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Studies of composition variability of oily wastewaters collected from harbour

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Abstract

Effluents from the ships containing the petroleum compounds are very dangerous for the marine environment, hence, they are pre-treated on ships and their concentrates are transferred in harbours for further purification. Oily wastewaters are very difficult for treatment; therefore this process is carried out in specialized wastewater treatment plants. The treatment of oily wastewaters is made a more difficult by the fact that the wastewaters supplied are very different in composition. In this work was carried out the evaluation of variability of the composition of wastewaters collected from oily wastewater treatment plant, which was transferred from a harbour. Several parameters characterizing the actual wastewater (oil content, oil droplet size distribution, pH, salt concentration, surface tension, COD/TOC) were measured. The samples for analysis were collected over a period of 2 months.

Introduction

Different types of wastes are generated on the ships such as ballast, domestic, black and grey waters, and oily bilge waters, which are harmful for the marine environment. Particularly dangerous are bilge waters, which include petroleum and petroleum-derived products, the components of which exhibit the carcinogenic properties. Bilge waters are collected at the bottom of the ships and besides oil and grease leaking from the engine room; they contain compounds from all wastes generated in the ship.

Ship-generated wastes are diluted by seawater (e.g. leakage, cargo hold washing water) which causes that their volume is excessively increased and there is a need to discharge wastewater from ship. In order to limit the pollution of seas, the ships are equipped with the devices removing oil from wastes to a level 5 ppm (MARPOL convention). The concentrate of oily wastewater generated in the ships is conveyed into storage tanks in harbours. These wastes are further treated with use of different methods in on shore installations.

The treatment of oily wastewater can be performed using (usually integrated) various chemical or physical processes such as flotation, separation by centrifuge, filtration, and coagulation [1-4]. The microfiltration (MF) and ultrafiltration (UF) processes are most often utilized for oily wastewater treatment [4, 5]. Ship-generated wastewaters contain such a large amount of oils, that these oils can be recovered. In the considered installation of harbour (Poland) the oily wastewaters collected from ships are first stored into the equalizing tank, in order to achieve the separation of oil and water under the gravitational forces. Wastewaters taken from the bottom of this tank are rich in oil. This fraction is transported to dehydration installation, where with the use of heating procedure and chemical treatment, an oil fraction is obtained, which is then transported to a further treatment in refinery, whereas the aqueous phase is discharged into the balance tank. Residue oil is removed from the aqueous phase by using coagulation and flotation, and effluents obtained from these processes are subjected to the treatment by biological methods before discharge into environment.

The presence of surfactances in the waste significantly decreased the efficiency of waste treatment by coagulation and flocculation. Moreover, a composition of wastewater collected from harbour is varied, which deteriorates the effectiveness of the deoiling in the coagulation/flotation process. A discharge of poorly deoiling effluents caused disturbances in the operating of biological wastewater treatment plant. In this case a membrane processes can be applied for separation of such waste. A concentrate obtained from these processes (e.g. by water evaporation) even with the enhanced amount of oil can be recycled for waste re-purification in the deoiling installation.

The possibility of water evaporation from brine allows using the membrane contactors to desalinate hypersaline water or saline wastewater treatment [6-9]. The porous non-wetted hydrophobic membranes are assembled in the membrane contactors [6, 7, 10]. Their application is very attractive in the case when wastewater treatment by traditional methods is difficult or expensive, especially for oily wastewaters such as bilge water or wastewater generated in the process of hydraulic fracturing [11-13]. However, the hydrophobic membranes are intrinsically prone to fouling by hydrophobic contaminants due to the strong hydrophobic-hydrophobic interaction [14, 15]. The capillary polypropylene membranes were not-wetted during separation of bilge water [12] and oilfield produced water [16].

A serious limitation associated with the application of membrane technology is a decline of modules yield caused by fouling and scaling of the membranes [9]. There are two types of membrane fouling for oily wastewater treatment: reversible and irreversible fouling [6]. The reversible fouling occurs due to external deposition of sludge or colloidal particles on the surface and in the pores. A flux decline caused by reversible fouling can be easily recovered with mechanical cleaning or pure water rinsing or backwashing [6-9]. The other type is irreversible fouling, which leads to flux decline due to a strong physical or chemical sorption of solutes and particles on the surface and in the membrane pores. A flux decline caused by irreversible fouling can be recovered only by washing with acid or alkali solutions. However, the initial permeability of irreversibly fouled membranes cannot be restored even with the use of aggressive cleaning methods.

