

The effect of additives on the treatment of oil-in-water emulsions by vacuum evaporation

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Abstract

A simple batch vacuum evaporation process for the treatment of several oil-in-water (O/W) emulsions is reported. The experiments were carried out with waste emulsions from an industrial copper rolling process and with model emulsions prepared in the laboratory. No detailed information on the formulation of the industrial waste O/W emulsions was available. Several model emulsions were formulated using the same base oil (an 85–15% (w/w) mixture of a synthetic poly- α -olefin and a trimethylol propane trioleate ester, respectively) and one of the three following surfactants: Brij-76 (polyethylene glycol octadecyl ether, non-ionic), CTAB (hexadecyltrimethyl ammonium bromide, cationic), and Oleth-10 (glycolic acid ethoxylate oleyl ether, anionic). Experimental results show a strong influence of operating conditions, such as pressure or bath temperature, on the evaporation performance. As a general trend, the higher the values of these parameters, the higher the pollutant content in the obtained aqueous effluent. The presence of surfactants increase the evaporation rate, especially at low operating vacuum pressures, the solubility of oil molecules in water and the evaporation temperature of model O/W emulsions. Furthermore, COD reductions higher than 99.5% for the treated waste O/W emulsions were achieved.

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1. Introduction

One of the most extended industrial applications of oil-in-water (O/W) emulsions is their use in some metal-machining operations, such as rolling, grinding or cutting, where lubrication and cooling of the piece–tool contact are needed at the same time. These metalworking fluids lose their functional properties with use, because of the severe operating conditions, and need to be replaced. As a consequence, a great volume of oily wastewater is produced that has to be treated before its disposal, in order to obtain an aqueous effluent free of oil and others additives. Furthermore, water concentration in the oily effluent would be as low as possible.

Several techniques have been proposed for the treatment of waste O/W emulsions, such as deep bed filtration, coagulation, flocculation, centrifugation, flotation, ultrafiltration, liquid–liquid extraction and microwave radiation [1–6]. These treatments can physically separate the waste emulsion into an

aqueous effluent and a more concentrated O/W emulsion. Unfortunately, soluble organic matter contained in the waste emulsion may be present in the aqueous effluent at high concentrations, and in most cases there is a high water concentration in the oily effluent. An alternative such as vacuum evaporation could be an efficient treatment process because of the high chemical oxygen demand (COD) reduction that can be achieved (90–100%). This process is strongly recommended in those operations where the aqueous phase has to be reused.

Although in some existing plants this technique is used for the treatment of waste O/W emulsions, its performance has not been fully studied and very scarce information can be found in the literature [7]. Several works have studied the influence of operating conditions on the use of vacuum evaporation for water desalination [8] and treatment of landfill leachate [9]; the increase of the heat transfer to the feed increased the evaporation rate but decreased the quality of the final aqueous effluent (condensate). Oil evaporation mechanisms from O/W emulsions [10,11] and droplet evaporation from surfactant solutions or O/W emulsions on a heat surface [12–20] have been studied by several authors. The role of emulsifiers on the evaporation process and the effect of the heat flux were

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analysed in these works: the presence of surfactants delays the evaporation, specially when they have a long hydrocarbon chain [18], or when they are present at concentrations much higher than the CMC (critical micelle concentration) [17].

In this work, a simple batch vacuum evaporation process for the treatment of several O/W emulsions is reported. Experiments were carried out with waste emulsions from an industrial copper rolling process (Cunext Copper Industries, S.L., Córdoba, Spain) and with model emulsions prepared in the laboratory. The addition of surfactants to the O/W emulsions formulated in the laboratory was carried out in order to ascertain their effect on the evaporation process.

2. Materials and methods

Evaporation experiments were developed in an evaporator Büchi R205, consisted of a rotating flask immersed in a heating bath, where the O/W emulsion sample is control-heated to the adequate temperature. The vapour is condensed in a water-refrigerated column and it is collected in a flask. The process was carried out at low pressure by means of a vacuum pump and a pressure control device. The vapour temperature is continuously measured. In order to ensure a good mixing, the rotational speed in the feed flask was set at 60 rpm.

The quality of the aqueous effluents (condensates) was evaluated by chemical oxygen demand (COD) analyses, following the reactor digestion method using a Hach DR2010 spectrophotometer.

