Elimination of fuel spills from effluent using cloud point extraction methods

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ABSTRACT

Cloud point extraction procedure was used to remove hydrocarbons from aqueous streams coming from fuels storage centre. This real effluent was characterized by a high chemical oxygen demand (COD = 7000 mg O$_2$/L) due to significant concentration of hydrocarbons as gasoline diesel and kerosene. Two biodegradable non-ionic surfactants (Lutensol AO7 and Triton X-114) were employed to treat this effluent. First, the phase diagrams of the binary systems, water–surfactant and the pseudo-binary system, water–surfactant–hydrocarbons were determined. The effect of sodium sulphate on water–surfactant–hydrocarbons systems was studied. The experimental results, with respect to surfactant wt.% and temperature, were expressed in term of residual (soluble) chemical oxygen demand (COD$_S$), residual concentrations of surfactant in the dilute phase ($X_{t,w}$) converted to chemical oxygen demand (COD$_{TA}$) and the volume fraction of coacervate (ϕ_C) at the equilibrium. The results obtained for each parameter were represented on three-dimensional diagrams using an empirical fitting method. For instance, COD can be decreased from 7000 mg O$_2$/L to 50 mg O$_2$/L and 30 mg O$_2$/L, using Triton X-114 and Lutensol AO7, respectively at room temperature. However, the extraction extent of such effluent was found to be low at basic pH, which may be useful for surfactant regeneration.

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1. Introduction

The environmental pollution problem is still relevant as many industrial activities continue to generate various pollutants, including organic substances such as hydrocarbons, which could create significant harmful effects. Faced to more restrictive regulations, oil companies must treat their effluents before disposal [1]. However, anaerobic decomposition of petroleum hydrocarbons for example leads to extremely low rates of degradation [2], *n*-alkanes in the C1–C4 ranges are biodegradable only by a narrow range of specialized hydrocarbon degraders; and *n*-alkanes, *n*-alkyl aromatics, and aromatics above C22 are generally not available to degrading microorganisms. Therefore, hydrocarbons are among the potential environmental pollutants. The municipal sewers limit their discharge to 100 ppm, according to the European Union norm (CE 858-1). However, this norm limits hydrocarbons discharge to 10 ppm in nature. Unless properly treated, such compounds spread on the water surface (negative adsorption) and form oil films preventing gas exchange between air and water which, as a result, induce respiration suffocation due to a lack of oxygen. Indeed, carbon dioxide produced by breathing, accumulates in their cells and decreases the pH in which they live. Moreover, because of its great

capacity of penetration in the ground, oily wastewater, without further decontamination before disposal, constitutes a very serious threat for groundwater.

In general, remedies to oil spills and oil slicks comprise mechanical, physical-chemical and/or biological treatments [3–6]. During oil slicks, emulsions are formed as a result of the presence of natural surfactants in crude oil (e.g. asphaltenes). Phase separation needs the addition of a demulsifier in order to reach an optimum formulation corresponding to the minimum emulsion stability [7]. Petroleum molecules are eventually degraded by microorganisms but the rate of abiotic elimination, mainly determined by the ratio of surface to volume of petroleum in sea water, cannot be neglected. Oil dispersion is favoured by low interfacial tension and chemical dispersants forming emulsions or microemulsions increase the surface area of the spill [8–10]. Surfactants have been used in two original methods of recovering crude oil: oil processing products or oil residues spilled on a water surface being disclosed. The first one consists of making an anti-adhesive polysiloxane matrix from a hydrolyzable silane derivative reacting with a polyoxyethylenic surfactant, trapping the hydrocarbon into the matrix and removing the silicone/hydrocarbon solid residues from the water surface by conventional mechanical means (e.g. netting) [11]. In the second one, a ferrofluid is prepared by adsorbing sodium oleate on magnetite (Fe$_3$O$_4$), then by dispersing the particles into crude oil, kerosene or cyclohexane and adding a non-ionic surfactant to the dispersion. By using the ferrofluid, which is an effective disper-

Table 1
PNA contribution classes (wt.%) to light straight run naphta (LSRN), heavy straight run naphta HSRN, kerosene and gasoil.

	LSRN	HSRN	Kerosene	Gasoil
Paraffins	87.53	52.57	59.52	62.36
Naphthenics	09.92	37.63	22.83	20.28
Aromatics	02.44	09.09	17.65	17.36
Unidentified hydrocarbons	00.11	00.71	–	–

Data provide by the laboratory of the society NAFTEC (Arzew, Algeria).

Table 2
Chemical composition of the light straight run naphta (LSRN[a]).

Compound	wt.%
n-Paraffins	
n-Propane	0.32
n-Butane	12.32
n-Pentane	23.24
n-Hexane	17.57
n-Heptane	0.44
i-Paraffins	
i-Butane	1.66
i-Pentane	12.08
2.2-Dimethyl butane	0.25
2.3-Dimethyl butane	1.44
2-Méthyl pentane	9.68
3-Methyl pentane	5.53
2.2-Dimethyl pentane	0.12
2.4-Diméthyl pentane	0.46
2.2.3-Trimethyl butane	0.04
3.3-Dimethyl pentane	0.06
2-Methyl hexane	0.85
2.3-Dimethyl pentane	0.50
3-Methyl hexane	0.97
Naphthenics	
Cyclopentane	0.97
Methyl cyclopentane	4.40
Cyclohexane	2.98
1.1-Dimethyl cyclopentane	0.39
1-cis 3-dimethyl cyclopentane	0.29
1-trans 3-dimethyl cyclopentane	0.23
1-trans 2-dimethyl cyclopentane	0.46
Methyl cyclohexane	0.20
Aromatics	
Benzene	2.44
Unidentified hydrocarbons	0.11

