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Removal of Petroleum Pollutants from River Water by Centrifugation

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Abstract: Hydrocarbons belong to the compounds most occurring in surface waters and groundwater. The presence of petroleum compounds in such waters brings significant changes to their physicochemical and organoleptic characteristics even at very low concentrations, like 0.01 g/m^3. Petroleum compounds significantly affect living organisms. Pollution of these components is dangerous for biological life due to the formation of films and an emulsified layer that shuts off atmospheric oxygen. The dissolved compounds and heavier fractions are toxic and insoluble in both water and sediment. The purpose of this study was to make a preliminary analysis of purified flowing water with petroleum pollutants of an industrial origin. In order to attain this objective, the centrifugation speed, centrifugation time, centrifugation temperature and the addition of silica sand in different concentrations were measured. The identification and quantitative determination of petroleum compounds was made by fluorescent analysis.

Keywords: surface waters, petroleum, fluorescent analysis, TPH

JEL codes: Q01, Q25, Q53

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1. Introduction

The treatment of water only as an inexhaustible resource and transport medium led to excessive consumption of water resources, pollution and the atrophy of aquatic organisms involved in the self-purification process of waters. After these, there has been a kind of return to the water-related ecosystems. The growing population and the demand for good water caused the need for more sustainable development and even the development of new water management. Optimized water management in urban planning processes is critical to the quality of life and security of the

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inhabitants. For this reason, there is a necessity to analyze the impacts of human actions, look for ways to counteract the harmful effects of these activities and to achieve a sustainable development (Gacek and Gajewski, 2015).

Ingredients present in water can be generally divided into being either inorganic (mineral) and organic. The largest and most common group of organic compounds that pollute surface and groundwater are hydrocarbons and their derivatives. Some groups of these pollutants have been indicated (Synak et al., 2010):

- aliphatic hydrocarbons derived from petrol (C6 – C12 carbon content);
- aliphatic hydrocarbons derived from mineral oil (C12 – C37 carbon content);
- monocyclic aromatic hydrocarbons used as solvents and reagents in the chemical industry (i.e. benzene, toluene, ethylbenzene, xylene – BTEX);
- polycyclic aromatic hydrocarbons (PAHs) mainly derived from automotive exhaust gases, wet and dry deposition, as well as abrasion of automotive tires, asphalt, and uncontrolled sources.

Harmful to humans, the primary constituents of petroleum are aromatic and unsaturated hydrocarbons and hetero-organic compounds that contain sulphur, nitrogen and oxygen (Żółtowski, 2004).The degree of the toxicity of oils differs and depends on the structure of the components, and they generally pose a risk to soil and water. According to the Polish law, the allowable discharge limit is 10-15 mg/dm^3 for mineral and synthetic oils and 100-150 mg/dm^3 for plant and animal fats (Rozporządzenie Ministra Środowiska z dnia 18 listopada 2014). Such requirements caused the need to remove oily substances that are present in wastewater as an oil/water emulsion. The complex nature of the systems containing oil substances means that the purification processes usually consist of several steps. The first one is aimed at removing free oil from the emulsion or suspension. Gravity separation and centrifugation are most commonly used for this purpose.

2. Material and methods

2.1. Sample collection and preparation

The water samples contaminated with mineral oils were collected from a depth of five to ten centimeters below the surface of river water, and five one-liter glass samplers were used. The collector was filled several times until the total volume of five liters was gathered for each sample. The samples were stored in five one-liter amber glass jars and kept in dark containers, at room temperature. The storage time was always shorter than 8 hours (Hounslow, 1995: 14). All glassware and cells used in this work were carefully washed with sulphuric acid and rinsed successively with distilled water and n-hexane. The solvent selected for the sample extractions and standard solution was n-hexane.

