



Extraction of humic acid by coacervate: Investigation of direct and back processes

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ABSTRACT

The two aqueous phases extraction process is widely used in environmental clean up of industrial effluents and fine chemical products for their reuse. This process can be made by cloud point of polyethoxylated alcohols and micellar solubilization phenomenon. It is commonly called “coacervate extraction” and is used, in our case, for humic acid extraction from aqueous solution at 100 mg/L. The surfactants used are alcohol polyethoxylate and alkylphenol polyethoxylate. Phase diagrams of binary water/surfactant and pseudo-binary are plotted. The extraction results are expressed 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). For each parameter, the experimental results are fitted to empirical equations in three dimensions. The aim of this study is to find out the best compromise between E and ϕ_c . The comparison between experimental and calculated values allows models validation. Sodium sulfate, cetyltrimethylammonium bromide (CTAB) addition and pH effect are also studied. Finally, the possibility of recycling the surfactant has been proved.

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1. Introduction

Humic substances are polyelectrolytic macromolecules having high molecular weights [1–4]. They are significant in aquatic systems for several reasons. They give yellow brown color to water [5] and can complex metals [6,7] and organic pollutants such as pesticides [8]. They are precursors to the formation of mutagenic halogenated compounds in water after chlorination [9]. Especially humic acid represents the major advantage of the natural organic matter in soil and surface water [1]. However, its presence in raw water can significantly affect the quality during the purification process [10]. It is widely agreed that trihalomethanes (THMs), one of disinfection byproducts, can be generated by step chlorination in water treatment when they contain humic acid [11]. Several researches have been carried out as an alternative for the degradation of aquatic humic substances [12–15]. Besides, different techniques for treatment of contaminated release with humic acid, have been proposed such as: biological treatment [16], filtration [17,18], adsorption [7,9], ozone oxidation [19], heterogeneous photocatalysis [20,21], coagulation and ion exchange [22], electrochemistry [23], photocatalytic treatment [24,25].

The present work concerns the study of cloud point extraction (CPE) as a method of recovery and valorization of humic acid of aqueous solution using the powerful solubilizing characteristic of nonionic surfactant aqueous solutions. In effect, above a line of low critical demixing point of such systems defined as cloud point (t_c), aqueous solutions of most nonionic polyethoxylated (or in the presence of polyethylene glycol electrolyte) form two phases: the coacervate, rich in surfactant, and the dilute phase. In the latter, the surfactant concentration is close to its critical micelle concentration (cmc). Therefore, due to the micellar solubilization property of the surfactant, hydrophobic, amphiphilic or even ionic solutes have been extracted in the coacervate after increasing the temperature above its critical value T_c . The extraction process with two aqueous phases, initially applied to the case of metal ions in the presence of chelating agent [26], was later applied to many chemical species: various metal ions, small organic molecules and biological molecules [27,28]. This technique allows moving toward Green Chemistry. The small volume of the biodegradable surfactant-rich phase obtained by using the cloud point methodology, permits to set up an experimental process of lower cost, better extraction efficiency and lower toxicity than those using organic solvents. This fact is particularly attractive, because the “Green Chemistry” concept can be employed here. CPE is considered to be convenient and environmentally safe alternative to extraction with organic solvents [28,29]. Many advantages were claimed to CPE compared to conventional liquid–liquid extraction, including high extraction

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efficiency, ease of waste disposal and the use of non-toxic and less dangerous reagents [29].

2. Materials and methods

2.1. Reagents

The surfactants used in this work are biodegradable nonionic surfactants:

- 1) A polyethoxylated octylphenol known as "Dowfax 20B102", supplied by Dow Chemical company. It has the chemical formula $C_{16-18}H_{33-37}-\Phi-(OCH_2-CH_2)_9-OH$ and belongs to the family of ethoxylated alkylphenols (EPA).
- 2) An alcohol polyethoxylate (AE) experienced by Lutensol ON 30 and equivalent to $C_{10}H_{21}(OCH_2-CH_2)_3OH$. It is provided by BASF.

These surfactants warranted great deal of research, both theoretically [30] and experimentally [25]. They are not so expensive and have excellent extraction performances. Humic acid was supplied by Sigma–Aldrich.

2.2. Methods

2.2.1. Cloud point

Aqueous solutions of ethoxylated alcohols and ethoxylated alkylphenols are sensitive to temperature, because their hydrophilic groups to desolvate gradually during heating [31–33]. The determination of cloud point was made by using the apparatus Mettler FP 900 which consists of the operating FP900, a control unit, and several measuring cells. The cell temperature measurement is performed with a highly accurate sensor Pt100 (probe), integrated in the body of a furnace. In the lower part of the cloud point measuring cell, PF81C is a light source and an optical fiber which illuminates the three specimens. The light passing through the specimens is converted by three photoelectric cells into electrical signals proportional to the intensity remains. The light transmission is measured continuously while the cell temperature increases linearly with the heating rate chosen. The cloud point designates the temperature at which the single limpid phase is troubled, as a result of the appearance of a second phase.

