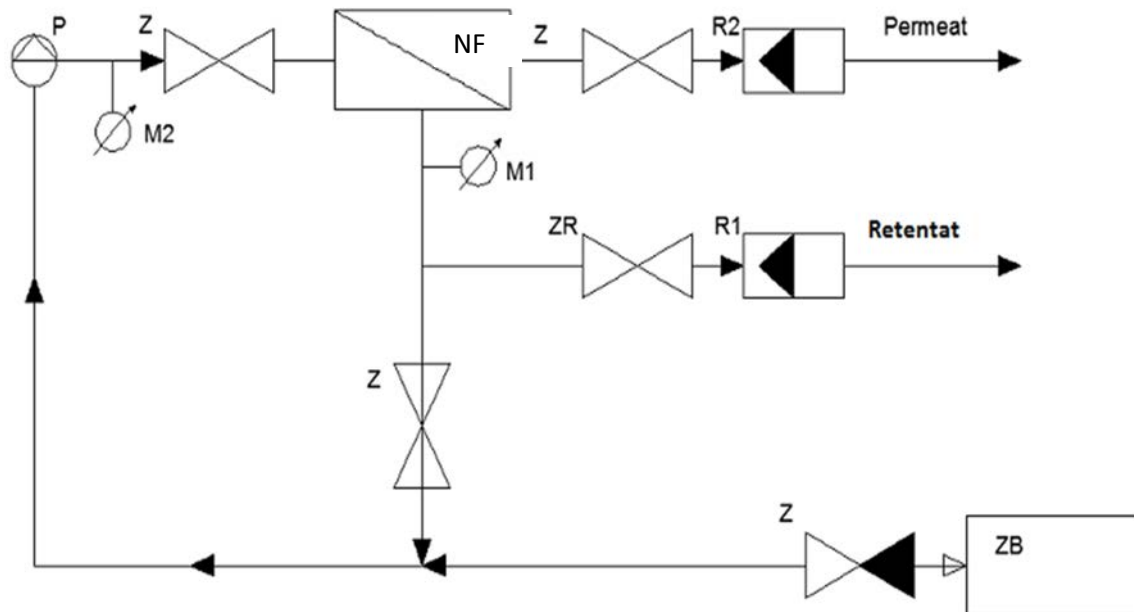


Fig. 1. Installation diagram of the nanofiltration process used for research. P – pump; Z – control valves; NF – spiral nanofiltration membrane; R1, R2 – rotameters; M1, M2 – manometers; and ZB – pressure water tank.

The retention coefficient (Fig. 2) of the isomers of trimethylbenzene, tetrabutylbenzene, *m*-xylene, *p*-xylene, and ethylbenzene was found to range from 32% to 58%. Efficiency of removing BTEX was definitely higher. Xylene and ethylbenzene are monoaromatic hydrocarbons and are from the BTEX group, thus it can be assumed that other aromatic hydrocarbons from this group (*o*-xylene, toluene, and benzene) may have an impact on the higher total BTEX retention factor. This effect could have been caused by the interaction of the tested compounds with the membrane [13,15–17]. It was also observed that the removal process was stable without large differences in retention coefficient, which indicates that only the separation mechanism in the nanofiltration process is probably used here.

The study of aliphatic hydrocarbons removal (Table 2 and Fig. 3) showed that *n*-alkanes up to C_{22} reached the retention rate of about 100%, while for those from C_{23} to C_{33} , the factor gradually decreased. The minimum retention factor was below 75%. This is probably due to the fact that the efficiency of petroleum hydrocarbons removal in nanofiltration is also influenced by the spatial configuration of a molecule, the particle radius, and the average particle size. Sometimes, these parameters largely determine the separation properties than the molar mass alone [16,18,19]. It was also observed that the removal process was more effective with the time of the nanofiltration process. The observed effect of increasing impurities removal degree over time was probably the result of increasing membrane surface blockage with a layer of impurities, which constituted an additional separation barrier. An inverse relationship was observed for C_{10} – C_{12} .