[a] Used at 92% (v/v) in light fuel (essence) formulation; data provide by the laboratory of the society *NAFTEC* (Arzew, Algeria).

sant, and an oil slick drawing apparatus equipped with permanent magnets, the oil can be selectively removed and recovered without adversely affecting the marine ecosystem [12]. It also makes sense that the rate of bioremediation increases with the dispersion state of the oil. Thus, a nonylphenol ethoxylate enhances the biodegradation of 2% (w/v) Bow River crude oil by a mixed bacterial culture substantially [13]. A psychrotrophic *Acinetobacter* sp. is able to grow on *n*-dodecane in cold environments and to produce biosurfactants [14]. Another biosurfactant, consisting of a polysaccharidic chain with hydrophobic ester-linked fatty acid (C_{10}–C_{14}) substitutions may disrupt oil slicks. It makes a stable emulsion whose biodegradation by marine microorganisms is greatly enhanced due to the strong adhesion of the latter onto the oil surface [15]. Oxidation rates of alkanes by cells of *Rhodococcus* sp. 094 in the stationary growth phase (but not in the exponential growth phase) were stimulated by surfactants of intermediate hydrophile lipophile balance (HLB) values (8–12) [16].

It is widely recognised that pollution comes from leaking underground fuel storage tanks. For that reason, it is necessary to develop a simple, clean, effective and environmentally friendly process as a "two aqueous phase extraction" method to separate hydrocarbon (mineral oil, gasoil, diesel, kerosene and fuel additives, etc.) from effluent. In such a mixture, small amount of fuel additives (detergent, corrosion inhibitor, anti-rust, antiwear, antioxidant, anti-foam, anti-hoarfrost, dispersants, extreme pressure agents, knocking corrector, dyes and lubricant for height capacity motors) could be found [17]. The oily wastewater (O/W emulsion) collected from a fuel storage and marketing centre of "NAFTAL" company in Oran (Algeria) provides an excellent example. Such effluent was characterized by a high chemical oxygen demand (COD around 7000 mg O_2/L). The PNA (paraffins, naphthenics and aromatics) contribution to the stored fuel is given in Tables 1 and 2. Indeed, the oily phase is generally constituted of hydrocarbon. Most hydrophobic compounds (hydrocarbons) present in this (O/W) emulsion can then be solubilized in non-ionic surfactant micelles and concentrated in the small volume of coacervat after phase separation beyond the cloud point of the surfactant [18].

2. Background

Cloud point extraction (CPE) is one of the most promising, environmentally-friendly, energy-saving processes for aqueous effluent purification. This achievement appears as an answer to the current restricted use of organic solvents (volatile organic compounds, VOC), often toxic, on a large scale. Owing to the existence of a lower consolute point curve in their phase diagrams, water/polyethoxylated non-ionic surfactant systems offer an interesting opportunity of getting rid of VOC. Coacervat extraction is also sought as an environmentally benign separation process comparing to microemulsion [19] and reverse micelles [20] extraction. These are hardly considered because of the involvement of volatile organic compounds.

The origin of phase separation in CPE with increasing temperature, lies in a delicate balance between repulsive and attractive solute–solute and solute–water interactions, associated with entropy increase. Above the cloud point of the solution, solubilization and concentration of hydrophobic or amphiphilic substances occur. This operation, known as liquid-coacervate or cloud-point extraction (CPE) [21–23], was first applied to metal ion separation in the presence of a chelating agent [24]. It allows removing organic pollutants (hydrocarbons, e.g., polycyclic aromatic hydrocarbons [25], volatile organic solvents [26], phenols [27,28], alcohols [29,30], amines [31], dyes [32,33], molecules of biological interest [34], herbicides [35] or various organic compounds [36–40]) and/or heavy metal-containing electrolytes under cationic or anionic forms, without chelating agents [41]. Scaling-up of CPE has been attempted with continuous rotating disk contactor [42] or a variation of a mixer-settler device [41].

Surfactants suitable for cloud point extraction process should be weakly soluble in water (to restrict surfactant loss in the dilute phase); have a low cloud point (to reduce heating requirement); solubilize pollutants (especially oil); form an easily separable phase; be readily disposable at fair price; have low toxicity; and biodegradable. The aim of this work is to apply the CPE to treat and purify effluents containing hydrocarbons (complex mixture of saturated, unsaturated, cycloalkanes, aromatic hydrocarbons, and fuel additives) (Tables 1 and 2). Two non-ionic surfactants (Triton X-114 and Lutensol AO7) were investigated in this work. The effects of temperature, surfactant concentration, effluent pH solution, as well as the addition of sodium sulphate on extraction extent were also evaluated which allow performing extraction tests at low temperatures (between 15 °C and 38 °C) to avoid excessive heating and reduce energy costs in a high scale cloud point extraction process. This work has been also focused on the comparison between ethoxylated alkylphenols non-ionic surfactants type (represented by Triton X-114) and ethoxylated alcohols (represented by Luten-

sol AO7) in target solutes (hydrocarbons) extraction. Ethoxylated alcohols (EA) which are easily and quickly biodegradable, have been used as good alternative to alkyl phenol ethoxylate (APE) because of the toxic intermediate substances generated from their biodegradation process such as alkylphenol molecules [43,44].

