Simultaneous elimination of dissolved and dispersed pollutants from cutting oil wastes using two aqueous phase extraction methods

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A B S T R A C T

Oily wastewater experimental study has been accomplished using two aqueous phases extraction methods on the basis of phase separation properties of non-ionic surfactants above the so-called cloud point curve and the solubilization phenomena of coacervate micelles (surfactant rich phase). Two commercial ethoxylate fatty alcohol surfactants (Oxo-$C_{10}E_3$, Oxo-$C_{15}E_7$) were employed to treat three kinds of cutting oil wastewater, in order to define the conditions promoting cutting oils emulsions destabilization and cloud point extraction possesses simultaneously. Before extraction test, the phase diagrams of binary water/surfactants systems were drawn and the effect of some cutting oil additives on water–surfactant systems was, therefore studied. The results of oily wastewater extraction with respect to wt.% surfactant and temperature were expressed in terms of chemical oxygen demand (COD) of the dilute phase before and after extraction, residual chemical oxygen demand (COD_R), residual concentrations of surfactant in the dilute phase ($X_{t,w}$) converted to chemical oxygen demand (COD_T) and the volume fraction of coacervate (ϕ_c) at the equilibrium. The results obtained for each parameter which were also represented on three dimensional diagrams using an empirical smoothing method were in agreement with the experimental ones, where the COD_R was reduced from 55 to 1.1 $g\,O_2\,l^{-1}$.

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1. Introduction

Lubricants, cutting fluids and degreasant are the most important polluting agents for both environment and operators during the manufacturing of metals. In machining processes such as metal-turning, milling, drilling and in particular when the metal removal operations are conducted at high speeds and low pressures, the regulation of heat generation and the lubrication of the contact point are achieved by pouring an oil-in-water emulsion, the so-called "*cutting fluid emulsion*".

A cutting fluid concentrate usually contains a mineral oil, a surfactant mixture, and in some cases water and various additives which are employed to exhibit comparable specifications of commercial concentrates in their resistance to bacterial growth and low corrosion capacity [1]. During their use, cutting fluids loose their properties and effectiveness because of their thermal degradation and production of suspended metal particles. The oils have therefore to be replaced periodically and the organic wastes generated have to be taken away and treated. Consequently, a significant amount of these products (especially chlorate, bore and also heavy

metals) has caused serious contamination of natural ecosystems. On the water surface, cutting oil form a thin film on which harms oxygen water from the atmosphere; indeed this causes the ecosystem perturbations [2]. Moreover, because of their great capacity of penetration in the ground, they constitute a very serious threat for groundwater. Therefore, it is necessary to treat this effluent before disposal [3–6]. The significant developments of the formulations of cutting oils as well as the preparation of the synthetic or semi-synthetic emulsions complicate some more the issue of the purification of these effluents which is attributed to the stability of these emulsions. Moreover, it has been reported [7–13] that some conventional methods especially evaporation, membrane or chemical separation generate a concentrated stream which is more harmful than the original waste. Accordingly, no ideal solution was reported in the literature to resolve such problem; where the combination of two or more treatment processes was the sole issue to increase the purification efficiency.

Conventional biological wastewater treatment processes are often used for the elimination of organic pollution, but, in the case of cutting oil emulsions (usually corresponding to a petroleum cut). The high complexity of such hydrocarbon mixture (aromatic or naphtenic nature), make it highly resistant to biodegradability. Besides, the antibacterial agents which were frequently used in the commercial cutting oil formulation, increase the difficulty of the biologic treatment [9,18]. The micro and ultrafiltration was largely

Nomenclature

cmc	critical micellar concentration
COD	chemical oxygen demand
COD_R	total residual chemical oxygen demand
COD_T	chemical oxygen demands of surfactant
CPE	cloud point extraction
DDL	light scattering detector
ELSD	light scattering detector
HPLC	high performance liquid chromatography
T	Temperature (°C)
T_c	cloud point Temperature (°C)
UV	ultraviolet
X_t	surfactant wt. %

Greek letter

ϕ_c	volume fraction

investigated where the application of different ultrafiltration membranes was tested [7,10–12]. Therefore, in membrane separation processes, care is needed to avoid membrane fouling, which may be reversible or irreversible [12].

Since conventional treatment methods (evaporation, phase separation, filtration) are often inefficient or environmentally unacceptable, the development and application of new method is highly necessary. Recently, new interest on micellar extraction based on the phase separation at cloud point temperature in the non ionic surfactant solutions was developed. The cloud point extraction method (CPE) was firstly adopted by Watanabe et al. [13] for the extraction of metal ions. This method has been extensively investigated for perconcentrating and separating metal ions, organic pollutants as well as proteins, hormones and viruses [10–23]. CPE is considered to be convenient and environmentally safe alternative to extraction with organic solvents [24]. Many advantages were claimed to CPE compared to conventional liquid–liquid extraction, including high extraction efficiency, ease of waste disposal and the use of non-toxic and less dangerous reagents.