For the extraction tests, 10 mL of solution containing the surfactant concentrations (1–12 wt.%) and the solute (humic acid at 100 mg/L) in deionized water, were heated in a precision oven for 2 h to reach equilibrium. The heating temperature range was chosen from the cloud point temperature to about 20 °C. In effect, for the surfactant Lutensol ON 30, the temperature range is (27–47 °C) while that for Dowfax20B102 is (33–53 °C). The volumes of both phases were registered. A small amount of the dilute phase was taken using a syringe and analyzed.

2.2.2. Analysis

The concentration of Dowfax 20B102 in the dilute phase was achieved by high performance liquid chromatography reverse phase, under the following conditions: RP18 column (ODS), 95 bar pressure, eluent $H_2O/CH_3CN/CH_3OH$, 7.5/60/32.5 (vol.%), flow rate 1 mL/min and 260 nm wavelength detector (UV).

For Lutensol ON 30, the light scattering detector LS 31 (EUROSEP instruments) was used. The three parameters to optimize the sensitivity of the detector were the flow of air into the nebulizer, the temperature of the evaporator and the gain of the photomultiplier. During the analysis, the air pressure was set to 1 bar, the evaporator temperature fixed at 55 °C and the gain of photomultiplier was

equal to 400 mV. Humic acid concentration was determined using the spectrophotometer (SAFAS type MC2) at 400 nm.

3. Results and discussion

3.1. Binary and pseudo-binary phase diagrams

Organic solubilizes can interact with the surfactant polar head group or with its hydrophobic length after solubilization in micelles. According to their chemical nature, organic compounds can vary the surfactants cloud point [31,34]. The cloud point increasing of Lutensol ON 30 and Dowfax 20B102 surfactants by humic acid addition, this phenomenon is especially noticeable for low surfactant concentrations. This indicates a significant interaction between humic acid and the surfactant. Indeed, the surfactants solubility in water was increased by inducing the cloud point increase [34,35]. Furthermore, even at very low concentration (0.1 wt.%), the presence of CTAB significantly enhances the cloud point of Lutensol ON 30. To explain this phenomenon, various mechanisms have been suggested including formation of micelles, solubilization and complex formation. The incorporation of ionic surfactant into the nonionic micelles causes electrostatic repulsion between the micelles, thus hindering the coacervate phase formation and raising up the cloud point [36,37].

4. Modeling of extraction

The extraction results of humic acid from its aqueous solutions at 100 mg/L by different surfactants, according to two variables: wt.% surfactant (X_t), and temperature (T), were expressed by three responses (Y): percentage of extracted solute (E), residual concentrations of solute ($X_{s,w}$) in the dilute phase and the coacervate volume fraction at equilibrium (ϕ_C) [34,38]. For each parameter determined and by considering central composite designs [39], the results were analyzed 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 computing data against experimental results. The quadratic correlation was chosen to give the slope and the regression coefficient (R^2) closer to unity.

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

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

The quadratic equations for the properties (E , $X_{s,w}$, $X_{t,w}$ and ϕ_C), whose reliability was checked, are as follows:

$$E_{(\text{Dowfax})} = 26.993 + 11.314X_t + 1.21T - 0.103X_tT - 0.395X_t^2 - 8.788 \cdot 10^{-3}T^2 \quad (2)$$

$$E_{(\text{Lutensol})} = 14.687 + 5.592X_t + 2.607T - 0.033X_tT - 0.216X_t^2 - 0.027T^2 \quad (3)$$

$$X_{s,w}(\text{Dowfax}) = 106.276 + 0.063X_t - 2.92T - 0.125X_tT + 0.344X_t^2 + 0.03T^2 \quad (4)$$

$$X_{s,w}(\text{Lutensol}) = 83.753 - 2.485X_t - 2.543T - 0.051X_tT + 0.225X_t^2 + 0.027T^2 \quad (5)$$

$$X_{t,w(\text{Dowfax})} = 106.276 + 0.063X_t - 2.92T - 0.125X_tT + 0.344X_t^2 + 0.03T^2 \quad (6)$$

$$X_{t,w(\text{Lutensol})} = 0.506 + 0.035X_t - 0.023T - 1.046 \cdot 10^{-3}X_tT - 1.159 \cdot 10^{-3}X_t^2 + 3.11 \cdot 10^{-4}T^2 \quad (7)$$

$$\phi_{C(\text{Dowfax})} = 0.403 + 0.479X_t - 0.027T - 0.009X_tT - 0.001X_t^2 + 4 \cdot 10^{-4}T^2 \quad (8)$$

$$\phi_{C(\text{Lutensol})} = 0.2939 + 0.0009X_t - 0.0136T - 0.002X_tT - 0.0054X_t^2 - 0.0006T^2 \quad (9)$$

