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Proceedings of European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

# Treatment of waste oil-in-water emulsions from a copper metalworking industry by vacuum evaporation: effect of operating conditions

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## Abstract

The efficiency of treatment of synthetic and semi-synthetic waste oil-in-water (O/W) emulsions by vacuum evaporation is evaluated. A previous destabilisation/centrifugation stage increases the quality of the final aqueous effluent. However, proper selection of a coagulant salt or flocculant is required. A comparison of laboratory-scale evaporation results and those obtained in an industrial evaporator shows a good agreement.

Keywords: O/W emulsions, vacuum evaporation, metalworking, coagulant, pH

## 1. Introduction

Oil-in-water emulsions are commonly used in metalworking industries for lubrication and cooling purposes. These fluids lose their functional properties with aging and generate waste oily emulsions that must be properly treated before disposal in order to remove the free, soluble and emulsified oil. Different techniques are being used for this purpose, such as sedimentation, centrifugation, deep bed filtration, ultrafiltration, and evaporation [1-4]. Previous works have indicated that the best discharge levels are obtained by combining several of the aforementioned techniques [5,6].

Evaporation is a suitable technique for treatment of oily wastewaters since a high quality aqueous effluent is achieved and because the resulting recovered oil has a low water content, so it can be used for energy recovery. Moreover, evaporative treatment of synthetic and semi-synthetic emulsions is more effective than other techniques, because of the low oil concentrations in these emulsions. Processes such as ultrafiltration, centrifugation or coagulation tend to separate the oily phase from the emulsion but all the water-soluble compounds remain in the aqueous phase, leading to high COD values in the discharge effluent [3].

The main drawback of the evaporation process is that it is an energy-intensive thermal process for treating these wastes, although under vacuum conditions the energy costs are lower. Factors such as the heat transfer rate [7-9] and operating pressure [2,10] play important roles in the performance of evaporators. Moreover, if compounds with a vapor pressure similar to that of water are present in the oil/water emulsion, they may pollute the vapor condensate [1].

The composition of the emulsion, including the type of emulsifiers employed and their concentrations affect the evaporation process, since high concentrations may decrease the evaporation rate, especially for emulsifiers containing a very long hydrophobic chain [11-14]. Furthermore, if foaming develops, it will provide more air/water interfacial area, increasing the water evaporation rate [15], but it may also affect the quality of the condensate because of entrainment of some feed. Moreover, non-ionic surfactants enhance evaporation more than ionic surfactants [16].

## 2. Materials and methods

Evaporation experiments were carried out using a Büchi R205 evaporator, which consisted of a rotating flask immersed in a heating bath, in which the O/W emulsion sample was heated to the desired temperature. The vapor was condensed in a water-condenser and collected in a receiving flask. The process was carried out at low pressures by means of a vacuum pump and a pressure control device. The vapor temperature was continuously recorded. In order to ensure good mixing, the rotor speed of the feed flask was set at 60 rpm.

Waste oil-in-water emulsions were provided by a local copper manufacturing company. These emulsions were generated in different parts of the process:

*i.* A synthetic emulsion, used for cooling in the melting process (Multiroll), made from a 2% (v/v) commercial concentrate in water. Commercial name: Multiroll Cu, Zeller+Gmelin.

*ii.* A semi-synthetic emulsion, used for lubrication and cooling in the smoothing process (Unopol), with 13-14% (v/v) commercial concentrate in water. Commercial name: Unopol G560, Fimitol ZD 56 GF.

*iii.* A semi-synthetic emulsion, used in a wire drawing process (Divinol), made from a 5% (v/v) commercial concentrate, based in naphthenic hydrocarbons containing both anionic and non-ionic surfactants, in water. Commercial name: Multidraw Cu MF, Zeller+Gmelin.

Table 1 presents some characteristics of the waste O/W emulsions, which had been used for 8 months, 3 months and 1 year, respectively.

The qualities of the feed and aqueous effluents (condensates) were evaluated in terms of analyses for chemical oxygen demand (COD), turbidity, conductivity and biological oxygen demand ($BOD_5$). The COD analysis was carried out by the reactor digestion method [17] using a Hach DR2010 UV spectrophotometer. Turbidities were measured using a Hach ratio XR turbidimeter. The conductivity meter used was a Crison Micro CM 2202. $BOD_5$ was determined using a WTW Oxitop IS6.

