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# Use of integrated process of petroleum removal from water

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ABSTRACT

Petroleum compounds appear in the surface and underground water in increasing concentrations. This is due to the emergence of new risks associated with the production, transport, use, and disposal of hazardous waste substances. These pollutants have a strong toxic impact on the organism, hence they should be removed using the most effective methods. This paper deals with the removal of petroleum compounds from water using a combination of classical and membrane methods. Coagulation and reverse osmosis were applied. The study used model water, i.e. distilled water enriched with a mixture of diesel fuel and gasoline. The aim of the study was to determine the possibility of petroleum removal during the hybrid process. The model water was subject to the coagulation process using $Al_2(SO_4)_3 \cdot 18H_2O$, then filtered and subjected to the reverse osmosis process. Determination of petroleum hydrocarbons in the model water was made after coagulation and reverse osmosis.

*Keywords:* Coagulation; Water; Petroleum hydrocarbons; Reversed osmosis

## 1. Introduction

Petroleum pollution, resulting from human activities, degrade the environment, including a negative impact on living organisms, and consequently on human beings. Given the prevalence of petroleum use, we need to be aware of the consequences of environmental pollution due to petroleum products. Particularly dangerous are disasters occurring in land and sea transport [1,2] because they cause serious point and area pollution, which negatively affects not only the ecosystems, but also the supra-local economy [1]. Petroleum-origin products penetrate the soil and then directly to waters along with sewage and stormwater that wash out the surfaces of streets and roads. Removal of dispersed petroleum pollutants from water is difficult and quite frequently becomes real only when combined with several unit processes in a meaningful model [2]. The investment and operation of such technological systems involves large financial outlays at times. There are still attempts to find ever newer and cheaper technological solutions including water purification of petroleum products or heavy metals [3–6]. Implementation of two unit processes at one stage of the technological system could increase the purification efficiency, which, in consequence, can lower the costs. The process that was used to remove the petroleum hydrocarbons from water is the combination of volume coagulation with the

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membrane process. In order to solve the problem, the possibility of petroleum hydrocarbons removal from water was determined [7].

## 2. Materials, experimental procedure (coagulation, reversed osmosis)

Model water consisted of distilled water and a 1:3 mixture of petroleum and diesel fuel was used in the study. The mixture composition was based on the amount and type of fuel sold in the domestic market in 2008–2010 [8]. In the model water, after coagulation and the reversed osmosis process (RO), the mineral oil index (IOM) was determined as the fractions of hydrocarbons in the range of $C_7$–$C_{35}$, as well as benzene, toluene, ethylbenzene, and xylene (BTEX).

During the study, the petroleum derivatives were removed in the process of volume coagulation combined with RO. The coagulation process required a traditional coagulant—aluminum sulfate (VI) $Al_2(SO_4)_3{\cdot}18H_2O$.
Laboratory tests included following series:

(1) coagulation using different dose of general coagulants (50, 100, 150, and 200 mg/L) along with constant share of petroleum compounds;
(2) coagulation using different share (0.1 $cm^3$–499.19 μg/L, 0.125 $cm^3$–598.38 μg/L, 0.15 $cm^3$–1152.75 μg/L) of fuels mixture and constant dose of coagulant.

Parameters of the coagulation process during tests:

(1) duration of rapid mixing − 60 s and 1,000 rpm;
(2) duration of slow mixing (flocculation) − 30 min, 50 rpm;
(3) filtration on filter paper in order to protect membrane.

The solution after filtration was sampled to determine the IOM and BTEX, and then the remaining part was subject to the reverse osmosis system. In RO process, water, in which the best effect of tested substances removal was achieved, was used. The RO process was carried out on the installation with spiral membrane made of aromatic polyamide. The RO worked in a continuous system with partial recirculation of the concentrate. Membrane filtration tests were conducted at 20˚C under the pressure of 1.2 MPa and linear velocities over the membrane from 0.8 to 1.0 m/s. Before the measurements, deionized water was passed through the membrane to determine the maximum permeate flux, and then the tests were conducted. After testing, the membrane was washed again with distilled water, thereby determining the change in the transport properties of the membrane after operating. Efficiency of the RO process was rated

