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Phenol and benzenoid alcohols separation from aqueous stream using cloud point extraction: Scaling-up of the process in a mixer-settler

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ABSTRACT

In the present work, the cloud point extraction (CPE) of three organic pollutants (phenol,benzyl alcohol and 1-phenylethanol) with aqueous solutions of biodegradable alkoxylated nonionic surfactants (TERGITOL 15-S-7 and SIMULSOL NW342), is investigated. First, the partial phase diagrams of the water–surfactant binary systems are established. Then, the effects of organic pollutants and sodium chloride on the cloud point (T_c) are determined. Extraction efficiency is evaluated by the following responses: percentage of solute extracted, E (%), residual concentrations of solute and surfactant in dilute phase ($X_{s,w}$, and $X_{t,w}$, respectively) and volume fraction of coacervate at equilibrium (ϕ_c). Three-dimensional empirical correlations are used for fitting the experimental results. The comparison between experimental and calculated values allows model parameter identification. Based on these data, CPE was implemented in a continuous mixer-settler device. The feasibility of a multi-stage crossflow process for the purification of samples containing phenol using SIMULSOL NW342 was tested. Six stages were required to reduce the pollutant concentration below the allowed level (0.3 ppm), which proves the efficiency of CPE in the treatment of wastewaters.

1. Introduction

From the wide variety of organic pollutants, phenol, benzyl alcohol and1-phenylethanol were chosen for this study. Phenol is considered as one of the major water pollutants. Even at very low doses, it is still very dangerous because of its persistence, toxicity, ecotoxicity and bioaccumulation [1–5]. The Environmental Protection Agency (EPA) and the French legislation limit its allowedconcentration in surface waters to 0.3 mg/L [6,7]. For phenol removal, solvent extraction, adsorption, but also ion exchange, polymerization, electro-coagulation, membrane-based separations and biological methods have been found effective [1,4,8–10]. In soap, perfume and flavor industries, benzyl alcohol is employed as such in bar soap fragrances and in the form of its esters. It is also used in the polymer industry and in the manufacture of car tires. Its photocatalytic degradation has been investigated [11]. 1-Phenylethanol is mainly a coproduct of the oxidation step of ethylbenzene, whose hydroperoxide is used to convert propylene to its oxide. It is then valorized through dehydration to styrene. It can be burnt in a chemical incinerator equipped with a post combustion and epuration system [12].

The laws and regulations on wastewater treatment are becoming increasingly strict. Therefore, there is a strong trend to develop efficient methods for the removal and/or recovery of toxic species in the environment [13]. Among others, Cloud Point Extraction (CPE) appears to be a relatively simple and ecologically safe technique. In fact, the aqueous solutions of most polyethoxylated nonionic surfactants become cloudy and start to separate into two phases, coacervate and dilute phase, as soon as temperature rises above their cloud point, T_c [14]. This phenomenon is the basis of the CPE process [15–20]. This latter avoids the use of an organic solvent, produces small sludge volume and requires low energy consumption. This process is very efficient for treating water containing various contaminants including dissolved or dispersed organic matter [21–40]. This method of water purification was also applied to the extraction of metal ions using diverse appropriate chelates [15,41–44] and without chelates [45–49]. Associated to the cloud point value, the main factors in surfactant selection are its biodegradability, toxicity and ecotoxicity. The use of CPE offers an interesting alternative to conventional extraction systems. This technique allows moving toward Green Chemistry. Many advantages were claimed to CPE compared with conventional liquid-liquid extraction: CPE is an efficient and selective process that works continuously, saves energy and can be scaled up [50–54]. On the basis of this finding, the batch CPE of phenol, benzyl alcohol and 1-phenylethanol from aqueous solution was investigated in the present work. The effects of

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Nomenclature

Symbols

Symbol	Definition
BA	Benzyl alcohol
cmc	Critical micelle concentration
E	Extent of extraction (%)
PE	1-phenylethanol
PH	Phenol
T_c	Cloud point (temperature)(°C)
V_r	Stirrer speed
$X_{s,w}$	Mass fraction of solute in the dilute phase after extraction
$X_{t,w}$	Mass fraction of surfactant in the dilute phase after extraction
X_t	Initial surfactant mass fraction
$X_{PH,F}$,$X_{PH,S}$,$X_{PH,E}$,$X_{PH,R}$	Mass fraction of solute in the feed, solvent, extract and raffinate phase, respectively
$X_{t,F}$,$X_{t,S}$,$X_{t,E}$,$X_{t,R}$	Mass fraction of surfactant in the feed, solvent, extract and raffinate phase, respectively
ϕc	Volume fraction of coacervate

temperature, surfactant concentration and decantation time on solute extraction extent were also studied. For this purpose, two polyalkoxylated nonionic surfactants were used: TERGITOL 15-S-7 and SIMULSOL NW342. The initial pollutant concentration used in water was 0.2 wt.%. Using these data, the continuous multi-stage crossflow cloud point extraction was implemented in a mixer-settler. As a model system, phenol was extracted using SIMULSOL NW342. The mixer-settler can be easily arranged in battery for counter-current multi-stage process. Each mixer-settler couple can be considered as a theoretical stage. This equipment offers the advantage to operate with highly unequal phase fractions. This technology is able to operate with high flow rates, and can be useful for wastewater treatment.

