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THE EFFECT OF DEMULSIFIER AND DEWATERING AGENT ON SEPARATION OF PHASES FROM OILY WATER

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Environmental pollution with crude oil and its derivates has become a growing problem due to their toxic and carcinogenic effects on live organisms. Proper collection and treatment of oily wastewaters is very important for prevention and disabling of harmful effects on the environment. The most important step in the oily wastewater treatment process is separation of oil and aqueous phase. Consequently, it is important to examine the conditions which enable the maximum separation effect and provide satisfactory quality of the aqueous phase before discharge into natural recipients. This paper examines the effects of temperature and addition of demulsifier and dewatering agent on phase separation in oily wastewaters. The best separation rate and the highest quantity of the aqueous phase are achieved with the addition of demulsifier in concentration of 500 mg/l and the dewatering agent in concentration of 500 mg/l at 60 °C. The quality of the aqueous phase after separation shows low values of mineral oils and high COD (Chemical Oxygen Demand) values due to the remaining demulsifier and dewatering agent in aqueous phase. For that reason it is necessary to use additional treatments, such as adsorption on active carbon or biological treatment before discharge into natural waters.

Key words: oily wastewater, demulsifier, dewatering agent.

Utjecaj dodatka deemulgatora i sredstva za obezvodnjavanje na razdvajanje faza u zauljenoj otpadnoj vodi. Zagađenje okoliša sirovom naftom i njenim derivatima postaje sve veći problem zbog toksičnog i kancerogenog djelovanja na žive organizme. Odgovarajuće prikupljanje i obrada zauljenih otpadnih voda je ključna u sprječavanju i smanjenju njihovog štetnog utjecaja na okoliš. U cilju učinkovitije obrade ovakvih voda nužno je ispitati uvjete pri kojima se postiže najbolje odvajanje uljne od vodene faze, kao i kakvoću vode koja se nakon pročišćavanja ispušta u okoliš. U ovom radu je ispitan utjecaj dodatka demulgatora i sredstva za obezvodnjavanje na separaciju uljne od vodene faze pri različitim temperaturama. Najveća brzina razdvajanja faza i najveći volumen izdvojene vodene faze je postignut kod dodatka deemulgatora u koncentraciji od 500 mg/l i sredstva za obezvodnjavanje u koncentraciji od 500 mg/l pri temperaturi od 60 °C. Vodena faza nakon odvajanja sadrži nisku koncentraciju mineralnih ulja i visoke vrijednosti KPK (kemijske potrošnje kisika) zbog zaostalog deemulgatora i sredstva za obezvodnjavanje. Iz tog je razloga nužno primijeniti dodatno pročišćavanje ovakve vode, npr. biološkom obradom ili adsorpcijom na aktivnom ugljenu, prije ispusta u prirodne recipijente.

Ključne riječi: zauljena otpadna voda, deemulgator, sredstvo za obezvodnjavanje.

INTRODUCTION

Emulsions are colloid systems which are characterized as dispersion of one liquid in another (e.g. oil in water or water in oil). They cause serious environmental problems in spills of crude oil or ballast waters in the sea, in industrial processes e.g. in food industry where their remaining in the equipment represents a major problem [1-3].

Investigations show increase of pollution of natural waters due transport of crude oil, normal municipal activities in the oil industry and particularly accidents in oil exploitations and storage [4-6]. These activities produce huge quantities of oily wastewaters in environment and their collecting prior to treatment is an extremely complex process. The collected oily wastewaters are usually very stable emulsions and have no tendency to separate into the aqueous and the oil phase. One of methods for their separation is the addition of demulsifiers and dewatering agents that support separation of phases and decrease the water content in the oil phase. Demulsifiers change surface properties between oil and water, enabling linking up of oil drops so that they become a separated phase [7, 8]. Due to the difference in density, they easily separate into aqueous and oil layers. Demulsifiers are usually added in low concentrations, depending on the emulsion type and mechanism of its activity.

This paper examines the effect of concentration of a commercial demulsifier and a dewatering agent on the efficiency of gravitational separation of phases in oily wastewater at different temperatures. After phase separation, it is necessary to determine the concentrations of mineral oils and the chemical oxygen demand (COD) in the aqueous phase, before making any decision about its discharge into natural waters.

