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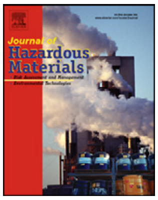

Extraction of humic acid by coacervate: Investigation of direct and back processes

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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 $\phi_{C.}$ 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.

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 $C_{16-18}H_{33-37}$-Φ-$(OCH_2{-}CH_2)_9{-}OH$ 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 désolvate 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 solubilizates 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.

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

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:

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

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

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

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