Table 1. Characteristics of the waste O/W emulsions studied

| | **COD (mg/L)** | **Turbidity (NTU)** | **Conductivity (µS/cm)** | **BOD$_5$ (mg/L)** | **pH** |
|---|---|---|---|---|---|
| **Multiroll** | 29600 | 58500 | 5750 | 315 | 9.0 |
| **Unopol** | 304800 | 29300 | 4820 | 155 | 8.5 |
| **Divinol** | 158700 | 58500 | 1673 | 188 | 8.3 |

A selection of the flocculants/coagulants and their concentration was made by centrifugation tests, in order to evaluate the efficiency of the destabilisation/centrifugation pre-treatment stage for oil removal. Centrifugation experiments were performed in a Wifug Labor 50 batch centrifuge, working at 3000 rpm for 15 minutes. In order to break the emulsion, different coagulant salts and flocculants were used: $CaCl_2$ and $AlCl_3{\cdot}6H_20$ (Panreac S.L., Barcelona, Spain) as coagulant salts and the flocculant NALCO 71243 (NAL, a quaternary polyamine) supplied by Nalco Europe (Leiden, The Netherlands).

## 3. Results and discussion

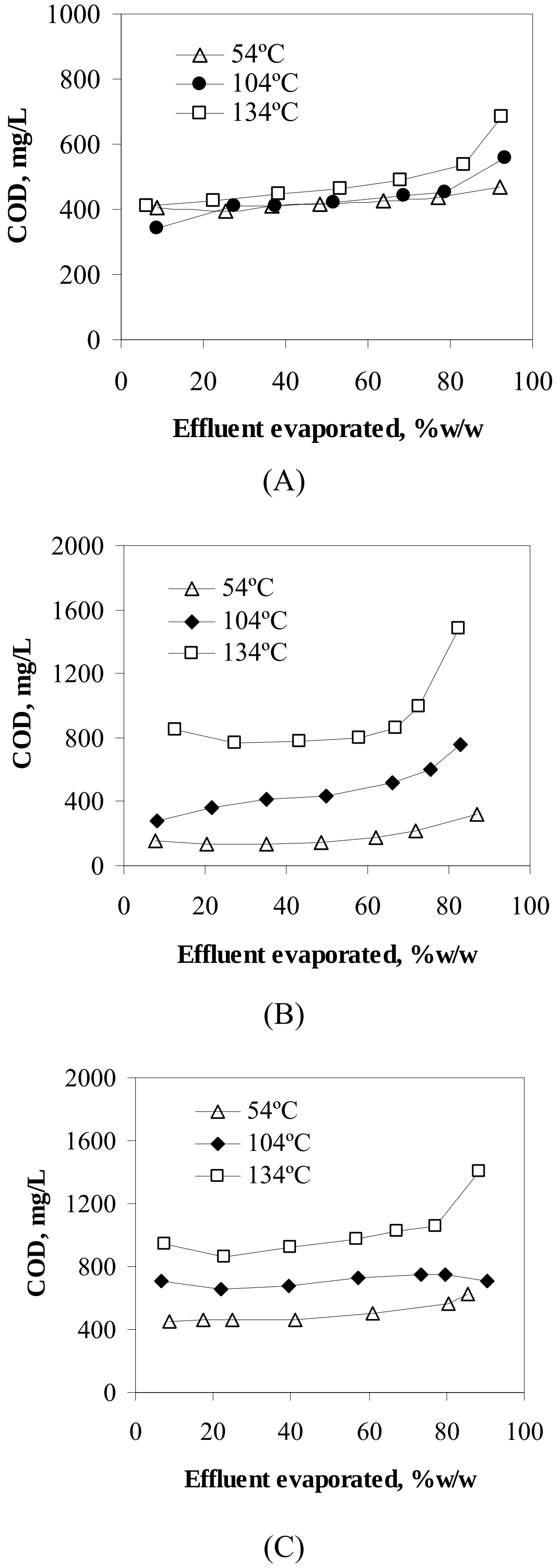
### *3.1. Effects of heat transfer rates*

The rate of heat transfer to the feed sample is a key parameter in evaporation, since it influences the bubble size [8], bubble life, and the manner in which bubbles break [7]. An increase in the temperature of the heating fluid enhances the evaporation rate, but decreases the quality of the condensate [18].

