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Removal of Tannic Acid From Aqueous Solution by Cloud Point Extraction and Investigation of Surfactant Regeneration by Microemulsion Extraction

H. Ghouas¹ · B. Haddou¹ · M. Kameche¹ · J. P. Canselier² · C. Gourdon²

Abstract The aim of this work is the extraction of tannic acid (TA) with two commercial nonionic surfactants, separately: Lutensol ON 30 and Triton X-114 (TX-114). The experimental cloud point extraction results are expressed by four responses to surfactant concentration and temperature variations: extent of TA extraction (E), remaining solute ($X_{s,w}$) and surfactant ($X_{t,w}$) concentrations in dilute phase and volume fraction of coacervate (Φ_c) at equilibrium. An empirical smoothing method was used and the results are represented on three dimensional plots. In optimal conditions, the extraction extent of TA reaches 95 and 87 % using TX-114 and Lutensol ON 30, respectively. Sodium sulfate, cetyltrimethylammonium bromide (CTAB) addition and pH effect are also studied. Finally, the possibility of recycling of the surfactant is proved.

Keywords Extraction · Tannic acid · Nonionic surfactant · Coacervate · Cloud point · Microemulsion

Abbreviations

E	Extraction efficiency (%)
$X_{s,w}$	Residual concentration of tannic acid g/L
Φ_c	Volume fraction of coacervate phase
$X_{t,w}$	Concentration of residual surfactant g/L
X_t	Initial concentration of surfactant (%)

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T	Temperature (°C)
T_c	Cloud temperature (°C)
CMC	Critical micelle concentration
CPE	Cloud point extraction
HLB	Hydrophile-lipophile balance
CTAB	Cetyltrimethyl ammonium bromide
TA	Tannic acid

Introduction

The toxicity of naturally occurring polyphenolic compounds, e.g. tannins, to microorganisms and to aquatic flora and fauna [1, 2] makes their removal from wastewater relevant. Two types of tannins (hydrolyzable and condensed ones) were first distinguished, the former being found more toxic than the latter [3]. Four classes are now listed [4]: gallotannins, ellagitannins, complex tannins and condensed tannins. Tannic acid, commercially available, is hydrolyzable and belongs to the first class [5, 6]. The structure of pure tannic acid corresponds to that of a polyester of glucose and gallic acid (IUPAC name: β -D-Glucose pentakis(3,4-dihydroxy-5-((3,4,5-trihydroxybenzoyl)oxy) benzoate or 2,3-dihydroxy-5-(((2R,3R,4S,5R,6R)-3,4,5,6-tetrakis ({3,4-dihydroxy-5-[(3,4,5-trihydroxyphenyl)carbonyloxy]phenyl)carbonyloxy) oxan-2-yl]-methoxy)carbonyl)phenyl 3,4,5-trihydroxybenzoate) but the commercial compound may also contain esters of glucose and quinic acid. Its LD50 are 5 g kg⁻¹ (mice, oral) and 2.26 g kg⁻¹ (rat, oral) [7]. Tannic acid is commonly found in the human diet including tea, beans, grapes, strawberries, etc., and regarded as a safe food additive. It has antimicrobial activity, anticarcinogenic and

antimutagenic potentials and its antioxidant properties protect from cellular oxidative damage [8, 9, 11]. Through hydrolysis, hydrolyzable tannins decompose into mixtures containing gallic acid and pyrogallol, which show enhanced antioxidant and antimicrobial activities [6, 12]. However, ingestion of large quantities of tannins may result in adverse health effects [13]. Tannins may injure the intestinal mucosa [14], alter intestinal secretions [15], inhibit digestive enzymes [16] and increase the excretion of endogenous proteins [16]. Tannin components have also been implicated in the high levels of cheek and esophageal cancers in some regions of the world, and to produce other physiological effects such as immune response, hepatotoxicity and lipid metabolism [9]. Tannic acid (TA) is generally considered as one of the polyphenolic pollutants which may cause severe threats to the environment [17]. It may cause serious problems by reacting with chlorine disinfectants, form carcinogenic disinfection by-products during drinking water production [2, 18, 19] and make wastewater with distinguished color [20]. Large quantity of hydrolyzable tannin in wastewater with strong color is harmful to microorganisms, animals and humans, protein precipitation and decreased utilization in mammals [17, 21–28]. Furthermore, TA has toxicity for aquatic species such as algae, phytoplankton, fish, and invertebrates [17, 26–29]. TA enters the water body, coming from plant medicine, paper, leather, coir and cork processing industries and textile dyeing and tanning [10, 26, 30, 31]. Therefore, TA must be removed from water and wastewater to protect flora and fauna before effluent is discharged into the environment.

