New Hydrocarbon Bioproducts: Searching for Effective Methods for Their Removal from Water in the Event of a Spill

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Abstract

The petrochemical industry produces chemicals that form the basis for a wide range of products that are crucial to our daily lives. In particular, aromatic hydrocarbons (including BTX: benzene, toluene and xylene) are very important petrochemical raw materials. In many cases, hydrocarbon products, obtained from fossil fuels such as crude oil, can be acquired from alternative carbon feedstock like biomass. One example can be the production of aromatic biohydrocarbons from ethyl alcohol previously obtained from plants. However, it should be noted that these bioproducts can pose a threat to the environment during transport and storage similar to those caused by crude oil. Especially, when they leak and seep into the water. In this regard, the question arises of whether oil dispersants, which can be one of the manners of response ways in aquatic environments affected by crude oil spills, are also effective in the case of leaks of these liquid hydrocarbon bioproducts?

The aim of the study was to evaluate the effectiveness of the EXOdis OS6 dispersant in the dispersion of liquid aromatic biohydrocarbons (Ekobenz Sp. z o.o., Poland) in a 3.3% NaCl solution and in Baltic Sea water. For comparative purposes, the effectiveness of this dispersant in dispersing crude oil from the Grabownica, Magdalena and Wańkowa reservoirs (Carpathians, Poland) was also presented. The study was conducted using the "baffled flask test" research procedure. The aromatic biohydrocarbons and crude oil content in the water was determined by UV-Vis spectroscopy.

Furthermore, this study used infrared spectroscopy to examine the effect of dispersant use on the interaction of tested aromatic biohydrocarbons with kaolinite, a clay mineral that can be a component of marine bottom sediments.

Keywords: *aromatic biohydrocarbons, oil spill, effectiveness of dispersant, baffled flask test, IR spectroscopy, UV-Vis spectroscopy*

1. Introduction

Chemicals produced by the petrochemical industry constitute the fundamental raw materials for a vast array of products essential in daily life. Notably, aromatic hydrocarbons (including benzene, toluene and xylene) are key intermediaries in the production of many of these materials [1]. The chains of transformations that aromatic hydrocarbons undergo after they are formed can be long before a suitable product appears in front of the consumer. For example, most of the benzene produced is used to produce ethylbenzene, which is then used to fabricate styrene. The polymerisation of styrene produces the important polymer polystyrene. Polystyrene is also used to produce ABS (acrylonitrile butadiene styrene) resins. On the other hand, over 20% of the benzene produced is used to produce cumene, which is then used to produce phenol and acetone. Phenol is used in the production of phenolic resins, bisphenol A, pharmaceutical products, solvents, and various plastics with different physicochemical properties and, therefore, diverse applications [2].

Recently, new methods have been developed for producing aromatic hydrocarbons, including BTX hydrocarbons, which accounts for 30% of current petrochemical production by weight [1,3]. One of the methods is production of BTX by catalytic pyrolysis of different types of plastic-waste [4-6]. The other method is production of biohydrocarbons and/or their derivatives from plant material [7-10]. The most common process routes for obtaining bioaromatics from various type of biomass are gasification, pyrolysis and hydrolysis [8]. These highly valuable initiatives for obtaining bioaromatic hydrocarbons limit the exploitation of fossil fuel deposits and reduce CO_2 emissions.

However, it should be noted that these bioproducts can pose a threat to the environment during transport and storage similar to those caused by crude oil. Especially, when they leak and seep into the water. Aromatic hydrocarbons are toxic and are widely listed on the priority substances list developed by the U.S. Agency for Toxic Substances and Disease Registry [11]. The priority list ranks 275 substances are considered to pose the greatest potential threat to human health. The list includes benzene, xylenes (total), toluene and naphthalene, occupying positions 6, 65, 75 and 82, respectively. Of the 100 compounds on this list (in addition to the aromatic hydrocarbons mentioned above), 36 compounds contain benzene in their structure (these are mainly chlorine-containing compounds).

As new hydrogen bioproducts are introduced to the market, questions arise about the best and proper method of removing them if they leak into the aquatic environment. In this regard, the question arises whether oil dispersants, which can be one of the manners of response in a aquatic environments affected by crude oil spills, are also effective in the case of leaks of these liquid bioproducts?