The extraction method includes simultaneously cloud point and solubilization phenomenon of non-ionic surfactants medium. Thus, most of polyethoxylated non-ionic surfactants in aqueous solutions form two phases above the cloud point (T_c): a surfactant-rich phase (coacervate), and a dilute phase, in which the concentration of the surfactant is close to its critical micelle concentration (cmc) [15,16,18,21]. Therefore, the hydrophobic components initially present in the solution and bound to the micelles will be favourably extracted to the surfactant-rich phase after increasing the temperature above T_c.

CPE has been widely adopted in our laboratory [18,21,24] to treat the pollution of different effluents including phenols, benzyl alcohol and colorants from water, where coacervate regeneration method was proposed. On the basis of these findings, the cloud point extraction of three mineral cutting oils wastes: HMP (TotalFinaElf, France), HMI (Motul, France) and Tasfalout 22B (NAFTEC, Algeria), respectively was investigated in the present work. The effects of temperature, surfactant concentration, effluent pH solutions, as well as the addition of sodium sulphate (a strong salting-out electrolyte) on oils solutes extraction were also achieved.

2. Experimental

2.1. Reagents

Two commercial ethoxylated alcohols (Oxo-$C_{15}E_7$, Oxo-$C_{10}E_3$) which were used during this work were purchased from BASF and

Table 1
Emulsifiable concentrates composition of Tasfalout 22B cutting oil

Component	wt.%
Oil (spindle)	78
Sodium sulfonates	10–19.9
Borate alkenylamide	10–19.9
Alkyl amide	5–9.9
Hexylene glycol	1–4.9
Diethyl glycol monobutyl ether	1–4.9
Alkanolamine	3.2
Dodecanol	0.5–4.5
N–N dimethylene bismorpholine	2.4

SEEPIC, respectively. The cloud points of these surfactants at 1 wt. % in water were 47 °C and 2 °C, respectively. Three types of cutting oil were used in this study: HMP from TotalFinaElf (France), HMI from Motul (France) and Tasfalout 22B produced by the petroleum industry NAFTEC (Algeria). The approximate compositions of the emulsifiable concentrates of this last cutting oil is given in Table 1. The pH values of the solutions were adjusted between 2 and 13 by adding hydrochloric acid and sodium hydroxide as appropriate.

2.2. Apparatus

The determination of the cloud point was carried out using a Mettler FP 900 apparatus: temperature of the sample placed in a cell was measured using a precise sensor placed in a small oven. At the bottom of the measuring cell, there is a luminous source and an optic driver which illuminates the sample. The crossed sample light was converted by photoelectric cell into an electric signal proportional to the transmitted light intensity. The transmission of light was measured continuously, while the cell temperature increased linearly according to the chosen heating rate. The cloud point indicates the temperature at which the unique limpid phase becomes cloudy which induce a transmission decrease.

Surfactant concentration in, the dilute phase was determined using HPLC analyser. The chromatographic conditions were as follows: column RP18 (ODS), pressure 95 bar, with the following mobile phase $H_2O/CH_3CN/CH_3OH$, 7.5/60/32.5 (v/v/v) using the Evaporative Light Scattering Detector (ELSD). The ELSD enables the analysis of the chemical compounds which show no absorption in the UV range as polyethoxylated alcohols surfactants. The principle of its operation is the introduction of an eluent from the HPLC column onto the top of a heated diffusion tube, followed by spraying with an aide of stream of nitrogen gas. When passing through the diffusion tube, the sprayed beads are evaporated so the mist formed in the nebulizer contains only non-volatile particles of the substance under examination, which leave the column together with the eluent used for separation. The particles are introduced onto a light beam and scatter it. Measured at a constant angle, the scattered light is proportional to the concentration of the substance under analyses [25–27]. The sensitivity of the evaporative light scattering detector (DDL 31, EUROSEP Instruments) was optimised by the control of the air flow rate in the atomizer (relative pressure: 1 bar), were the evaporator temperature was 55 °C and the photomultiplier gain was 400 mV.

The chemical oxygen demands (COD) of the initial solution (effluent) and of the dilute phase after extraction were measured with METROHM 776 DOSIMAT apparatus. Surfactant concentration was converted to COD data using calibration equation.

2.3. Procedures for cloud point extraction

The O/W emulsion of cutting oil has been prepared in water at 2 wt.% of emulsifiable concentrates, as used usually in the industry

at pH equal to 9.12. For the extraction tests, 10 mL of solution containing the surfactant (at concentrations of 1, 4, 7, 10 or 13 wt.%) and cutting oil emulsion, were poured into graduated cylinders and heated in a precise thermostated bath during 24 h, to reach the phase separation (dilute phase and coacervate). The heating temperature range varies from the cloud point temperature to about 20° above. The volumes of both phases were registered and small amount of the dilute phase was pumped using a syringe and analysed by HPLC for the surfactant concentration determination. The content of organic pollutants is expressed in term of the chemical oxygen demands (COD), of the initial solution (effluent) and of the dilute phase after extraction. Using METROHM 776 DOSIMAT apparatus. A mixture of 4 mL of diluted effluent samples (before and after extraction), 1.5 mL of potassium dichromate and 3.5 mL of sulphuric acid was shaken and heated to 180 °C for 2 h. The samples were then cooled and titrated with a freshly standardized 0.12 N iron (II) ammonium sulphate solution in the presence of ferroin as indicator (colour change from purple-blue to red after addition of V_1 mL). The same operation was done with 4 mL of distilled water as a standard solution (addition of V_2 mL). The COD (mg O_2/L) was then calculated using the following equation:

$$COD = \frac{8000 \times 0.12(V_2 - V_1)}{4} \qquad (1)$$

3. Results and discussion

3.1. Phase diagrams of binary and pseudo-binary systems

When the cutting oil emulsifiable concentrates were added to water at 2 wt.% we obtained an O/W emulsion with a milky color which prevented the cloud point detection of water/surfactant/cutting oil emulsifiable system. Hence, the phase diagrams of such system can not be plotted. Therefore, it was firstly necessary to plot the phase diagrams of water/surfactant as a function of temperature before the extraction test of cutting oil wastes consequently the cloud point extraction domain (two-phase zone) can be identified approximately for each surfactant This information allowed (Fig. 1).

In general, surfactant properties vary regularly with the carbon number (i) of the hydrophobic chain and the degree of ethoxylation (j). For example, the cloud point increases as j increase and decreases when i increase in any homologous series of polyethoxy-
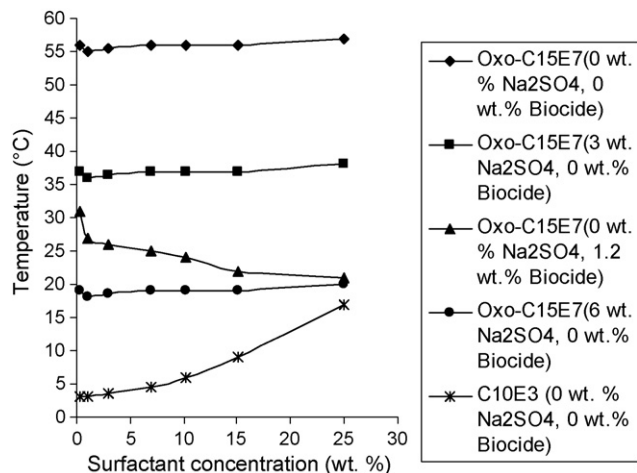

Fig. 1. Effect of biocide and Na_2SO_4 on the cloud point temperature of Oxo-$C_{15}E_7$ and Oxo-$C_{10}E_3$.
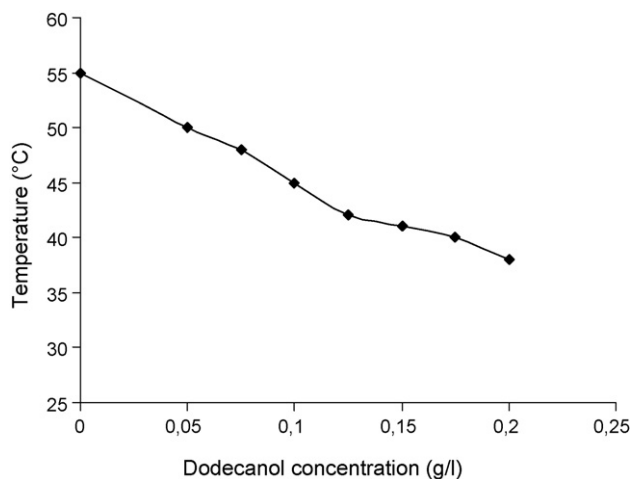

Fig. 2. Effect of dodecanol on the cloud point temperature of an aqueous solution at 10 wt.% of Oxo-$C_{15}E_7$.

lated non-ionic surfactants (C_iE_j). Thus, the critical temperature of n-$C_{10}E_3$ ($T_c \cong 3$ °C) is lower than the ambient one, while that of n-$C_{15}E_7$ is located near 55 °C (Fig. 1).

Like phenol and benzyl alcohol [18,21], 'Biocide' was found to lower significantly the cloud point of the Oxo-$C_{15}E_7$, which caused a pronounced depression of the cloud point to room temperature. Indeed, this indicates a significant interaction between this cutting oil additive and the surfactant. We note that "Biocide" (N–N dimethylene bismorpholie) is added to cutting fluid formulation to prevent bacteria proliferation (Table 1). In general, organic solubilizates can interact with the surfactant polar head group or with its hydrophobic length after solubilization in micelles. Organic compounds can vary the surfactants cloud point according to their chemical nature [18,21,28]. As shown in Fig. 2 the dodecanol solubilized in Oxo-$C_{15}E_7$ micelles lowers its cloud point temperature. As given in Table 1, this solute is also an additive (co-surfactants) to cutting fluid formulation.

Fig. 1 shows also the cloud point decreasing of Oxo-$C_{15}E_7$ by sodium sulphate. This phenomenon was due to the salting-out of the surfactant which was induced by the solvated electrolyte. Therefore, cloud point can be adjusted at low temperature by a simple control of surfactant and salt concentrations, which could reduces the heating energy cost in large scale cloud point extraction processes. Salt addition can also be applied in the extraction of heat sensitive products. However, electrolyte does not contribute equally between the dilute phase and coacervate, and its addition increases the density of the dilute phase. This makes phases separation easier in some non-ionic surfactant systems [29,30].