Several treatment technologies have been reported for the removal of TA, such as chemical oxidation, adsorption–coagulation combined systems [32], electrochemical process [29, 33], ultrafiltration [34], biological process [35], and adsorption [1, 2, 13, 17, 18, 20, 22, 24–27, 29, 33–35]. In the present work, cloud point extraction (CPE) was investigated to extract and recover tannic acid from aqueous effluents. For this purpose, the solubilization properties of micellar solutions of nonionic surfactants were turned to account. The effect of sodium sulfate, cetyltrimethyl ammonium bromide (CTAB) addition and pH was studied in this respect.

Various solutes can be extracted into the coacervate (surfactant-rich phase) after a temperature rise above the cloud points of non-ionic surfactants. The CPE process has been widely applied in the separation of metal ions, small organic and biological molecules [36–41]. Avoiding the use of organic solvents and applied with biodegradable surfactants, CPE is an environmentally-friendly technique as well as an efficient and selective process that works continuously, saves energy and can be easily scaled up [42, 43]. However, in order to establish micellar extraction

processes as an alternative to conventional solvent extraction processes, recycling of the surfactant as well as product recovery from the micellar phase is essential [44–47]. The influence of pH on the partitioning of ionizable solutes is an important parameter to control the extraction and back extraction efficiency from coacervate [48–50]. In this paper, the recovery of a complex molecule as tannic acid from nonionic surfactant micellar phase by pH changing was found to be impossible. Hence, Winsor I microemulsion extraction was investigated as an alternative method for surfactant recycling.

Winsor I microemulsion is made of an oil in water (*Wm*) phase coexisting with an excess oil phase, whereas water in oil (*Om*) phase coexisting with an excess water phase leads to Winsor II microemulsion system [51]. The type of microemulsion is also strongly affected by the nature of the nonionic surfactant [52]. Shen et al. [53] investigated the effect of the HLB of the nonionic surfactant on the type of microemulsion. A hydrophobic nonionic surfactant (of low HLB) forms Winsor II microemulsion and a hydrophilic nonionic surfactant, like TX-114 (HLB = 12.4), is more soluble in water and allows the formation of Winsor I microemulsion.

Generally, Winsor I microemulsions are formed by hydrophobic organic solvents (with a high $\log P$). In such systems, nonionic surfactant mainly partitions into the *Wm* phase. However, a hydrophilic organic solvent (low $\log P$) forms Winsor II microemulsions in which the nonionic surfactant mainly partitions into the *Om* phase [54]. Temperature also largely controls the type of microemulsion [55]. In water/Triton X-100/n-butyl acetate system, the type of microemulsion changes from Winsor I at 6 °C to Winsor II at 50 °C [53]. In this paper, downstream processing of the CPE of tannic acid with TX-114 was investigated. Separation using Winsor I microemulsion extraction of tannic acid from the coacervate phase by selection of the solvent as excess oil phase, was achieved. Diethyl ether ($\log P = 0.85$), petroleum ether ($\log P = 3.1$) and cyclohexane ($\log P = 3.2$) were selected to study the effect of this parameter ($\log P$) on the back-extraction of tannic acid from nonionic surfactant aqueous solution at 20 °C.

Materials and Methods

Materials

In the present work, coacervate extraction is based on the use of two biodegradable nonionic surfactants [49, 50, 56–58]. The polyethoxylated octylphenol mixture, known as “Triton X-114” (TX-114) and having the average formula $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{C}(\text{CH}_3)_2-\Phi-(\text{OCH}_2-\text{CH}_2)_{7.5}\text{OH}$ (abbreviated as

C8ΦE7.5), was supplied by Sigma-Aldrich. Its critical micelle concentration (CMC) was 0.2 mM (at 25 °C) and its cloud point (T_c) at 1 wt% in water was 23 °C. The second surfactant was a polyethoxylated alcohol known as Lutensol ON 30, equivalent to $C_{10}H_{21}(OCH_2-CH_2)_3OH$. It was provided by the Badische Anilin- und Soda-Fabrik (BASF) company; its cloud point at 1 wt% in water was about 25 °C and its CMC was 0.024 mM (at 25 °C). Cetyltrimethyl ammonium bromide (CTAB) was purchased from Alfa Aesar; its CMC was $1.3 \cdot 10^{-3}$ mol/L (at 25 °C). Tannic acid (CAS Number 1401-55-4, empirical formula $C_{76}H_{52}O_{46}$, molar mass 1701.20) was supplied by Sigma-Aldrich.