Oil dispersants are typically formulated as mixtures of surfactants dissolved in one or more solvents. The application of these chemical agents on the oil spill layer reduces surface tension and promotes micelle formation, which leads to the fragmentation of the crude oil into tiny droplets. Such dispersed fractions are subsequently biodegraded by microorganisms, which then become part of the trophic chain, serving as food for protozoa and nematodes [12-14]. The application of chemical dispersants in oil spill response strategies consti-

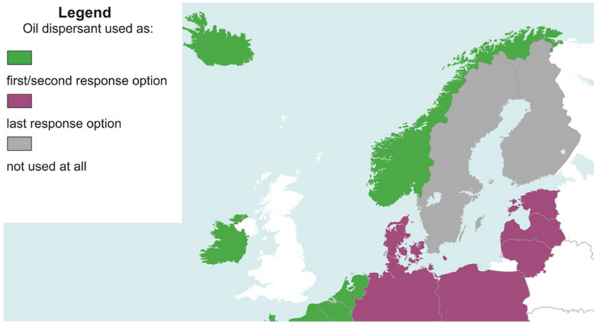

Fig. 1. Dispersant usage in selected European countries in the Baltic Sea region according to EMSA – European Maritime Safety Agency [19]
Rys. 1. Wykorzystanie dyspergatorów w wybranych krajach europejskich regionu Morza Bałtyckiego według EMSA – Europejskiej Agencji Bezpieczeństwa Morskiego [19]

Tab. 1. Chemical composition of EXOdis OS6 [28]
Tab. 1. Skład chemiczny EXOdis OS6 [28]

Chemical name	CAS (Chemical Abstracts Service) registry number
2-(2-butoxyethoxy)ethanol	112-34-5
alcohols, C_{12-14}, ethoxylated	68439-50-9
2-aminoethanol	141-43-5
sodium hydroxide	1310-73-2

tutes a trade-off between mitigating acute surface impacts on coastal biota and introducing toxic compounds into the water column. An oil film persisting on the surface of the water poses a significant health risk to avian species and air-breathing marine fauna. Conversely, chemical dispersion enhances the bioavailability of hydrocarbons in the water column; thereby increasing exposure of aquatic organisms to the toxic effect of both the dispersed oil and the dispersant itself [15].

The first large-scale use of dispersants took place in 1967 off the coast of Great Britain. In the Torrey Canyon tanker catastrophe, 100,000 tons of Kuwaiti crude oil spilled into the waters, and 3,000 tons of detergents were used to disperse it [16,17]. Currently, despite their disadvantages, dispersants are approved for use in many countries as the first, second or last option for responding to oil spills into the aquatic environment. Figure 1 shows dispersant usage in selected European countries in the Baltic Sea region [18,19].

Fortunately, according to statistics from the International Tanker Owners Pollution Federation (ITOPF), the number of crude oil spills from tankers is steadily decreasing (database from 1970 to the present) [20]. However, the threat of spills remains real; stemming from the fact that approximately 90% of the world's crude oil is transported by tankers [21,22]. Therefore, tanker sea routes and port areas are the most vulnerable to spills. The Baltic Sea is one of the world's busiest waters. The closed nature of the body of water, combined with the high degree of urbanisation along the coast and the intensive industrial activity of the Baltic basin countries, makes the sea particularly vulnerable to pollution with oil derivatives. It plays a key role in shipping, including as a corridor for crude oil exports from Russia [23-26]. Many ports, including the Gdańsk Oil Port, are becoming increasingly active. In 2024, the oil port in Gdańsk received 489 tankers and handled 38.8 million tons of crude oil and liquid fuels [27]. The transport by sea of other oily substances such as biofuels and other oily substances like liquid biohydrocarbons is also becoming increasingly important.

There is therefore a need to conduct studies which simulate the behaviour of these new products in the aquatic environment in order to design the most effective strategy for their removal in the event of a potential future spill. Therefore, there is a need to test oil dispersants not only for crude oil spills but also for spills of other oily liquids. In this context, the objective of the present study was to conduct experimental investigations assessing the efficiency of the oil dispersant EXOdis OS6 in treating liquid aromatic biohydrocarbon samples (Ekobenz Sp. z o.o., Poland). The dispersant EXOdis OS6 was evaluated for its effectiveness in dispersing liquid aromatic biohydrocarbons in both a 3.3% NaCl solution and in Baltic Sea water. For comparative purposes, the dispersant's performance was also inspected on crude oil obtained from the Grabownica, Wańkowa and Magdalena fields (Carpathian Mountains, Poland). In addition, the study investigated the impact of dispersant application on the interaction between the tested aromatic biohydrocarbons and kaolinite, a clay mineral that can occur in marine bottom sediments.

2. Materials and Methods

2.1. Materials

The EXOdis OS6 dispersant (PCC Exol SA, Brzeg Dolny, Poland) is a synthetic, commercially available specialized alkaline surfactant blend designed to remove crude oil and oil-based spills in open waters. The main chemical composition is presented in Table 1 [28].