EXPERIMENTAL

Materials

- oily wastewater
- demulsifier EB: AQUALIFE EB 9300,
- Dewatering agent DW: AQUALIFE DW 7000, supplied by the Gaeta s.r.l. company [5].

The examinations have been performed on samples of oily wastewater originating from a ship's ballast tank. The 5 litres of sample is taken and stored in polyethylene vessel at room temperature. Experiments are performed during 24 hours after sampling. The sample was not transparent; it was completely emulsified and dark brown. The experiments were carried out by adding different quantities of demulsifier or the demulsifier with the dewatering agent into a vessel containing 200 mL of oily wastewater. The emulsions are homogenised by mixing with propeller stirrer during 5 minutes at 120 rpm, than mixing is stopped and separation of phases were monitored by measuring of heights of oily and aqueous phase. Nine samples were prepared with and without the addition of the demulsifier in the concentration range of 500-3000 mg/l, and nine samples with and without the addition of the demulsifier and the dewatering agent in the equal concentration range of 250-1500 mg/l, at 40 °C and 60 °C as shown in Table 1. The heights of separated phases until the equilibrium were monitored in all vessels, and the results were compared to those obtained for the sample without the addition of any agents. After phase separation, the concentrations of mineral oils and COD (Chemical Oxygen Demand) were determined in the aqueous phase. Mineral oils were determined using the FT-IR spectrometry at wave lengths of 3.38 μm using Spectrum One Perkin Elmer instrument. COD was determined by the standard dichromate method [10].

Table 1. Concentrations of the demulsifier (EB) or the demulsifier and the dewatering agent (DW) in samples examined.

Tablica 1. Koncentracije deemulgatora (EB) i sredstva za obezvodnjavanje (DW) u ispitivanim uzorcima.

Sample	temperature 40 °C	
	concentration of EB mg/l	concentration of DW mg/l
EB0T40	0	0
EB500T40	500	0
EB1000T40	1000	0
EB2000T40	2000	0
EB0DW0T40	0	0
EB250DW250T40	250	250
EB500DW500T40	500	500
EB1000DW1000T40	1000	1000
	temperature 60 °C	
EB0T60	0	0
EB500T60	500	0
EB1000T60	1000	0
EB2000T60	2000	0
EB3000T60	3000	0
EB0DW0T60	0	0
EB250DW250T60	250	250
EB500DW500T60	500	500
EB1000DW1000T60	1000	1000
EB1500DW1500T60	1500	1500

RESULTS AND DISCUSSION

The effect of demulsifier addition on phase separation

The experimental results of separation of oil and aqueous phases in samples of oily wastewater with and without the addition of the demulsifier in the range of 500-3000 mg/l, at temperatures of 40 °C and 60 °C are shown in Figures 1 and 2 respectively. In the sample without the demulsifier (EB0T40), the separation starts at 65 minutes and takes place very slowly, and the maximum reached ratio of the height of the aqueous phase and the total height of the emulsion equals $\alpha = 0.1$. The addition of the demulsifier in the concentration of 500 mg/l (EB500T40) provides for fast separation in the first 10 minutes, slowing down until the equilibrium is reached. The increase in the demulsifier concentration does not increase the height of the aqueous phase, and the maximum reached ratio $\alpha = 0.6$. In the sample without the demulsifier the increase in temperature from 40 °C to 60 °C increases value α from 0.1 to 0.3 [11]. The addition of the demulsifier increases the separation rate and the height of the aqueous phase in equilibrium. The increase in the demulsifier concentration increases the separation effect and the maximum reached value of $\alpha = 0.76$. Consequently, the addition of the demulsifier is more effective than the increase in temperature.