3. Materials and methods

3.1. Reagents

The alkyl phenol ethoxylate (APE) non-ionic surfactants, Triton X-114 (occtyl phenol polyethylene glycol ether), was supplied by Sigma–Aldrich. Its critical micellar concentration was 1.7×10^{-4} M ant its cloud point at 1 wt.% in water was 24 °C. The ethoxylated alcohols (EA) obtained from fatty oxo alcohol ethoxylation, Lutensol AO7 (equivalent to $C_{15}H_{31}$ (OCH_2–CH_2)$_7$OH), was provided by BASF. The cloud point of this surfactant at 1 wt.% in water was at 46 °C and its critical micellar concentration was 4.6×10^{-4} M. The pH values of the solutions were adjusted between 1 and 12 by adding drops of aqueous solutions of H_2SO_4 (0.1 N) and $Ca(OH)_2$ (1.5 g/L).

3.2. Apparatus

The determination of the cloud point was carried out using a Mettler FP 900 apparatus. The temperature of the sample placed inside 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 designates the temperature of the unique limpid phase which becomes cloudy, inducing a transmission decrease.

The surfactant concentration in the dilute phase was determined using HPLC. The chromatographic conditions were as follows: column RP18 (ODS), 1 mL/mn, with the following mobile phase H_2O/CH_3CN/CH_3OH, 7.5/60/32.5 (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 alcohol 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 the aid of stream of nitrogen gas. When passing through the diffusion tube, the sprayed beads were evaporated so the mist formed in the nebulizer contained only non-volatile particles of the substance under examination, which left the column together with the eluent used for separation. The particles were introduced onto a light beam and scattered it. Measured at a constant angle, the scattered light was proportional to the concentration of the substance under analyses [45–47]. 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). The evaporator temperature was fixed at 55 °C and the photomultiplier gain was 400 mV.

The COD of the initial effluent solution and of the dilute phase after extraction were measured with a METROHM 776 DOSIMAT apparatus. The surfactant concentration (from 0.05 to 0.15 wt.%) was converted to COD using the calibration equation.

3.3. Procedures for cloud point extraction

The considered release of hydrocarbons in water (O/W) was a very complex mixture of lubricating-oil and fuels dispersed in water. For the extraction tests, 10 mL of solution containing the surfactant (at concentrations of 1, 4, 7, 10 or 13 wt.%) and effluent (O/W emulsion with the presence of 3 wt.% of Na_2SO_4 using Triton X-114 and 6 wt.% of Na_2SO_4 when Lutensol AO7 was used), 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 varied from the cloud point temperature to about twenty degrees above. The volumes of both phases were registered and a 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 was expressed in terms of COD, of the initial effluent solution and of the dilute phase after extraction. Using the METROHM 776 DOSIMAT apparatus, a mixture of 4 mL of diluted effluent samples (before and after extraction), 1.5 mL of 0.1 N 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 carried out with 4 mL of distilled water as a standard solution (addition of V_2 mL). The COD_R (mg O_2/L) was then calculated using the following equation:

$$COD_R = 8000 \frac{0.12(V_2 - V_1)}{4} \tag{1}$$

4. Results and discussion

4.1. Cloud point extraction domain

When the temperature of an aqueous solution containing a non-ionic surfactant is raised above its cloud point (CP), the solution can be separated onto two phases: a surfactant-rich phase (coacervate), and a dilute phase, in which the concentration of the surfactant is close to its critical micellar concentration (cmc). The temperature of phase separation is concentration dependent. A consolute curve may be determined in terms of concentration and temperature, above which the solution consists of two phases in equilibrium and below which a single isotropic phase exists (Fig. 1). CP varies with temperature from one surfactant to another [48–54]. Hence, cloud point temperature of TX-114 aqueous solution increases with TX-114 concentration from 24 °C to approximately 30 °C, while the critical temperature of Lutensol AO7 (Oxo-$C_{15}E_7$) was above 46 °C (Fig. 1). For homologous series of non-ionic surfactants (having a hydrophobic head group and a hydrophilic tail) the CP increases with decreasing length of the hydrocarbon chain and increasing length of the oxyethylene chain (ethoxylation number, E) [25]. Having nearly the same ethoxylation number (E) and the same number of carbons in the hydrocarbon chain length, Triton X-114 (iso-C_8H_{17}–C_6H_4–$E_{7,5}$) and Lutensol AO7 (Oxo-$C_{15}E_7$) should have a normally close critical temperature. However, the comparison between such surfactants is difficult (surfactant from different families). One can notice that the presence of a benzene ring in the hydrocarbon chain makes the surfactant (Triton X-114) more hydrophobic and then less soluble in water. Hence, it was first necessary to plot the phase diagrams of water/surfactant as a function of temperature before the extraction test of hydrocarbons from the oily wastewater. Consequently, the two-phase zone (cloud point extraction domain) can be identified for each surfactant (Fig. 1).

One can see in Fig. 1 that, like in the presence of phenols, alcohols and amines [25,26,28,29,35,36], the CP of Triton X-114 and Lutensol AO7 were lowered by hydrocarbons present in the effluent.