4.1. Extraction efficiency

Fig. 2 represents the three-dimensional isoresponse curves of the studied properties smoothed by the quadratic model (Eqs. (2) and (3)). Fig. 3a shows that the extent of humic acid extraction (*E*) increases with *X_t*. In this work, *E* reaches 98% for 10% Lutensol ON 30. However, the temperature increase has slight effect of humic acid extraction. This trend was also observed by other researchers in other extraction systems [34,35,38]. Indeed, the temperature raise induces simultaneous and opposite effects: it increases the concentration of solute in the micellar aggregates as a result of the decrease of (*φ_C*) [38]. Besides, one can notice that the extraction extent obtained with Lutensol ON 30, is higher than observed using Dowfax 20B102. The presence of a benzene ring in the hydrophobic chain of Dowfax 20B102, seems to have a negative effect on humic acid solubilization.

4.2. Concentration of residual humic acid (*X_{s,w}*)

Fig. 3 represents the three-dimensional isoresponse curves of the studied property (*X_{s,w}*), smoothed by the quadratic model (Eqs. (4) and (5)). In this figure, it is shown that the concentration of humic acid in the dilute phase *X_{s,w}* decreases as *X_t* and *T* increase. Hence, the first contact between the surfactant and the effluent solutions, allows solute concentration reduction to about 10 and

60 times using Dowfax 20B102 and Lutensol ON 30, respectively (Table 1).

4.3. Concentration of residual surfactant (*X_{t,w}*)

The concentration of residual surfactant (*X_{t,w}*) is a very important parameter. The high loss of surfactant in the dilute phase can compromise the process reliability. Indeed, the presence of another contaminant in the dilute phase, is sufficient to make the process useless. Although these surfactants are known by their good biodegradability proprieties, it would be detrimental to squander them in the dilute phase.

The behavior of (*X_{t,w}*) according to *X_t* and *T* is shown in Fig. 4 (smoothed by the quadratic model Eqs. (6) and (7)). This figure shows that the residual concentration of surfactant is low at high temperature and low surfactant concentration. These results are in good agreement with previous studies using polyethoxylated alkylphenols [37] as well as other polyethoxylated alcohols [38]. Indeed, the heating desolvates gradually the surfactant hydrophilic groups and thus it reduces its hydrophilic character. In general, the desolvation energy of the surfactant molecule can be associated with its energy transfer from the hydrophilic (aqueous solution) to the hydrophobic medium (micellar system). One can notice in Fig. 4 that the remaining concentration of Lutensol ON 30 in the dilute phase after the extraction, is higher than that obtained using Dowfax 20B102. Such result can be explained by the fact that the cmc of Lutensol ON 30 (cmc = 0.2 g/L) is higher than that of Dowfax 20B102 (cmc = 0.08 g/L). Hence, Lutensol ON 30 is more soluble in water than Dowfax 20B102.

4.4. Volume fraction of coacervate

In order to increase the concentration factor of solute, a minimal volume fraction of coacervate (*φ_C*) should be obtained when temperature increases. In effect, according to Fig. 5, the smoothed value of *φ_C* using Eqs. (8) and (9) is low at high temperature and low surfactant concentration. However, high surfactant concentrations induce more surfactant loss in the dilute phase (Fig. 4). Although the surfactant is biodegradable, this loss is not economical. So the optimization of the process needs to compromise between the four studied parameters *E*, *X_{s,w}*, *X_{t,w}* and *φ_C*. It should be pointed out that this observation had also been done either by us and others [34,37,38,40]. Indeed, less surfactant concentration should be used to have a smaller volume fraction of coacervate. On the basis of this finding, optimal values of *φ_C* (i.e. 0.1 and 0.3) were obtained using 4 wt.% Dowfax 20B10 and 4 wt.% Lutensol ON 30 at 50 °C and 40 °C, respectively.