3.2. Modelling of the results

The organic pollutants of cutting oil were measured by the chemical oxygen demand (COD) method. The total residual of dilute phase after cloud point extraction, COD_R, includes that due to surfactant remaining into this phase (concentration close to cmc, [18–22]), COD_T, and that due to soluble pollution in water and no extractible by the surfactant, COD_S.

Hence, COD_R content in the dilute phase can be calculated according to Eq. (2)

$$COD_R = COD_T + COD_S \qquad (2)$$

The extraction results by the two non ionic surfactant, Oxo-$C_{10}E_3$ and Oxo-$C_{15}E_7$, are expressed by the three following "responses" (Y): total residual chemical oxygen demand (COD_R), residual COD_T

Table 2
Somme experimental results of the extraction parameters (COD_R, COD_T, ϕ_c and COD_R/COD_I)

	(X_t, T)	COD_R (mg O_2/L)	COD_T (mg O_2/L)	Coacervate volume fraction	COD_I/COD_R [a]
HMP, Oxo-$C_{15}E_7$	(4, 60)	1134.20	149.15	0.29	48.88
	(4, 65)	976.43	110.26	0.25	56.78
	(13, 70)	1530.20	354.20	0.80	36.23
HMI, Oxo-$C_{15}E_7$	(4, 60)	690.20	234.11	0.27	78.89
	(4, 65)	2285.29	210.41	0.22	23.86
	(13, 80)	3138.32	259.58	0.25	47.83
T22B, Oxo$C_{15}E_7$	(4, 65)	1689.84	75.45	0.41	20.84
	(4, 70)	1812.67	108.45	0.32	19.43
	(13, 70)	3189.45	170.67	0.61	11.04
T22B, Oxo-$C_{10}E_3$	(4, 10)	5174.20	892.09	0.10	6.80
	(4, 15)	4312.52	750.92	0.13	8.17
	(13, 20)	6844.45	853.97	0.20	5.14

[a] COD_I = 55.12 (g O_2/L) for HMI, 54.45 for HMP and 35.23 for Tasfalout 22B.

due to surfactant remaining in the dilute phase and coacervate volume fraction at equilibrium (ϕ_c) with respect to wt.% surfactant (X_t), and temperature (T) variations. For each response determined, by considering central composite designs [31], the results were analysed by an empirical fitting. In this method, the experimental values can be used to determine, the polynomial model constants which were adjusted. The models were checked by plotting computed vs. experimental data. The best correlation correspond to that giving the slope and regression coefficient (R^2) closest to 1. Thus, the quadratic correlation was judged to be the most adequate for all our systems:

$$Y = a_0 + a_1X_t + a_2T + a_{12}X_tT + a_{11}X_t^2 + a_{22}T^2 \qquad (3)$$

Such correlation provides an excellent response surface build.

3.2.1. Total residual chemical oxygen demand (COD_R)

As an example of soluble and dispersed pollution (O/W emulsion), we dealt with mineral cutting oils (HMP, HMI and Tasfalout 22B). The process of extraction by Oxo-$C_{10}E_3$ and Oxo-$C_{15}E_7$ is accompanied by demulsification. The initial COD (COD_I) of HMP
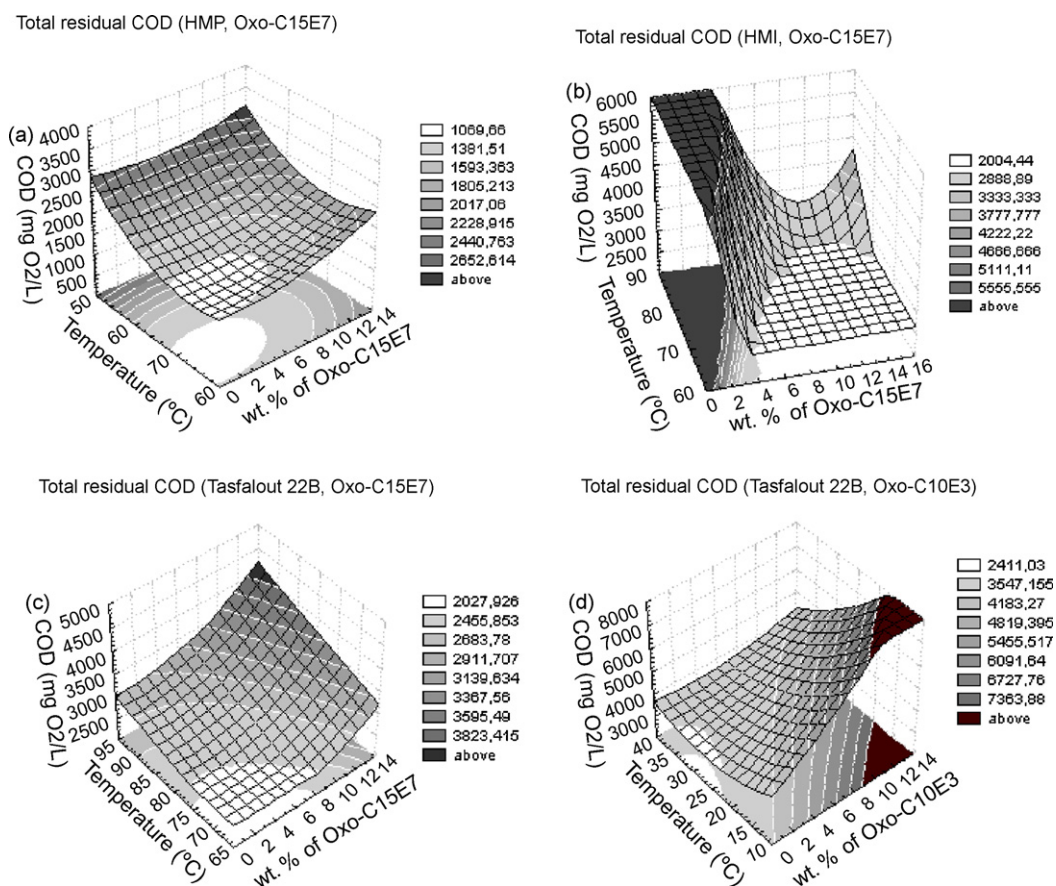
Fig. 3. Three-dimensional isoresponse curves smoothed by a quadratic model (Eqs. (4)–(7)): (a) $COD_{R(HMP, Oxo-C_{15}E_7)} = f(X_t, T)$; (b) $COD_{R(HMI, Oxo-C_{15}E_7)} = f(X_t, T)$; (c) $COD_{R(T22B, Oxo-C_{15}E_7)} = f(X_t, T)$; (d) $COD_{R(T22B, Oxo-C_{10}E_3)} = f(X_t, T)$.

