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The use of coagulation and reverse osmosis for petroleum hydrocarbons removal from water

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ABSTRACT

Petroleum compounds appear in the surface and ground 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 living organisms, hence they should be removed using the most effective methods. The 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 synthetic water, that is, distilled water enriched with a mixture of diesel fuel and gasoline.

Keywords: Coagulation; Water; Petroleum hydrocarbons; Reverse osmosis

1. Introduction

The most common cause of pollution of the natural environment with petroleum-derived substances is extremely problematic spills [1–3]. The issue of aquatic systems contamination with petroleum products became more important, because their high concentrations were detected not only in surface waters, but also in some groundwater intakes. The awareness of the problem resulted in the development of techniques aimed at removing oil products from the aquatic environment [3,4].

There are known processes dedicated ca. to removal of petroleum compounds from water as: chemical oxidation and membrane techniques (microfiltration and ultrafiltration). However, there is no system that includes efficient removal of petroleum products including benzene, ethylbenzene, toluene, *ortho-*, *meta-*, *para-*xylene (BTEX), and aliphatic hydrocarbons. In the available literature, there are several studies on combining different methods to remove all compounds of a given group, by modifying the process parameters. Presented results of researchers dealing with the problem of hydrocarbons removal from water [2,5] and previous own research indicate that it is appropriate to evaluate the effectiveness of removing the BTEX and aliphatic hydrocarbons from water and to determine the mechanisms of their separation in integrated systems by combining the classical method with the high-pressure membrane method.

The aim of the study was to determine the possibility of petroleum components removal during the hybrid process. The synthetic water was subjected to the coagulation process using $Al_2(SO_4)_3 \cdot 18H_2O$, then filtered and subjected to the reverse osmosis (RO) process. The determination of petroleum hydrocarbons in the synthetic water was made after coagulation and RO.

2. Methods

2.1. Subject of study

The experiments were carried out using synthetic water, which was made on redistilled water matrix enriched with a mixture of diesel oil and gasoline (MP). The mixture comprised of petrol and diesel oil in the ratio of 1:3 volumetric (MP). The ratio of fuel mixture resulted from the quantity and type of fuels sold on the domestic market in 2008–2010 [5].

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Benzene, ethylbenzene, toluene, *ortho-*, *meta-*, *para-*xylene (BTEX), and aliphatic hydrocarbons (*n*-alkanes) from dodecane to tetratriacontane ($C_{12}H_{26}$ to $C_{34}H_{70}$) were selected for the tests [6]. In the article, instead of systematic, a simplified name for particular C_{12}–C_{34} hydrocarbons was used. In water used for testing (Table 1), that is, redistilled water with MP, higher concentrations of BTEX and *n*-alkanes, exceeding the environmental concentrations were used, because the adopted order of magnitude facilitated the procedure of sample preparation and increased the accuracy of conducted measurements [6].

2.2. Technological research

Technological research was carried out in various variants: as a single volume coagulation process, single-stage RO and in the integrated system of volume coagulation – RO.

Aluminum coagulants, iron salts (PIX), and hydrolyzed aluminum coagulants (PAX) were used for coagulation in preliminary experiments. Coagulant doses were calculated based on the absorption spectrum in the range of 250 ÷ 350 nm to determine the concentration of organic matter (SUVA) in water. Following doses were used: PIX – 72 mg/dm^3, PAX – 8 mg/dm^3, 5% $A1_2(SO_4)_3\cdot18H_2O$ – 12 mg/dm^3. The most effective coagulant, which was 5% $A1_2(SO_4)_3\cdot18H_2O$, was selected for further tests. The applied doses of 5% $A1_2(SO_4)_3\cdot18H_2O$ were 6, 12, 24, and 36 mg/dm^3.

Prepared sample of synthetic water of a volume of 2 L along with the set dose of the mixture of diesel oil and gasoline was subjected to a coagulation process. All coagulation tests were carried out at room temperature. Such prepared samples were subjected to the mixing process carried out on a magnetic stirrer in two phases: fast mixing – 2 min, 1,000 rpm, slow mixing – 20 min, 50 rpm, and then to sedimentation – 45 min.