Table 1
Some experimental results of the extraction parameters (*E*, *X_{s,w}*, *φ_C*, *R²* and *X_{s,0}/X_{s,w}*).

| [<i>X_T</i> (wt.%), <i>T</i> (°C)] | <i>E</i> (%) | <i>X_{s,w}</i> (mg/L) | <i>X_{t,w}</i> (wt.%) | <i>φ_C</i> | <i>X_{s,0}/X_{s,w}</i> ^a |
|---|-------------------------------|-------------------------------|-------------------------------|-------------------------------|---|
| Lutensol ON 30 | <i>R</i> ² = 0.994 | <i>R</i> ² = 0.990 | <i>R</i> ² = 0.968 | <i>R</i> ² = 0.957 | |
| [2, 30] | 76.681 | 23.319 | 0.102 | 0.060 | 4.288 |
| [2, 36] | 79.864 | 20.136 | 0.090 | 0.050 | 4.966 |
| [2, 42] | 81.080 | 18.920 | 0.078 | 0.050 | 5.285 |
| [6, 36] | 92.201 | 7.799 | 0.087 | 0.200 | 12.822 |
| [6, 42] | 94.027 | 5.973 | 0.072 | 0.070 | 16.742 |
| [10, 42] | 98.340 | 1.660 | 0.115 | 0.050 | 60.240 |
| Dowfax 20B102 | <i>R</i> ² = 0.989 | <i>R</i> ² = 0.995 | <i>R</i> ² = 0.959 | <i>R</i> ² = 0.962 | |
| [1, 36] | 67.026 | 32.974 | 0.024 | 0.075 | 3.032 |
| [1, 42] | 70.012 | 29.988 | 0.021 | 0.050 | 3.334 |
| [1, 48] | 71.089 | 28.911 | 0.012 | 0.030 | 3.458 |
| [5, 42] | 88.102 | 11.898 | 0.041 | 0.300 | 8.404 |
| [5, 48] | 89.017 | 10.983 | 0.023 | 0.100 | 9.104 |
| [9, 48] | 92.287 | 7.713 | 0.051 | 0.150 | 12.965 |

^a *X_{s,0}* = 100 mg/L (initial concentration of humic acid).

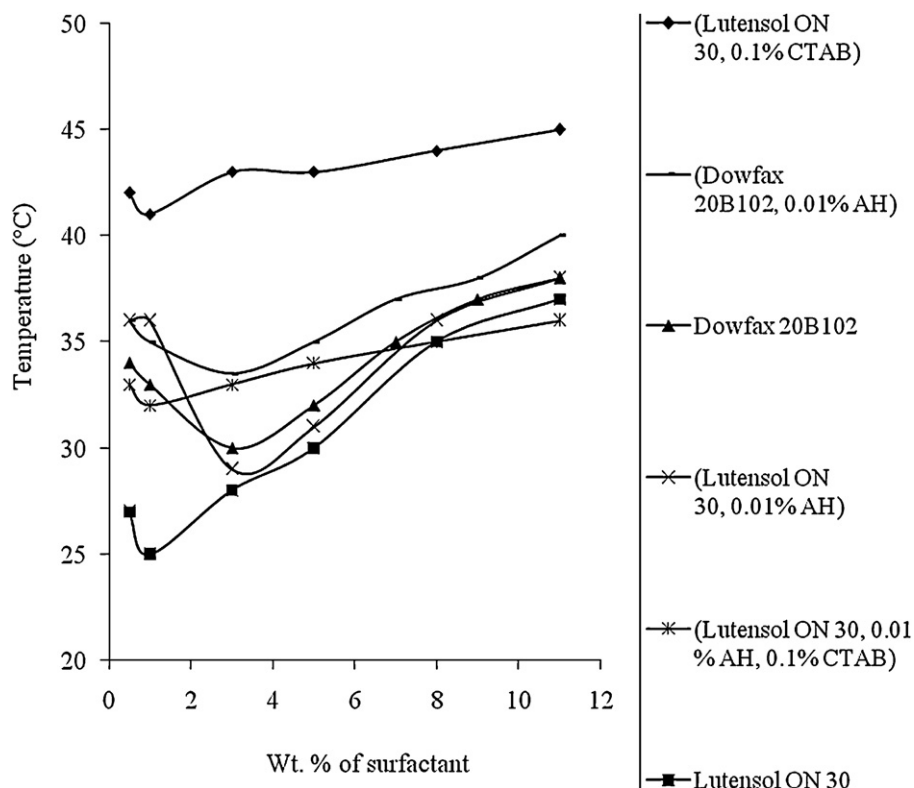


Fig. 1. Effect of humic acid and CTAB on the cloud point of Lutensol ON 30 and Dowfax 20B102.