and HMI effluents were about $55\,g\,O_2/L$, while initial COD of Tasfalout 22B effluent was about $35\,g\,O_2/L$. The quadratic model for the property studied (residual COD_R) vs. X_t and T gives the following equations:

$$COD_{R(HMP,Oxo-C_{15}E_7)} = 14,090 + 88.454X_t - 394.889T$$
$$-1.72X_tT + 5.846X_t^2 + 2.975T^2 \qquad (4)$$

$$COD_{R(HMI,Oxo-C_{15}E_7)} = -27,470 - 1969X_t + 813.295T$$
$$+2.647X_tT + 72.957X_t^2 - 4.056T^2 \qquad (5)$$

$$COD_{R(T22B,Oxo-C_{15}E_7)} = 216.247 - 72.698X_t + 18.334T$$
$$+0.687X_tT + 7.85X_t^2 + 0.073T^2 \qquad (6)$$

$$COD_{R(T22B,Oxo-C_{10}E_3)} = 5183 + 519.169X_t - 207.84T$$
$$-14.674X_tT + 8.692X_t^2 + 3.71T^2 \qquad (7)$$

The reliability of Eqs. (4)–(7) was checked by plotting computed data vs. experimental values. Fig. 3 represents the corresponding three-dimensional isoresponse curves smoothed by the quadratic models (Eqs. (4)–(7)). At constant X_t, the COD increases with temperature (Fig. 3a–c and Table 2), which could probably due to the

increase of the water solubility of certain additives of the emulsion. Thus, the significant temperature rise beyond the cloud point has a negative effect on the extraction with Oxo-$C_{15}E_7$ (Fig. 3a–c). Whereas, at lukewarm temperatures it has been noticed maximal reduction of COD effluent using Oxo-$C_{15}E_7$ (Fig. 3d). The total residual COD values obtained with HMI emulsion are, approximately, two time higher than that obtained in the case of HPM effluent (Fig. 3a and b and Table 2).

The most favourable areas for cloud point extraction are thus located in the lightest color zones in Fig. 3. The best performance-cost compromise of the process, based on minimum surfactant consumption, led to optimal surfactant concentrations lying between 2 and 5 wt.% for HMP and Tasfalout 22B emulsions. Whereas, for HMI emulsion it seems to be between 3 and 6 wt.%. In these zones, the total residual COD results are about 1100 mg O_2/L for HMP emulsion, and 2000 mg O_2/L for HMI and Tasfalout 22B emulsions. The cloud point extraction of such soluble and dispersed pollutant allows a ca. 78-fold COD reduction in optimal conditions (COD_I/COD_R in Table 2).

From Fig. 3c and d, we can deduced that Oxo-$C_{10}E_3$ is less effective than Oxo-$C_{15}E_7$ for Tasfalout 22B emulsion extraction, based on their total residual COD data. However, extraction using Oxo-$C_{10}E_3$ can be achieved at room temperature with less energy cost.