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) or $Ca(OH)_2$ (1.5 g/L).

The organic solvents used for surfactant recycling (diethyl ether, petroleum ether, cyclohexane and iso-butanol) were supplied by Sigma-Aldrich.

Methods

Cloud Point Extraction

The determination of the cloud point was carried out using a Mettler FP 900 apparatus. The cloud point designates the temperature at which the clear liquid phase becomes cloudy.

For the extraction tests, 10 mL of solution containing the surfactant (at concentrations of 1–12 wt% and tannic acid at 100 mg/L in deionized water, were settled in a precision oven for 2 h. In effect, for the surfactant Lutensol ON 30, the temperature range was 30–45 °C while that for TX-114 was 25–40 °C. For tannic acid and TX-114, the dilute phase was analyzed by RP-HPLC under the following conditions: column RP18 (ODS), pressure 95 bar, flowrate 1 mL/min; $\lambda = 260$ nm, mobile phase $H_2O/CH_3CN/CH_3OH$, 42.5/50/7.5 (v/v) (tannic acid), $H_2O/CH_3CN/CH_3OH$, 7.5/60/32.5 (TX-114).

For Lutensol ON 30, the light scattering detector LS 31 (EUROSEP instruments) was used under the following conditions: air pressure 1 bar, evaporator temperature 55 °C and the gain of the photomultiplier (400).

Microemulsion Back-Extraction

The Winsor I microemulsion was formed by mixing 5 mL of coacervate, diluted with an equal volume of water, and 10 mL of organic solvent and it was kept in a thermostated water bath at 20 °C. After complete phase separation and excess oil removal, tannic acid was determined spectrophotometrically in the remaining W_m phase. Separately, Winsor II microemulsion extraction was used to determine TX-114 in the W_m phase using iso-butanol as the Om

phase. The sample was diluted with the same volume of iso-butanol and incubated in a 20 °C water bath for over 6 h. The organic solvent phase was carefully driven out by stripping of the solvent with nitrogen gas. The residue (TX-114) was then weighed.

Results and Discussion

Binary and Pseudo-Binary Phase Diagrams

When mixed with micellar solutions, organic solubilizes may interact with the surfactant polar head group or its hydrocarbon chain. Thereby, the anorganic solute can raise or lower the surfactant cloud point [59–62]. One can notice in Figs. 1 and 2 the cloud point increase of Lutensol ON 30 and TX-114 by tannic acid addition.

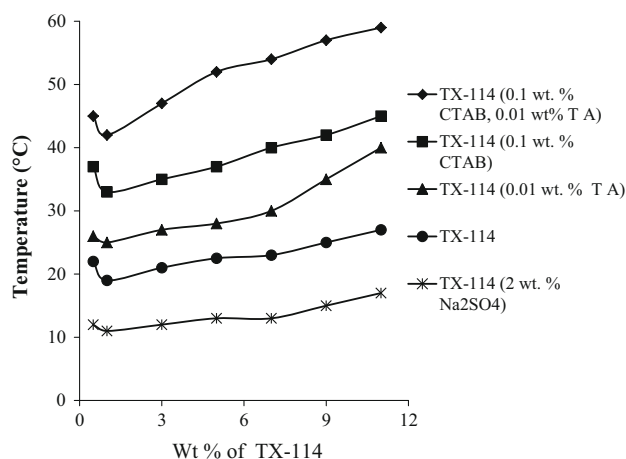


Fig. 1 Effect of tannic acid and CTAB on the cloud point curves of Lutensol ON30 and TX-114

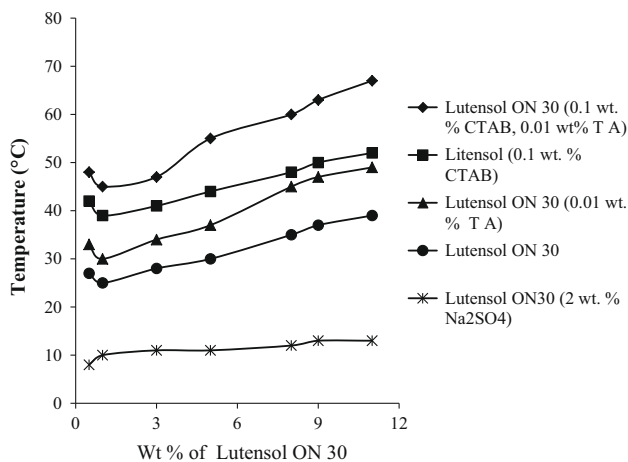


Fig. 2 Effect of sodium sulfate on the cloud point curves of Lutensol ON30 and TX-114