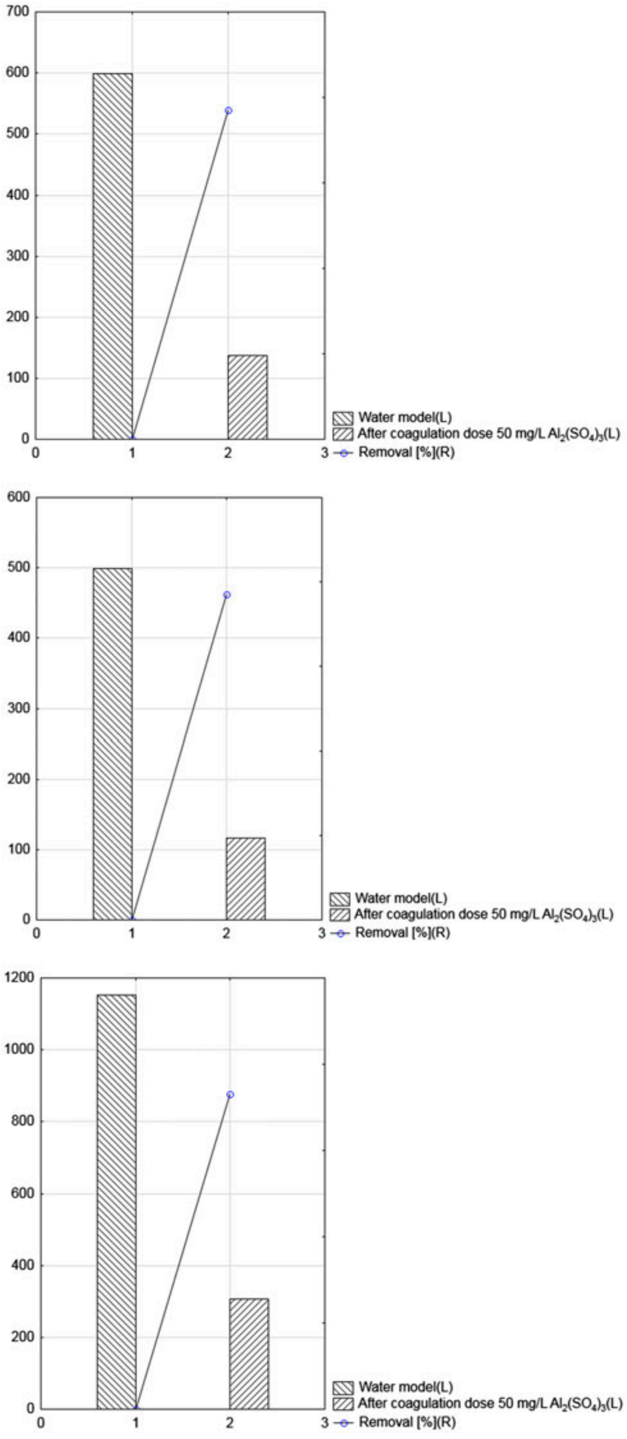

Fig. 1. Effect of petroleum hydrocarbons removal depending on a coagulant rate and concentrations of test compounds in water.

based on the measurement of the volume permeate flux ($J_v$) and a chemical analysis of the permeate and feed. Presented results of petroleum hydrocarbons are expressed as IOM and BTEX. During the RO process, samples for tests were collected every 10 min.

## 3. Methods of analysis of hydrocarbons

Determinations of analyzed petroleum aliphatic hydrocarbons from $C_7$ to $C_{35}$ were performed in accordance with Polish Norm PN-C-04643 using a gas chromatograph coupled with a spectrometer VARIAN 4000. The device was equipped with a column VF-5MS 30 m × 0.25 mm × 0.25 μm. The stationary phase was a polydimethylsiloxane with 5% share of phenol groups. Helium was the carrier gas. Aliphatic hydrocarbons were extracted from water by means of a liquid–liquid technique using hexane. After aqueous and organic layers separation, the eluate was transferred to volumetric flasks, and then dried with anhydrous magnesium sulfate ($MgSO_4$ pure grade). The temperature program: 40℃ (5 min) up to 130℃ (0 min), with a temperature increment of 10℃/min to 300℃; temperature of the transfer line 230℃; and ion source temperature 180℃.

## 4. Result and discussion

Research upon the coagulation process was carried out for concentrations of petroleum hydrocarbons in the model water from 410 to 1,152 μg/L. Using varying doses of the highest effect of petroleum, hydrocarbons removal from water was obtained when the lowest dose of 50 mg/L was applied.

The removal effects ranged from 75 to 81% (Fig. 1). The resultant hydroxide, products of coagulant hydrolysis—$Al(OH)_3$—contributed to the reduction of the oil dispersion, the molecules of which might be absorbed on their surface [9]. The coagulant proved to be quite efficient, since 81% of petroleum hydrocarbons removal was achieved expressed as the IOM for $Al_2(SO_4)_3$. This result was fully satisfying. The use of primary coagulants for the removal of petroleum hydrocarbons was mainly focused on neutralizing the electric charge of the double electron layer of oil molecules, as most petroleum compounds are hydrophobic materials that exhibit a low-affinity energy for water, while high for petroleum compounds. Thus, the coagulation efficiency increases significantly [3,10,11].