3.2.2. Chemical oxygen demand due to the surfactant residual concentration (COD_T)

The quadratic equations for the property COD_T (residual chemical oxygen demand due to surfactant concentration in the dilute
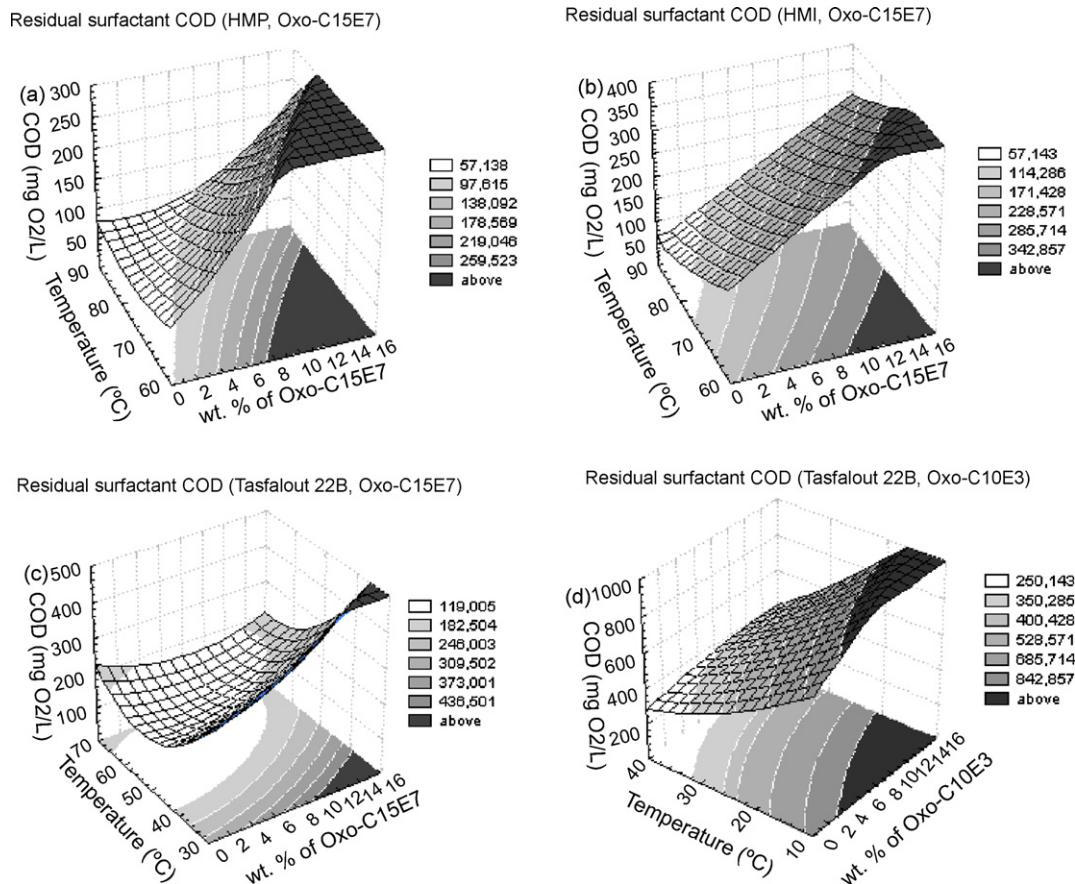

Fig. 4. Three-dimensional isoresponse curves smoothed by a quadratic model (Eqs. (8)–(11)): (a) $COD_{T(HMP,Oxo-C_{15}E_7)} = f(X_t, T)$; (b) $COD_{T(HMI,Oxo-C_{15}E_7)} = f(X_t, T)$; (c) $COD_{T(T22B,Oxo-C_{15}E_7)} = f(X_t, T)$; (d) $COD_{T(T22B,Oxo-C_{10}E_3)} = f(X_t, T)$.

phase after extraction), whose accuracy was checked, are as follows:

$$COD_{T(HMP,Oxo-C_{15}E_7)} = 726 + 73.392X_t - 18.298T - 0.869X_tT$$
$$+ 0.958X_t^2 + 0.118T^2 \qquad (8)$$

$$COD_{T(HMI,Oxo-C_{15}E_7)} = 912.413 + 26.308X_t - 16.973T$$
$$- 0.085X_tT - 0.0515X_t^2 + 0.074T^2 \qquad (9)$$

$$COD_{T(T22B,Oxo-C_{15}E_7)} = 1113 + 26.667X_t - 38.797T$$
$$- 0.636X_tT + 1.026X_t^2 + 0.362T^2 \qquad (10)$$

$$COD_{T(T22B,Oxo-C_{10}E_3)} = 1036 + 49.97X_t - 33.96T$$
$$- 0.866X_tT - 0.432X_t^2 + 0.29T^2 \qquad (11)$$

Fig. 4 represents the three-dimensional isoresponse curves of the studied property (COD_T) for different couples of cutting oil emulsion–surfactant, smoothed by the quadratic model (Eqs. (8)–(11)). From Fig. 4a–d it is clear that, the COD due to the residual surfactant concentration in the dilute phase after demulsification and extraction process, is lower at low surfactant concentration, X_t, and pass through a minimum at height temperature. The behaviour of COD_T according to X_t and T is generally similar for all cutting

oil emulsion–surfactant couple. However, COD_T due to Oxo-$C_{10}E_3$ was higher than that obtained with Oxo-$C_{15}E_7$ (Fig. 3 and Table 2). Thus, the first surfactant was more soluble in water than the second.

Moreover, polyethoxylated alcohols (AE) have been choose in our work, due to their satisfactory biodegradable activities [32,33]. Hence, COD_T can be eliminated naturally by biodegradability mechanism.

