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Use of porous materials to remove oil contaminants from water

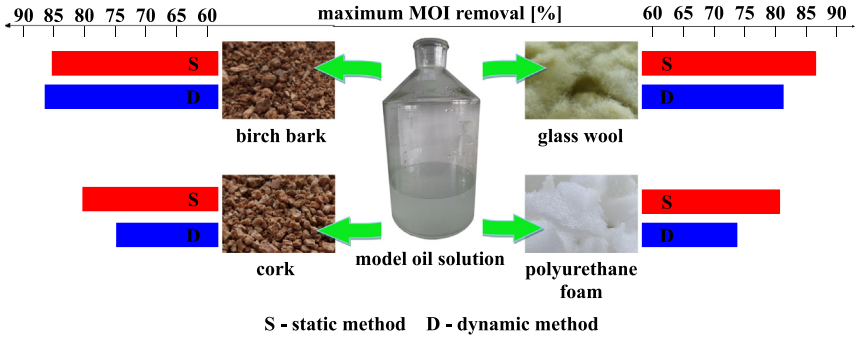
Adam Gołub *, Janina Piekutin

Technical University of Białystok, 45A Wiejska Str., 15-351 Białystok, Poland

HIGHLIGHTS

- Many sorbents efficiently remove oil contaminants.
- The most effective removal of MOI and n-alkanes are birch bark and glass wool.
- Polyurethane foam and cork are not effective in removing MOI and n-alkanes.
- n-Alkanes are more effectively removed than MOI.

GRAPHICAL ABSTRACT



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ABSTRACT

The purpose of the research was to remove petroleum substances from water using porous materials. Birch bark, cork, glass wool and polyurethane foam were used for the study. The model solution was distilled water enriched with a mixture of petrol and diesel fuel in a volume ratio of 1:3. The model water used had 3 different concentrations of oil substances. The research included petroleum substances expressed as mineral oil index and aliphatic hydrocarbons, n-alkanes (from C7H16 to C38H78). The process of oil substances removal was carried out applying two methods: static and dynamic. Based on the research, it was found that materials the most effective in lowering the index of mineral oil and C7H16–C38H78 n-alkane concentrations were both birch bark and glass wool, both static and dynamic, while cork and polyurethane foam were less effective. In addition, concentration of C7H16–C38H78 n-alkanes was lowered in each measurement series to a greater extent than the mineral oil index.

1. Introduction

Oil contaminants entering the water are a complex mixture of various hydrocarbons: aliphatic (C_nH_{2n+2}), naphthenic (i.e. cycloalkanes) and aromatic (Muir and Bajda, 2016). There are many sources of oil substances in the water. The most important of these are: natural gas seeps from the seabed and ocean floor, drilling in the bottom, leakage of oil extraction and transportation facilities, inland and marine navigation, emergency floods (e.g. collisions or breakdowns of tankers), road and air transport, waste petroleum-based industrial installations, and storm water from urban areas (Gutteter-Grudziński, 2012; Polkowska and Błaś, 2010).

The tragic effects of oil spills on water have led to the development of a number of methods for removing such contaminants from the aquatic environment. Among actions taken to reduce the negative effects of oil spills, the first is the observation and control of the pollution source and protection of human life and safety. The term "response actions" includes strategies, equipment, technologies and approaches used to remove spilled contaminants and mitigate the potential effects of such spills (Fingas, 2016). Basic strategies for controlling the oil spill in seas and coasts include (Fingas, 2016; Adebajo et al., 2003):

* Corresponding author.
E-mail address: a.golub@doktoranci.pb.edu.pl (A. Gołub).

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- source control,
- surveillance and monitoring,
- use of mechanical equipment,
- use of dispersants,
- controlled burns in situ.

Often, several methods are used to remove oil stains. Their choice depends on the size of the spill, nature of water and the weather, but there are no universal de-oiling systems that can be used in any case. A method that deserves special attention is the use of porous materials, i.e. sorbents, which are readily available, simple to use, cheap, and most importantly, non-toxic to the environment.

Sorption is a physical method of oils removal in which the process of their absorption and adsorption takes place. The effectiveness of sorbents in the removal of pollution depends on (Dies et al., 2007):

- surface expansion,
- physical and chemical characteristics of the surface,
- inter-phase liquid-solid tension,
- dimensions of fibrils, grains or pores,
- oil viscosity.