5. Parameters affecting extraction efficiency

5.1. Effect of sodium sulfate

One can see clearly in Fig. 6 that the electrolyte increases the extraction extent (E%) of humic acid. The presence of the electrolyte induces a decrease in the solubility of humic acid in water by salting-out phenomenon. According to Saito and Shinoda [41], the addition of electrolyte to non-ionic surfactant solutions increases their hydrocarbon solubilization capacity, by lowering cmc. This behavior may be the result of an increase in micellar number in

the presence of electrolyte. So, the addition of electrolyte to non-ionic surfactants solutions increases their solubilization capacity toward organic solute and consequently improves the efficiency of its coacervate extraction (Fig. 6).

5.2. Effect of cetyltrimethylammonium bromide (CTAB): extraction by mixed micelles

When nonionic and ionic surfactant co-exist together, they interact and provide additional beneficial properties to the system. This interaction results in most cases by a specific association and

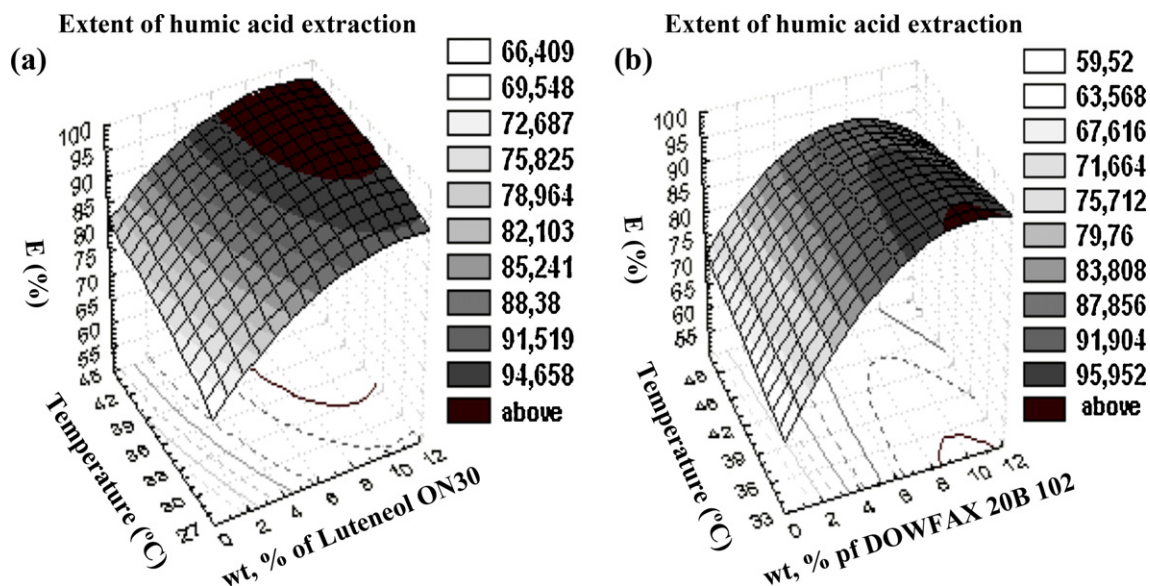
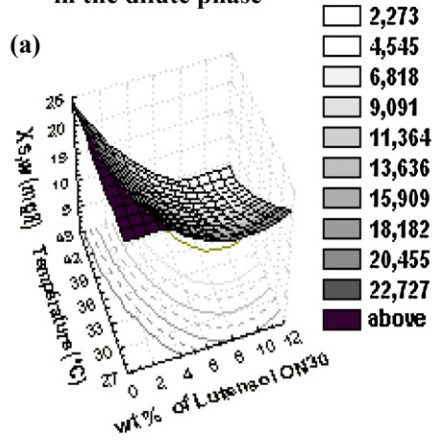


Fig. 2. Three-dimensional isoresponse curves smoothed by a quadratic model, $E(\%) = f(X_i, T)$, calculated by the quadratic model (Eqs. (2) and (3)).