In the conducted tests, the RO process was carried out in a continuous system with partial recirculation of the concentrate on a small RO station. The research was performed on a composite membrane made of an aromatic polyamide by Dow Filmtec (USA) with a spiral module and cross-flow filtration. Installation in the RO station was made of stainless steel. Process parameters were experimentally determined as follows:

Volumetric permeate flow for distilled water
$J_w = 5.32 \times 10^{-6}$ m^3/m^2 s, (ΔP = 1.2 MPa)

NaCl retention coefficient (concentration 1 g/dm^3,
ΔP = 1.2 MPa) – 98%.

The osmotic membrane, during the prefiltration, was subjected to conditioning by filtering the redistilled water to stabilize the volumetric permeate stream. Then, the research on filtration in a cross-pattern of synthetic water prepared on the basis of redistilled water with the addition of MP, at the transmembrane pressure range of 1.0 ÷ 1.2 MPa, changing the pressure in intervals by 0.1 MPa with feed temperature in the range of 20°C and degree of water recovery from 30% to 90% at a linear feed rate of 1.1 m/s, were started.

The RO research system was rinsed when the efficiency dropped by 10% or the content of hydrocarbons in the treated water increased noticeably or the differential pressure increased by 15% as compared with the reference state. The cleaning was carried out using a multistage membrane product (EnCh 016 acidic) to remove $CaSO_4$ and $CaCO_3$, then (EnCh 006 alkaline) to eliminate microbial contamination [6]. The system was then rinsed with redistilled water. The efficiency of the RO process was established by determining the volumetric dependence of the permeate flux on the time at the given pressure, as well as by the retention coefficient of the petroleum hydrocarbons. The comparison of the stream of redistilled water before and after the process of membrane filtration of contaminated water enabled to determine the contamination of the diaphragm of reversible and irreversible nature.

Table 1
Quality of model water for technological research in terms of BTEX and *n*-alkanes content

Water type	Redistilled + MP^a
Temperature (°C)	20
Absorbance (UV254-350) (cm^{-1})	0.043–0.402
ΣBTEX (mg/dm^3)	0.800–35.00
$\Sigma C_{12}H_{26}$-$C_{34}H_{70}$ (µg/dm^3)	13.00–115

MP^a – a fuel mixture consisting of diesel fuel and gasoline at 1:3 ratio.

2.2.1. Integrated systems

The study of the effectiveness of oil derivatives removal in integrated systems consisted of the purification of a synthetic water by coagulation followed by RO. Membrane filtration was carried out as in the single-stage process. Before the actual measurements, the redistilled water was passed through the membrane to determine the maximum permeate flux, then the appropriate tests were carried out. After the appropriate tests, the membrane was rinsed again with redistilled water to determine the change of transport properties of the membrane after the treatment process. The effectiveness of the water filtration process was evaluated based on the volumetric permeate flux (J_v) measurement and its chemical analysis.

2.3. Analytical methodology

Determinations of petroleum hydrocarbons (*n*-alkanes, BTEX) in water were made using gas chromatograph 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 (Na_2SO_4). Concentrated extract was subjected to separation and detection on a GC-MS instrument. The carrier gas used was helium with 6.0 purity. Aliphatic hydrocarbons were extracted from water applying liquid–liquid method using hexane.

3. Results and discussion

Iron sulfate, aluminum sulfate, and PAX 16 were used in the preliminary tests of the coagulation process. Following doses: PIX – 72 mg/dm^3, PAX – 8 mg/dm^3, 5% $A1_2(SO_4)_3\cdot 18H_2O$ – 12 mg/dm^3 were applied. Aluminum sulfate turned out to be the most effective for BTEX removal (Fig. 1).