It is well known that most electrolytes when dissolved in water decrease the solubility of an organic component. The occurrence of such phenomenon leads to the salting-out, referring to reduced solubility, and salting-in for the reverse effect. Compounds that cause
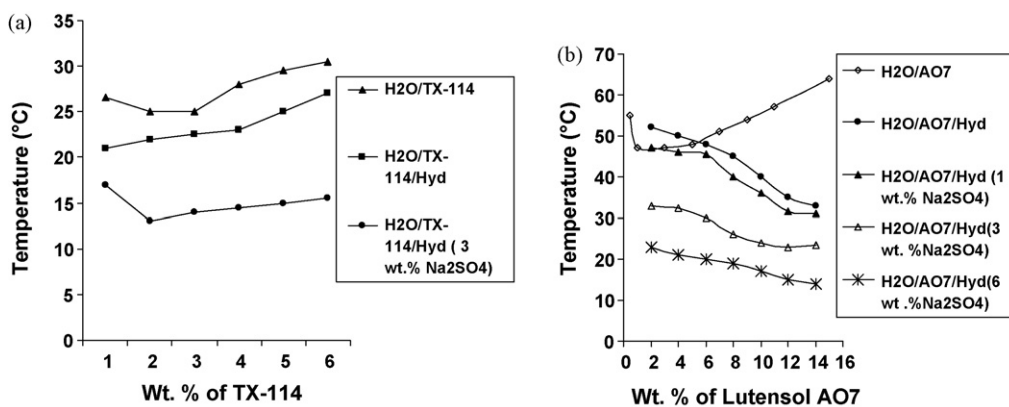
Fig. 1. Effect of hydrocarbons and sodium sulphate on the cloud point temperature of: (a) TX-114; (b) Lutensol AO7.

increase in aqueous solubility are called hydrotropes or chaotropes [55]. Fig. 1 shows that the presence of Na_2SO_4, decreases the CP of the mixture containing water, hydrocarbons and surfactant. The CP decrease is generally due to dehydration of the ethylene oxide (EO) chain by the salt [56]. The Na_2SO_4 influence on the CP of Triton X-114 and Lutensol AO7 follows the lyotropic (opposite of hydrotrope) series. Anions with a low lyotropic number, high hydration, or strong water-structure-making tendency decrease the CP. For example, SO_4^{2-} is two times more effective than Cl^- [28,56–60]. Therefore, it is possible to adjust the cloud point to room temperature ($22\,^\circ$C) by a simple control of surfactant and Na_2SO_4 concentrations (at 3 wt.% with TX-114 and 6 wt.% using Lutensol AO7), and reduce the heating energy cost of the large scale cloud point extraction. This may have also an application for brine effluent. Furthermore, the electrolyte does not contribute equally between the dilute phase and coacervate, and its addition increases the density of the dilute phase. This makes the separation of both phases easy using Lutensol AO7.

4.2. Extraction of hydrocarbon spills by coacervat

The organic pollutant concentration in the effluent was measured by COD analysis. The total residual COD_R of dilute phase after cloud point extraction includes the surfactant COD_{TA} remaining in this phase (surfactant concentration converted to COD [27,30,33,41]), and that due to soluble pollution in water and less extractible by the surfactant, COD_S.

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

$$COD_S = COD_R - COD_{TA} \qquad (2)$$

The extraction results by the two non-ionic surfactants, Triton X-114 and Lutensol AO7, are expressed by the three following "responses" (Y): soluble chemical oxygen demand (COD_S), residual COD_{TA} 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 variations (T). By considering central composite designs, for each parameter determine [61], the results were analysed by an empirical fitting. In this method, the experimental values can be used to determine, the adjusted polynomial model constants. The models were checked by plotting computing data against experimental results. For a constant oil concentration in the effluent (COD $\approx$ 7000 mg O_2/L), the quadratic correlation was chosen to give the slope and the regression coefficient (R^2) close to unity.

$$Y = a_0 + a_1 X_t + a_2 T + a_{12} X_t T + a_{11} X_t^2 + a_{22} T^2 \qquad (3)$$

Such correlation allowed building the response surface. However, one could not allow physical significance to the portion of horizontal planes corresponding to the maximum value of the response.

4.2.1. Soluble chemical oxygen demand, COD_S

The quadratic equations for the properties (COD_S), whose reliability was checked by plotting computed data vs. experimental values, are as follows:

$$COD_{S(TX-114)} = (1.3085 - 0.0398X_t - 0.1488T + 0.0007X_tT$$
$$+ 0.0034X^2 + 0.0044T^2) \times 10^3 \qquad (4)$$

$$COD_{S(LT-AO7)} = 933.5343 + 1.0865X_t - 162.3434T + 0.2372X_tT$$
$$+ 0.5841X^2 + 6.1378T^2 \qquad (5)$$

The reliability of Eqs. (4) and (5) was checked by plotting computed data vs. experimental values.

Fig. 2 represents the corresponding three-dimensional isoresponse curves smoothed by the quadratic models (Eqs. (4) and (5)). In comparing Fig. 2a and b, we notice that soluble (residual) chemical oxygen demand (COD_S) obtained using the system: Lutensol AO7/6 wt.% of Na_2SO_4 was higher than that obtained by the system: TX-114/3 wt.% of Na_2SO_4. Hence, TX-114 seems to be widely more efficient for hydrocarbon extraction than Lutensol AO7. Since both surfactants have almost the same ethoxylation number (EO = 7), this difference may certainly be caused by the presence of a benzene ring in the hydrocarbon chain length of Triton X-114 (iso-C_8H_{17}–C_6H_4-$E_{7,5}$). This latter seems to have more capacity towards hydrocarbons and fuel additive solubilization and extraction. Therefore, it is more effective than Lutensol AO7 to trap and concentrate them in the micelle cores of the coacervat. The addition of Na_2SO_4 is favourable for cloud point extraction of hydrocarbons and fuel additives by the salting-out phenomena.