The model O/W emulsions prepared in the laboratory were formulated using an 85–15% (w/w) mixture of a synthetic poly- α -olefin (PAO-10) and trimethylol propane trioleate ester (TMP), respectively, as base oil. Three different surfactants, supplied by Sigma–Aldrich, were added to stabilise the emulsion: Oleth-10 (glycolic acid ethoxylate oleyl ether, anionic, CMC = 20 mg/L), Brij-76 (polyethylene glycol octadecyl ether, non-ionic, CMC = 200 mg/L), and CTAB (hexadecyltrimethyl ammonium bromide, cationic, CMC = 350 mg/L). Their critical micelle concentration (CMC) was determined at 20 °C by surface tension measurements using a Krüss K-8 tensiometer, following the Du Noüy's platinum ring method.

All the emulsions were prepared with a 3% (w/w) base oil content but at different emulsifier concentrations: 0.5, 1.0 and 2.0 times the CMC. First, the base oil was blended with the emulsifier by stirring on a hot plate. Their respective amounts were adjusted to achieve the required oil and emulsifier concentrations after the dilution with water. Then, this concentrate was dispersed in deionised water (Millipore Elix 5 deioniser) in the

required proportion using a homogeniser Heidolph DIAX 900, at 10,000 rpm during 10 min.

Some tests were carried out using surfactant solutions without oil and with emulsions without surfactant in order to know their influence on water evaporation. Table 1 shows the COD values for all emulsions and solutions prepared in the laboratory.

The waste O/W emulsion generated in an industrial copper rolling process was provided by the manufacturing company, Cunext Copper Industries, S.L. (Córdoba, Spain). Their composition was unknown and proprietary of the manufacturer company. Before being treated, the waste emulsion was homogenised following the same procedure used for the model O/W emulsions. Turbidity and conductivity of feed and condensate effluents from the treatment of this waste emulsion were also measured using a turbidimeter Hach ratio XR and a conductimeter Crison micro CM 2202. The initial water content of the waste emulsion was measured according to the normalised method ISO 662:1998. The waste emulsion characteristics were the following: 98.5% (w/w) water content, 31,840 mg/L COD, conductivity: 965 μ S/cm, and turbidity: 9210 NTU.

3. Results and discussion

3.1. Model O/W emulsions prepared in the laboratory

The influence of operating pressure and emulsifier concentration on the evaporation process for model O/W emulsions were studied. The heating bath temperature was fixed at the lowest value that allows arising the boiling temperature of water at the operating pressure, in order to reduce energy consumption and to obtain a better condensate quality (aqueous effluent), as it has been previously reported [8,13,14].

Fig. 1 shows the evolution of evaporation temperature (T_v) along time for pure water, surfactant solutions, emulsions without surfactants and surfactant-stabilised emulsions. The operating pressure was 10 kPa and surfactant concentration, if any, was the CMC for all cases. It can be seen in Fig. 1 that lower evaporation temperatures correspond to the emulsions without surfactants. As a general trend, the higher the evaporation temperature, the faster the evaporation process, as shown in Fig. 2, where the evaporation rate (E), expressed as the volume of sample evaporated (mainly water) per unit time, is shown at two different operating pressures. The different behaviour of the emulsion without the emulsifier is more noticeable at 10 kPa.

Moreover, the presence of surfactants has another effect on the pollutant content of the aqueous effluent (Fig. 3). COD values are higher for the emulsions stabilised with surfactants than for

Table 1
COD values (mg/L) of model O/W emulsions and surfactant solutions before being treated

	Surfactant concentration (times CMC)									
	No surfactant	Non-ionic			Cationic			Anionic		
		0.0	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0
Surfactant solution	~0	240	455	855	300	505	1,200	25	45	85
O/W emulsion	1400	21,850	22,480	26,600	9130	13,250	17,750	1720	7680	8260