The waste composition has a significant influence on the scaling and fouling intensity. Therefore, the studies about the variability of the composition of sewage subjected to treatment are very important in the design of membrane technology..

Experimental

The oily wastewater used for this study was supplied from harbour wastewater treatment facility. The samples of wastewaters collected from ships and also after coagulation/flotation processes at different periods of time (over 2 months) were utilized for studies of wastes composition.

The determination of the total organic carbon (TOC) was performed using an analyzer Multi N/C (Analytic Jena) with the detection limit of 0.02 mg/L. The oil concentration in examined samples was determined by means of the oil analyzer HORIBA OCMA 310. The turbidity of water was determined using the turbidimeter 2100 AN IS (HACH, USA) with the detection limit of 0.01 NTU.

The electrical conductivity and total dissolved solids (TDS) of solutions were measured with a 6P Ultrameter (Myron L Company, USA). This meter was calibrated for measurements as NaCl using TDS/Conductivity standard Solution (Myron L Company).

The surface tension of liquid and the membrane contact angle significantly affect the membrane wettability. The measurements of these parameters were performed using apparatus Sigma 701 microbalance (KSV Instrument, Ltd., Finland) applying the Wilhelmy plate method.

The waste composition (anion and cation concentrations) was determined using an ion chromatography method with conductivity detector (850 Professional IC, Herisau Metrohm – Switherland, equipped with Metrohm A Supp5-250 and Metrosep C2-150 analytical columns).

The COD (Chemical Oxygen Demand) tests have been carried out using the method developed by HACH LANGE GmbH (Germany). Appropriately diluted wastewater samples were mixed with the working solution (LCI 1000) and mineralized in the apparatus Thermostat LT200.

The COD values were read using a DR 2800 spectrophotometer (HACH LANGE. The calibration of measurements were carried out using Chemical Oxygen Demand Standard Solution 1000 mg/L COD (HACH LANGE).

Results

The studies were performed with samples of wastewaters (Table 1) collected from deoiling installation at intervals of several days. The examined samples had the colour from light to dark brown and they exhibited a high turbidity. A sample filtration through a filter paper (5 μm) demonstrated that wastewater contained 0.064-1.9 g/L of suspended solids (s.s). The turbidity of shaken samples amounted to 27.7-154.3 NTU. These values decreased during the wastes storage, which indicated their sedimentation. The values in the range of 17-55 NTU were obtained after 5 days of storage, which indicated that sedimentation proceeds slowly. Slightly sediment sewage containing the least suspension, in addition, the resulting precipitate was unstable, caused a small swirl of liquid to increase the turbidity again.

Table 1. The samples of bilge water collected from treatment plant

No.	TDS [mg/L]	Conductivity [mS/cm]	pH	Turbidity			Suspended solids [g/L]
				[NTU] mixed	[NTU] 4 days	[NTU[5 days	
1	6601	11.90	6.97	66.6	42.3	36.6	0.381
2	6613	11.91	7.1	87.8	54.8	49.9	0.487
3	6107	10.98	6.97	27.7	23.5	17.7	0.064
4	6608	11.90	7.12	87.3	53.5	45.2	0.536
5	6595	11.88	8.6	87.8	50.7	49.2	0.376
6	6384	11.49	6.8	28.7	25.5	25.6	0.072
7	6590	11.87	6.6	76.7	57.4	52.1	0.244
8	6487	11.66	7.3	91.9	48.1	46.3	0.410
9	6627	11.92	7.4	154.3	57.4	55.5	1.896
10	6664	11.97	6.8	68.3	50.2	47.9	0.176
11	6531	11.77	7.1	110	46.9	41.2	1.365
12	6496	11.67	7.3	38.3	29.8	26.3	0.110
13	6572	11.79	6.7	71.7	47.7	42.3	0.211
14	6566	11.85	7.9	87.3	46.9	41.2	0.498
15	6547	11.82	8.3	87.8	46.7	42.3	0.511

The tested samples exhibited significant differences in the filtration rate (Table 2). For example, the filtration of sample No.9, containing 1.89 g s.s/L was very slow, but filtration of the sample No.8 containing more than 4 times less slurry was similarly slow. Such a result indicates that the rate of filtration depended not only on the thickness of the resulting filter cake, but also on the structure of the resulting sediment. This conclusion is confirmed by the filtration results obtained for sample No.3, containing 0.064 g s.s/L, which also filtered slowly despite such low turbidity (27.7 NTU). The samples No.7 and 13 contained similar amount of suspended solids (0.24 and 0.21 g/L) and similar values of NTU (76.7 and 71.7) respectively, but different filtration rate was also obtained in this case (Table 2).