Residual concentration of humic acid in the dilute phase



Residual concentration of humic acid in the dilute phase

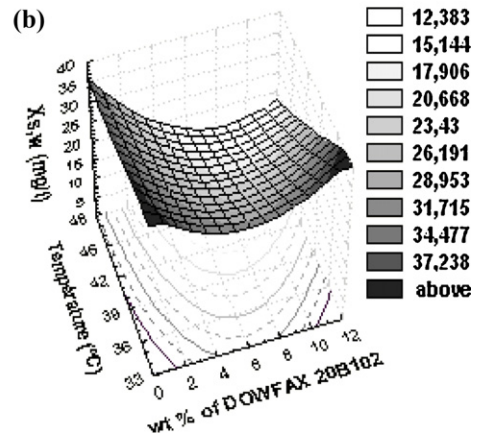
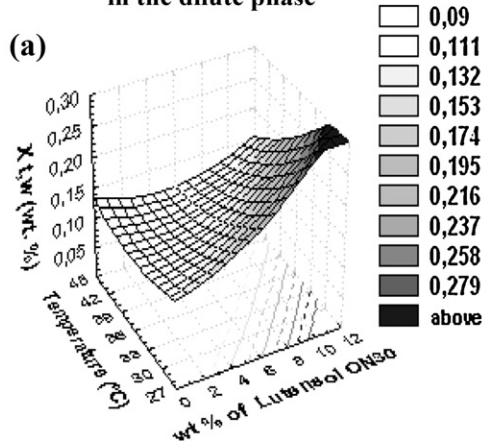


Fig. 3. Three-dimensional isoresponse curves smoothed by a quadratic model, $X_{s,w} = f(X_i, T)$, calculated by the quadratic model (Eqs. (4) and (5)).

Residual concentration of surfactant in the dilute phase



Residual concentration of surfactant in the dilute phase

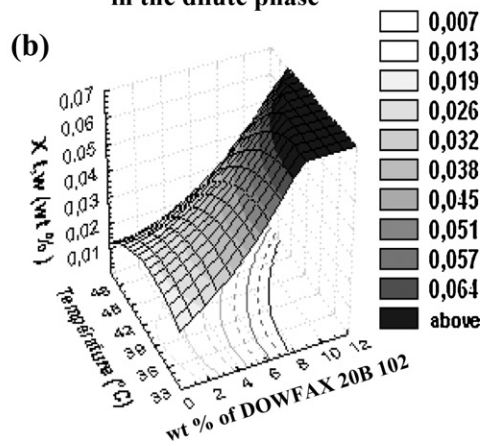
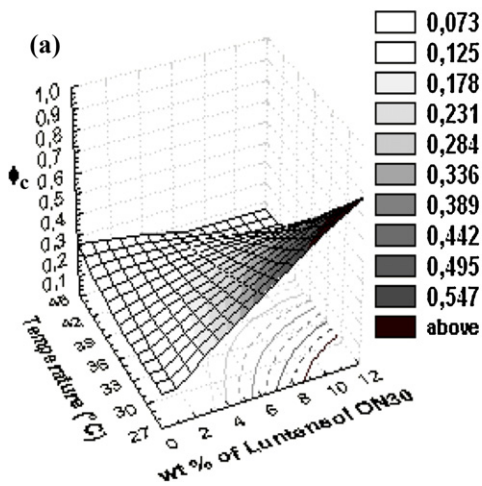


Fig. 4. Three-dimensional isoresponse curves smoothed by a quadratic model, $X_{t,w} = f(X_i, T)$, calculated by the quadratic model (Eqs. (6) and (7)).

Volume fraction of coacervate



Volume fraction of coacervate

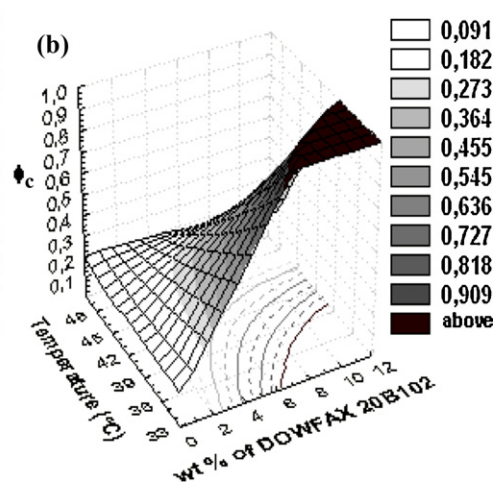


Fig. 5. Three-dimensional isoresponse curves smoothed by a quadratic model, $\phi_c = f(X_i, T)$, calculated by the quadratic model (Eqs. (8) and (9)).

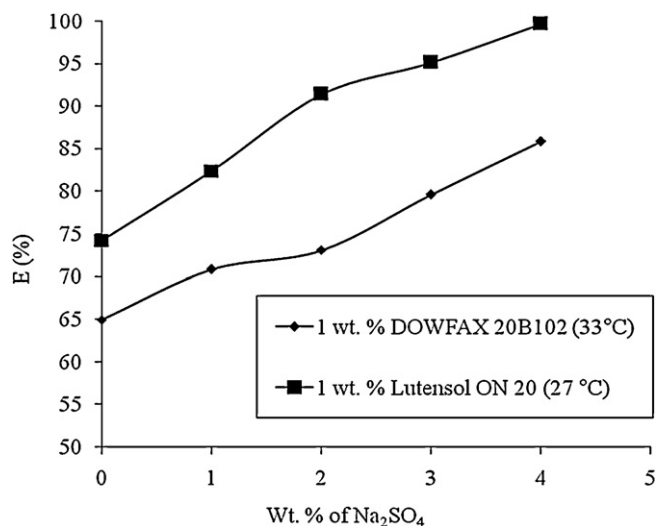


Fig. 6. Effect of the Na₂SO₄ on the extraction extent of humic acid (E%).