After the coagulation process, water was introduced into the RO system. During this (Table 1), IOM ranged from 39% at the highest concentration of 306 μg/L to 90.6% at 267 μg/L (Table 1). It was observed that the index decreased to some point with a subsequent increase. During removal of BTEXs, the retention coefficient varied with the same trends as for IOM: it was high at the beginning, then decreased and increased again in all test series.

Worse removing effects along with treatment time in RO is probably related to the surface charge of the membrane [12,13] and the phenomenon of compounds adsorption on its surface. This is based on the

Table 1
IOM and BTEX concentration in permeate

| | IOM | Toluene | Ethylbenzene | m + p xylene | o-xylene |
|---|---|---|---|---|---|
| Initial concentration, μg/L | 116.55 | 0.22 | 0.07 | 0.26 | 0.12 |
| Retention coefficient, % | 53.4 | 44.4 | 85.6 | 84.3 | 82.7 |
| | 70.4 | 82.2 | 99.9 | 99.7 | 99.9 |
| | 81.5 | 67.6 | 85.6 | 88.3 | 91.3 |
| | 61.6 | 21.3 | 75.6 | 78.3 | 81.3 |
| | 43.9 | 49.7 | 28.2 | 41.3 | 48.1 |
| Initial concentration, μg/L | 267 | 0.43 | 0.11 | 0.35 | 0.34 |
| Retention coefficient, % | 78.8 | 81.5 | 74.6 | 82.3 | 89.4 |
| | 74.8 | 95.4 | 100.0 | 99.9 | 100.0 |
| | 76.6 | 95.4 | 100.0 | 97.1 | 100.0 |
| | 60.4 | 64.9 | 46.9 | 53.6 | 79.4 |
| | 52.0 | 64.2 | 46.9 | 50.7 | 82.3 |
| Initial concentration, μg/L | 306 | 0.99 | 0.27 | 0.85 | 0.37 |
| Retention coefficient, % | 88.5 | 88.7 | 77.5 | 81.1 | 81.1 |
| | 34.5 | 75.8 | 81.3 | 84.6 | 83.8 |
| | 59.2 | 85.9 | 92.5 | 91.7 | 91.9 |
| | 42.6 | 78.8 | 81.8 | 85.4 | 85.2 |
| | 48.9 | 62.7 | 77.5 | 79.9 | 83.8 |

interaction between the membrane surface and the compound as well as the formation of hydrogen bonds. As a result of charge saturation of the membrane surface, there occurs a decrease in the retention of removed substances and the mechanism takes the form of dissolution and diffusion phenomena. Disruption of the separation mechanism in the membrane process is observed during contamination with