2. Materials and methods

2.1. Chemical species

The nonionic surfactants used in this work were obtained from Oxo-alcohol alkoxylation: SIMULSOL NW342 (cmc = 1.52 mmol/L at 15 °C), kindly provided by SEPPIC (Castres, France) and TERGITOL 15-S–7 (cmc = 1.22 mmol/L at 20 °C), a Dow Chemical specialty purchased from Aldrich, are mixtures of primary and secondary alcohol alkoxylates with the alcohol group located at various positions along the carbon chain. Phenol, benzyl alcohol and 1-phenylethanol were purchased from Aldrich and sodium chloride from VWR. The formulas and some properties of the species used in this work are listed in Table 1. Deionized water was used in all cases except for the HPLC analyses, carried out with ultrapure water.

2.2. Methods

2.2.1. Cloud point measurements

Cloud point measurements were carried out using a Mettler FP 900 apparatus. It consists of a FP90 control and operating unit, and a FP81C measuring cell dedicated to cloud point measurements. The cell temperature was measured with a Pt100 sensor; light transmission was measured continuously, while the cell temperature was increasing linearly according to the chosen heating rate. The cloud point corresponds to the temperature at which the limpid phase becomes cloudy, inducing a light transmission decrease.

2.2.2. Experimental conditions

For batch extraction tests, 30 mL of solution, containing the surfactant (at concentrations from 2 to 10 wt.%) and the solute (0.2 wt.%) in demineralized water, were poured into graduated cylinders and heated in a precision oven and kept during 24 h to reach equilibrium. The volumes of both phases (coacervate and dilute) were measured.

The dilute phase was analyzed. The residual pollutant and surfactant concentrations were determined by reversed-phase high-performance liquid chromatography: for the solutes, the conditions were as follows: column RP18 (ODS), 95 bar, mobile phase $H_2O/CH_3CN/CH_3OH$, 42.5/50/7.5 (v/v), flowrate 1 mL/min.; λ = 260 nm; t = 25 °C. The conditions were slightly different for the surfactant: mobile phase $H_2O/CH_3CN/CH_3OH$, 7.5/60/32.5 (v/v). The sensitivity of the evaporative light-scattering detector (DDL 31, EUROSEP Instruments) was optimized by the control of the air flowrate in the atomizer (relative pressure: 1 bar), the temperature of the evaporator (55 °C) and the gain of the photomultiplier (400 mV) [59–61].

The total capacity of the mixer-settler (Fig. 1); temptatively used by our research group in a previous work [21], was 9.5 L. However, the occupied volume was 7 L. The stirrer diameter was 6.5 cm and the mixing tank diameter was 8.5 cm. The cylindrical settler was 98 cm length and 10 cm diameter; the stirring speed could vary from 0 to 900 rpm. For the ternary water/Simulsol NW342/phenol system, the equipment was operated with equal volumes of the feed solution F (0.4 wt.% phenol) and the solvent S (8 wt.% surfactant); the mixture was maintained at 30 °C.

2.2.3. Extraction parameters

In order to find the optimal conditions of the two variables: wt.% surfactant (X_t), and temperature (T), allowing to obtain the best possible extraction results, we have worked out the best compromise between the four "responses", Y (E, $X_{s,w}$, $X_{t,w}$ and ϕ_c), defined as follows:

- The extraction yield E (%):

$$E(\%) = \frac{m_{s(in)} - m_{s(w)}}{m_{s(in)}} \times 100 \tag{1}$$

Where $m_{S(in)}$ and $m_{S(w)}$ represent the mass of the solute in the initial solution and in the dilute phase, respectively.

- The volume fraction of coacervate$_c$, i.e. the ratio of the volume of the coacervate, V_C, to the total volume ($V_C + V_w$),V_w being the volume of the dilute phase:

$$\phi_c = \frac{Vc}{Vc + Vw} \tag{2}$$

- The weight percentage of solute in the dilute phase:

$$X_{s,w}(\%) = \frac{m_{s(w)}}{m_w} \times 100 \tag{3}$$

with m_w: mass of dilute phase,

The weight percentage of surfactant in the dilute phase:

Table 1
Chemicals: formulas and properties.

Name (abbreviation)	Formula	Aqueous solubility at 25 °C (g/L)	log P [58]
SIMULSOL NW342 (Oxo-$C_{10}E_3P_4E_2$)	$C_{10}H_{21}$-$(OCH_2$-$CH_2)_3$-(O-CH_2 $CH(CH_3))_4$-$(OCH_2$-$CH_2)_2$-OH		
TERGITOL 15-S-7 ($C_{11-15}E_{7.3}$)	$C_{15}H_{31}$-(O-CH_2-$CH_2)_{7.3}$-OH		
Phenol (PH)	C_6H_5OH	82.8 [55]	1.5
Benzyl alcohol (AB)	$C_6H_5CH_2OH$	40 [56]	1.05
1-Phenylethanol (PE)	$C_6H_5CH(CH_3)OH$	20 (at 20 °C) [57]	1.42