Similar study was conducted by Santo et al. [7] and Demirci et al. [8], in which the authors showed that the use of aluminum sulfate coagulant was markedly more effective in removing petroleum substances from water than other coagulants such as iron sulfate or hydrolyzed aluminum coagulant (PAX). Organic compounds were probably complexed, aggregated, or sorbed on flocks of precipitated aluminum hydroxide. On the other hand, according to Pernitsky and Edywald [8–10], the presence of polymeric aluminum forms in solutions of polyaluminum chloride made them more effective in the destabilization of colloids with negative electric charge than in case of aluminum sulfate, removal of organic contaminants, and impurities causing the color and turbidity of water. It was also found that the effectiveness of polyaluminum chloride increases with increasing their alkalinity. In their opinion, prehydrolyzed coagulants reduce the pH of treated water compared with unhydrolyzed one to a lesser extent. The fundamental research carried out in the coagulation process (Fig. 2) showed that the *n*-alkanes were better removed at a dose of 24 mg $Al_2(SO_4)_3\cdot 18\ H_2O$, obtaining from 3% to 12% higher values in regard to other doses of the coagulant used. It was noticed that more volatile saturated aliphatic hydrocarbons were worse removed, probably due to easier dissolution in water. The *n*-alkanes removal rate, at the optimum dose, ranged from 43% to 58%. The optimal dose of the coagulant for *n*-alkanes was 24 mg/dm^3.

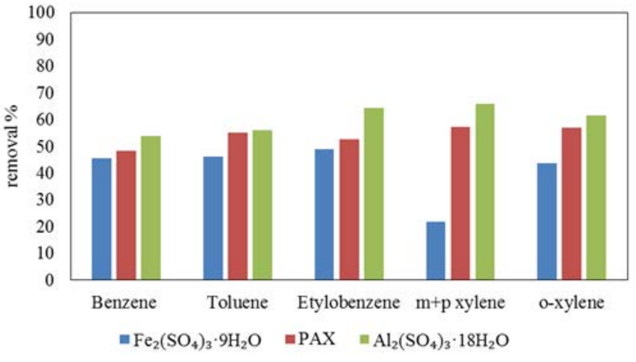

Fig. 1. Purification of water contaminated with petroleum hydrocarbons by coagulation using different coagulants.

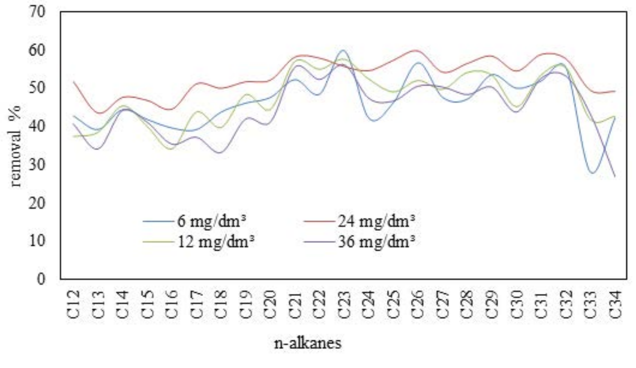

Fig. 2. Removal of *n*-alkanes from water during the coagulation process.

The effective dose of coagulant for (Fig. 3) BTEX contaminants elimination was 12 mg/dm^3, resulting in removal of 64% for ethylbenzene and xylenes, 51% toluene, and 44% benzene. The lowest effects for benzene could be associated with the highest, amounting to 1.78 mg/dm^3, solubility of benzene in water and an octanol/water partition coefficient equal to 2.13, which indicates on a low ability of benzene to be sorbed on the surface of flocs. It was noted that the effect of oil derivatives removal was higher for aluminum sulfate with flocculant in relation to the coagulant itself [6,10–12]. By removing hydrocarbons, it was shown that attention should have been paid to the type of compounds being removed, because the optimal dose for *n*-alkanes was higher than in the case of BTEXs.

The highest removal results after RO for BTEX (Table 2) were obtained in all series for *o*-xylene at the level of 87%, while the lowest retention coefficients were obtained for benzene ranging from 49% to 85.9%.

The lower removal effects along with the treatment time (Table 2) in RO was probably related to the surface charge of the membrane [6,12,13] and phenomenon of adsorption of compounds on the membrane surface. Interaction between the surface of the membrane and the compound and the formation of hydrogen bridges lies at the basis of this phenomenon.