2.2. Extraction

The extraction procedure was carried out according to the method by Lumex Ltd. M 01-5-2007, based on GOST standards (GOST standards 2001). In the laboratory, a 100 cm^3 aliquot from a one-liter sample was filtered through a quantitative filter paper medium (Eurochem), homogenized and transferred into a 250 ml separating funnel. 10 ml of hexane was taken with a glass pipette and the sample vessel was rinsed with it. The hexane was poured into the separation funnel and vigorously shaken for at least one minute. Next, the layers were separated. These final extracts were analyzed by a UV-fluorescence spectroscopy in order to determine the concentrations of the dissolved total petroleum hydrocarbons (TPH). The same procedure was applied to another four-liter aliquot, except for the filtration step. Then centrifugation tests were designed.

2.3. Design of centrifugation tests

The centrifugation tests took three parameters into consideration due to the influence they have on the efficiency of centrifugation (Hamacher et al., 2000; Bilo'o and Ngassoum, 2013). The ranges of the chosen parameters are as follow: 2000 – 6000 rpm for rotation speed, 10 – 30 min for centrifugation time, two centrifugation temperatures (Huang et al., 2011; Pawlak et al., 2008): 20°C and 55°C (± 2°C) and 0.8 – 1.0 mm, 0.4 – 0.7 mm and under 0.4 mm for the grain size of the silica used in the centrifugation. The sand was treated with hydrochloric acid, then purified with distilled water. It was used in about 3% of the weight of each water sample. All of the centrifugation tests were realized for four times. For preliminary tests, in order to verify the effect of a parameter, the other parameters had fixed values. The concentration of the TPH from the best extraction rate was characterized.

2.4. UV-fluorescence analysis

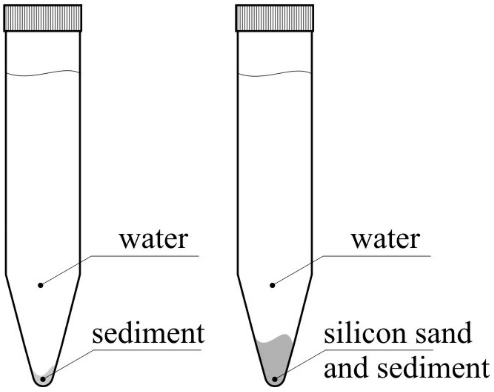
The extracts were analyzed by a UV-fluorescence spectrometry (Fluorat®-02-3MModel) at 270 nm excitation wavelength. The fluorescence intensities were measured at 315 nm (Boeker and Grondelle, 2002), using the TPH (total petroleum hydrocarbons) solution in n-hexane as a quantitative standard. The results show the content of the TPH in the n-hexane extract.

The research method of fluorescence made it possible to estimate the concentrations of the ppm level. The method's admissible maximum relative uncertainty is 40% for very small TPH concentrations (0.02 to 0.50 mg/dm^3) and 25% for a 0.50 to 50.00 mg/dm^3 concentration at a confidence level equal to 95%.

2.5. Sample collection after centrifugation

Water samples were centrifuged in the 10 ml tubes shown in Figure 1. After centrifugation, 80% of the water from the top of each tube was collected.

Figure 1. Tubes after centrifugation



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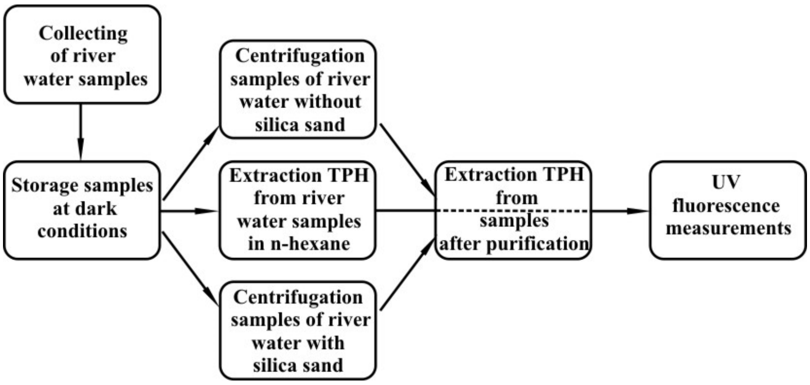
2.6. The algorithm of the research method

The algorithm of the research method is shown in Figure 2.