The liquid aromatic biohydrocarbons sample was received from Ekobenz Sp. z o.o. (Bogumiłów, Poland). The physico-chemical parameters of these liquid aromatic biohydrocarbons are gathered in Table 2. The data comes from the manufacturer's product technical description [29]. Additionally, prior to the experiments, density and viscosity at 20°C were measured using a pycnometer and an Ubbelohde viscometer, respectively.

The crude oil samples from Grabownica, Wańkowa and the Magdalena reservoirs examined in this study comes from the old collections of the Department of Petroleum Engineering, Faculty of Drilling, Oil and Gas, AGH University of Kraków and were used for study without any prior preparation. Table 3 presents selected parameters characterizing crude oil from Grabownica, Wańkowa and Magdalena reservoirs (the Carpathian reservoirs, Poland). The crude oils tested differed in density and viscosity. Measurements of these two parameters

Tab. 2. Physico-chemical parameters of the liquid aromatic biohydrocarbons tested in this study [29]. *This work
Tab. 2. Parametry fizykochemiczne ciekłych aromatycznych biowęglowodorów badanych w niniejszym badaniu [29]. *Ta praca

Parameter	Value
Density at 15°C [g/cm^3]	0.900 – 0.970 *0.9422
Kinematic viscosity [20°C, m^2/s]	*11.08 x 10^{-6}
Content of hydrocarbons [%, v/v]: aromatic nonaromatic	 92.0 – 98.0 2.0-8.0
Composition of aromatic hydrocarbons [%, m/m]: single-ring two-ring three or more rings	 50.0 – 73.0 26.0 – 45.0 1.0 – 5.0

Tab. 3. Characteristics of crude oils from the Grabownica, Wańkowa and Magdalena reservoirs according to [30-33]. *This work
Tab. 3. Charakterystyka rop naftowych ze złóż Grabownica, Wańkowa i Magdalena według [30-33]. *Ta praca

Parameter	Value		
	Grabownica	Wańkowa	Magdalena
Density [g/cm^3]	0.8154, *0.8156	0.8595, *0.8597	0.8591, *0.8595
Kinematic viscosity [20°C, m^2/s]	*18.55 x 10^{-6}	*12.86 x10^{-6}	*14.28 x10^{-6}
Paraffin [%]	0.4-0.5	3.3	6.1
Sulfur [%]	0.26-0.27	0.77	0.19
Acid number [mg KOH/g]	0.22-0.30	0.20	0.06
Asphaltene [%]	0.2	2.1	0.7
Resins [%]	17.3-22.9	33.6	16.7
Porphyrins [μg/kg]	0.0067	0.2491	0.1857

at 20°C were carried out experimentally for this study using a pycnometer and an Ubbelohde viscometer. Further, Table 3 shows the literature data oconcerning the selected parameters characterizing the crude oils tested [30-33].

Kaolinite natural was purchased in Sigma-Aldrich (Germany). The analytically pure dichloromethane (CH_2Cl_2) used in the extraction process and the sodium chloride (NaCl) necessary to prepare a substitute of synthetic seawater were purchased from WARCHEM Sp. z o.o. (Poland). Water from the Baltic Sea was sampled from the region of the Słowiński National Park in Poland. The water was filtered through a soft paper filter.

2.2. UV spectroscopy

Detection of studied samples in water was performed using ultraviolet (UV) spectroscopy. All UV spectra (with an accuracy of 1 nm) in the range of 190–800 nm were recorded using a UV-Vis spectrometer (Shimadzu UV-1700, Japan).

2.3. IR spectroscopy

All FT-IR (Fourier Transform Infrared) spectra of samples were recorded using an Avatar 360 FT-IR spectrometer (Thermo Nicolet, USA). The spectra of the KBr pellets were collected each time at room temperature in the spectral range of 3600–400 cm^{-1} with 256 scans at a spectral resolution of 2 cm^{-1}.

2.4. "Baffled flask test" procedure for assessing the efficiency of oil dispersant

The dispersibility of crude oils using the baffled flask test (BFT) is determined by comparing the total mass of crude oil introduced into synthetic seawater with the mass of crude oil present in the aqueous layer below the top layer of crude oil after testing under specific experimental conditions [34-36]. In this work, the same method was used to assess the dispersibility of a liquid aromatic hydrocarbons sample (Fig. 2). Each time, 100 μL of crude oil or liquid aromatic hydrocarbons was carefully added to a baffled flask containing 120 ml of artificial seawater (3.3% NaCl solution [37]) at the brine surface. Then, 4 μL of dispersant EXOdis OS6 was applied to the centre of the oil slick, ensuring direct contact with the oil phase without prior contact with water. The baffled flask containing the sample was then shaken on an orbital shaker at 200 rpm for 10 minutes. After 10 minutes of shaking, the flask was removed from the shaker for 10 min. After these 10 minutes of standing, 3 mL of the remaining solution in the bottom tap of the flask was removed. Another 30 mL of solution was collected for analysis. The dispersed crude oil or aromatic hydrocarbons content of this sample was determined.