By carrying out the RO process after coagulation, there was a significant increase in the retention coefficient (Fig. 4) observed for *n*-alkanes from 25% to 40% in relation to the effects obtained in the coagulation process. Coagulation removes molecules with higher molecular weight, while smaller colloids and organic substances with lower molecular mass can settle on the membrane surface, creating a cake that can be removed by chemical methods. However, if fouling is hydrodynamically reversible, addition of a coagulant may lead to an increase in resistance and a decrease in membrane permeability [11,14–17].

Values of the permeate flux varied depending on the process and ranged from 1.08 (Fig. 5(a)) for a single process to 1.45 m^3/m^2 h × 10^{-6} (Fig. 5(b)) for an integrated system. Coagulation reduced the amount of impurities on membrane and this caused the permeate flux to increase in comparison to a single-stage process [6,13,14]. It was due to the presence of hydrocarbons or colloidal substances, which

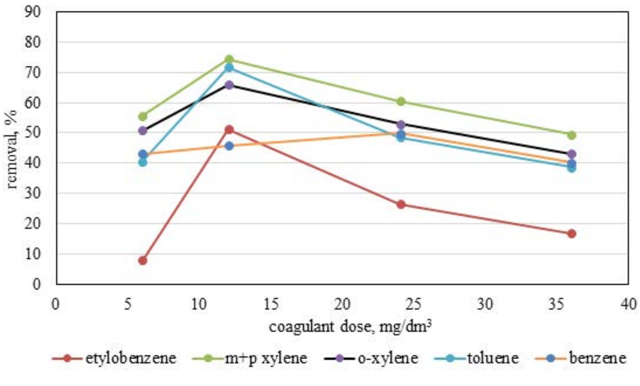

Fig. 3. The effect of aluminum sulfate dose on BTEX coagulation process.

Table 2
BTEX concentration after coagulation and retention rate after reverse osmosis

	Time of sampling (s)	Benzene	Toluene	Etylobenzene	*m*+*p* xylene	*o*-xylene
Concentration after coagulation (μg/dm³)		**0.146**	**0.512**	**0.982**	**1.765**	**0.14582**
Retention coefficient (%)[a]	600	85.9	82.2	99.9	99.7	99.9
	1,200	78.4	77.6	85.6	88.3	85.3
	1,800	68.8	64.4	75.6	84.3	82.7
	2,400	49.2	49.7	68.2	41.3	78.1
Concentration after coagulation (μg/dm³)		**0.410**	**1.229**	**1.519**	**4.391**	**0.410**
Retention coefficient (%)[a]	600	85.3	95.4	100.0	99.9	100.0
	1,200	72.6	95.4	100.0	82.3	100.0
	1,800	60.3	81.5	74.6	71.1	89.4
	2,400	59.8	64.2	46.9	50.7	82.3
Concentration after coagulation (μg/dm³)		**1.819**	**3.717**	**5.855**	**12.778**	**1.819**
Retention coefficient (%)[a]	600	85.2	88.7	92.5	91.7	91.9
	1,200	78.5	75.8	81.3	84.6	81.1
	1,800	68.5	85.9	77.5	81.1	83.8
	2,400	58.7	62.7	77.5	79.9	83,8

[a] Samples were taken every 600 s.

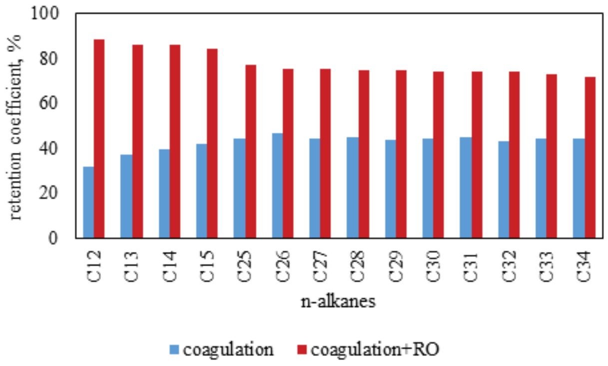

Fig. 4. Change in the retention coefficient of *n*-alkanes after coagulation process and after coagulation with RO.