One can notice also in Fig. 2 that for a constant concentration of surfactant, the (COD_S) generally increases with temperature, due probably to the increase of the water solubility of hydrocarbons and fuel additives at height temperature. Thus, the significant temperature rise beyond the cloud point has a negative effect on the extraction. At higher temperatures, these products are note easily extractable in coacervat and remain in the dilute phase. Besides, Fig. 2 shows that at constant temperature, COD_S increases slightly when operating at high surfactant concentration. The minimum value of COD_S was therefore obtained when extraction was conducted at room temperature, i.e. (between $16\,^\circ$C and $21\,^\circ$C for TX-114/3 wt.% Na_2SO_4 system, COD_S values were
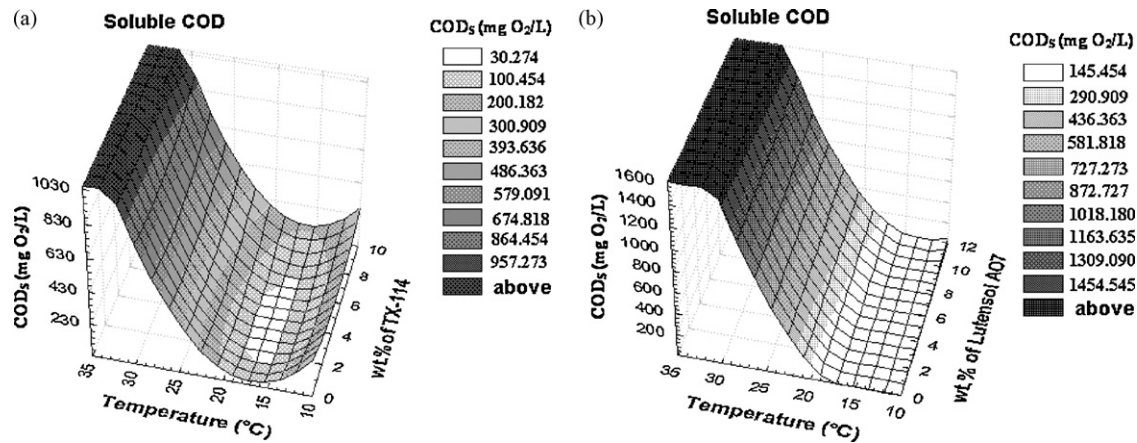
Fig. 2. Three-dimensional isoresponse curves smoothed by a quadratic model (Eqs. (4) and (5)): (a) $COD_{s(TX-114)} = f(X_t, T)$; (b) $COD_{s(AO7)} = f(X_t, T)$.

less than 120 mg O$_2$/L). Whilst, for Lutensol AO7/6 wt.% Na$_2$SO$_4$ system, between 15 °C and 19 °C, CODs values were between 50 and 113 mg O$_2$/L. At optimal conditions of temperature and surfactant concentration (Fig. 2a and b), cloud point extraction of hydrocarbons allowed a *ca.* 140-fold COD reduction using Lutensol AO7 (from 7000 mg O$_2$/L to 50 mg O$_2$/L), and a *ca.* 244-fold when Triton X-114 was used (from 7000 mg O$_2$/L to 30 mg O$_2$/L). The most favourable areas for cloud point extraction were thus located in the lightest colour zones in Fig. 2. The best performance-cost compromise of the process, based on minimum surfactant consumption, led to optimal surfactant concentrations ranging between 2 and 5 wt.%.

4.2.2. Chemical oxygen demand due to surfactant residual concentration (COD$_{TA}$)

The results of the residual chemical oxygen demand (COD$_{TA}$) due to the surfactants (TX-114, Lutensol AO7) concentration in the dilute phase after extraction were exposed as an example. The quadratic equations for the property COD$_{TA}$ whose accuracy was checked are as follows:

$$COD_{TA(TX-114)} = (1.7313 + 0.0819X_t + 0.0304T + 0.0002X_t T$$
$$- 0.0047X_t^2 - 0.0010T^2) \times 10^3 \quad (6)$$
$$COD_{TA(LT-AO7)} = 526.7972 - 0.6346X_t - 2.7366T + 0.2051X_t T$$
$$- 0.1587X_t^2 - 0.04661T^2 \quad (7)$$

The surfactant loss in the diluted phase during the CP extraction is a very important parameter. The process became inefficient

if a new pollutant is detected in the dilute phase after extraction. Indeed, biodegradable surfactant (as polyethoxylated alcohol and alkylphenol polyethoxylated) was used due to their satisfactory biodegradable activities [43,44]. However, surfactant loss in the diluted phase is not economic even when the surfactant is biodegradable. Fig. 3 represents the corresponding three-dimensional isoresponse curves fitted by the quadratic models (Eqs. (6) and (7)). It is shown that, for both surfactants (TX-11 and Lutensol AO7), residual chemical oxygen demand (COD$_{TA}$) due to the surfactant remaining in dilute phase after extraction were low at high temperature and low surfactant concentration. Thus, the surfactant concentration in dilute phase after extraction, increases with X_t and decreases at high temperatures. This is a classical behaviour of non-ionic surfactants which are less soluble in water at high temperature (cloud point phenomenon principle) [27,30,33]. In addition, one can see in Fig. 3 that, COD$_{TA}$ due to TX-114 (cmc = 7×10^{-4} M) was higher than that obtained with Lutensol AO7 (cmc = 4.6×10^{-4} M). Therefore, the first surfactant was more soluble in water than the second one, in agreement with the cmc values.