Figure 2. The algorithm of the research method



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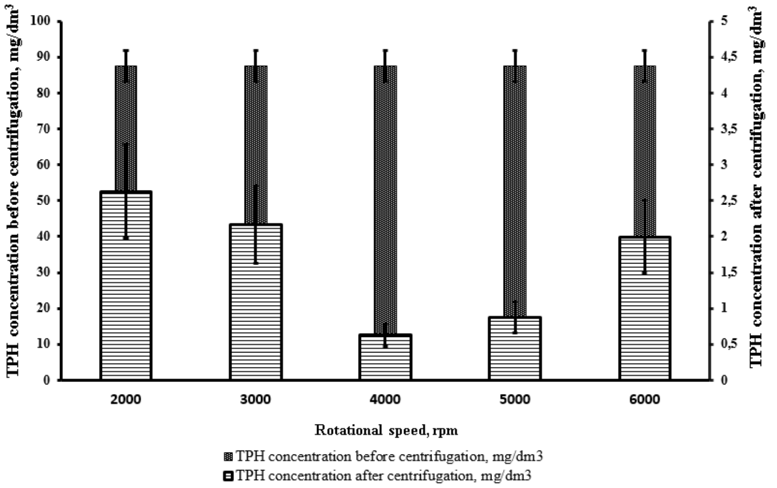
3. Results and discussion

3.1. Results at different centrifugation rotational speed, room temperature and time 30 min

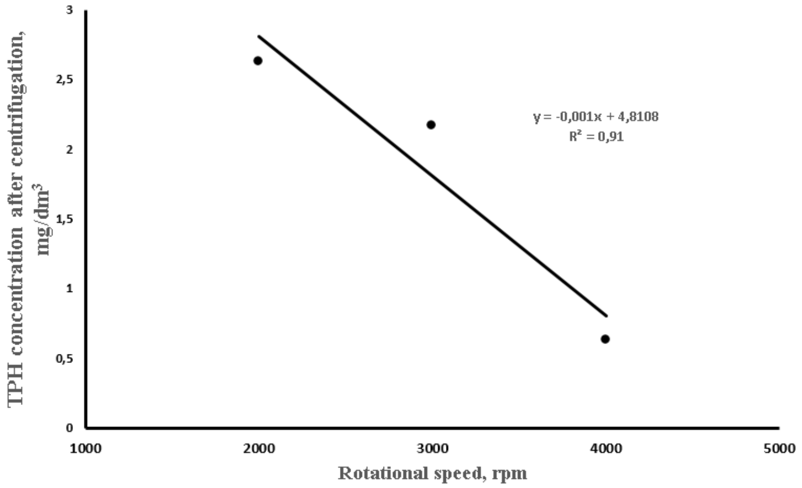
After the measurements of the purification by centrifugation at different rotational speeds, the different rates of the water purification from petroleum compounds containing the TPH were achieved. A negative correlation between the concentration of the TPH in the water and the rotational speed up to 4000 rpm was noted (Figure 3 and Figure 4). It can be described by the linear function: y = -0.001x + 4.8108. The degree of the linear fit is 0.91.

Figure 3. The concentration of the TPH before and after centrifugation (at 30 min and 20°C)



Source: Author’s own elaboration

Figure 4. The correlation between the concentration of the TPH in the water after centrifugation and the rotational speed up to 4000 rpm.