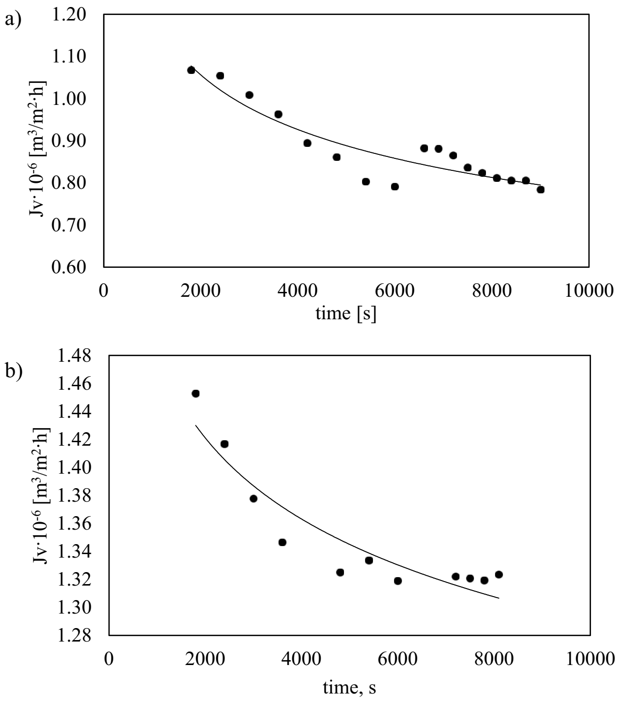

Fig. 5. Volumetric permeate flux in a single and integrated process: (a) RO single process and (b) RO after coagulation.

were probably suspended in the treated water, while they became destabilized under coagulation conditions and formed larger aggregates, which ultimately affected the membrane efficiency [1,12,13,18,19]. Aggregation of small colloidal particles induced by coagulation led to the formation of larger particles in the filter cake layer, which as an effect reduced the relative resistance and the cake characterized with greater compressibility [12]. Specific resistance and compressibility of the filter cake are closely related to the mechanism of destabilization of dissolved colloids and organic substance [19,20]. Gupta et al. [21] noted that resistance of the cake composed of coagulation flocs was less than the resistance caused by floating flocs and organic substances that did not coagulate during water purification (coagulation/ultrafiltration).

After the RO process, the relative permeability of the membrane was calculated from the average volumetric flux of permeate and volumetric water flux.

Relative flux was calculated from the following formula:

$$\alpha = \frac{J_v}{J_w}$$

where α = relative flux; J_v = volumetric permeate stream; and J_w = volumetric water stream.

The obtained value $\alpha = 0.59$ indicated on the phenomenon of blocking the surface of the membrane under the influence of impurities present in water. It was greater in the integrated process, which indicated that coagulation increased the performance of the membrane. Contaminants present in tested water probably aggregated and adsorbed on the flocks of precipitated coagulant and were partially removed outside the system during the sedimentation process. Coagulation reduced the phenomenon of membrane blocking. Studies showed that greater adsorption on the membrane occurred at the beginning of the process. After washing, the membrane's capacity for redistilled water was similar ($\alpha_w = 0.75$). Values of relative water permeability coefficient were $\alpha < 1$ for both simulated water and membrane washing. The size of these coefficients indicated that the membrane was blocked (fouling) by organic matter [22–26]. It should be assumed that this was influenced by the nature of petroleum hydrocarbons and their affinity to the material of the membrane. The performance of coagulation before the membrane process undoubtedly brought benefits in relation to membrane operation and probably contributed to the creation of reversible fouling.

4. Conclusions

The following conclusions were drawn from the conducted research:

- It was found that removal of individual hydrocarbons from the BTEX group and *n*-alkanes in the coagulation process yielded to different efficiencies.
- The coagulation process decreased the adsorption of contaminants on the membrane surface and improved hydraulic performance of the membrane.
- Results of the research allowed for the analysis of petroleum hydrocarbons removal in the unit processes and in the integrated system as well as to establish the mechanism of tested compounds removal in the RO process.

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