It was shown (Table 2 and Fig. 2) that the removal of *n*-alkanes from water during the nanofiltration process is about 20%–50% more effective than that of BTEXs,

methylbenzene, and tetrabutylbenzene isomers. According to the research conducted by Park and Barnett [21], removal of these compounds reached the level of 65% in a single nanofiltration process of purifying the water from petroleum compounds. Therefore, nanofiltration is included in the technological purification process, which allows for obtaining better quality water. Such a system was used at the water treatment plant in Mery-sur-Oise in France [13,14]. In order to ensure the correct operation of the nanofiltration modules, extensive pre-treatment of water was applied. During removal of tested petroleum compounds, on the membrane surface, there is probably a process of adsorption of petroleum compounds that are hydrophobic and at the beginning of the process, the substance adsorbs on the membrane and then passes through it by diffusion/convection [19–23]. Removal retention is also influenced by factors related to the membrane properties and the membrane-forming material [24]. Taylor and Jacobs [19], based on the results of pesticide removal tests using eight commercial membranes for reverse osmosis and nanofiltration (ACM-4, X-20, TFC-ULP, PVD-1, CPA/IF940524, BW-30, SH, and DL), showed that water quality does not have any significant impact on the retention factor for low-molecular-weight compounds, while membrane material exerts a significant effect [25–29].

Mixed separation mechanisms occurred in the nanofiltration process, one of them was adsorption, which probably affected the more effective removal of larger aliphatic hydrocarbon from water (Fig. 3). An additional factor is the high value of analyzed *n*-alkane partition coefficient. Smaller particles probably sorb in the coating layer.

Verliefde et al. [30] showed the removal process be affected by hydrophobic interactions between membrane and solute. It was further suggested that hydrophobic solutes could diffuse into hydrophobic membranes more easily