Source: Author's own elaboration

The rate of purification at a rotational speed of 2000 rpm against the reference sample (water taken from the river water – 87.5 mg/dm^3 TPH in n-hexane extract) was 97% (Figure 5). The concentration of the TPH was 2.63 mg/dm^3 in the extract. Increasing the speed of rotation of the centrifuge resulted in further purification of the samples. The rate of purification was 17% with reference to the samples treated at the speed of 2000 rpm. A significant decrease in the TPH contamination in the samples occurred when the purification was at 4000 rpm. The percentage of purification with reference to a sample purified at the speed of 3000 rpm was 71%. A further increasing the rotational speed wrongly affected to the purification of the water samples. A positive correlation of the concentration of the TPH in the water as a function of the rotational speed from 4000 rpm to 6000 rpm was noted (Figure 6). It can be described by the linear function: $y = 0.0007x – 2.2593$. The degree of the linear fit is 0.88. However, the purification efficiency for 4000 rpm and 5000 rpm is comparable. The percentage of the water purification as a function of the rotational speed can be described by the second degree polynomial function $y = - 0.4051x^2 + 2.7234x + 94.391$.

Figure 5. The correlation between the concentration of the TPH in the water after centrifugation and the rotational speed at and above 4000 rpm.

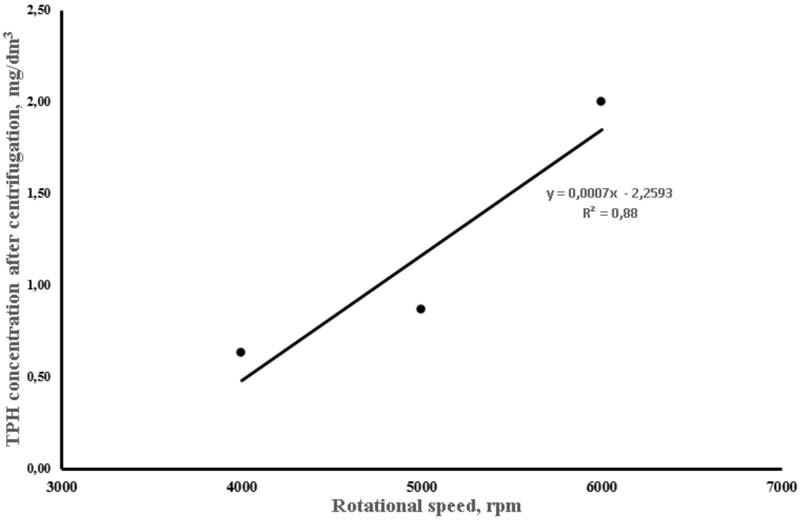


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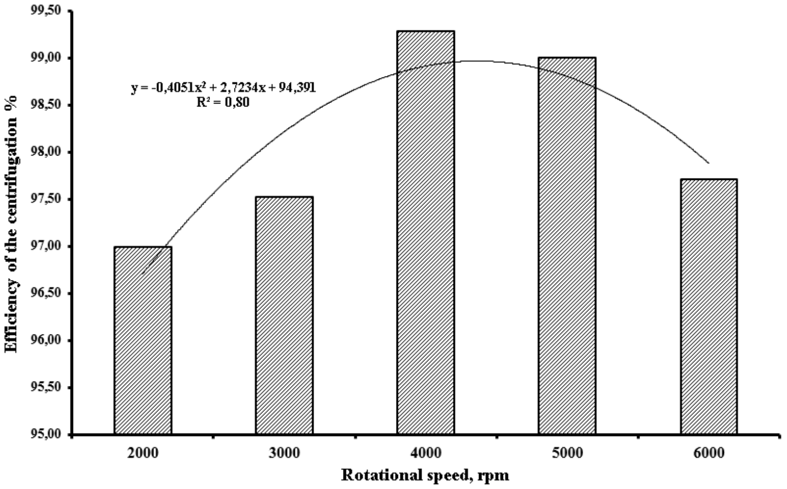
Figure 6. The efficiency of the centrifugation at various rotational speeds, at 30 min and 20°C