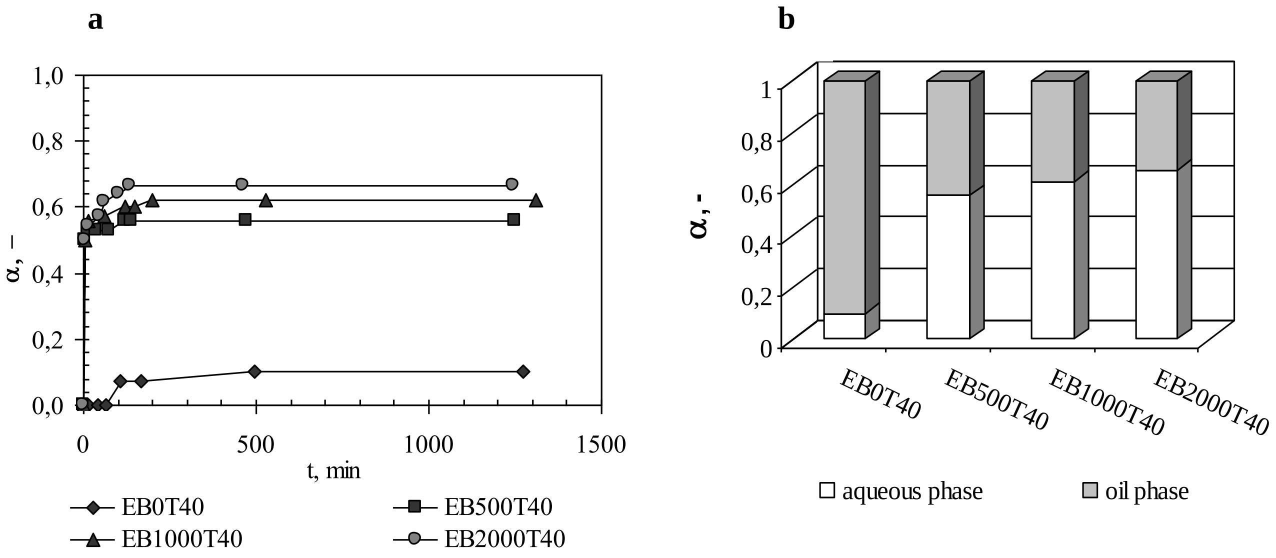

Figure 1. Monitoring of phase separation with the addition of the demulsifier at 40 °C (a). The equilibrium heights of the aqueous and the oil phase (b). **Note:** α is the ratio of the oil or aqueous layer height divided by the total layer height.

Slika 1. Vremensko praćenje razdvajanja faza uz dodatak deemulgatora pri 40°C (a). Visine vodene i uljne faze u ravnoteži (b). **Napomena:** α je omjer visine uljne ili vodene faze i ukupne visine sloja.

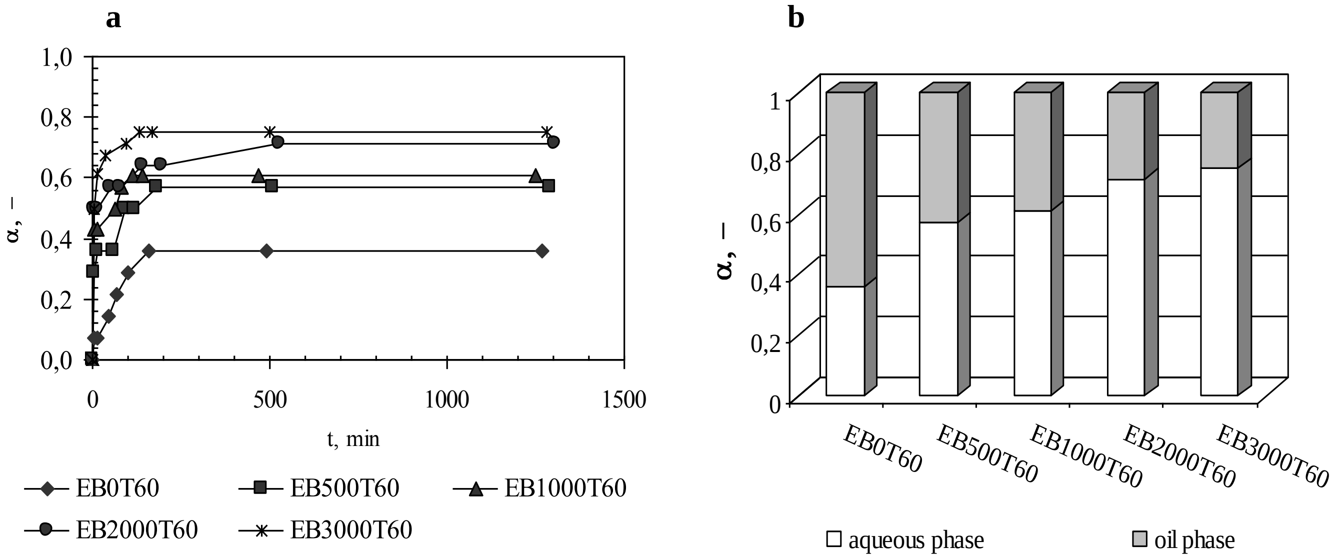

Figure 2. Monitoring of phase separation with the addition of the demulsifier at 60 °C (a). The equilibrium heights of the aqueous and the oil phase (b).