The impact of several factors, such as the number of ethylene oxide units of the surfactant, the additives (electrolytes and organic compounds) on the cloud point has been studied by several researchers [62–68]. In fact, the water solubility of organic compounds can be lowered in the presence of electrolytes by the salting-out phenomenon [65]. Indeed, the change of cloud point remains imperceptible in the case of addition of a low amount (less than 0.01 M) of NaCl to non-ionic surfactant system [49]. However, at higher concentrations (≥ 0.1 M), NaCl reduces the cloud point [63]. Figures 1 and 2 show the cloud point lowering of TX-114 and Lutensol ON 30 by Na_2SO_4 . The salting-out phenomenon favors the weakening of surfactant head–water interaction [64, 65, 68]. Therefore, salt addition can save the heating energy cost of a large scale cloud point extraction. One can also notice in Fig. 1 that the cloud points of $\text{H}_2\text{O}/\text{TX-114}$ and $\text{H}_2\text{O}/\text{Lutensol ON 30}$ systems increase significantly upon addition of a small amount of CTAB (0.1 wt%). The formation of mixed micelles by incorporation of the ionic surfactant into the nonionic micelles introduces electrostatic repulsion between aggregates, thus hindering coacervate formation and thereby increasing the cloud point dramatically [49, 69, 70].

Smoothing of Extraction Results

The results of tannic acid (TA) extraction from its 100 mg/L aqueous solutions with TX-114 and Lutensol ON 30 were expressed by four ‘‘responses’’ (Y): percentage of TA extracted (E), remaining concentrations of TA ($X_{s,w}$) and surfactant ($X_{t,w}$) in the dilute phase and coacervate volume fraction at equilibrium (Φ_c) [62, 63, 71]. For each parameter determined by considering central composite designs [72], the results were analyzed using an empirical fitting method. The experimental values are used to determine the adjustable polynomial model constants. The models were checked by plotting computed data against experimental results. The quadratic correlation was chosen to give the slope and regression coefficient (R^2) closest to unity.

$$Y = a_0 + a_1X_t + a_2T + a_{12}X_tT + a_{11}X_t^2 + a_{22}T^2 \quad (1)$$

Where X_t is the initial concentration of surfactant (%) and T is the temperature. Such a correlation allows building the response surface. The quadratic equations for the properties (E , $X_{s,w}$, $X_{t,w}$ and Φ_c), are as follows:

$$E_{(\text{TX-114})} = 13.945 + 6.992X_t + 2.307T - 0.005X_tT - 0.336X_t^2 - 0.030T^2 \quad (2)$$

$$E_{(\text{Lutensol})} = 16.486 + 2.845X_t + 1.000T + 0.029X_tT - 0.0000987 \times 10^{-3}X_t^2 - 0.999 \times 10^{-1}T^2 \quad (3)$$

$$X_{s,w}(\text{TX-114}) = 6.390 + 2.202X_t + 0.115T + 0.01X_tT + 0.012X_t^2 - 0.014T^2 \quad (4)$$

$$X_{s,w}(\text{Lutensol}) = 2.626 + 8.452X_t + 0.012T - 0.190X_tT + 0.230X_t^2 - 0.013 \times 10^{-1}T^2 \quad (5)$$

$$X_{t,w}(\text{TX-114}) = 0.389 + 0.045X_t - 0.019T - 0.013 \times 10^{-1}T^2X_tT + 2.567 \times 10^{-3}X_t^2 + 0.267 \times 10^{-3}T^2 \quad (6)$$

$$X_{t,w}(\text{Lutensol}) = 0.082 + 0.070X_t - 6.032 \times 10^{-3}T - 0.109 \times 10^{-2}X_tT + 0.262 \times 10^{-3}X_t^2 + 0.076 \times 10^{-3}T^2 \quad (7)$$

$$\Phi_c(\text{TX-114}) = 1.967 + 0.162X_t - 0.105T - 0.003X_tT + 0.019 \times 10^{-1}X_t^2 + 0.014 \times 10^{-1}T^2 \quad (8)$$

$$\Phi_c(\text{Lutensol}) = 0.969 + 0.150X_t - 0.040T - 0.025 \times 10^{-1}X_tT + 0.001X_t^2 + 0.003 \times 10^{-1}T^2 \quad (9)$$

Extraction Results: Effects of Temperature and Nonionic Surfactant Concentration

Efficiency

Figure 3 represents the three-dimensional iso-response surfaces of the studied properties smoothed by the quadratic model (Eqs. 2–3). This figure shows that the extent of tannic acid extraction (E) increases with X_t . In this work, E reaches 95 and 74 % at 12 wt% TX-114 and Lutensol ON 30, respectively. In agreement with previous findings in other extraction systems, temperature variations have a slight effect on tannic acid extraction [49, 50, 62, 71, 73]. Hence, propitious conditions (X_t and T) for best CPE results are situated in the darkest colored zones.