Nevertheless, previous studies have shown that a very hot surface could have a negative effect on the quality of the condensate, since a vapor layer is formed between the emulsion and the surface, which decreases the rate of heat transfer to the emulsion [9]. This situation was avoided in this work through rotation of feed flask to keep the emulsion well mixed and to obtain more uniform heat transfer.

Since the heating temperature plays a key role, some experiments were carried out at constant pressure but at several bath temperatures. The operating pressure was fixed at 10 kPa and the bath temperatures were 100, 150 and 180 ºC. These values produce concomitant temperature differences between the bath and the evaporating emulsion of 34, 104 and 134 ºC, respectively.

The effects of the difference between the bath temperature and the evaporation temperature ($\Delta T_{BE}$) on the effluent quality (Figure 1) evaporation rate (Figure 2), and the final volume of oil waste (Figure 3) are shown. The operating pressure was fixed at 10 kPa for all tests.



(A)

(B)

(C)

Figure 1. Effect of $\Delta T_{BE}$ on COD values of aqueous effluent obtained after evaporation at 10 kPa for the three O/W emulsions: Multiroll (A), Unopol (B) and Divinol (C)

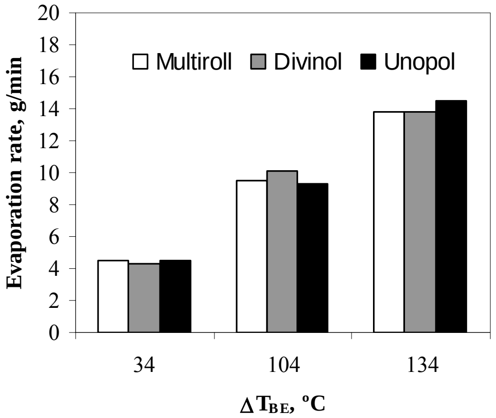


Figure 2. Effects of $\Delta T_{BE}$ on evaporation rates for waste O/W emulsions at 10 kPa

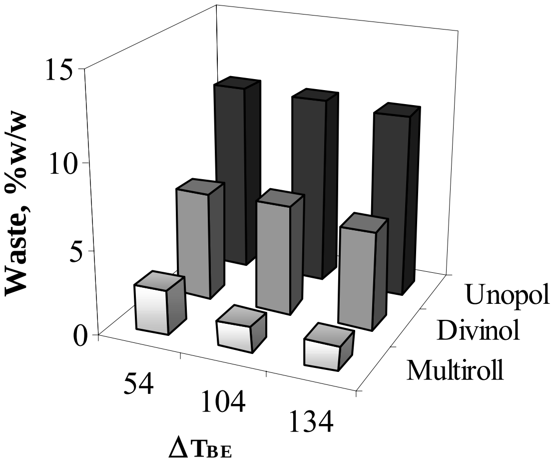


Figure 3. Weight percentages of waste remaining after evaporation of the three O/W emulsions at different $\Delta T_{BE}$

Examination of Figure 2 clearly indicates an increase of the evaporation rate with increasing $\Delta T_{BE}$. However, the COD of the condensate became higher as $\Delta T_{BE}$ increased, especially for the semi-synthetic emulsions (Figure 1). Similar results were observed in previous studies [18]. These results were attributed to evaporation of the most volatile components of the oil. The synthetic emulsion (Multiroll) yielded the lowest volume of final waste (Figure 3), because synthetic emulsions do not contain oil. For all cases, a slight decrease in this volume was observed as $\Delta T_{BE}$ increased.