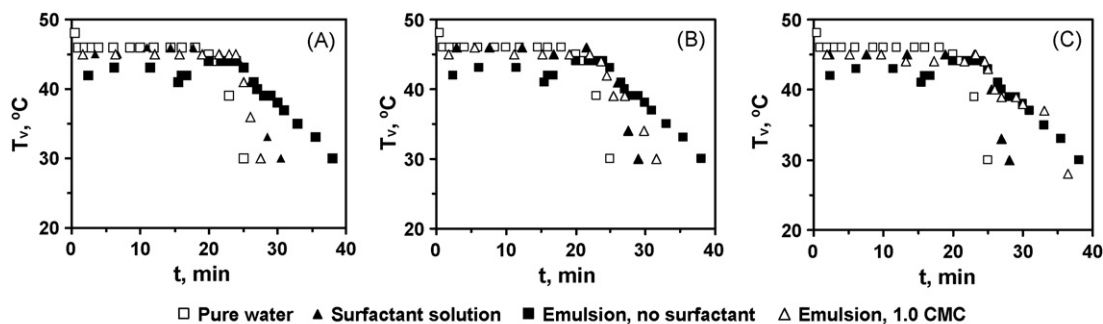


Fig. 1. Evolution of evaporation temperature along time for pure water, surfactant solution, emulsion without surfactant and emulsion with non-ionic (A), cationic (B) and anionic (C) surfactants (operating pressure = 10 kPa; surfactant concentration = 1.0 CMC).

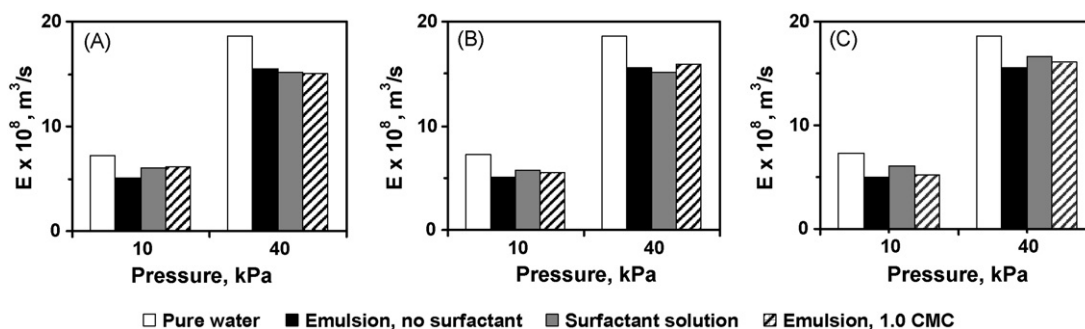


Fig. 2. Evaporation rate at different operating pressures for pure water, surfactant solution, emulsion without surfactant and emulsion with non-ionic (A), cationic (B) and anionic (C) surfactants (surfactant concentration = 1.0 CMC).

those without surfactants. It has been reported that this behaviour is due to the increase of the solubility of the oil molecules in water by means of micelle formation. A water film is created between oil droplets, and it will play a key role in the evaporation process. Further, during the evaporation, the dispersed oil droplets cream to the surface but remain separated from the vapour phase by a thin water film [10]. The oil, in order to be evaporated, has to diffuse across this water film and surfactant micelles may enhance this diffusion [11]. It is also observed that COD values for surfactant solutions are very low.

As it is also shown in Fig. 2, an increase of operating pressure from 10 to 40 kPa enhances about 2.5 times the evaporation rates. There are several factors that could explain this behaviour. Firstly, the heat flux transferred to the sample flask is higher in the case of 40 kPa since the temperature gradient (difference between the water boiling temperature and the minimum heating

bath temperature needed to achieve the water evaporation) is 54 °C for 10 kPa and 105 °C for 40 kPa pressure. Arguably, high temperatures cause a decrease in surface tension and then in the rate of bubbles formation [13,14]. Further, elevated temperatures enhance the solubility of oil and emulsifier molecules, so the water has less resistance to diffuse and evaporate through oil droplets or layers [12].

The operating pressure has also an important effect on the quality of the obtained aqueous effluent. Fig. 4 shows that the COD values of the aqueous effluents obtained for all emulsions working at 40 kPa are higher than those obtained at 10 kPa until 75–80% of the initial volume of the emulsion sample is evaporated, due to the higher heat flux that causes the presence of organic compounds in the condensates. From then on, the COD value at 10 kPa increases rapidly, while it remains approximately constant at 40 kPa for the overall experiment, due to the difficulty