In comparing Fig. 3a and b, we notice that the extent of tannic acid extraction (E) obtained using TX-114 is higher than that obtained with Lutensol ON 30. The presence of more EO units in TX-114 could provide it with higher solubilization (in the palisade) and extraction capacities towards tannic acid.

Residual Concentration of Tannic Acid ($X_{s,w}$)

Figure 4 shows that the percentage of remaining tannic acid in the dilute phase, $X_{s,w}$ decreases as X_t increases, but it increases slightly with T . Thus, beyond the cloud point, excessive heating is not favorable for CPE [62]. Hence, at propitious conditions of X_t and T (light colored zones), solute concentration reduction in the dilute phase was about 40 and 60 times using Lutensol ON 30 and TX-114, respectively.

Fig. 3 Extraction extent of tannic acid $E (%) = f(X_t, T)$, calculated by the quadratic model (Eqs. 2, 3)

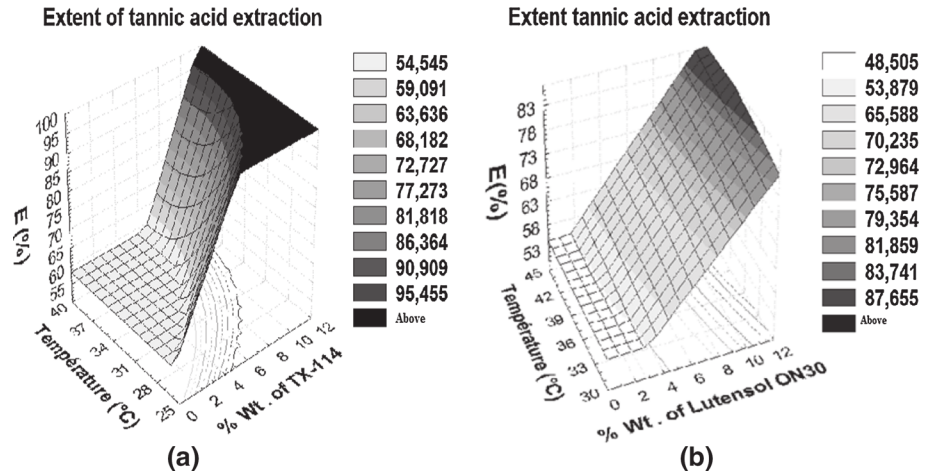
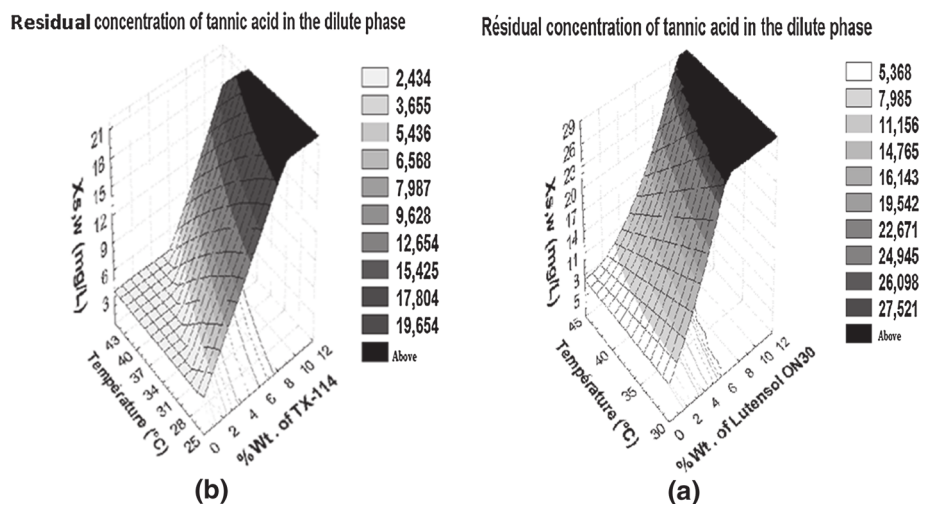