The content of crude oil and liquid aromatic biohydrocarbons in the samples was analyzed using UV-Vis spectroscopy, after three extractions with dichloromethane (3 x 5 mL CH_2Cl_2) and adjusting the volume to 20 mL. A series of standard solutions for crude oil from the Magdalena and Grabownica deposits was prepared according to the procedure described by Venosa et al. [34]. Procedure for preparation of calibration curves was as follows:

a) artificial seawater was a 3.3% NaCl solution in distilled water according to standard ASTM F3251-17 [37],

b) stock solutions of crude oils were obtained by mixing 18 mL of dichloromethane with 2 mL of crude oil and 80 μL of dispersant,

c) series of standard solutions on the basis of which calibration curves were prepared were obtained by adding the appropriate volume of the stock solution (obtained in accordance with point b), i.e. 20, 50, 70, 100, 150, 200 and 250 μL to 30 mL of synthetic seawater (obtained in accordance with point a). Then, three extractions were carried out with dichloromethane (3 x 5 mL CH_2Cl_2), and then the volume of the final extract was adjusted to 20 mL. Standard solutions were prepared in duplicate,

d) next, UV-Vis spectra were measured in the range of 800–190 nm for the final extracts (standard solutions),

e) as described in the method presented by Vendoza et al. [34], a calibration curve was plotted as the dependence of the theoretical concentration of crude oil in the artificial seawater on the surface area under the absorption band in the 340–400 nm range,

f) determination of the concentration of dispersed crude oil in the sample based on its measured signal (area under the

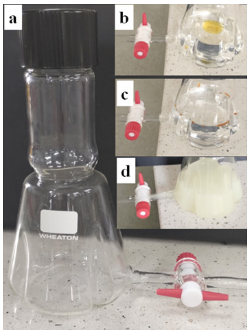

Fig. 2. The baffled flask test: a) the baffled flask used for testing the dispersant effectiveness, b) liquid aromatic biohydrocarbons introduced onto the brine surface before BFT, c) view after introducing of EXOdis OS6 dispersant onto liquid aromatic biohydrocarbons spill d) view after baffled flask test

Rys. 2. Badanie w kolbie z przegrodami: a) kolba z przegrodami używana do badania skuteczności dyspergatora, b) ciekłe węglowodory aromatyczne wprowadzone na powierzchnię solanki przed BFT, c) widok po wprowadzeniu dyspergatora EXOdis OS6 na rozlaną ciekłą frakcję węglowodorów aromatycznych d) widok po badaniu w kolbie z przegrodami

absorption band in the 340–400 nm range) and a previously determined calibration curve (via linear regression).

The same measurement method (Vendoza et al. [35]) was tested to determine the content of liquid aromatic biohydrocarbons (Ekobenz Sp. z o. o.) in the samples. The calibration curve, plotted in the same way, also showed a strong linear relationship. Therefore, the measurement methodology for aromatic hydrocarbons was the same as for crude oil testing.

2.5. Study of the interaction of tested liquid aromatic biohydrocarbons with kaolinite

In the work the examination of the effect of EXOdis OS6 dispersant use on the interaction of studied aromatic biohydrocarbons with kaolinite was also studied. Brine (3.3% NaCl solution) was poured into 300 mL flasks and 0.25 g of kaolinite was added. Then, 100 µL of tested aromatic biohydrocarbons were added to the brine surface, with the dispersant EXOdis OS6 added to some of the samples. The samples were shaken on an orbital shaker at 200 rpm and observed at several time intervals.

In addition, when in all samples (after 2 days) the kaolinite had settled to the bottom, infrared spectra of these sediments were measured.

3. Results

3.1. Evaluation of the EXOdis OS6 dispersant effectiveness

The aim of this study was to evaluate the dispersion efficiency of tested aromatic biohydrocarbons sample in 3.3% NaCl solution and water from Baltic Sea using the EXOdis OS6 dispersant. For comparison, the effectiveness of the EXOdis OS6 dispersant on crude oil from the Grabownica, Wańkowa and Magdalena reservoir was also assessed.