3.2.3. Coacervate volume fraction at equilibrium (ϕ_c)

For the properties ϕ_c regarding the different cutting oil emulsion–surfactant couples, the quadratic model provides the following equations:

$$\phi_{c(HMP,Oxo-C_{15}E_7)} = 0.306 + 0.24X_t - 0.01T - 2.783 \times 10^{-3}X_tT$$
$$+ 1.306 \times 10^{-3}X_t^2 + 0.085 \times 10^{-3}T^2 \qquad (12)$$

$$\phi_{c(HMI,Oxo-C_{15}E_7)} = 1.535 - 0.045X_t - 0.026T + 3.238 \times 10^{-4}X_tT$$
$$+ 1.875 \times 10^{-3}X_t^2 + 0.11 \times 10^{-3}T^2 \qquad (13)$$

$$\phi_{c(T22B,Oxo-C_{15}E_7)} = 1.81 + 0.059X_t - 0.029T - 0.01 \times 10^{-3}X_tT$$
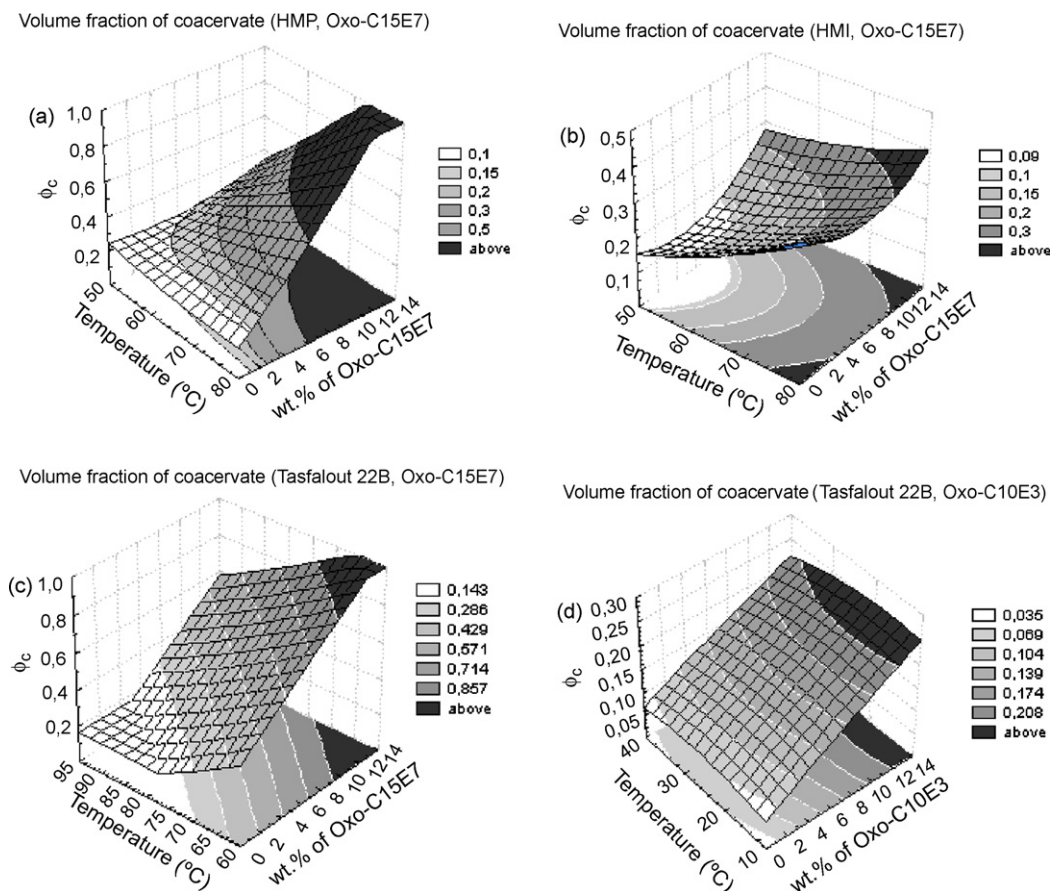$$- 1.062 \times 10^{-4}X_t^2 + 0.072 \times 10^{-3}T^2 \qquad (14)$$

Fig. 5. Three-dimensional isoresponse curves smoothed by a quadratic model (Eqs. (12)–(15)): (a) $\phi_{c(HMP,Oxo-C_{15}E_7)} = f(X_t, T)$; (b) $\phi_{c(HMI,Oxo-C_{15}E_7)} = f(X_t, T)$; (c) $\phi_{c(T22B,Oxo-C_{15}E_7)} = f(X_t, T)$; (d) $\phi_{c(T22B,Oxo-C_{10}E_3)} = f(X_t, T)$.
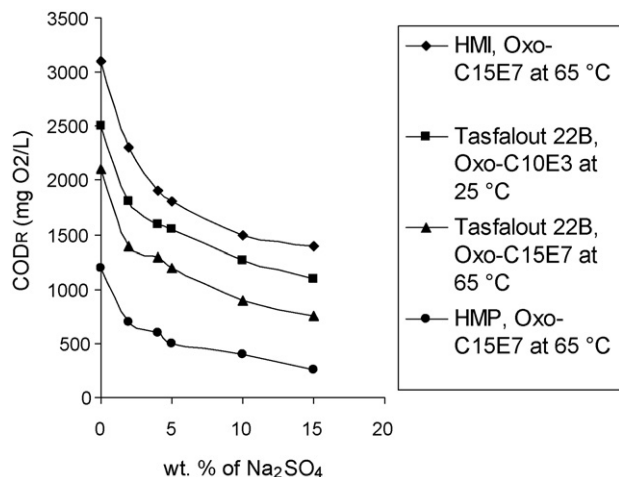
Fig. 6. Effect of sodium sulphate on the total residual chemical oxygen demand (COD_R) in the dilute phase after extraction with 2 wt. % of surfactant.