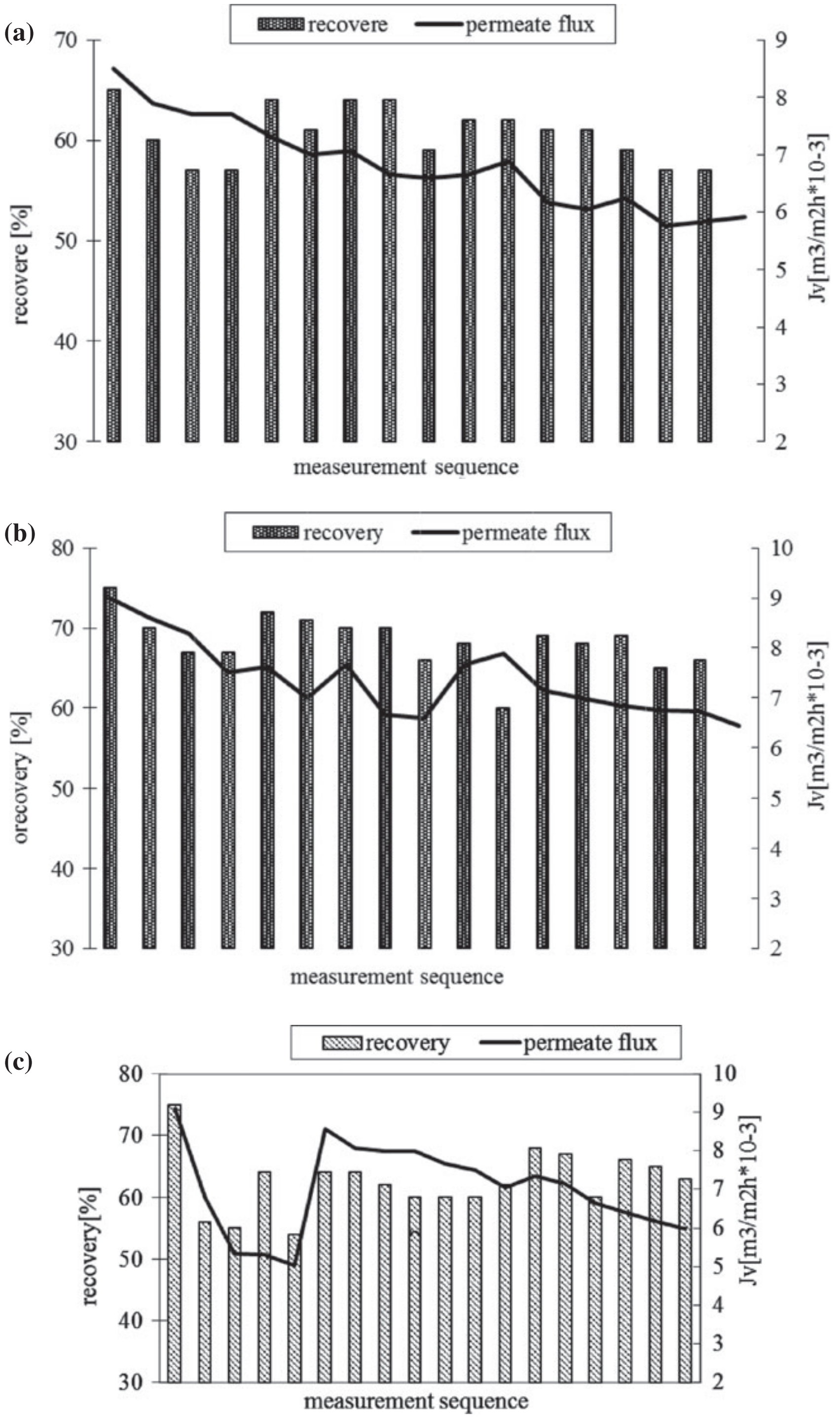

Fig. 2. Influence of IOM concentration in the feed on the water recovery and permeate flux during treatment of model water after coagulation using $Al_2(SO_4)_3 \cdot 18H_2O$. (a) Initial concentration 116 μg/L, (b) initial concentration 267 μg/L, and (c) initial concentration 306 μg/L.

organic sediments and changes in the concentration of micropollutants removal (filtration under concentrating conditions, a process pressure increase) [12,13]. When using polyamide membranes with hydrophobic properties [14], the permeate flux decline is particularly high at the beginning of the process and amounts at a concentration (Fig. 2(a) and (b)) of 116 μg/L IOM to $9 \times 10^{-3}$ m$^3$/m$^2$ h and after 30 min of the process to $7.5 \times 10^{-3}$ m$^3$/m$^2$ h at a concentration of 267 μg/L $J_v$ $8.5 \times 10^{-3}$ m$^3$/m$^2$ h and $7.7 \times 10^{-3}$ m$^3$/m$^2$ h after 30 min. However, the largest change was observed at the highest concentration in the feed 306 μg/L $J_v$, it was $9 \times 10^{-3}$ m$^3$/m$^2$ h, while after 40 min of the process, $J_v$ amounted to $5 \times 10^{-3}$ m$^3$/m$^2$ h. Rinsing of the membrane restored its selectivity, the permeate flux, and recovery. The results presented in Fig. 2 are confirmed by the literature data quoted in the work [14,15,16].

The realization of the membrane process and selection of process parameters are important factors affecting the separation efficiency of petroleum substances. It was found (Fig. 2) that the greater degree of recovery assumed, the higher average volume permeate flux and the higher retention rate are achieved. The study also revealed a decline in the degree of water recovery along with increasing the concentration of petroleum hydrocarbons: 116 and 306 μg/L in the feed (Fig. 2(a) and (c)). The decrease in the hydraulic performance of membranes is associated with an increase in the intensity of modules blocking and deterioration of their separation characteristics. Lowering the linear flow velocity of the liquid has to be associated with an increase in the polarization layer thickness and an increase in the component concentration on the surface of the membrane.

## 5. Conclusion

The system coagulation–reverse osmosis, by utilizing the synergistic effect, makes it possible to achieve greater efficiency of water purification as compared to the unit processes, possibly at slightly higher investment and operating costs. It should be, however, taken into account that a combination of these processes can also reduce the retention of the removed compounds as a result of scaling of the membrane by compounds used for coagulation.

Combining the conventional process with the membrane system allowed for achieving the level of water recovery from 58 to 75%.

The tests indicate that the mechanism of membranes blocking by petroleum substances was not fully recognized and it is problematic due to several factors.

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