Appearance of all tested samples (4 mL) on the surface of 3.3% NaCl solution (40 mL) is presented in Fig. 3a. Figures 3b and 3c also show the appearance of these samples after shaking on an orbital shaker, both with and without the addition of the dispersant (160 µL). After the shaking process, a slight blurring of the liquid-phase boundary can be observed in the tested samples, particularly evident in the case of crude oil from the Magdalena reservoir and aromatic biohydrocarbons (Fig 3b). The addition of the EXOdis OS6 dispersant results in dispersion of the liquid hydrocarbons throughout the entire water column in all tested samples (Fig 3c).

The quantitative assessment of the degree of dispersion both aromatic biohydrocarbons and crude oil from Grabownica and Wańkowa reservoir was carried out using the baffled flask test described by Vendoza et al. [35]. Therefore, the efficiency of the EXOdis OS6 dispersant was determined by comparing the total mass of aromatic biohydrocarbons (or crude oil) introduced into synthetic seawater with the mass of aromatic biohydrocarbons (or crude oil) present in the aqueous layer below the top layer of crude oil after testing under the experimental conditions described in the experimental section (2.4).

The calibration curves illustrate the relationship between the relative integration of the absorption band in the 340–400 nm range and the concentration of aromatic biohydrocarbons (or crude oil) in a 3.3% NaCl solution. It was found, the calibration curve for aromatic biohydrocarbons samples, also showed a strong linear relationship (R2=0.995 and R2=0.996 for 3.3 Nacl solution and water from Baltic Sea, respectively). This means, that the method described by Vendoza et al. [34] can be successfully applied not only to crude oils but also for the tested aromatic biohydrocarbons samples.

Table 4 presents the obtained results for the dispersion efficiency of aromatic biohydrocarbons and three crude oils in the 3.3 % NaCl solution and water from Baltic Sea using the EXOdis OS6 dispersant. Its efficiency for the tested aromatic biohydrocarbons is relatively high, amounting to 64.69% (and 56.43 for water from Baltic Sea). In contrast, the efficiency of this dispersant for crude oils is in the range of 44.02-69.07 % (and 43.69-56.93 % for water from Baltic Sea).

Differences in the dispersion efficiency of crude oils undoubtedly result from their varying chemical compositions and, consequently, their physicochemical properties. The literature includes studies in which demonstrated that dispersant efficiency depends on crude oil pour point, viscosity, and composition, particularly wax and asphaltene content [39-41]. It also depends on experimental conditions, such as the salinity, composition, and temperature of the water in which the oil is dispersed [42,43].

The difference in dispersion efficiency of the three tested crude oils undoubtedly results from the fact that each of them has a different viscosity (Table 3 and 4). Literature studies indicate that dispersants are usually less effective on viscous oil [39]. This may explain why the EXOdis OS6 dispersant proved least effective for crude oil from the Grabownica res-

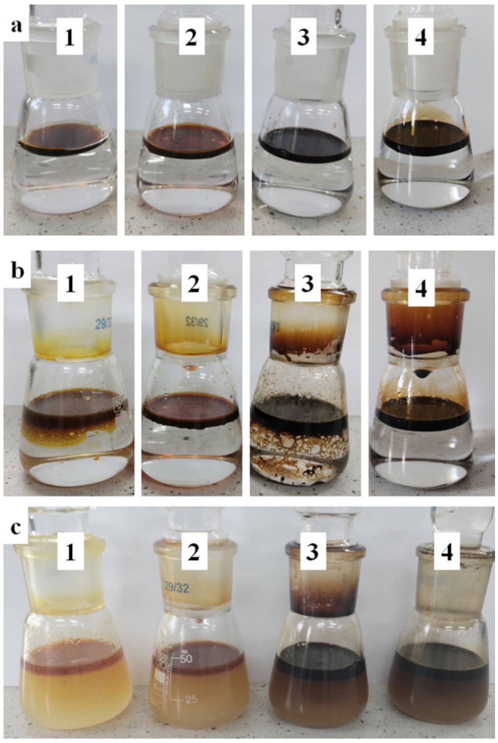

Fig. 3. View of tested samples (4 mL of sample on the surface of 40 mL of 3.3% NaCl): 1) aromatic biohydrocarbons (Ekobenz Sp. z o. o.), 2) crude oil from Grabownica reservoir, 3) crude oil from Magdalena reservoir, 4) crude oil from Wańkowa reservoir. Samples: a) before shaken, b) after shaken on an orbital shaker at 200 rpm for 30 minutes without dispersant, c) after shaken on an orbital shaker at 200 rpm for 30 minutes with dispersant EXOdis OS6