4.2.3. Coacervate volume fraction at equilibrium (ϕ_C)

For the properties ϕ_C regarding the two surfactants (TX-11 and Lutensol AO7), the quadratic model provides the following equations:

$$\phi_{C(TX-114)} = 0.0937 + 0.0612X_t - 0.0042T - 0.0013X_t T$$
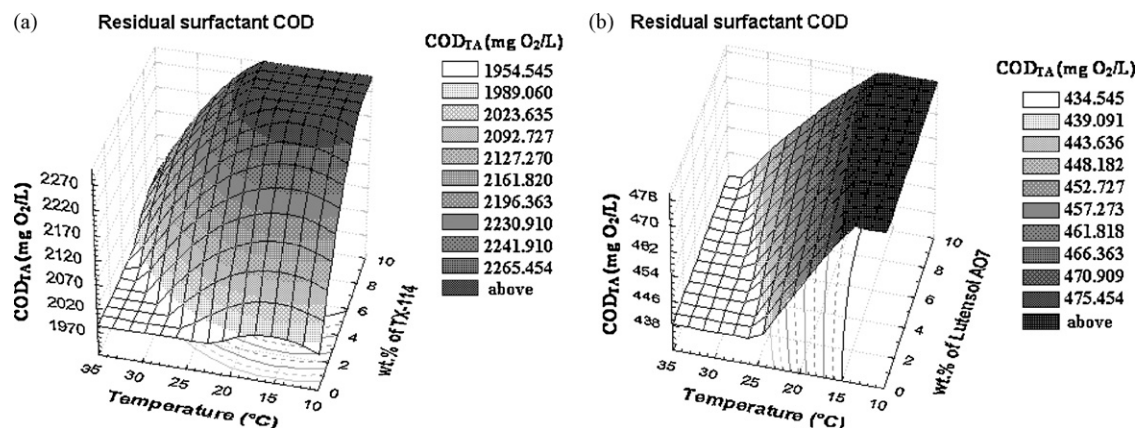$$+ 0.0009X_t^2 \quad (8)$$

Fig. 3. Three-dimensional isoresponse curves smoothed by a quadratic model (Eqs. (6) and (7)): (a) $COD_{TA(TX-114)} = f(X_t, T)$; (b) $COD_{TA(AO7)} = f(X_t, T)$.
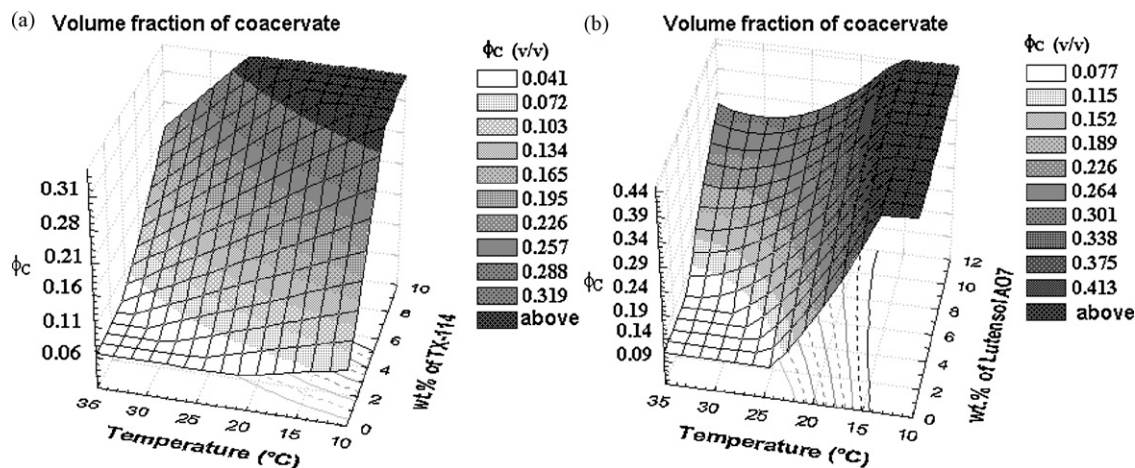
Fig. 4. Three-dimensional isoresponse curves smoothed by a quadratic model (Eqs. (8) and (9)): (a) $\phi_{C(TX-114)} = f(X_t, T)$; (b) $\phi_{C(AO7)} = f(X_t, T)$.

$$\phi_{C(LT-AO7)} = 1.2661 - 0.0005X_t - 0.0727T + 0.0015X_tT$$
$$- 0.0011X_t^2 + 0.00091T^2 \qquad (9)$$

In contrast to solvent liquid–liquid extraction where the volume fraction is constant, ϕ_C depends upon temperature and surfactant concentration in cloud point extraction method. Indeed, it is possible to adjust this parameter to low value (e.g. $\phi_C = 0.02$) by a simple control of T and X_t in order to increase the treated effluent volume. Fig. 4 shows that the behaviour of ϕ_C according to