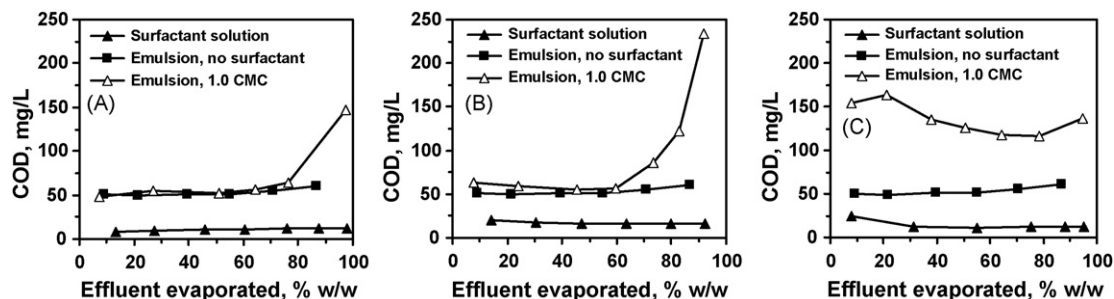


Fig. 3. COD content in the aqueous effluent as a function of the effluent evaporated for surfactant solution, emulsion without surfactant and emulsion with non-ionic (A), cationic (B) and anionic (C) surfactants (operating pressure = 10 kPa; surfactant concentration = 1.0 CMC).

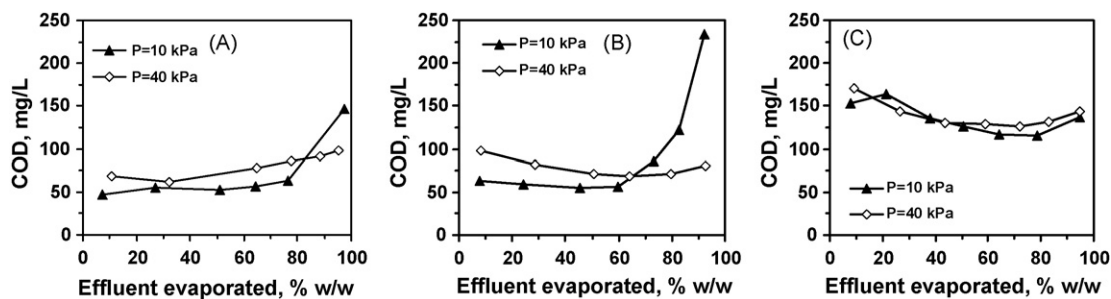


Fig. 4. Effect of operating pressure on COD content in the aqueous effluent for emulsions stabilised with non-ionic (A), cationic (B) and anionic (C) surfactants (surfactant concentration = 1.0 CMC).

to evaporate water from emulsions with high oil and surfactants content [8,9,15]. The increase of COD values at the end of the evaporation process was more perceptible for those emulsions stabilised by cationic and non-ionic surfactants. The COD content of the aqueous effluent for anionic surfactant-stabilised emulsion was higher but it remained more constant along the test.

The emulsifier type and concentration are expected to exert some influence on the evaporation behaviour since the addition of these compounds will modify several properties involved in the evaporation process, such as droplet size distribution, zeta potential and surface and interfacial tensions. It has been reported that oil solubility in water is largely increased when the emulsifier concentration exceed the CMC value. Electrostatic repulsions or steric barriers between oil droplets also play a key role since the water film between droplets is closely related to these interactions, specially at high oil concentrations, i.e., at the end of evaporation process. Water films are thicker and water evaporation is more facilitated for high electrostatic repulsions. Hence, these water films are thinner when non-ionic emulsifiers are used [10,11]. Furthermore, the interfacial tension is also related to the facility of oil molecules to diffuse in the aqueous phase and vice versa and to coalesce forming larger oil droplets.

Fig. 5A shows the effect of emulsifier concentration on the evaporation rate. There is not a clear trend in the experimental data, and only the emulsions stabilised with the cationic surfactant showed a higher evaporation rate when surfactant concentration was increased. Similar results were obtained when the