the formation of new and original structures that can lead to synergistic effects. These micelles are known as “mixed micelles”. The cloud temperature analysis (Fig. 1) allows us to confirm the formation of mixed micelles. One can see clearly that the cloud point of 1 wt.% Lutensol ON 30 rises dramatically in the presence of CTAB.

Mixed micelles have positive effects on the extraction ratio of humic acid (E%). One can see in Fig. 7 that E increases significantly with increasing CTAB concentration. The positive charge of CTAB molecules increases the affinity of the negatively charged humic acid toward the micellar aggregates [42], such results was obtained in other systems using mixed micelles [37].

5.3. Effect of pH on extraction rate of humic acid: recycling of surfactant

Humic substances are mixtures of weak acid polyelectrolytes, widely spread out in soil and natural aquatic environments [37,43]. Following the complexity of their chemical nature, a large number of models have been developed to describe their acid-base properties [44,45]. Models known as continuous distribution of acidity constants values (expressed in terms of $pK_i = -\log K_i$), have been developed. In this model, the acidity distribution of humic

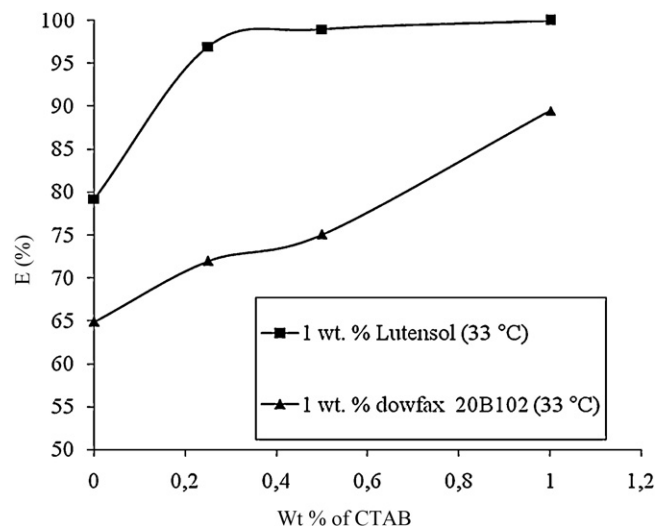


Fig. 7. Effect of CTAB on the extraction extent of humic acid (E%).

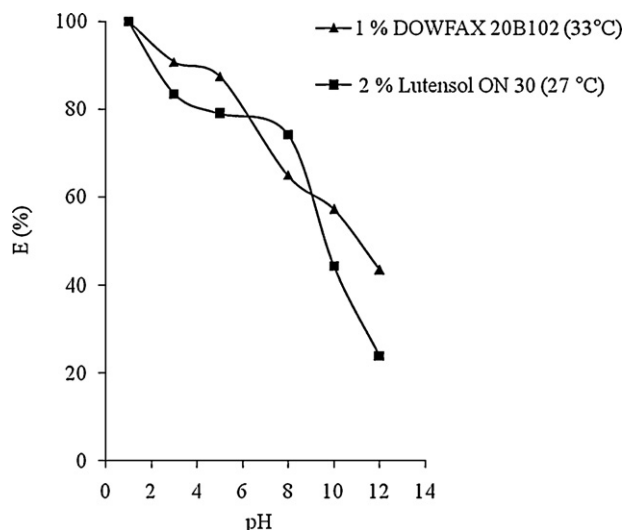


Fig. 8. Effect of pH on the extraction extent of humic acid (E%).

substances molecules may be expressed by several functions [46–48]. Posner [48] showed that the dissociation constants of humic acid can be described by a model of pK_i values distribution of its acid sites ($4.0 \leq pK \leq 9.0$), whereas the relative concentration of each site is normally distributed according to the pK_i values.



It is also well known that the solute–micelle interactions are strongly influenced by solute ionization [38]. After the deprotonation of a weak acid or the protonation of a weak base, slight interactions may occur with the surfactant. In these conditions, a small amount of those species may solubilize, unlike neutral molecules. Consequently, a small amount of ionized solute can be extracted.