### *3.2. Effect of operating pressure*

The effect of the operating pressure was studied at a constant $\Delta T_{BE}$ value of 105ºC. The influence of this parameter was analysed in previous studies, but not at constant $\Delta T_{BE}$ [1,2]. Three different pressures were studied (10, 25 and 40 kPa) for bath temperatures of 100, 150 and 180ºC, respectively. The experimental results –COD of the aqueous effluent, evaporation rate and the final volume of oil waste after evaporation – are shown in Figures 4 to 6.

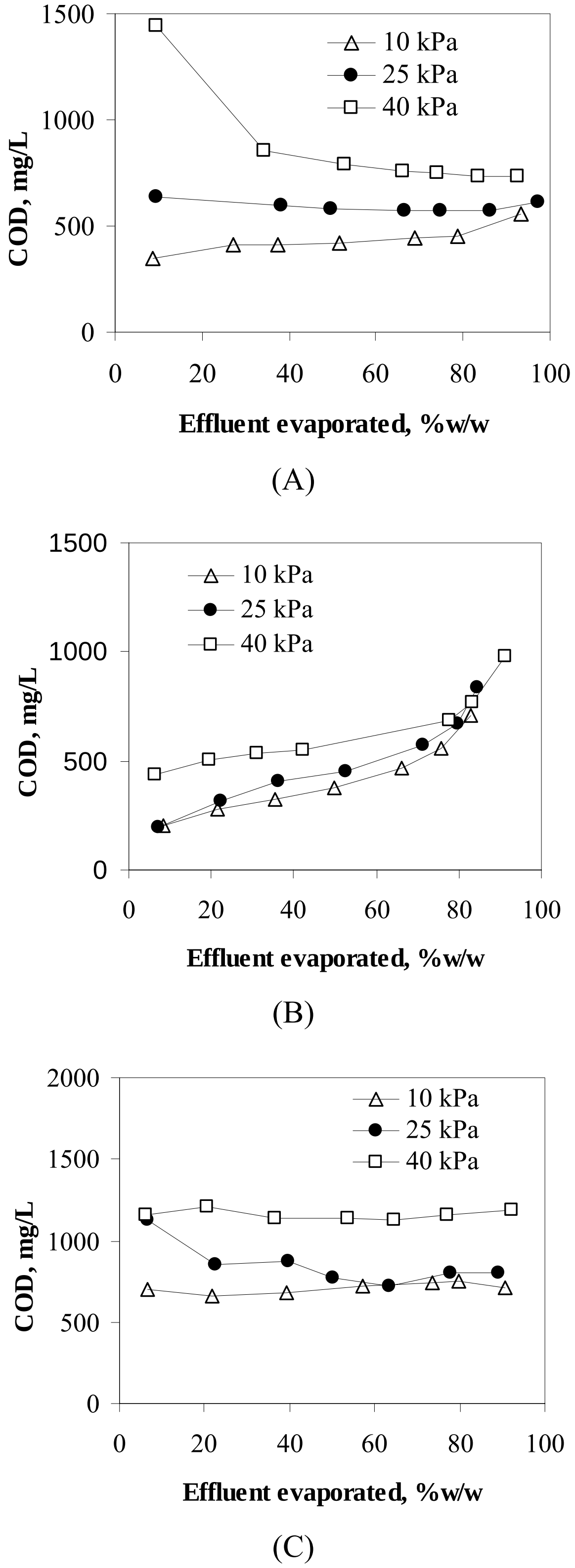


Figure 4. Effect of operating pressure on COD of aqueous effluent obtained after evaporation at a $\Delta T_{BE}$ of 105ºC for three O/W emulsions: Multiroll (A), Unopol (B) and Divinol (C).

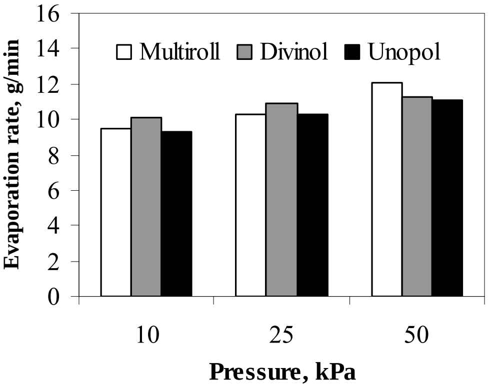


Figure 5. Effects of operating pressure on the evaporation rate of O/W emulsions at a $\Delta T_{BE}$ of 105ºC

Increases in the evaporation rate and COD values are observed when the operating pressure was increased. However, the increases are not as large as those observed for evaporation at different values of $\Delta T_{BE}$. No significant changes in the final volume of the oily wastes were observed when the operating pressure increased. Once again, the Unopol emulsion rendered the highest volume of concentrate oily waste as might be expected, because it is the most concentrated metalworking fluid. Nevertheless, the COD values of the condensate for this emulsion are similar to those of the other fluids.