Slika 2. Vremensko praćenje razdvajanja faza uz dodatak deemulgatora pri 60 °C (a). Visine vodene i uljne faze u ravnoteži (b).

The effect of demulsifier and dewatering additions on phase separation

Separation of phases in the samples of oily wastewater has been performed using the demulsifier and the dewatering agent in the same concentrations, with the total concentration equal to the addition of the demulsifier in previous experiments. Figure 3 shows the experimental results of the separation of the oil and the aqueous phase in oily wastewaters with and without the addition of the demulsifier and the dewatering agent (EB+DW) in the range of 500-2000 mg/l, at the temperature of 40°C. The addition of the demulsifier and the dewatering agent shows the same phase separation rate as in samples with the demulsifier only (shown in Figure 1). But the height of the aqueous phase is much higher, which means that the separation is more effective. The increase of the addition from 250 mg/l to 500 mg/l improves phase separation and the maximum of the aqueous phase is α = 0.78 for the EB500DW500T40 sample. The comparison of results for samples with the demulsifier and samples with the demulsifier and the dewatering agent shows a similar effect on the separation rate. However, better efficiency is observed in samples containing the demulsifier and the dewatering agent. It is probably due to better removal of water from the oil phase. The same experiments were performed at 60 °C for the whole concentration range of 500-3000 mg/l and the results are shown in Figure 4. The increase of separation efficiency is observed with the increase of concentration of the demulsifier and the dewatering agent from 250 mg/l to 500 mg/l, and the maximum ratio of aqueous phase is α = 0.9 for the EB500DW500T60 sample. The increase in concentration of the demulsifier and the dewatering agent of 1000 mg/l and 1500 mg/l each decreases the separation effect, which was not observed in samples at 40 °C and samples with the demulsifier only. This behaviour of oily wastewater emulsions can be explained by the effect of temperature on the dewatering agent and changes of surface tensions between the oil and the aqueous phase [12-14].

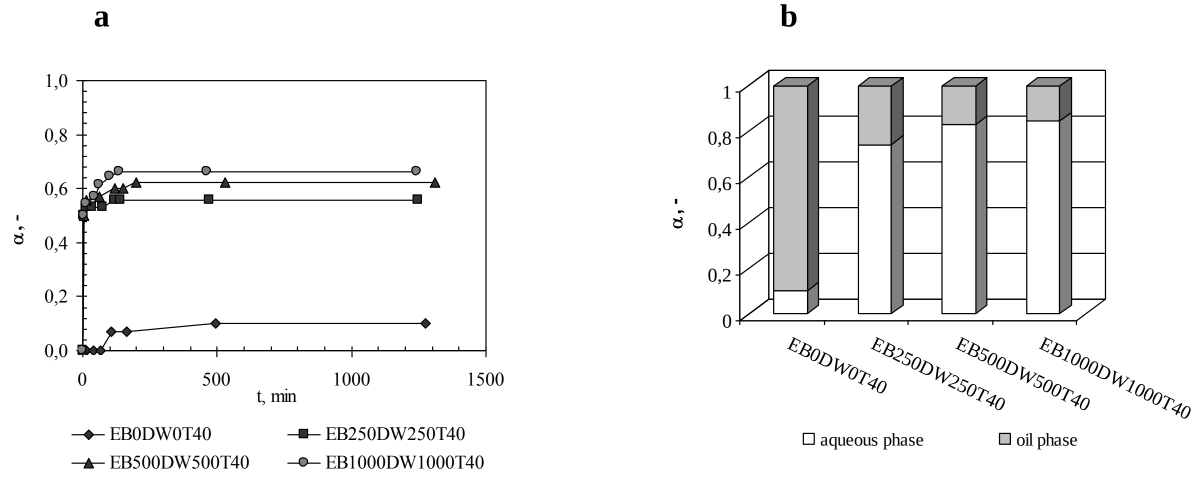

Figure 3. Monitoring of phase separation with the addition of the demulsifier and the dewatering agent at 40 °C (a). The equilibrium heights of the aqueous and the oil phase (b).