Rys. 3. Widok badanych próbek (4 ml próbki na powierzchni 40 ml 3,3% NaCl): 1) biowęglowodory aromatyczne (Ekobenz Sp. z o. o.), 2) ropa naftowa ze złoża Grabownica, 3) ropa naftowa ze złoża Magdalena, 4) ropa naftowa ze złoża Wańkowa. Próbki: a) przed wytrząsaniem, b) po wytrząsaniu na wytrząsarce orbitalnej z prędkością 200 obr./min przez 30 minut bez dyspergatora, c) po wytrząsaniu na wytrząsarce orbitalnej z prędkością 200 obr./min przez 30 minut z dyspergatorem EXOdis OS6

Tab. 4. Efficiency of dispersant EXOdis OS6

Tab. 4. Skuteczność dyspergatora EXOdis OS6

Efficiency of dispersant [%]	Aromatic biohydrocarbons (Ekobenz Sp. z o. o.)	Crude oil (Grabownica reservoir)	Crude oil (Wańkowa reservoir)	Crude oil (Magdalena reservoir)
3.3 % NaCl solution	64.69	56.80	44.02	69.07
Water from Baltic Sea	56.43	56.93	43.69	50.56

ervoir (56.80% for 3.3 solution of NaCl and 56.93% for water from Baltic Sea) compared to crude oil from the Magdalena reservoir (69.07% for 3.3 solution of NaCl and 50.56% for water from Baltic Sea). Although crude oil from the Grabownica field has the lowest density, it is also characterized by higher viscosity. The best-dispersed oil is from the Magdalena reservoir, despite having the highest paraffin content of 6.1%, as shown in Table 3. It is suspected that long-chain linear paraffins are resistant to dispersion due to their cohesive nature [44]. On the other hand, oil from the Grabownica reservoir, one of the largest oil deposits in the Polish Carpathians, has very low paraffin content [45]. These results indicate that paraffin content is not the primary factor determining dispersion efficiency; rather, other components of crude oil play in this study a decisive role. The weak dispersion effect of the oil from the Wańkowa reservoir is difficult to explain. The specific composition of this oil certainly accounts for its low degree of dispersion. The tested crude oils also differ in their content of asphaltenes, resins, sulfur as well as in their acid number. These properties of the oils may also influence the effectiveness of oil dispersion [46-48]. They also differ in porphyrin content, which can migrate easily to the water/oil interfaces and can alter the surface tension during the formation of water-oil emulsions [46]. Water salinity mainly affects the dispersion efficiency of crude oil from the Magdalena reservoir. For brine (3.3% NaCl solution) it is 69.07% and decreases by 18.51% for water from the Baltic Sea, the salinity of which is along its southern shore 75 g/kg [49].

As can be observed, the sample of tested aromatic biohydrocarbons is also well dispersed by the EXOdis OS6 dispersant in the 3.3% NaCl solution, with a dispersion degree of 64.69%, which falls within the range of crude oils examined in this study. Dispersant efficiency is lower in the Baltic Sea water and equals 55.43%.

Study of the interaction of tested liquid aromatic biohydrocarbons with kaolinite

The presence of a crude oil dispersant in sediment–seawater systems enhances the formation of oil–mineral aggregates, thereby promoting the transfer of hydrocarbons from the surface oil slick to the sediment phase. For example, the dispersant Corexit EC9527A increased the mass percentage of total petroleum hydrocarbons in the sediment phase from 6.9% (without dispersant) to 90.1% [50]. What is more, the presence of clay

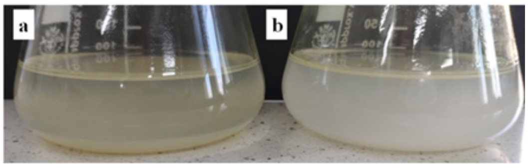

Fig. 4. View of samples after shaken on an orbital shaker at 200 rpm (30 min) of 0.25 g kaolinite in 3.3% NaCl solution with contact of 100 μL of tested aromatic biohydrocarbons putted on the brine surface (a – with the 4 μL of dispersant EXOdis OS6, b – without the dispersant)

Rys. 4. Widok próbek po wytrząsaniu na wytrząsarce orbitalnej przy 200 obr./min (30 min) 0,25 g kaolinitu w 3,3% roztworze NaCl w kontakcie ze 100 μl badanych aromatycznych biowęglowodorów naniesionych na powierzchnię solanki (a – z 4 μl dyspergatora EXOdis OS6, b – bez dyspergatora)