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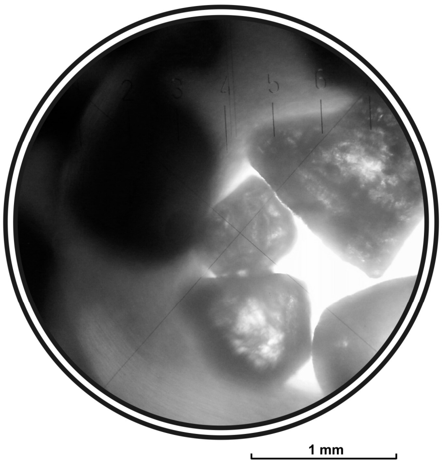
3.2. Results at centrifugation at 4000 rpm with silica sand in time 30 min

After the selection of the most effective speed of 4000 rpm for water purification from the TPH, the centrifugation with the addition of silica sand (Sirotkina and Novoselova, 2005) of various granulations was made (Figure 7). The sand was used in about 3% of the weight of each water sample.The samples of water with the sand were shaken for 10 min at room temperature, then centrifuged for 30 min at the same temperature.

Figure 7. A micrograph showing grains of sand



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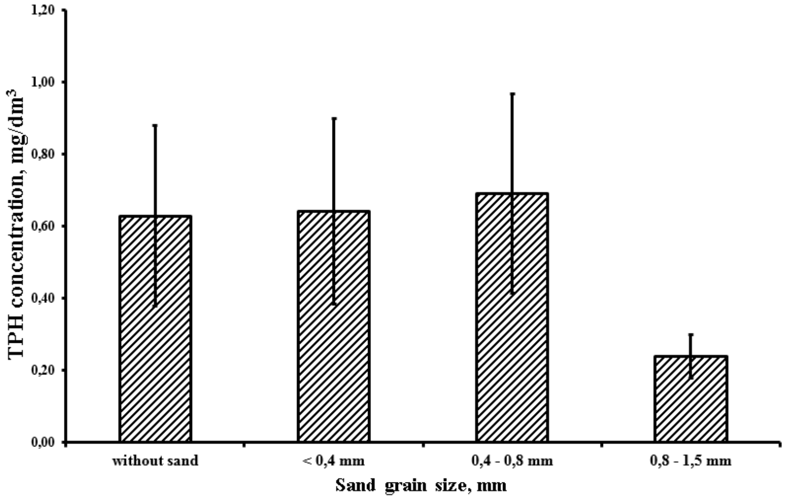
The results were compared with a reference sample where sand had not been added. The sand with a granulation below 0.4 mm and 0.4-0.8 mm did not show a statistically significant improvement of water purification. A significant decrease in the pollution by petroleum substances in water with the presence of sand with a granulation of 0.8-1.5 mm was observed (Figure 8). The results of the tests show that the concentration of the TPH decreases in the samples as follows: 0.63 mg/dm^3without sand and 0.24 mg/dm^3 with sand.The percentage of the purification with respect to the reference water sample purified at the speed of 4000 rpm was 62%.

Figure 8. The concentration of the TPH after centrifugation at 4000 rpm, at 30 min and 20°C



Source: Author’s own elaboration

3.3. Results at different centrifugation temperature, at 4000 rpm and time 10 min

The study also investigated the efficiency of centrifugation of the water samples with different levels of engine oil pollution. The labeling and the TPH content in the water samples are presented in Table 1.