In Fig. 8, the results show that the distribution of humic acid between aqueous and surfactant-rich phase, depends greatly on the solution acidity. The extraction ratio (E%) increases when the pH decreases (Fig. 8). This behavior can be explained by the transformation of humic acid to the neutral molecular form at acid pH. The neutral form of humic acid interacts strongly with the micellar aggregates of nonionic surfactant. This phenomenon was also observed with fulvic acid ($pK_a = 4.15$) [49]. Hence, separation of humic acid is favored by acid pH.

Indeed, pH is the key-parameter for surfactant regeneration. Several works have been done on the recycling and recovery of surfactant solution after the extraction steps, by a simple pH control [38,50,51]. This requires two steps: the first one concerns the back-extraction of solutes from coacervate while the second one relates to the regeneration of the surfactant.

After a first extraction process of humic acid (as weak acid) at 4 wt.% of Lutensol ON 30 and 40 °C, the coacervate pH was increased beyond its pK_a equal to 9.0, using Ca(OH)₂ to give a complete dissociation of the solute (Table 2) [38,48]. Hence, 87.15% of humic acid extracted at 40 °C can be released from the coacervate to a new dilute phase (at 75 °C and pH 12.4). It is the maximum pH which can be reached using Ca(OH)₂ with a solubility limit of 1.53 g/L [52].

Moreover, the previous coacervate was separated into two new phases at 75 °C: a small quantity of the aqueous phase containing the concentrated solute, and a new coacervate phase containing most of the surfactant. In order to use the surfactant again, it is necessary to decrease its pH and to precipitate the base (Ca(OH)₂). Therefore, it is better to choose an acid forming an insoluble salt with the base cation, such as H₂C₂O₄.

Table 2
Conditions for regeneration of coacervate.

| [Ca(OH) ₂] (g/L) in the coacervate | pH of coacervate | Concentration (mg/L) of humic acid release from the coacervate |
|--|------------------|--|
| 0 | 7.62 | 13.60 |
| 0.05 | 8.24 | 26.15 |
| 0.12 | 9.56 | 31.14 |
| 0.24 | 10.08 | 38.89 |
| 0.36 | 11.12 | 46.72 |
| 0.65 | 11.56 | 57.06 |
| 0.75 | 11.89 | 72.62 |
| 1.25 | 12.21 | 75.24 |
| 1.53 | 12.40 | 77.91 |

Table 3
Results of three cycle regeneration of Lutensol ON 30 coacervate.

| Settings | Surfactant from the first back extraction | Surfactant from the second back extraction | Surfactant from the third back extraction |
|---------------------|---|--|---|
| Es (%) | 96.587 | 81.298 | 69.758 |
| X _{Ts} (%) | 11.23 | 10.13 | 8.97 |
| Et (%) | 93.58 | 84.41 | 74.75 |

Table 3 summaries the results of surfactant reuse for three successive cycles after back-extraction of humic acid, solubilized in Lutensol ON 30 micelles. The first stage extraction was performed at 40 °C using 10 wt.% of surfactant whereas the back extraction was achieved at 75 °C. One can notice that the extraction extent (Es%) recovered after humic acid release at pH 12.4 using fresh surfactant, is higher than that obtained with recycled surfactant. As the back extraction of humic acid is around 87% at pH 12.4, micelles keep 13% of the humic acid concentration at each extraction/back-extraction stage. Therefore, Es decreases using recycled surfactant. Table 3 shows also that the surfactant concentration obtained after humic acid release from coacervate (X_{Ts}%), decreases after the surfactant recycling. Indeed, at each extraction/back-extraction stage, a small amount of surfactant is lost in the dilute phase, inducing a lower surfactant recovery percentage.

6. Conclusion

Coacervate extraction was used to separate humic acid from water. The best compromise between the parameters governing the extraction effectiveness (surfactant concentration and temperature) was found using a suitable experimental design and three-dimensional empirical curve fitting. The study showed that cloud point extraction technique was able to remove soluble pollutants from effluent. Extractions at temperatures ranging between 40 °C and 50 °C, allowed to obtain the extraction extents 94% and 97% using 4 wt.% of Dowfax 20B102 and Lutensol ON 30 respectively. Whereas low surfactant concentration (<5 wt.%) should be used to have smaller volume fraction of coacervate. Na₂SO₄ and CTAB increased the extraction extent of humic acid. The extraction of the solute was high at acid pH range. Moreover, extraction extent obtained with Lutensol ON 30 was higher than that using Dowfax 20B102. However, humic acid was less extractible at pH above its pK_a. Indeed, the pH can be a key-parameter for surfactant regeneration in cloud point extraction process of humic acid. The surfactant recycling in a cloud point extraction process seems to be possible at pH > pK_a of the solute.

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