X_t and T was generally similar for both surfactants (TX-11 and Lutensol AO7). The values of ϕ_C were low at high temperature and at small surfactant concentration. Hence, in order to increase the concentration of solute, a minimal volume fraction of coacervate (ϕ_C) should be obtained when temperature increases. In contrast, high temperature was unfavourable for efficient extraction extent (Fig. 2), while, high surfactant concentrations induced more surfactant loss in the dilute phase (Fig. 3). Therefore, a minimum value of ϕ_C was obtained above 30 °C (Fig. 4) at low surfactant concentrations (2 wt.% of TX-114 and 4 wt.% of Lutensol AO7). Such
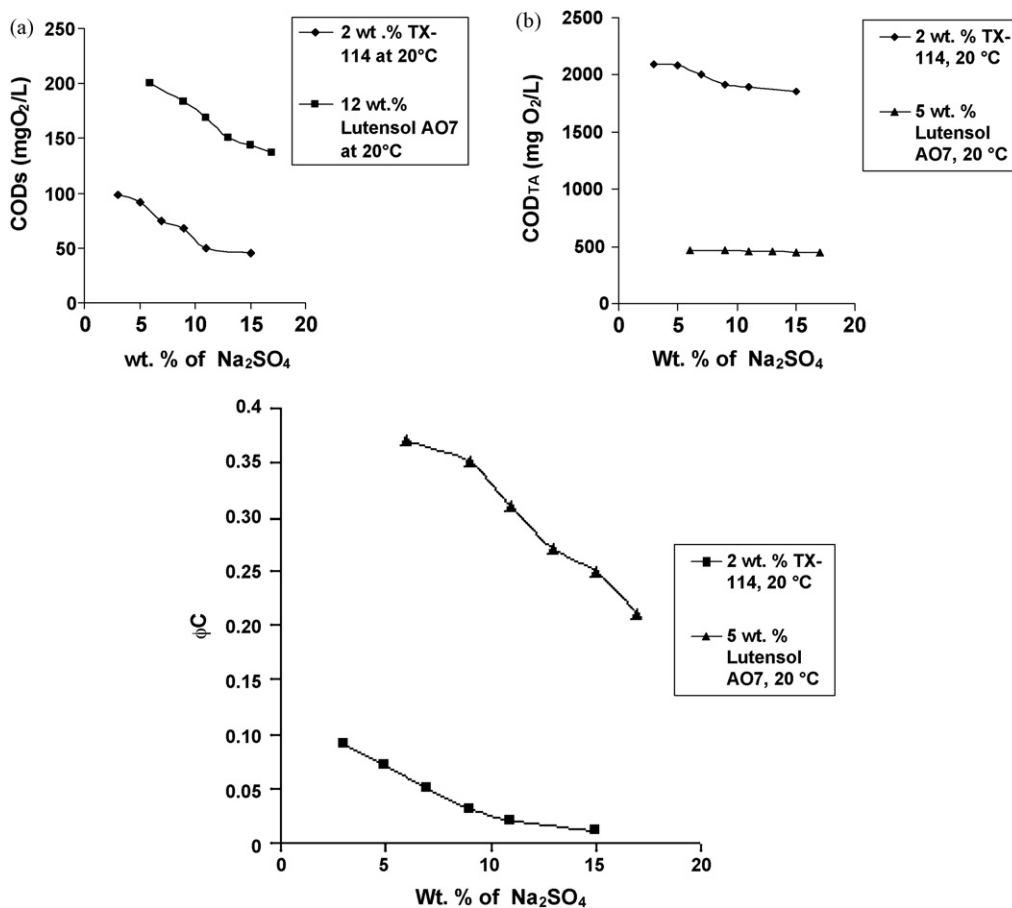

Fig. 5. Extractions with 2 wt.% of TX-114, and 5 wt.% of Lutensol AO7 at 20 °C; effect of sodium sulphate on: (a) the soluble chemical oxygen demand, COD_s; (b) the chemical oxygen demand due to the surfactant residual concentration, COD_{TA}; (c) the coacervate volume fraction at equilibrium, ϕ_C.

Table 3
CODs and surfactant recovery extent E (%) during three extraction/regeneration stages.

	1st surfactant regeneration	2nd surfactant regeneration	3rd surfactant regeneration
CODs (mg O$_2$/L)	45.1	57.8	72.3
E (%): extent of surfactant recovery from coasevate[a]	95.5	90.0	88.6

[a] Conditions of coacervate regeneration: [Ca(OH)$_2$]: 1.53 mg/L; pH 12.1 [26].

conditions seemed to be insufficient to reduce CODs below the regulation value (120 mg O$_2$/L) (Fig. 2). Consequently, the optimization of the process was needed to compromise between the three studied parameters COD$_R$, COD$_T$ and ϕ_C. Therefore, 2 wt.% of TX-114% at 18 °C provided a volume fraction below 15% (v/v), and a good extraction yield, while optimum conditions for Lutensol AO7 were around 4 wt.% at the same temperature (18 °C).

4.2.4. Effect of sodium sulphate on CODs and ϕ_C

The CODs and COD$_{TA}$ evolution as a function of Na$_2$SO$_4$ concentration (wt.%) of H$_2$O/surfactant/hydrocarbons solution was shown in Fig. 5a and b. The sodium sulphate addition induced coacervate volume fraction reduction (Fig. 5c) due to the cloud point lowering of the surfactant solution (Fig. 1) [30]. Therefore, in the presence of salt, small coacervate volumes with a high surfactant concentration were obtained (Fig. 5c). According to Saito and Shinoda [58], the addition of 0.17 M of NaCl (equivalent to 1 wt.%) to non-ionic surfactant solutions increases their hydrocarbon solubilization capacity, by lowering cmc concentration. This behaviour may be the result of an increase in micellar number in this concentration region. As mentioned above, the salting-out effect resulted from the solvated electrolyte depended upon the hydrogen bonding between water molecules and the surfactant polar head group as well as with the hydrocarbons present in oily wastewater. Hence, hydrocarbons and surfactant molecules were less soluble in water in the presence of electrolyte and low values of CODs and COD$_{TA}$ were obtained at high concentrations of sodium sulphate (Fig. 5). However, a high value of CODs was obtained with Lutensol AO7 (Fig. 5a), while low value of COD$_{TA}$ was quoted using this surfactant (Fig. 5b). These results confirmed that Lutensol AO7 was less soluble in H$_2$O/hydrocarbons system than TX-114. However, TX-114 was widely more efficient for hydrocarbons extraction than Lutensol AO7. One can notice here that the extraction by TX-114 and Lutensol AO7 was accompanied by demulsification conducted by Na$_2$SO$_4$. In the absence of sodium sulphate, the extraction was possible at high temperature (above 25 °C and 45 °C using TX-114 and Lutensol AO7, respectively) [62].