The tested wastewater came from ships sailing on the Baltic Sea (salinity below 7 g/L), hence, the salinity of the majority of samples was at the similar level (Table 1 - TDS). In the case of sewage collected in the dock, where the ships were repaired, the salt concentration was twice lower (Table 3). However, this sewage contained significantly more oil impurities. Their content was significantly reduced in the process of coagulation and flotation. The solution obtained after these processes contained 11-38 mg/L of oil. The surface tension of samples of bilge water (after its filtration) was in the range of 38.9-42 mN/m. In the case of wastewater collected from dock, the

values of surface tension changed in the range of 49-54.1 mN/m. These results suggest that apart from salt and oil, oily wastewaters contained significant amounts of surface-active compounds.

Table 2. Relative rate of filtration the waste from Table 1

Filtration rate [250 ml/x hours]	Sample No.
Fast [250ml/0.2-0.5h]	5, 10, 13
Slow [250ml/1-4 h	3, 4, 7
Very slow [250 ml/24 h]	8, 9

Table 3. The oily wastewater collected from dock

Sample	TDS [mg/L]	Conduc. [mS/cm]	pH	NTU	TOC [mg/L]	IC [mg/L]	Oil [mg/L]	Surf.ten. [mN/m]	COD [mg/L]
B1	3085	5819	6.8	20.2	634	132.1	38.4	52.8	1750
B2	3024	5708	6.17	19.2	583	165.4	21.7	50.5	1602
K-1	2931	5535	7.71	26.1	377	116.2	20.1	53.1	889
K-1b	2925	5536	6.65	34.2	381	123.4	20.2	50.1	1112
K-2	2833	5363	7.39	48.1	632	166.2	21.2	51.6	1750
K1	2913	5505	6.91	63.5	274.8	112.8	12.7	54.1	708
K1B	2926	5529	6.12	40.3	508	131.8	11.8	49.0	1260
K2	2908	5496	7.02	94.8	367.2	166.2	13.7	51.6	1055
K2B	2834	5360	6.74	153	259.6	160.6	11.1	52.6	714

TOC tests showed that the samples contained significantly more carbon than would be due to the oil content. For the samples tested, the TOC content was in the range of 0.26-0.7 g/L. This indicates that a significant amount of other organic compounds, such as surfactants, is present in the wastewaters tested.

In Table 3 were presented the data describing the samples collected from dock, which were treated in the coagulation process (index “2”) and subsequently were subjected to flotation (index “1”). Odour of samples collected `from wastewater treatment plant was very intensive and indicated for the presence of hydrogen sulphide in some cases. The pH values were in the range 6.12-7.43 for these samples. The samples after flotation had a lower value of pH. The obtained values of NTU confirmed that the flotation process allowed to remove a significant fraction of suspended matter. A part of samples (1) and (2) were filtered through filter paper, the initial 2 L was stored in bottles (B1 and B2), and the remaining 20 L was collected in canisters K-1 and K-2), in which the samples were supplied (after rinsing them with tap water). After 2 weeks of storage, the pH of wastewater collected in these canisters increased and was different than initial pH measured for samples B1 and B2. Probably due to filtration, the samples were subjected to aeration, what enables the growth of aerobic bacteria. All the wastewaters become clearer during the next two months, and a 2-3 cm layer of settable solids was accumulated at the bottom of canisters. Moreover, odour of wastewaters was definitely less intensive due to biodegradation.

The ions concentration of tested wastewaters was presented in Table 4. Besides the prevailing concentration of NaCl, wastewaters also contain significant amounts of Ca^{2+}, Mg^{2+} and SO_4^{2-}. The sulphate concentration was in the range of 592-1388 mg/L, and taking into consideration a significant initial concentration of Ca^{2+} above 700 mg/L, the precipitation of $CaSO_4$ can take place when its concentration in the feed exceeds 2 g/L during the MD.