Sorbents most commonly used to remove oil spills can be divided into (Adebajo et al., 2003; Bandura, Franus, Panek, et al., 2015):

- inorganic mineral materials (e.g. diatomites, diatomaceous earth, perlites, clay minerals, zeolites, fly ash, activated carbons or silica gel);
- organic mineral materials (e.g. peat, sawdust, wood, waste bark, cellulose from paper production, cotton, kapok and rice husks);
- synthetic organic polymers (e.g. polypropylene, polyethylene, polyacrylate, polystyrene or polyurethanes).

Materials from the above groups were selected for the study. Glass wool is classified into inorganic mineral materials, birch bark and cork into organic mineral materials, while polyurethane foam into synthetic organic polymers.

The purpose of the research was to remove petroleum substances from the water using porous materials.

2. Materials and methods

The study used porous materials such as birch bark, cork, glass wool and polyurethane foam. Dimensions of particles are shown in Table 1.

The model solution consisted of distilled water enriched with a mixture of petrol and diesel fuel in a volume ratio of 1:3. This proportion of fuel mixture reflected the quantity and type of fuel supply on the domestic market in 2008–2010. In order to obtain an adequate degree of dispersion of oil substances in water, the sample was sonicated in a sonicator. Such prepared model water contained hydrocarbons that were the subject of analysis.

The research included petroleum products expressed as mineral oil index (MOI) and aliphatic hydrocarbons n-alkanes (from C_7H_{16} to $C_{38}H_{78}$). In Table 2 and Table 3 are shown different concentrations of oil substances in model water and their standard deviations. To compare effectiveness of different sorbents and methods Fisher's exact test was performed. It was assumed that probability value less than or equal to 0,05 means that the difference was statistically significant.

Table 1
Dimensions of particles of porous materials.

Sorbent	Dimension
Birch bark (grains)	0.1–1 mm
Cork (grains)	0.1–1 mm
Glass wool (squares)	2 × 2 cm
Polyurethane foam (squares)	1 × 1 cm

2.1. Methodology of technological research

The process of oil substances removal was carried out applying two methods: static and dynamic. The study was carried out in 3 repetitions on model water with the concentrations of petroleum substances listed in Tables 2 and 3.

2.1.1. Static method

In the static method, test samples were prepared by mixing 1 dm^3 of model water with 20 g of porous material and then allowed to stand for 1 h. In this way, the process was carried out for each porous material and three different concentrations of petroleum substances.

2.1.2. Dynamic method

The dynamic removal of oil substances was carried out in a column filled with 20 g porous material. The 500 ml model water was filtered through this column with a constant deposit load of 1.06 $m^3\ m^{-2}\ h^{-1}$. In this way, the process was performed for each porous material and model water of all prepared concentrations of petroleum substances.

2.2. Methodology of analytical research

Determinations of MOI and aliphatic hydrocarbons in each sample were made using a gas chromatograph coupled with VARIAN 4000 mass spectrometer. The analyte was separated on a VF-5MS column measuring 30 m × 0.25 mm × 0.2 mm. The stationary phase of the column was polydimethylsiloxane with 5% phenyl groups.

The procedure for sample preparation was divided into several stages: fixation, extraction, purification and concentration. The fixation of the sample consisted in its acidification using an inorganic acid to a pH of about 2.

Liquid-liquid extraction was used to isolate the compounds making up the n-alkanes. The separation was carried out at room temperature of ±20 °C on a magnetic stirrer at a rotational speed of about 800 RPM, using 50 ml of a 2:1 mixture of hexane and dichloromethane. After separation of the aqueous and organic layer, the eluate was transferred to volumetric flasks and then purified on florisil and dried over anhydrous sodium sulfate p.a. The extract was separated from the water sample and concentrated to a volume of 1.5 ml. The concentrated extract was subjected to GC/MS separation and detection with the following operating parameters:

- volume of injected sample: 1 μl,
- no carrier gas stream sharing (splittless mode),
- injector temperature: 250 °C,
- carrier gas flow rate: 1 ml/min,
- initial oven temperature: 40 °C — isotherm 5 min,
- final oven temperature: 300 °C — isotherm 20 min,
- temperature increase: 10 °C/min,
- transfer line temperature: 230 °C,
- ionic source temperature: 180 °C,
- range of scanned masses: 40–400 *m/z*.

Table 2
Concentration of petroleum substances in model water samples.

Series	MOI [μg dm^{-3}]		∑n-alkanes [μg dm^{-3}]	
	Average concentration	Standard deviation	Average concentration	Standard deviation
I	51.6	2.3	8.3940	0.4
II	67.8	2.8	9.4276	0.6
III	73.1	2.1	10.4276	0.6