Slika 3. Vremensko praćenje razdvajanja faza uz dodatak deemulgatora i sredstva za obezvodnjavanje pri 40 °C (a). Visine vodene i uljne faze u ravnoteži (b).

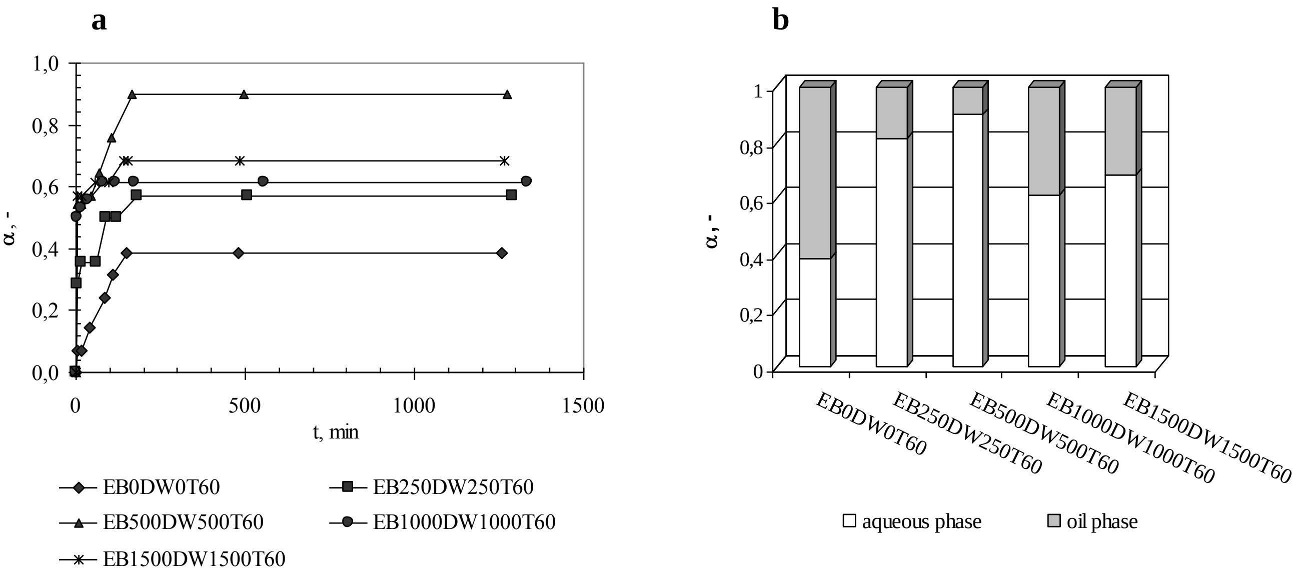

Figure 4. Monitoring of phase separation with the addition of the demulsifier and the dewatering agent at 60 °C (a). The equilibrium heights of the aqueous and the oil phase (b).
Slika 4. Vremensko praćenje razdvajanja faza uz dodatak deemulgatora i sredstva za obezvodnjavanje pri 60 °C (a). Visine vodene i uljne faze u ravnoteži (b).

Based on all the experiments performed, it may be concluded that the most effective separation of phases has been observed with the EB500DW500T60 sample, i.e. with mixing of oily wastewater with the demulsifier and the dewatering agent, each in concentration of 500 mg/l, at the temperature of 60°C.

The analysis of the aqueous phase after separation

Apart from the satisfactory separation effect, it is necessary to achieve the minimal content of water in the oil phase and the minimal content of oil in the aqueous phase. The quality of the aqueous phase is important as it is discharged into natural waters. This paper examines the quality of the aqueous phase by determination of mineral oils and COD. They are determined in samples of aqueous phases from emulsions which have shown the most effective separation of phases. Table 2 shows the results.

Table 2. The quality of the aqueous phase after separation.
Tablica 2. Kakvoća vodene faze nakon razdvajanja.