Fig. 4 Remaining concentration of tannic acid, $X_{s,w} = f(X_t, T)$, calculated by the quadratic model (Eqs. 4, 5)



Concentration of Residual Surfactant ($X_{t,w}$)

The surfactant loss in the dilute phase is a very important parameter. The process becomes inefficient if a new pollutant is detected in the dilute phase after extraction. Indeed, a biodegradable surfactant (polyethoxylated alcohol or alkylphenol) was used due to their satisfactory biodegradable activities [56, 57]. However, surfactant loss in the dilute phase is not economic even when the surfactant is biodegradable. Figure 5 represents the corresponding three dimensional iso-response curves fitted by the quadratic models (Eqs. 6, 7). It is shown that, for both surfactants (TX-114 and Lutensol ON 30) the behavior of $X_{t,w}$ is similar. This figure shows that increasing temperature (T) and lowering surfactant concentration allows residual surfactant concentration ($X_{t,w}$) reduction. Such results were obtained in previous studies with other polyethoxylated alcohols, in agreement with the lower aqueous solubility of alkoxyated nonionic surfactants at high temperature [50, 62, 63, 71]. In addition, one can see

in Fig. 5 that the residual TX-114 concentration is higher than that of Lutensol ON 30 (CMC = 0.024 mM), which is in agreement with the CMC values.

Volume Fraction of Coacervate

Figure 6a and b represent the iso-response surfaces of Φ_c vs X_t and T . When X_t increases, Φ_c increases almost linearly, due to the progressive enrichment of the coacervate in micelles. This increase in volume of the coacervate is also associated with the retention of water molecules by the hydrophilic groups of TX-114 and Lutensol ON 30. This observation was also made in previous studies using other micellar systems [49, 50, 61, 62, 71, 73–75]. So, it is advantageous to use less surfactant to have a smaller volume of coacervate. We also notice that the elevation of T reduces Φ_c , the coacervate becoming increasingly concentrated in surfactant. Indeed, the heat input tends to eliminate the hydration water molecules retained in the coacervate by hydrogen bonds with the polar head of the

Fig. 5 Remaining concentration of surfactant, $X_{t,w} = f(X_t, T)$, calculated by the quadratic model (Eqs. 6, 7)

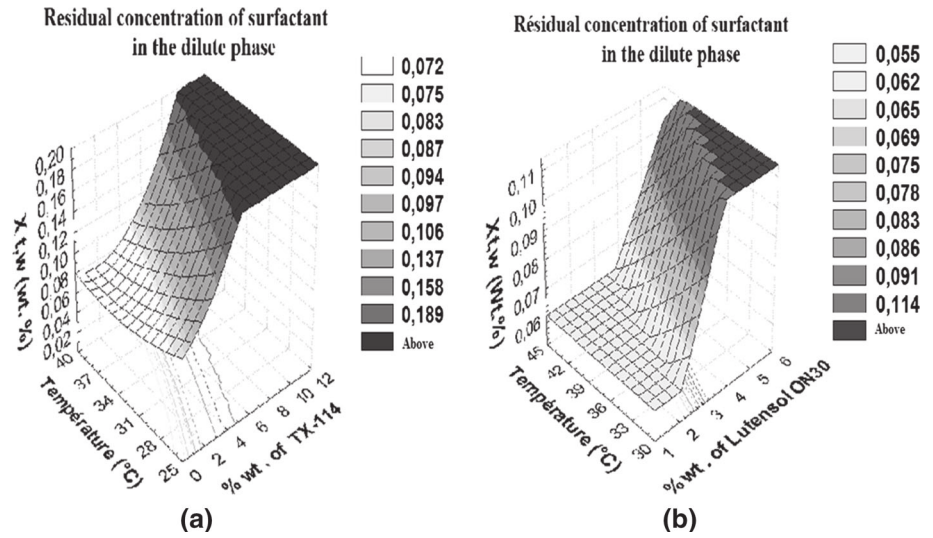
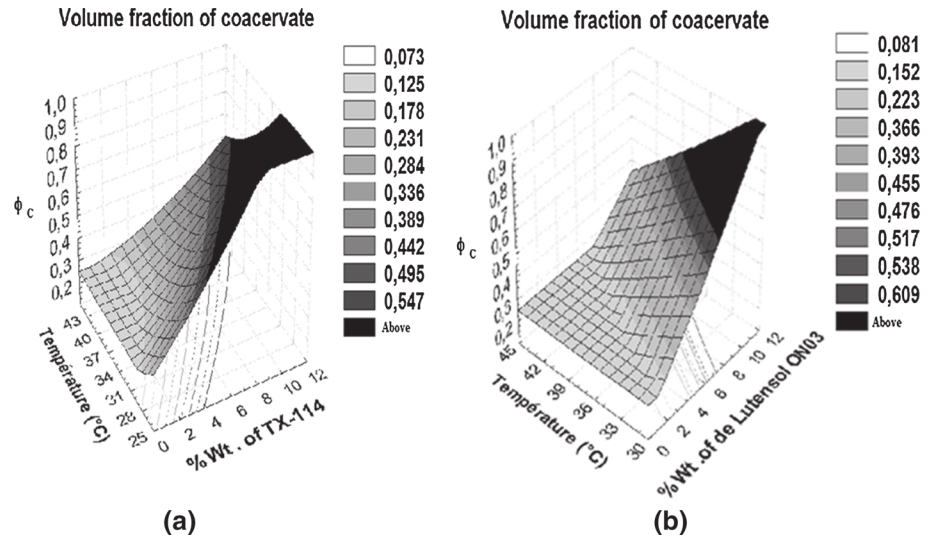