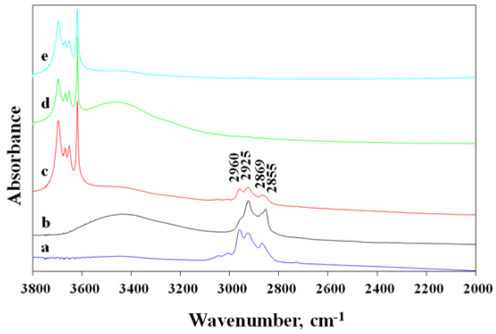

Fig. 5. FT-IR spectra in the range of 3800-2000 cm-1: a) aromatic biohydrocarbon sample, b) EXOdis OS6 dispersant, c) kaolinite sample, which were in contact with tested aromatic biohydrocarbons and dispersant, d) kaolinite sample, which were in contact with tested aromatic biohydrocarbons, e) pure kaolinite

Rys. 5. Widma FT-IR w zakresie 3800-2000 cm-1: a) próbka węglowodorów aromatycznych, b) dyspergator EXOdis OS6, c) próbka kaolinitu, która miała kontakt z badanymi węglowodorami aromatycznymi i dyspergatorem, d) próbka kaolinitu, która miała kontakt z badanymi węglowodorami aromatycznymi, e) czysty kaolinit

mineral like for example kaolinite (which is the most abundant clay mineral in ocean sediments, [48]) in oil-contaminated marine environments has been shown to enhances the growth of bacteria that degrade hydrocarbons [51,52]. Therefore, the research in this work additionally focused on how the use of the EXOdis OS6 dispersant affects the interaction of the tested aromatic biohydrocarbons with kaolinite.

View of samples, where tested aromatic biohydrocarbons interact with natural kaolinite (in 3.3% NaCl solution) is presented in Fig 4. As is seen in Fig. 4 aromatic biohydrocarbons without dispersant EXOdis OS6 are accumulated on the surface of the brine. The situation is different when the EXOdis OS6 dispersant is present in the system. In this case, the tested liquid aromatic biohydrocarbons are adsorbed onto clay particles. The kaolinite derived from the sample containing the dispersant exhibits a slightly yellow coloration.

Infrared technique analysis confirms observations indicating the adsorption of aromatic biohydrocarbons on kaolinite with the participation of the dispersant EXOdis OS6. Infrared spectra recorded for kaolinite samples, which were in contact with tested aromatic biohydrocarbons, with and without the presence of the dispersant, are presented in Figure 5. For comparison in Figure 5, spectra of the aromatic biohydrocarbon sample, pure natural kaolinite, and pure EXOdis OS6 dispersant are also shown.

As can be seen in Figure 5, the spectra of aromatic biohydrocarbons and dispersant in the spectral range of 3800-2000 cm-1 are dominated by bands originating from the stretching vibrations of the $-CH_3$ and $-CH_2-$ groups. Asymmetric stretching vibrations of the $-CH_3$ and $-CH_2-$ groups are observed at 2960 and 2925 cm^{-1}, respectively, while symmetric stretching vibrations of these groups are observed at 2869 and 2855 cm^{-1}, respectively.

In the spectrum of kaolinite that was in contact only with aromatic biohydrocarbons (without dispersant), these bands are not observed, indicating that kaolinite did not adsorb the aromatic biohydrocarbons, or their sorption was very low and undetectable by IR spectroscopy. This is supported by literature data, which indicate weak sorption of aromatic hydrocarbons like BTX on natural, unmodified kaolinite [52]. Wu et al. determined that the sorption efficiencies for benzene, toluene, and m-xylene are only 20.5, 27.11, and 46.47 mg/kg, respectively. Considering the nature of molecular bonding, hydrophobic interactions together with van der Waals forces are probably the main contributors to the adsorption of BTX molecules onto kaolinite surfaces [52].

Fig 5 shows the different situation for the sample where the kaolinite was in contact with both aromatic biohydrocarbons and EXOdis OS6 dispersant. The infrared spectrum clearly shows strong bands at 2960, 2925, 2869 and 2855 cm-1 originating from the dispersant and as well the aromatic biohydrocarbons.

In summary, visual observation (Fig. 4) and infrared spectroscopy (Fig. 5) indicate that aromatic biohydrocarbons are strongly adsorbed on the kaolinite surface after prior application of the Oxodis OS6 dispersant. The Oxodis OS6 dispersant most likely binds to kaolinite and modifies its surface charge characteristics, which is crucial for understanding the adsorption and/or desorption processes [53,54]. Similar observations were reported by Li et al. [54], who explored the dispersibility and stability mechanisms of kaolin in the oil phase with various surfactants, including sodium bis(2-ethylhexyl)sulfosuccinate (AOT), sorbitan monooleate (Span 80), sorbitan trioleate (Span 85), cetyltrimethylammonium bromide (CTAB), oleic acid (OA), and stearic acid (SA). They indicated that these dispersants were adsorbed on the kaolinite surface [53-55].