Moreover, during the MD process the feed is heated, which can result in the decomposition of the HCO_3^- ions and precipitation of $CaCO_3$ The TOC examinations demonstrated, that the content of inorganic carbon was at a level of 35-40 mg/L in the tested bilge water. This corresponds to the

concentration of HCO_3^- ions at a level of 178-205 mg/L. A significant large concentration of IC contained the wastewaters from dock (122-166 mg/L – Table 3).

Table 4. The ions composition of investigated bilge water (mg/L)

No. (from Tab. 1)	Cl	Br	NO3	SO4	Na	NH4	K	Ca	Mg
3	3974	130	104.8	704.8	2839.3		144.4	238	405.8
4	3233	589	497	1388	2708.5		180.9	431	741
5	4420	580		992.2	2541	16.6	121.7	742.4	480
7	3933	131		653.3	2364.7	47.9	117.8	732.6	380.5
10	4102	580		958.4	2353		74.3	694	501
12	3540	130		592.2	2137.8	37.3	109.1	561.5	381.5
15	3383	576		876.1	1969.4		71.2	495.2	464.7

The determination of oil content in the crude samples from docks was difficult. Wastewater contained beside emulsion also a large amount of free oil, which sticks to the walls of canister. The TOC analysis demonstrated that the oil concentration was 18 g/L, which is a definitely overstated value. Most probably this resulted from contamination of samples during its collection by droplets of free oil. The previous studies demonstrated that oil emulsion undergo breakdown and a layer of free oil is formed when the oil concentration in emulsion exceeds a value of 1 g/L. An analysis of oil content in wastewater samples from docks (Table 3) after coagulation and flotation demonstrated the concentration of oil residue at a level of 11-22 mg/L. The studies of oil content in the examined bilge water demonstrated the oil concentration at a level of 23-67 mg/L (Table 5). In this case the coagulation process allowed to reduce the oil concentration for example from 35 to 24 mg/L.

Table 5. Oil concentration in bilge water samples

No of sample	Oil concentration [mg/L]
4	28; 27.2
5	37; 40.8 and 40.8
7	23.6; 30.2
8	51.2; 56.4
A – after coagulation	37.5; 35.7; 35.2
B – after flotation	24.6; 24.1

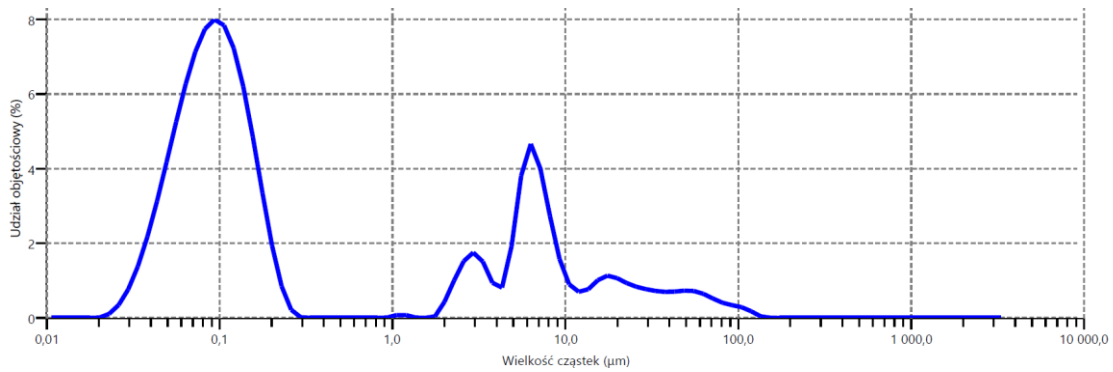

Fig. 1. Droplets size distribution

The investigations of oil droplet size distribution demonstrated that formed emulsion have at least two ranges of oil droplet size (bimodal distribution) – Fig.1. In the first range prevail the oil droplets with the diameters of 1-5 μm, whereas in the second range, in the range of 60-100 μm.

Conclusions

The performed studies confirmed, that the oily wastewaters generated in the ships are characterized by varied composition. With regard to this, the treatment of such wastewater should be performed with the utilization of processes, the effectiveness of which do not depend in a large degree, on the wastewater content and concentration.

The application of coagulation and flotation allows to remove a significant fraction of oil from wastewater, which in the majority of cases facilitate a further treatment of studied wastewater.

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