Fig. 6 Coacervate volume fraction, $\Phi_C = f(X_t, T)$, calculated by the quadratic model (Eqs. 8, 9)



surfactant (dehydration). Now, it will be essential to focus on the values of Φ_C because this parameter plays a decisive role in the implementation of the process and its progress. According to the results, the optimal Φ_C value for the couples Triton X-114/tannic acid and Lutensol 30/tannic acid is 0.03 at 45 and 40 °C, respectively.

Effect of Inorganic Salt on the Rate of Extraction, E (%)

Generally, after electrolyte addition, the organic compound solubility in water decreases. This behavior is related to the salting-out phenomenon. Thereby, hydrogen bonds between water molecule and both surfactant polar head group and tannic acid molecules become weaker than those observed in the absence of electrolyte. Hence, tannic acid and surfactant become less soluble in water and can be

easily concentrated in the coacervate [71, 73]. One can notice in Fig. 7 that electrolyte increases tannic extraction yield (E). According to [64], the presence of electrolyte in nonionic surfactant system makes it more hydrophobic and reduces thereby the critical micelle concentration (CMC) and T_c , which increases the surfactant solubilizing capacity and, consequently, improves the extraction efficiency (Fig. 7).

Extraction by Mixed Micelles

The formation of mixed micelles in the Lutensol ON 30/CTAB system is confirmed by the dramatic cloud temperature rise in the presence of cationic surfactant (Fig. 1). One can see in Fig. 8 that the extraction extent (E) of TA increases significantly with increasing CTAB concentration. Hence, additional beneficial properties can

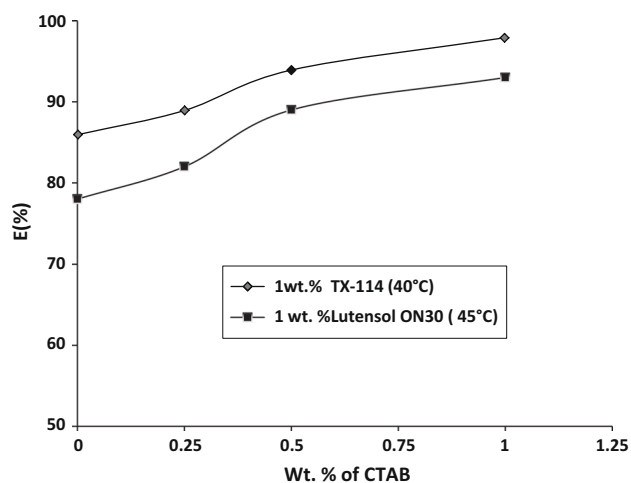


Fig. 7 Effect of Na_2SO_4 on the extraction extent of tannic acid, E (%)

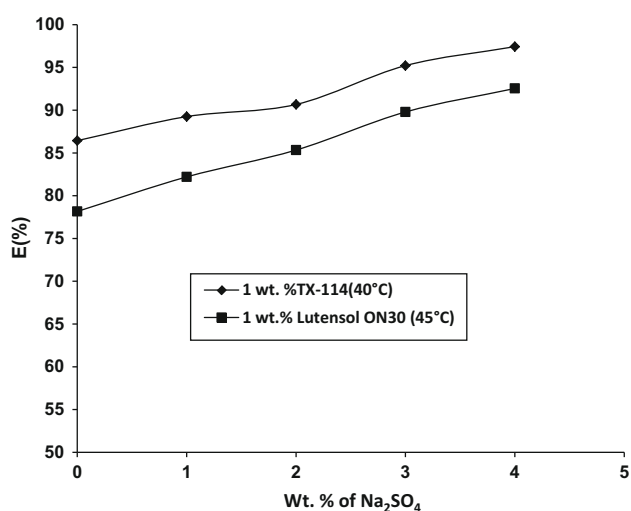


Fig. 8 Effect of CTAB on the extraction extent of tannic acid, E (%)

be observed when nonionic and ionic surfactants co-exist. The positive charge of CTAB molecules increases the affinity of the numerous electronegative phenolic oxygen atoms of tannic acid towards the micellar aggregates [76]. Such results were obtained in other systems using mixed micelles [49, 50].