COD values of aqueous effluents were analysed (Fig. 5B). There was a strong increase in the pollutant content above the CMC when the non-ionic surfactant (Brij-76) was used, likely due to the higher solubility of oil molecules, which were able to diffuse in the aqueous phase and get through the surface water layer to be evaporated. Electrostatic interactions play a more important role for the ionic emulsifiers. The addition of increasing concentrations of the cationic surfactant (CTAB) reduced the COD value of the aqueous effluent whereas for the anionic surfactant (Oleth-10) a maximum was obtained at the CMC value. A likely explanation for the performance of the cationic surfactant behaviour is that its concentration increase lowers the zeta potential and the interfacial tension, so the coalescence of oil droplets is enhanced, reducing their potential evaporation. The anionic surfactant behaviour is more difficult to explain and it is likely due to the combined effect of interfacial tension, zeta potential and oil solubility changes, without a clear correlation among these properties. It is important to point out that the CMC value of the anionic surfactant – and therefore, the concentrations used in this study – are much lower than the CMC of the other surfactants used.

3.2. Waste O/W emulsion

In this case, only the influence of operating conditions, such as pressure or bath temperature, is studied since there was no option to modify the composition of the waste O/W emulsion. Experimental results are shown in Figs. 6–8. Higher evaporation

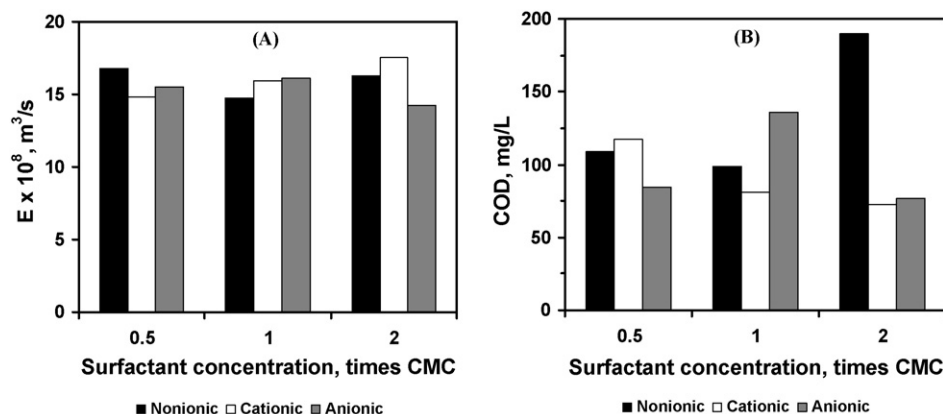


Fig. 5. Effect of surfactant concentration on the evaporation rates (A) and COD content of the aqueous effluent (B) for the evaporation of emulsions at 40 kPa.

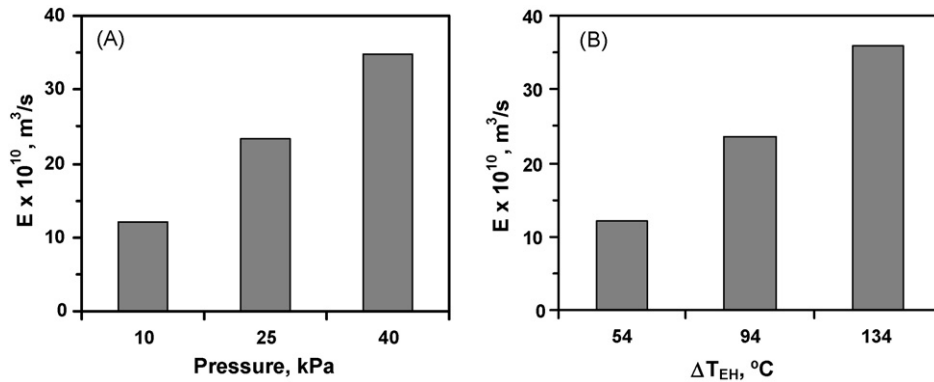


Fig. 6. Influence of operating pressure (A) and temperature gradient (B) on the evaporation rate for the waste O/W emulsion.