$$\phi_{c(T22B, Oxo\text{-}C_{10}E_3)} = -0.023 + 0.019X_t + 4.667 \times 10^{-3}T$$
$$-0.111 \times 10^{-3}X_tT - 1.389 \times 10^{-4}X_t^2$$
$$-8.889 \times 10^{-5}T^2 \qquad (15)$$

The behaviour of ϕ_c according to X_t and T is generally similar for all the cutting oil emulsion–surfactant couples (Fig. 5). According to Fig. 5a–d, the value of ϕ_c is low at high temperature and at small surfactant concentration (Table 2). Hence, In order to increase the concentration factor of solute, a minimal volume fraction of coacervate (ϕ_c) should be obtained when temperature increases. In contrast, high temperature is unfavourable for efficient extraction extent (Fig. 3), while, high surfactant concentrations induce more surfactant loss in the dilute phase (Fig. 4).This loss is not economic even when the surfactant is biodegradable. Consequently, the optimisation of the process needs to compromise between the three studied parameters COD_R, COD_T and ϕ_c.

Since water comprises from 90 to 98% of a water-based cutting fluid mixtures, the originality of the proposed ecologic method which can be employed for example, as a previous step to "Direct Flame Incineration", or "Catalytic incineration"; will permit the separation of water from the pollutants to avoid the destruction of the whole waste. On the other hand, due to the presence of sufficient oil in the coacervate, the incineration fuel cost may be substantially reduced.

Coacervate extraction can be used also before a evaporation–distillation process, where evaporation must be accelerated by heating. Unless waste heat is readily available from some in-plant source, the cost of evaporation of the total effluent stream is prohibitive. Evaporation of water from concentrated coacervate is more easy after the cloud point extraction where the volumes are considerably reduced. Cost can also be reduced using natural solar evaporation.

3.3. Effect of sodium sulphate on the total residual chemical oxygen demand (COD_R)

The total residual chemical oxygen demand (COD_R) of the couples cutting oil emulsion–surfactant as a function of Na_2SO_4 concentration is shown in Fig. 6. In general, electrolytes addition induced coacervate volume fraction reduction due to the cloud point lowering of non-ionic surfactant solution [16,18,21]. At con-

stant surfactant concentrations at a given temperature (T), the presence of Na_2SO_4 decreases both of the cloud point temperature (Fig. 1) and the values of ϕ_c, and increases the values of ($T-T_c$). Moreover, the addition of electrolytes to non-ionic surfactant solutions increases their hydrocarbon solubilization capacity, by lowering cmc concentration [18,21,34]. Such behaviour may be the result of an increase in micellar number in this concentration region [29,30,34].

Fig. 6 shows the decrease of COD_R with sodium sulphate concentration; for example at 15 wt.% of Na_2SO4 in HMP/Oxo-$C_{15}E_7$ system, all of the surfactant, the solubilized solutes (cutting oil additives) in micelles and the dispersed pollution (oil) were pushed out to the coacervate phase (salting-out effect). Indeed, the dilute phase became less concentrated in organic molecules and COD_R obtained was about 0.5 g O_2/L (Fig. 6). This concentration is almost 110 times less than that of the initial effluent concentration (55 g O_2/L). Consequently, we have deduced that the electrolyte doesn't contribute equally between the dilute phase and coacervate, and its addition increases the density of the dilute phase wish makes separation of both phases easy.

4. Conclusion

A new approach has been developed in the present work to treat and purify real effluents containing cutting oils emulsions. For this purpose, polyethoxylated alcohols surfactants (C_iE_j), which are easily and quickly biodegradable and therefore more environmentally friendly than alkyl phenol ethoxylate surfactants, were employed [32,35]. In special conditions, cutting oils emulsions can be broken using such non-ionic surfactant and heat. Hence, a demulsification and CPE possesses occur simultaneously. Accordingly, dispersed pollution (mineral oils) and dissolved pollution (surfactant, co-surfactant and cutting oils additives) can be concentrated and eliminated simultaneously into the coacervate phase. Therefore, soluble and dispersed pollutants (e.g. cutting oils additives) can be easily removed from effluents using two-aqueous phase extraction method. On the basis of these results, we have deduced that a good separation in all cutting oils surfactant systems was observed when 5 wt.% of electrolyte (Na_2SO_4) is added. At such optimal concentration, the residual COD, was reduced under 2 g/L (tolerate COD in purification stations). Moreover, coacervate extraction was found to be competitive with other purification processes of effluents polluted by soluble organic pollutants or cutting oils (physicochemical process, distillation, ultrafiltration etc.) [36–38]. Since the long-term goal of laws governing water pollution is "zero discharge", more work need to be done for the coacervate regeneration after first step extraction which is the main objective of our laboratory.

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