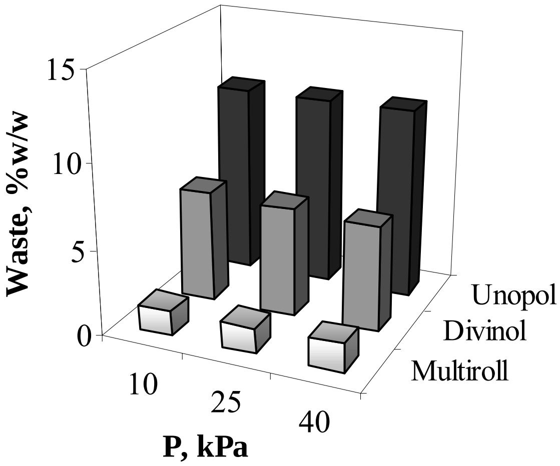


Figure 6. Percentage of waste obtained after evaporation of emulsions at ą $\Delta T_{BE}$ of 105ºC

### 3.3. Pre-treatment of the waste emulsions

Use of a destabilisation/centrifugation pretreatment stage to remove part of the initial oil content should lead to a better performance of an evaporation process, because this stage would permit one to operate with longer cycles, thereby reducing the frequency of cleaning steps and the associated energy costs [6]. Use of this stage led to good results in the treatment of mineral oil-in-water emulsions [2].

First, the three emulsions were treated by centrifugation (at 3000 rpm for 15 minutes) using different flocculant and coagulant salts, in order to determine the critical coagulant concentration (CCC). The best results were obtained using 500 ppm of the flocculant Nalco 71243 for the synthetic emulsion (Multiroll) and with 0.2 M $CaCl_2$ and 0.05 M $AlCl_3$ for the semi-synthetic emulsions Unopol and Divinol, respectively.

Subsequently, samples of 200 mL of each emulsion were allowed to settle for 16 hours after addition of the optimum concentration of flocculant and coagulant salts but prior to being evaporated. Properties of the resulting aqueous phases are shown in Table 2.

Table 2. Properties of the aqueous phases obtained after destabilisation/centrifugation and settling treatments for the emulsions Multiroll, Unopol, and Divinol

| **Emulsion** | **Additive** | **COD (mg/L)** | **Conductivity (μm/S)** | **pH** | **Turbidity (NTU)** |
|---|---|---|---|---|---|
| **Multiroll** | 500 ppm Nalco 71243 | 11150 | 2070 | 3.8 | 266 |
| **Unopol** | 0.2 M $CaCl_2$ | 34450 | 23700 | 7.9 | 19.7 |
| **Divinol** | 0.05 M $AlCl_3$ | 8575 | 2010 | 3.6 | 1580 |

Decreases in the evaporation rate were clearly observed after pretreatment of the emulsions. Pretreatment also leads to greater increases in the COD values of the effluent (Figure 7). These results could be explained by the change in pH that occurs on addition of demulsifiers (Table 2), because the pH influences the zeta potential of emulsions. The oil droplets exhibit less affinity for $H^+$ ions than for $OH^-$ ions [19]. Consequently, a decrease in pH decrease the net charge of the electric double layer around oil droplets, reducing the repulsive forces between oil droplets and enhancing coalescence [12]. Addition of a coagulant salt decreases the pH of the emulsion, because of formation of $Ca(OH)_2$ and $Al(OH)_3$ precipitates [20,21].