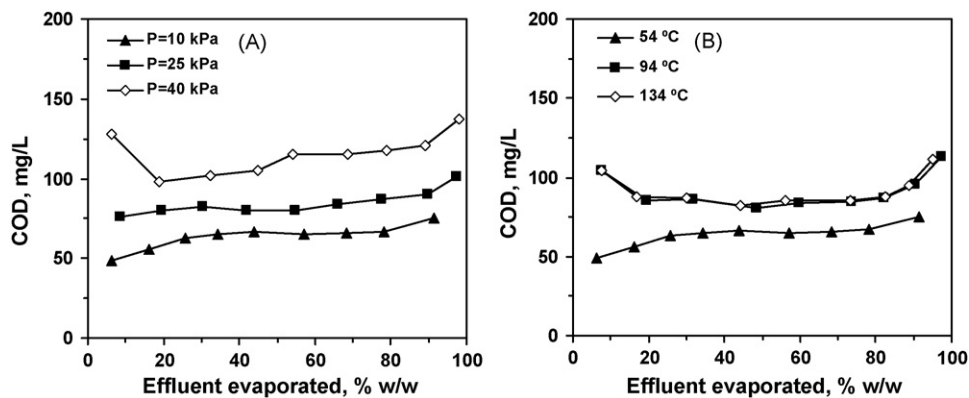


Fig. 7. Influence of operating pressure (A) and temperature gradient (B) on the COD content of the aqueous effluents obtained in the treatment of waste O/W emulsion.

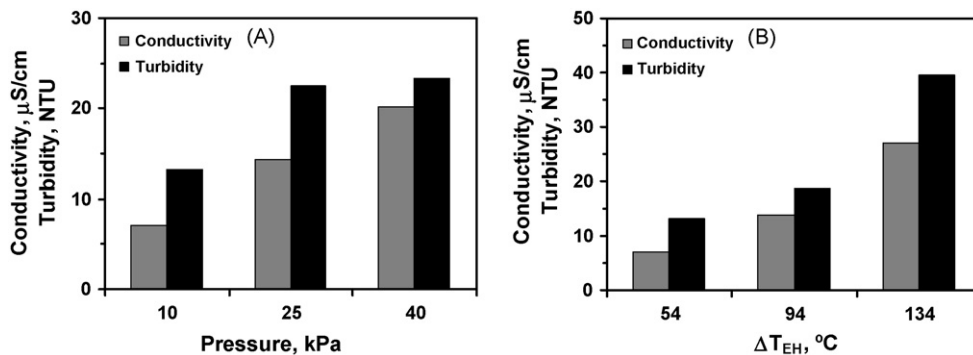


Fig. 8. Influence of operating pressure (A) and temperature gradient (B) on the conductivity and turbidity values of the aqueous effluents obtained in the treatment of waste O/W emulsion.

rates were reached when working at higher operating pressures, but also a lower quality of the aqueous effluent were obtained, with high COD, conductivity and turbidity values.

As it was previously explained [8,13,14], a higher bath temperature increases the heat flux, which produces shorter bubble life and an increase of oil solubility in water. In order to check it, different evaporation tests were carried out at 10 kPa and at several bath temperatures: 100 °C—the minimum temperature required to get the water boiling temperature in the feed flask –, 140 °C and 180 °C, corresponding to temperature gradients (ΔT_{EH}) of 54, 94 and 134 °C, respectively. It can be observed that an increase of the heat flux enhances the evaporation rate

but reduces the quality of the effluent. It is not noticed an apparent difference in the COD values between experiments carried out at bath temperatures of 140 and 180 °C, while conductivity and turbidity increase with heat flux, so it is supposed that there are more inorganic ions present in the effluent at the bath temperature of 180 °C. COD reductions higher than 99.5% were achieved for all tests.

4. Conclusions

The influence of operating conditions during the vacuum evaporation of several oil-in-water emulsions was studied in

this work. The addition of surfactants increases the evaporation rate, especially at low operating pressures, and the evaporation temperature of model O/W emulsions. The effect of the type and concentration of surfactants added to the model O/W emulsions was also studied since they affect to several interfacial properties related to the evaporation process, such as oil solubility, interfacial tension, interactions between oil droplets or oil droplets coalescence. Hence, the addition of non-ionic surfactant (Brij-76) at concentrations below its CMC value gave a final aqueous effluent with a better quality (lowest COD value), whereas the ionic surfactants performed better when they were added at concentrations above their CMC. As a general trend, the higher the operating pressures or temperatures, the higher the pollutant content in the obtained aqueous effluent. Furthermore, COD reductions higher than 99.5% were achieved when waste O/W emulsions were treated.

The results also indicate that a proper selection of additives, such as emulsifiers, biocides or corrosion inhibitors, is needed for the right formulation and the subsequent regeneration of metalworking O/W emulsions, in order to achieve aqueous effluents with low COD values.

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