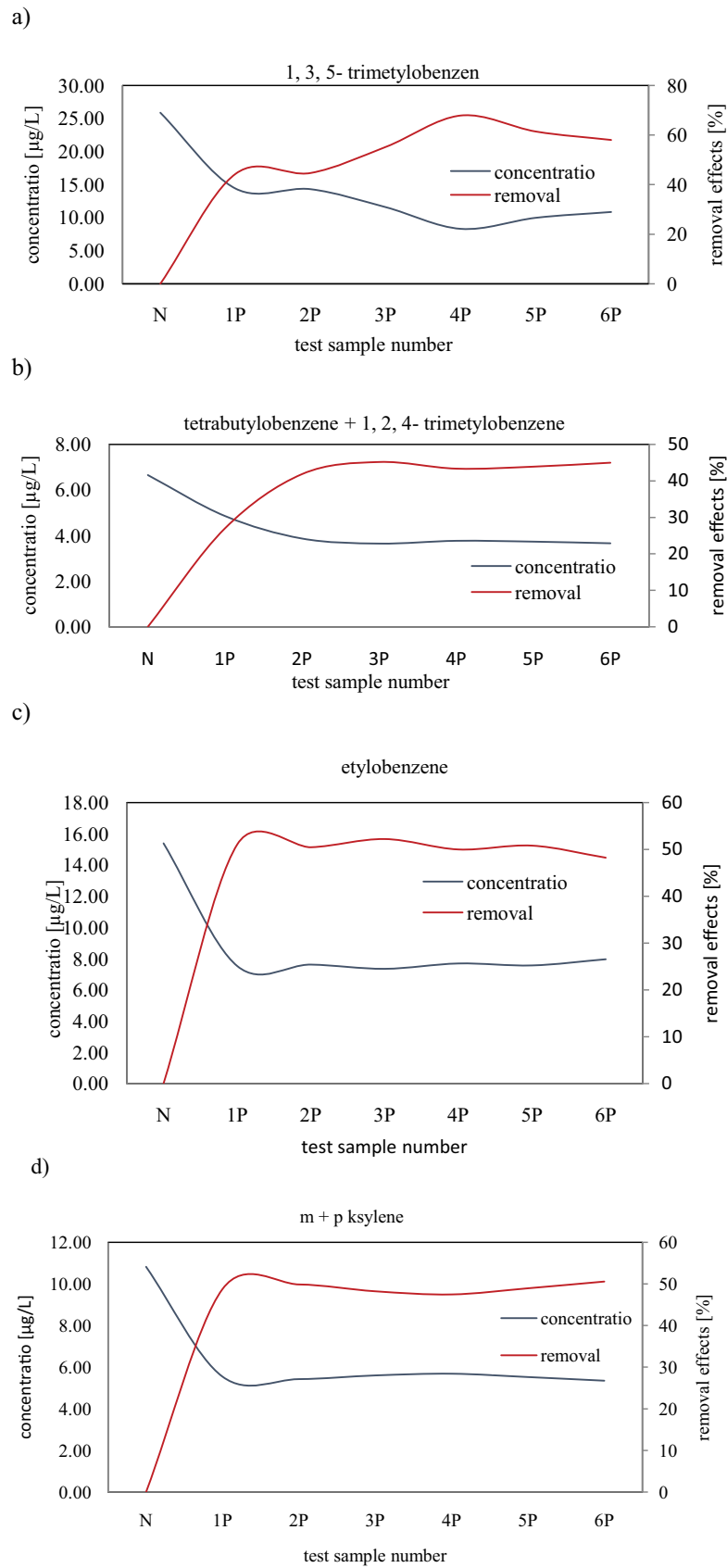


Fig. 2. Removal of selected monoaromatic hydrocarbons in the nanofiltration. (a) 1, 3, 5-trimetylobenzen, (b) tetrabutylbenzene + 1, 2, 4- trimetylobenzen, (c) etylobenzen, and (d) m + p ksylene. Where N-feed, P-permeate after 0.5 h.

Table 2
Concentrations of *n*-alkanes in the feed and permeate after the time

Aliphatic hydrocarbons	Concentration in feed (µg/L)	Concentration in permeate (µg/L) – filtration time 1.0 h	Concentration in permeate (µg/L) – filtration time 2.0 h	Concentration in permeate (µg/L) – filtration time 3.0 h	Concentration in permeate (µg/L) – filtration time 3.5 h
C10	1,306.6	3.061	1.244	5.477	6.38
C11	1,604.6	13.375	14.79	10.91	17.09
C12	1,221.1	19.49	18.56	24.71	20.03
C13	6,998.7	1.013	0.064	0.386	0.749
C14	4,472.8	2.625	2.615	2.322	2.154
C15	3,497.4	0.537	0.253	0.448	0.781
C16	3,253.7	0.499	0.421	0.54	0.751
C17	3,175.9	0.863	0.411	0.478	0.231
C18	2,721.9	0.517	0.635	0	0.478
C19	2,174.9	0.519	0	0.243	0.309
C20	1,894.9	1.317	0.491	0.373	0.454
C21	1,370.2	2.307	0.665	0.551	0.648
C22	1,091.2	9.408	1.897	1.569	1.514
C23	697.42	15.91	3.938	2.417	2.5
C24	438.58	18.34	5.25	3.385	3.155
C25	230.04	18.97	5.7	3.971	3.118
C26	95.042	1.566	0.554	0.367	0.312
C27	44.741	2.094	0.694	0.457	0.577
C28	18.971	1.815	0.584	0.422	0.453
C29	10.154	0.487	0.154	0.09	0.62
C30	3.1792	0.672	0.206	0.106	0.085
C31	1.9471	0.25	0.102	0.008	0.057
C32	0.4821	0.066	0.025	0.005	0.007
C33	0.1022	0.024	0.007	0.001	0.002

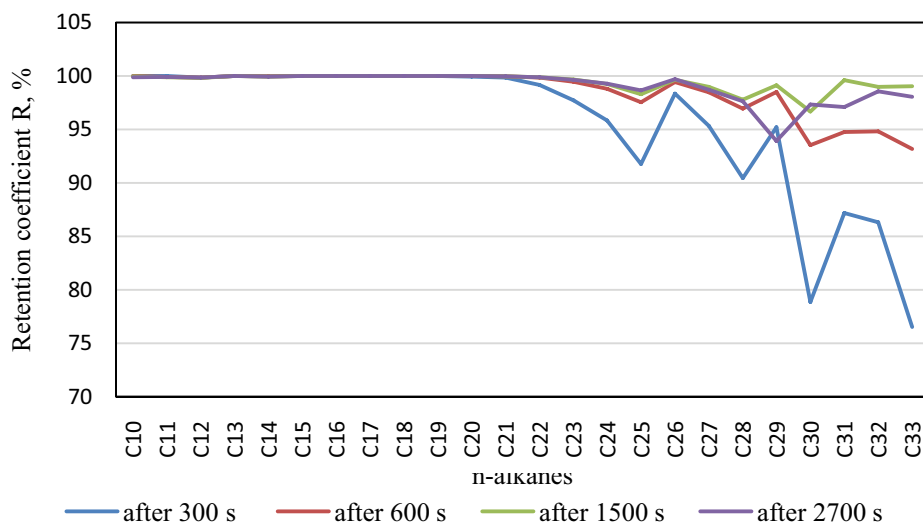


Fig. 3. Retention factors for aliphatic hydrocarbons in the nanofiltration process.

than hydrophilic solutes even with the same solute size, thus resulting in low rejection of the hydrophobic solute than the hydrophilic solute. Kimura et al. [31] pointed out that negatively charged organic compounds were highly (>90%)

removed by negatively charged NF membrane because of the electrostatic repulsion, while positively charged organic compounds were removed less than negatively charged organic due to electrostatic attraction.