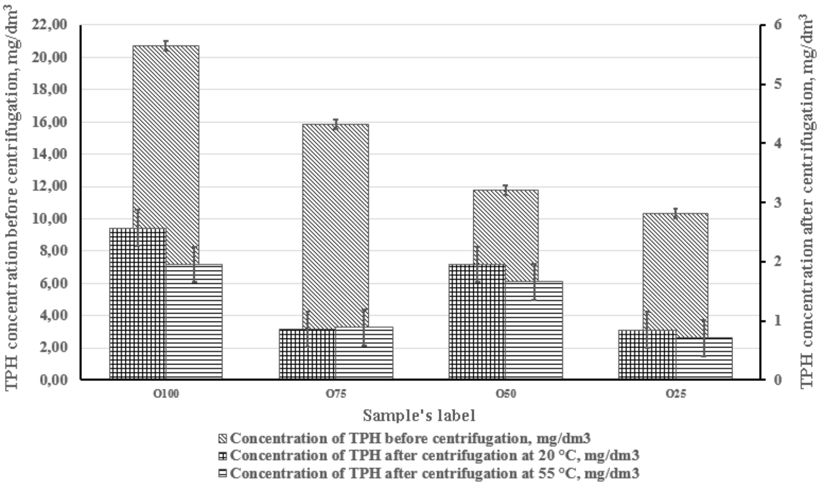
Table 1. The labelling and the TPH content in water samples

Sample	The concentration of the TPH before centrifugation, mg/dm^3	The concentration of the TPH after centrifugation at 20°C, mg/dm^3	The concentration of the TPH after centrifugation at 55°C, mg/dm^3
O100	20.70	2.57	1.95
O75	15.83	0.86	0.89
O50	11.80	1.95	1.66
O25	10.35	0.85	0.71

Source: Author’s own elaboration

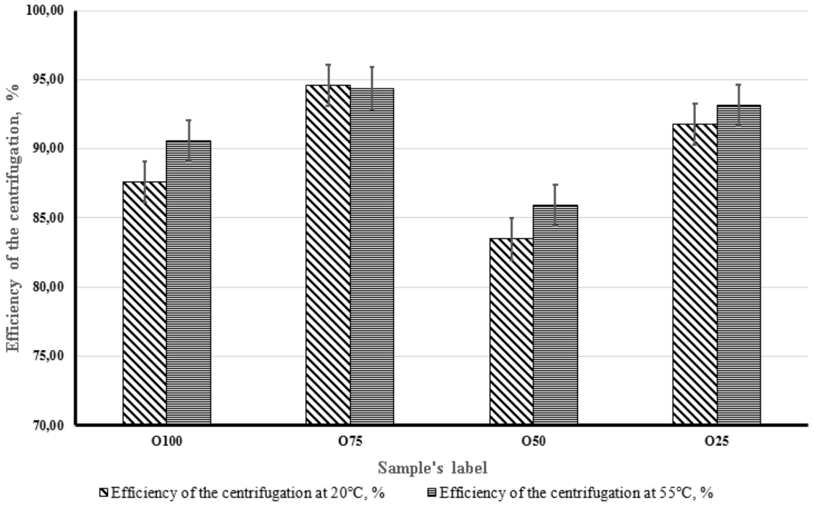
For these samples, two centrifugation temperatures were compared: 20°C and 55°C with a constant centrifugation speed of 4000 rpm and a centrifugation time of 10 min. For three samples, a slight improvement in the efficiency of the centrifugation of the TPH was observed at a higher temperature; however, the variation is found within the measurement uncertainty (Figure 9). One of the samples did not improve in the TPH centrifugation at a higher temperature. The centrifugation efficiency is in the range of (87 - 94)% for the tested samples at 20°C and in the range of (89 - 94)% for the tested samples at 55°C (Figure 10). Water purification by centrifugation within 10 min is more effective for less polluted samples, both at 20°C and 55°C.

Figure 9. The concentration of the TPH before and after centrifugation (at 10 min, 20°C and 55°C)



Source: Author's own elaboration

Figure 10. The efficiency of the centrifugation at different temperatures, at 4000 rpm and 10 min



Source: Author's own elaboration

4. Conclusion

The centrifugation of the water samples led to a reduction in the concentration of petroleum substances in the water to a level below the Polish law, (Rozporządzenie Ministra Środowiska z dnia 18 listopada 2014).

