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

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ABSTRACT

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}.

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

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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 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.

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

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