4. Conclusions

Valuable initiatives in the extraction of aromatic biohydrocarbons from biomass limit the exploitation of fossil fuel deposits and reduce CO_2 emissions. However, it should be noted that as new bioproducts appear on the market, solutions should also be developed to address environmental risks in the event of theirs potential leaks. Regardless of how they are produced, aromatic biohydrocarbons undoubtedly pose a serious environmental threat when released into water.

The research conducted indicates that the aromatic hydrocarbon sample (containing primarily mono- and di-cyclic hydrocarbons) behaves similarly to the three crude oil samples tested in the presence of oil dispersant. The dispersant's effectiveness was tested using the baffled flask method. The effectiveness of the EXOdis OS6 dispersant in dispersing liquid aromatic biohydrocarbons (Ekobenz Sp. z o.o., Poland) in a 3.3% NaCl solution was 64.69%. For comparison, the effectiveness of this dispersant was also tested for crude oil from the Grabownica, Wańkowa and Magdalena reservoirs (Carpathian Mountains, Poland) and equals 56.80, 44.02 and 69.07, respectively. The effectiveness of the EXOdis OS6 dispersant is slightly lower for crude oils from the Grabownica and Wańkowa reservoirs in less saline The Baltic Sea water. For crude oil from the Magdalena reservoir, the effectiveness decrease by as much as 18.51%. The effectiveness of the EXOdis OS6 dispersant in dispersing liquid aromatic biohydrocarbons in water from the Baltic Sea was also lowest and equals 56.43%.

Thus, although the use of the dispersant will significantly reduce the thickness of the slick on the water surface, it will significantly introduce toxic hydrocarbons into the water column, in larger quantities than in the case of crude oil, which often does not contain significant amounts of aromatic hydrocarbons.

It was also observed that the addition of the dispersant modifies the surface of kaolinite (a clay mineral that can be a component of marine bottom sediments), resulting in increased sorption of aromatic biohydrocarbons on its surface.

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Nowe bioprodukty węglowodorowe: poszukiwanie skutecznych metod ich usuwania z wody w przypadku wycieku

Przemysł petrochemiczny produkuje substancje chemiczne, które stanowią podstawę szerokiej gamy produktów niezbędnych w naszym codziennym życiu. W szczególności węglowodory aromatyczne (w tym BTX: benzen, toluen i ksylen) są bardzo ważnymi surowcami petrochemicznymi. W wielu przypadkach produkty węglowodorowe, pozyskiwane z paliw kopalnych, takich jak ropa naftowa, można pozyskiwać z alternatywnych surowców węglowodorowych, takich jak biomasa. Przykładem może być produkcja biowęglowodorów aromatycznych z alkoholu etylowego, wcześniej pozyskiwanego z roślin.
Należy jednak zauważyć, że te bioprodukty mogą stanowić zagrożenie dla środowiska podczas transportu i przechowywania, podobne do tego, jakie stwarza ropa naftowa. Zwłaszcza w przypadku wycieku i przesiąknięcia do wody. W związku z tym pojawia się pytanie, czy dyspergatory ropy naftowej, które mogą być jednym ze sposobów reagowania w środowiskach wodnych dotkniętych wyciekami ropy naftowej, są również skuteczne w przypadku wycieków tych ciekłych bioproduktów węglowodorowych?
Celem badań była ocena skuteczności dyspergatora EXOdis OS6 w dyspergowaniu ciekłych biowęglowodorów aromatycznych (Ekobenz Sp. z o.o., Polska) w 3,3% roztworze NaCl oraz w wodzie Morza Bałtyckiego. Dla celów porównawczych przedstawiono również skuteczność tego dyspergatora w dyspergowaniu ropy naftowej ze złóż Grabownica, Magdalena i Wańkowa (Karpaty, Polska). Badania przeprowadzono z zastosowaniem metody badawczej „testu kolby z przegrodami". Zawartość biowęglowodorów aromatycznych i ropy naftowej w wodzie oznaczono metodą spektroskopii UV-Vis. Ponadto, w badaniu wykorzystano spektroskopię w podczerwieni do zbadania wpływu zastosowania dyspergatora na interakcję badanych biowęglowodorów aromatycznych z kaolinitem, minerałem ilastym, który może być składnikiem morskich osadów dennych.

Słowa kluczowe: *aromatyczne biowęglowodory, wyciek ropy, skuteczność dyspergatora, badanie w kolbie z przegrodami, spektroskopia IR, spektroskopia UV-Vis*