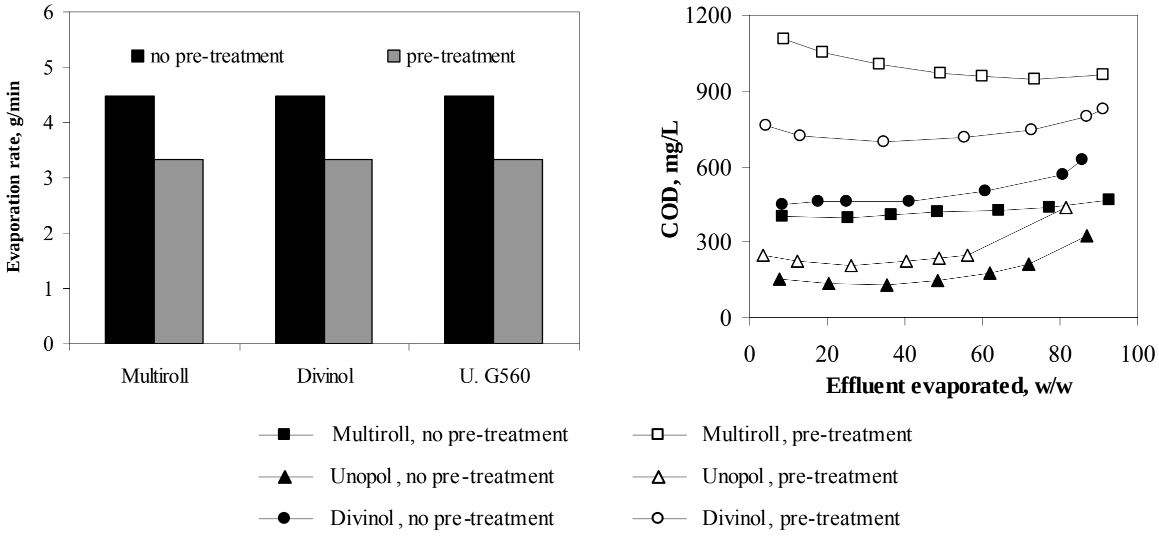


Figure 7. COD values of the aqueous effluents obtained after evaporation of emulsions at 10 kPa and $\Delta T_{BE}$ of 54ºC. Data were obtained from both samples not subjected to pre-treatment and samples pretreated in destabilisation/centrifugation and settling stages

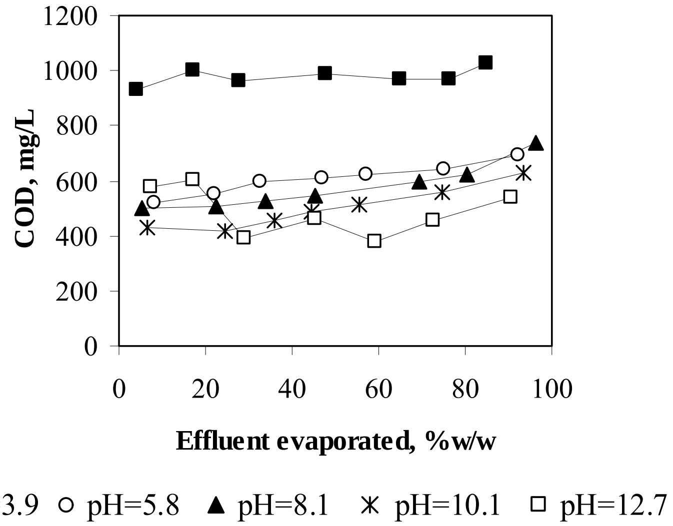


Figure 8. Effect of pH on the quality of the aqueous effluent obtained by evaporation of the Divinol emulsion after pre-treatment (10 kPa, $\Delta T_{BE}$ = 54ºC)

The effects of pH on the evaporation process were studied using samples of the Divinol emulsion. After the emulsion was destabilised and settled by addition of 0.05 M $AlCl_3$, the pH was adjusted with 1M NaOH. Between pH values of 5 and 10, a white precipitate was observed (probably $Al(OH)_3$). At a pH between 10 and 11, the precipitate turned a blue color that was characteristic of $Cu(OH)_2$. At higher pH, the precipitate disappeared and the solution became dark-blue, likely because of the formation of soluble compounds of $[Cu_n(OH)_{2n-2}]^{2+}$ [22]. These samples, prepared at different pH values, were evaporated and the quality of the resulting aqueous effluent was analysed. Figure 8 indicates that an increase in COD removal was achieved when the pH of the emulsion was raised by adding NaOH after centrifugation.