4.2.5. Effect of pH on COD$_S$

The solute–micelle interactions are strongly influenced by solute ionisation [63]. After the deprotonation of a weak acid or the protonation of a weak base (e.g. some fuel and lubricant additives), slight interactions may occur with the surfactant. In these conditions, a small amount of those species may be solubilize unlike neutral molecules (e.g. alkanes, olefins). Consequently, a small amount of ionised solute can be extracted. Fig. 6 shows that COD$_S$, in the dilute phase after extraction, was around 4500 mg O$_2$/L at basic pH. Hence, one can deduce that hydrocarbons separation was favoured by acid medium. It seemed to us that some fuel and lubricant additives are pH sensitive compounds. Such molecules dissociated in water (dilute phase) and had no more interactions with the polar head group of the surfactant in the coacervate micelles. Hence, those molecules remained in the dilute phase after extraction which induced COD$_S$ increasing (Fig. 6). The pH sensitive molecules able to be used as oil additives are stearic acid (antiwear additive), esters of chlorendic acid (extreme pressure additives) [64], the 2,4-dimethyl-6-*tert*-butylphenol, to prevent gumming in fuels, and as an ultraviolet stabilizer [65], and some fat-soluble dye as Sudan III (a lysochrome diazo dye) [33].
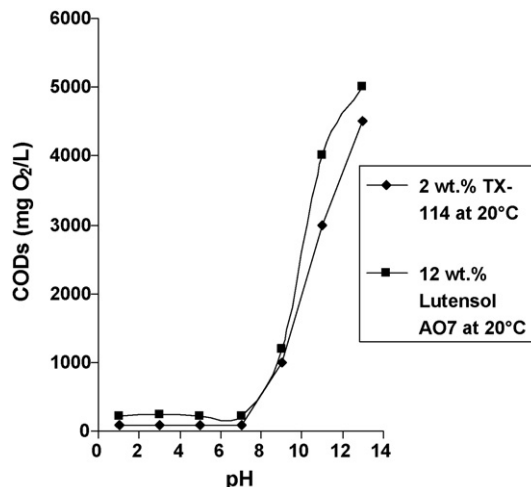

Fig. 6. Effect of pH on the soluble chemical oxygen demand (CODs) in the dilute phase after extractions with 2 wt.% of TX-114 and 5 wt.% of Lutensol AO7 at 20 °C.

Indeed, the pH may be employed in surfactant regeneration. In effect, after a first extraction of fuel spills at 18 °C, the coacervate pH was increased to a basic value using Ca(OH)$_2$ to give a complete dissociation of acid compounds. Moreover, the previous coacervate was separated into two new phases at 22 °C: (i) a small quantity of a brown floating phase where hydrocarbons was concentrated (W/O emulsion identified by conductimetry, and (ii) a new aqueous phase (coacervate) containing most of the surfactant (Table 1). In order to use the surfactant again, it was necessary to decrease its pH and to precipitate the base (Ca(OH)$_2$) using H$_2$SO$_4$. Starting with an extraction test using 2 wt.% of TX-114. Table 3 represents the results of a three time surfactant regeneration.

5. Conclusion

A CPE approach has been developed in the present work to treat and purify fuel spills. For this purpose, alkyl phenol ethoxylate (APE) non-ionic surfactants types (represented by Triton X-114) were compared to polyethoxylated alcohols surfactants (Lutensol AO7), which are easily and quickly biodegradable. So, they are more environmentally friendly than APE surfactants. The presence of hydrocarbons and Na$_2$SO$_4$ lowers the non-ionic surfactants cloud point. Most hydrocarbons were extracted at the first contact between surfactant and effluent. Hence, the COD of the effluent was reduced to about 140–233 time after extraction process. Subtracting the biodegradable COD due to surfactant (COD$_{TA}$), the results showed that after an initial effluent COD of 7000 mg O$_2$/L, two aqueous phases extraction allowed reduction of CODs below to 50 mg O$_2$/L and 30 mg O$_2$/L, using TX-114 and Lutensol AO7/6 wt.% Na$_2$SO$_4$ at 16 °C and 15 °C, respectively. The optimal surfactant concentrations needed to obtain a maximum reduction of soluble chemical oxygen demand (DCOs) were about 2 wt.% of Triton-X114, and 5 wt.% in the case of Lutensol AO7. On the other hand, a significant temperature rise beyond the cloud point decreased the extraction extent. The sodium sulphate reduced the coacervate volume fraction because of the cloud point lowering of the surfactant

solution, and also increased the solute extracted percentage. The recycling of a part of surfactant in a cloud point extraction process seemed to be possible at a pH between 10.5 and 12 (Fig. 6).

Nomenclature

ϕ_C	coacervate volume fraction
APE	alkyl phenol ethoxylate
cmc	critical micellar concentration
COD_R	total residual residual chemical oxygen demand
COD_s	soluble chemical oxygen demand
COD_{TA}	chemical oxygen demand due to the surfactant
CPE	cloud point extraction
GPC	gas phase chromatography
HPLC	high performance liquid chromatography
LT-AO7	Lutensol AO7
O/W	oil in water emulsion
PNA	paraffins, naphthenics and aromatics
T	temperature (°C)
T_c	cloud point temperature (°C)
VOC	volatile organic compounds
X_t	surfactant (wt.%)

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