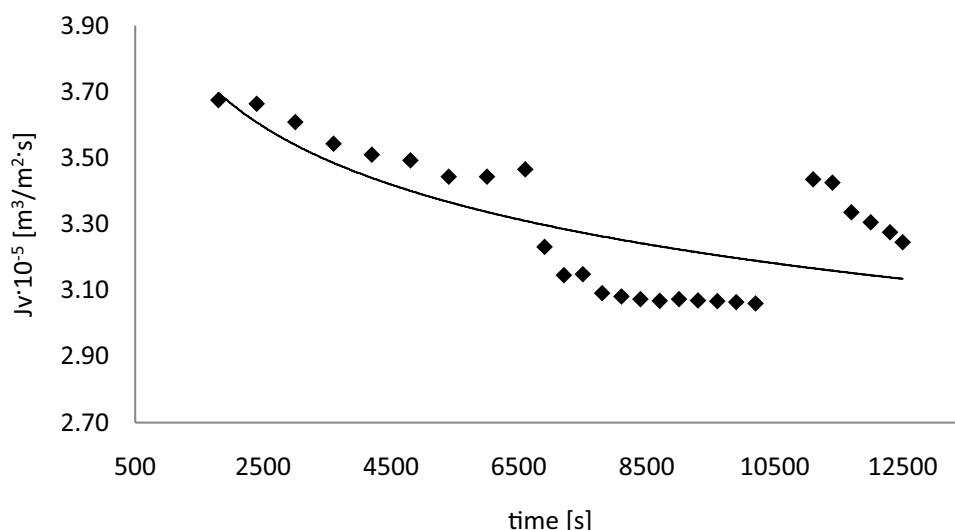


Fig. 4. Membrane permeate flux before rinsing up to 10,500 s of operation and after rinsing with deionized water from 11,000 s of process.

The research conducted for model waters with a high concentration of petroleum hydrocarbons revealed that the decrease in permeate flux [Fig. 4].

The permeate flux during nanofiltration has also a higher value ranging from 3.10 to 3.70×10^{-5} [$\text{m}^3/\text{m}^2 \cdot \text{s}$]. After 2.5 h, the system was rinsed and it was observed that the membrane blocking phenomenon occurred because the flux value was smaller amounting to J_v 3.5×10^{-5} [$\text{m}^3/\text{m}^2 \cdot \text{s}$] as compared to the flux at the beginning of the process. In a very short time, there was a decrease in the permeate flux reaching J_v 3.30×10^{-5} [$\text{m}^3/\text{m}^2 \cdot \text{s}$], which proves that it is not resistant to membrane blocking, and it also means that irreversible fouling appears, because rinsing was not enough to maintain constant performance [26–28]. The rate of flux recovery after 2.5 h was 32%. After the nanofiltration process, the relative permeability of the membrane for permeate was calculated from the average volumetric flow of permeate and volumetric water stream. The obtained value $\alpha = 0.61$ indicates the phenomenon of blocking the surface of the membrane under the influence of impurities contained in water. After washing, the membrane's capacity for redistilled water was similar to ($\alpha_w = 0.75$). During transport through the membrane, additional filtration resistance is generated, in addition to the resistance of the membrane itself, it is also caused by deposition of organic and inorganic compounds on the membrane surface. It should be noted that conducting the process for an extended time, in the concentrating system without the inflow of subsequent portions of feed, promotes the phenomenon of membrane fouling due to the increasing concentration of impurities in the feed tank.

4. Conclusions

Based on the conducted research, the following conclusions were drawn:

- The nanofiltration process can be an effective way of eliminating petroleum hydrocarbons from aqueous

solutions, however, in increasing the removal efficiency, the technological system should be expanded adsorption process or coagulation.

- Removal of *n*-alkanes from water in the nanofiltration process requires the definition of a membrane removal mechanism.
- The nanofiltration process is more effective for *n*-alkanes than for BTEXs.
- It was found that by removing hydrocarbons from the monoaromatic group and *n*-alkanes, different efficiency is obtained.
- When removing petroleum compounds on a commercial membrane, the structure of the selective layer should be known and the phenomenon construction of membrane blocking, and the improvement of the hydraulic performance of the membrane should be assessed.

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