Based on the studies in the centrifugation speed range 2000 - 6000 rpm, for 30 min centrifugation at 20°C, the most effective speed for purifying water from the TPH is 4000 rpm. For 30 min and 20°C, each of the centrifugation speeds resulted in at least 97% water purification. The speed of 4000 rpm at 30 min centrifugation and 20°C resulted in the purification of water from petroleum substances at the level of 99%.

The addition 0.30 g of 0.8 - 1.5 mm silica sand to the samples resulted in a significant improvement in water purification when compared to the reference sample without sand and smaller sand particle samples. Improvements in purification are estimated at 60% for 4000 rpm, 30 min centrifugation and 20°C. 0.8 - 1.5 mm silica sand showed the best sorbent properties for petroleum substances from all of the sand samples. The samples of water with silica sand with a particle size of 0.4 - 0.8 mm and below 0.4 mm were not purified more effectively than the reference sample without sand at a centrifugation speed of 4000 rpm, for 30 min centrifugation at 20°C.

The temperature increase impacts on the water purification from highly polluted motor oil samples was poor at 4000 rpm and 10 min. The efficiency of the water purification for both temperatures (20°C and 55°C) is very close. No interdependence was found between the initial concentration of petroleum substances in water and the efficiency of centrifugation. Further studies will predict research on the effect of temperatures between 20°C and 55°C at a simultaneously increased time for centrifugation. For the centrifugation time of 10 min, at a speed of 4000 rpm and each of the tested temperatures, the degree of purification was less than 95%.

Optimized water management is decisive for the quality of life and the security of people. For this reason, the purpose of the research was to develop a methodology for the preliminary purification of waters contaminated with petroleum substances in accordance with the Polish law concerning the conditions of the introduction of water and wastewater into the environment (Rozporządzenie Ministra Środowiska z dnia 18 listopada 2014). The TPH analysis in various water samples showed that the fluorescent TPH assay in the n-hexane extract has a great potential for the TPH analysis. It has been proven that an improved centrifugation technique is a simple and very effective way to counteract the harmful effects of human activities related to pollution of the aquatic environment by petroleum substances and to achieve sustainable development.

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Rozporządzenie Ministra Środowiska z dnia 18 listopada 2014 r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego, Dz.U. 2014 poz. 1800

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Usuwanie zanieczyszczeń ropopochodnych z wody rzecznej przez odwirowanie

Streszczenie

Węglowodory należą do związków najliczniej występujących w wodach powierzchniowych oraz gruntowych. Obecność złożonych związków ropopochodnych w wodach wywołuje istotne zmiany jej cech fizykochemicznych oraz organoleptycznych już przy bardzo niskich stężeniach rzędu 0,01 g/m^3. Związki ropopochodne należą do związków istotnie wpływających negatywnie na organizmy żywe. Zanieczyszczenie tymi składnikami jest niebezpieczne dla życia biologicznego na skutek tworzenia powierzchniowych i zemulgowanych warstw odcinających dopływ tlenu atmosferycznego, a także sedymentacji cięższych frakcji nierozpuszczalnych w wodzie oraz toksycznego oddziaływania związków rozpuszczonych. Celem niniejszego badania było przeprowadzenie wstępnej analizy nad oczyszczaniem wód płynących z zanieczyszczeń ropopochodnych pochodzenia przemysłowego. W celu osiągnięcia zamierzonego celu zbadano wpływ prędkości, czasu i temperatury wirowania oraz dodatku piasku krzemowego w różnych stężeniach. Identyfikację i oznaczenia ilościowe związków ropopochodnych dokonano za pomocą analizy fluorescencyjnej.

***Słowa kluczowe**:* wody powierzchniowe, substancje ropopochodne, analiza fluorescencyjna, całkowita zawartość węglowodorów.

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