Effect of pH on the Extraction Extent

The deprotonation of a weak acid or the protonation of a weak base increases the aqueous solubility of the solute and induces a reduction of surfactant-solute interactions. Under these conditions, only a small amount of ionized solute can be solubilized and extracted, unlike neutral molecules. Tannic acid is a weak organic acid ($\text{p}K_a = 10$), consequently its ionization is strongly dependent on pH.

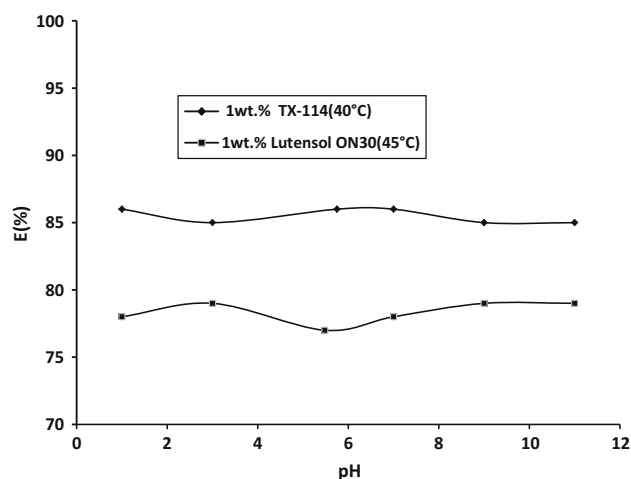


Fig. 9 Effect of pH on the extraction extent of tannic acid, E (%)

However, tannic acid extraction extent remains constant for all pH values (Fig. 9). Hence, the back-extraction of this solute from the coacervate was not possible by changing pH [77].

Winsor I Microemulsion Extraction

The results of reuse of the surfactant (coacervate of Triton TX-114) for two successive cycles after back-extraction of tannic acid using Winsor I Microemulsion extraction, are given in Table 1. The hydrophobic organic solvents, petroleum ether and cyclohexane, showed limited extractive capacity for tannic acid and most of acid was left in the W_m phase. In contrast, the more hydrophilic organic solvent, diethyl ether, extracted most of tannic acid into the excess oil phase and only two clear phases were observed.

Conclusion

The application of CPE for the removal of tannic acid from waste water is confirmed. Like other methods, this technique is capable of removing soluble pollutants from industrial effluents (Table 2). In order to optimize its operation, four parameters that control the effectiveness of this technique were analyzed, i.e. E , $X_{s,w}$, $X_{t,w}$ and Φ_c . The

Table 1 Results of regeneration of a coacervate of TX114

	Diethyl ether	Cyclohexane	Petroleum ether
Log P [70]	0.85	3.2	3.1
V (mL)	17	10	13
r (wt%)	95	85	70

V (mL) volume of excess oil phase, r (wt%) percent recovery of tannic acid

Table 2 Removal extent (%) of tannic acid with different separation methods

Separation methods of tannic acid	Removal extent (%)	References
Electrochemical oxidation	94.0	[33]
Adsorption-coagulation combined systems	87.5	[32]
Ultrafiltration and nanofiltration	78.0	[34]
Biological process	85.2	[35]
Adsorption on polyaniline adsorbent	90.0	[17]
Cloud point extraction	95.5	This work

choice of optimal conditions requires a compromise between all four parameters. Extraction percentages around 95 % for TX-114 and 87 % for Lutensol ON 30 were obtained at temperatures ranging between 40 and 45 °C, with very low coacervate volume fraction (0.03). In addition, the concentration factor of the solute can be increased when a minimal volume fraction of coacervate (Φ_c) was obtained at low X_t . Na_2SO_4 and CTAB increase the extraction extent of tannic acid but pH change shows no effect. Thereby, surfactant regeneration cannot be achieved by pH changing. Diethyl ether was selected for the stripping of organic compound from the coacervate using Winsor I microemulsion extraction.

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