Sample	mineral oils mg/l	COD mg O_2/l
EB1000T40	1.13	1471.2
EB2000T40	0.59	4229.8
EB2000T60	0.61	4045.9
EB3000T60	0.16	2942.5
EB250DW250T40	0.25	11586.0
EB500DW500T40	0.52	2942.5
EB500DW500T60	1.12	16916.2

The results show low values of mineral oils concentrations in aqueous phase which is suitable for discharge into natural waters and these values are below maximal allowed values for discharge into natural waters by Croatian low [15]. However, certain high COD values are due to the presence of the demulsifier and the dewatering agent in the aqueous phase. Specifically, the demulsifier and the dewatering agent are macromolecular organic compounds oxidative by oxidation agents such as dichromate. This is confirmed by determination of COD and BOD (Biochemical Oxygen Demand) in the aqueous solution of the demulsifier in the concentration of 500 mg/l, and in the aqueous solution of the demulsifier and the dewatering agent in the concentration of 500 mg/l each. Aqueous solutions have been prepared with river water due existence on microorganisms responsible for biodegradation in natural recipients [16]. The high observed COD values of 2390.8 mg O_2/l for the solution containing EB and 1957.4 mg O_2/l for the solution containing EB+DW confirm the oxidation of the demulsifier and the dewatering agent as previously assumed. The biodegradation of the dewatering agent and the demulsifier has been monitored by consumption of oxygen during 10 days. There is confirmed continuous oxygen consumption due to biodegradation of demulsifier and dewatering agent, as shown on Figure 5.

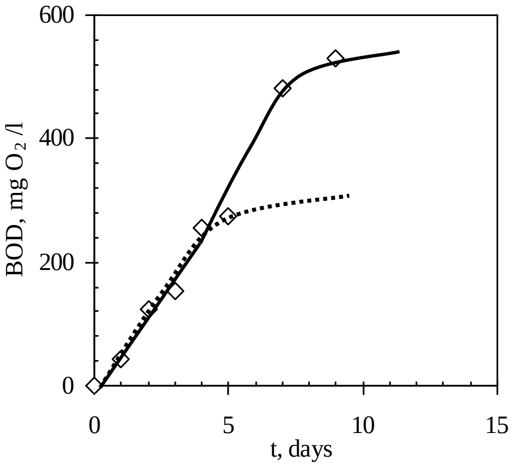

Figure 5. BOD in the aqueous solution of EB+DW prepared with river water.
Slika 5. BPK u vodenoj otopini EB+DW pripremljenoj u riječnoj vodi.

The values of BOD and the shape of the curve in Figure 5 indicate prolonged biodegradability and the presence of nitrogen in the molecules of additives. High values of COD in the aqueous phase indicate the need for additional treatment of the aqueous phase, e.g. adsorption on active carbon or biological treatment [13].

CONCLUSIONS

Based on the experiments performed and results obtained, it may be concluded that the addition of the demulsifier and the dewatering agent improves the separation of the oil and the aqueous phase in oily wastewater samples very effectively. The rate of separation can be monitored by measuring the height of the aqueous and the oil phase in a glass vessel. The effect of separation is determined as the ratio of the aqueous phase height and the total height of the emulsion. In the sample without additions at the temperature of 40°C, separation begins after 65 minutes, and continues very slowly. The addition of demulsifier increases the separation rate: most layers are separated during the first 10 minutes and the separation continues slowly until the equilibrium is reached. The increase of the demulsifier concentration increases the separation effect up to α = 0.6. In addition of demulsifier increase of temperature at 60 °C increases value α to 0.76. Effect of temperature on better separation is most observed at samples without addition (EB0T40 and EB0T60), where for all other samples it is less pronounced compared to effect of emulsifier addition. Because of that, it is more economical to perform the process with demulsifier at lower temperatures. The samples containing the demulsifier and the dewatering agent at 40 °C have shown better separation of phases compared to previous experiments and the ratio of separated aqueous phase has increased to α=0.78. It may be concluded that the addition of the dewatering agent and the demulsifier increases the effectiveness of this process. The best separation of the aqueous phase has been obtained in the EB500DW500T60 sample, and the increase in concentration does not contribute to better separation. The content of mineral oils is below the required values for discharge into natural waters according to the Croatian low [15], and high COD values in the separated aqueous phase indicate the needs for additional purification. Due observed biodegradability of demulsifier and dewatering in river water, a biological treatment could be suitable solution before discharge of treated water into natural water recipients.

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