### *3.4. Scale-up of the evaporation process*

Evaporation of the Unopol emulsion was carried out in an industrial evaporator for comparison with the results obtained on a laboratory scale. In this study, the waste emulsion had been used for 4 years. The properties of this emulsion prior to treatment are shown in Table 3. The industrial evaporator had a capacity of 60 L/h and the operating conditions were similar to those employed at laboratory scale (60 kPa, 180ºC).

Table 3: Initial properties of waste Unopol emulsion

| | **COD (mg/L)** | **$BOD_5$ (mg/L)** | **Turbidity (NTU)** | **Conductivity (µS/cm)** | **pH** |
|---|---|---|---|---|---|
| Unopol | 11600 | 102 | 7650 | 5550 | 9.1 |

Examination of Figure 9 reveals that no significant differences were observed between the two condensate products: the low pH and high conductivity reveal that probably small amounts of acid and salts were present in the industrial evaporator, because of the difficulty of removing accumulated deposits from the evaporator tubes during cleaning.

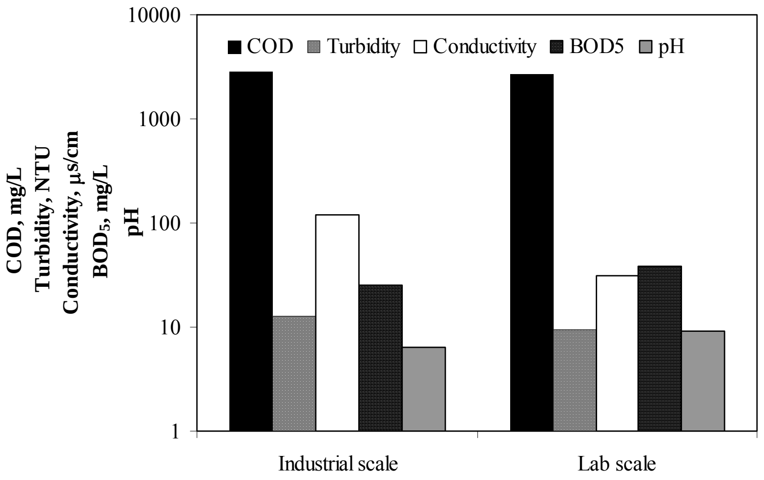


Figure 9. Properties of the aqueous effluent obtained after treatment of the waste emulsion Unopol by evaporation with the industrial and lab-scale evaporators

## 4. Conclusions

Evaporation is a suitable technique for treatment of synthetic and semi-synthetic waste O/W emulsions in that a 99% reduction in COD was achieved. However, the operating conditions play an important role in determining process efficiency since increases in the operating pressure and $\Delta T_{BE}$ increases the evaporation rate, but decreases the quality of the condensate.

By contrast, for the treatment of these waste O/W emulsions, the use of a destabilisation/centrifugation pre-treatment stage does not significantly improve either the evaporation rate or the quality of the condensate. In all cases proper selection of the destabilisation agent and pH adjustment are needed because reactions of these chemicals with ions present in the emulsion result in negative effects on the evaporation process.

Experimental results obtained after the evaporation of emulsions at laboratory and industrial scales show similar results. Hence, a direct scale-up would be feasible.

### Acknowledgments

Two of the authors, G. Gutiérrez and A. Cambiella, were the recipients of pre-doctoral fellowships from FPI and FPU Programmes (MEC, Spain), respectively. Financial support by the Ministerio de Educación y Ciencia (MEC, Spain) and the European Commission (project Ref.: CTQ2004-01413, European Regional Development Fund) is also gratefully acknowledged. This study was co-financed by the Consejería de Educación y Ciencia del Principado de Asturias (Plan I+D+i 2001-2004, Ref.: COF04-50).

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