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An efficient cloud point extraction of mixed organic-inorganic pollutants using an ionic liquid as extractant: separation of the red Bemacid dye from nickel (II) in saline medium and optimization through factorial design methodology

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ABSTRACT

This study concerns to the cloud point extraction of red Bemacid dye from an aqueous solution sulfate medium without and with nickel (II) presence using 1-butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl) imide ($BMIM^+$, NTf_2^-) ionic liquid as extractant in the presence of a nonionic surfactant (Triton X-100). A two-level factorial design and response surface methodology was used to evaluate the effects of parameters affecting extraction efficiency: pH (4.0–8.0), mass % of Triton X-100 (2%–10%), Na_2SO_4 (8%–10%) and red Bemacid dye concentration (10–100 ppm). Mathematical model has been developed to predict the effect of each variable and their interactions in the response (dye removal). A comparison between the predicted values using the model equation and the experimental values showed correlation coefficients higher than $R^2 > 0.998$. The response of factorial design (dye removal) showed a high elimination of dye removal with a yield of elimination of 96%. The study of mixture "red Bemacid dye and Ni^{2+}" shows that the selectivity of cloud point extraction was 100% for the red Bemacid dye and 0% for Ni^{2+}.

Keywords: Red Bemacid dye; Cloud point extraction; Triton X-100; Nickel; Selectivity; Sulfate medium

1. Introduction

Textile industries release toxic and carcinogenic chemicals in its aqueous effluents causing environmental and economic problems [1–3]. Nowadays, synthetic organic dyes are found in various fields, but especially in the textile industry. The reversing dyes in nature cause injury to human health and affect the environment [4]. The presence of dyes in wastewater, generated by the textile industries, even at low concentrations of 1 mg L^{-1}, leads to the alteration of the esthetic properties and transparency of public effluents, having a direct repercussion on the environment [5]. Dyes removal from industrial effluents is a big challenge since most dyes are light and heat stable, rich in organic matter, present a complex aromatic structure and most of them are not biodegradable [6,7]. The discharge of industrial wastewaters containing nickel (II) to the environment has been on the increase as a result of rapid intensification of industries. Numerous techniques have been used for the removal of heavy metals from industrials effluents such as: ion exchange, reverse osmosis, adsorption, precipitation, phyto-extraction, ultra-filtration and cloud point extraction (CPE) [8,9].

The later method has been reported [10] to be an efficient extraction method for dyes and metals. This method requires small amount of relatively non-flammable and non-volatile surfactant and uses a small quantity of solvent, being friendly with the environment [2,11].

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Ionic liquids present unique properties such as non-volatility (negligible vapor pressure), thermal stability, non-flammable nature, lower reactivity and a strong ability to dissolve a large variety of organic and inorganic compounds. Due to this, thorough studies should be made on the extraction of rare earth (lanthanides plus Sc and Y) and heavy metals [12–17]. The high density of imidazolium-based ILs relative to water makes them excellent extractants. The difference typical density between ionic liquids and water, favors rapid settling in phase-separation devices [18]. On the other hand, their miscibility with water can be complete or partial. This behavior is mainly due to the nature of the anion, which forms hydrogen bonds.

In this study, azoic red Bemacid from textile industry (Soitex-Algeria), was tried to pre-concentrate and eliminate using CPE. The main parameters affecting the removal of the dye were studied. Factorial experimental design methodology of 2^4 was used in the statistical planning of experiments, in order to obtain linear empirical relationship linking the response of the process (extraction yield) to four factors: initial pH, Triton X-100, Na_2SO_4 and the red Bemacid concentration in the presence of $BMIM^+$, NTf_2^- (100 ppm). The aim of this study was the comparison between the extraction of red Bemacid in an aqueous medium without and with Ni^{2+} (mass ratio of 4%) and observation of the metal effect on dye extraction.

2. Materials and methods

2.1. Materials and instruments

T-Octylphenoxypolyethoxyethanol (Triton X-100; $n = 9{,}10$ with HLB = 13.5), the critical micelle concentration (CMC) of Triton X-100 is 3.0×10^{-4} M (at 25°C) and the cloud point at 1 wt.% in water was 68°C; 1-Butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl) imide ($BMIM^+$, NTf_2^-) ionic liquid; $NiSO_4.7H_2O$, H_2SO_4; NaOH. The pH values of the solutions were adjusted in the range 4–8 by adding sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) as appropriate. Sodium sulfate (Na_2SO_4) was used to lower the cloud temperature and to facilitate at room temperature (25°C).

All reagents were provided by Sigma-Aldrich (Sarl Prochima Sigma –Tlemcen Algeria).

The red Bemacid N-TF is a dye (λ_{max} = 505 nm, $C_{24}H_{20}ClN_4NaO_6S_2$, M = 583.0 g mol^{-1}), water-soluble due to the presence of sulfonate or carboxylate groups. It is often difficult to know the chemical composition of this dye, since the confidentiality of the chemical composition is generally preserved [19]. Currently, the textile industry of Soitex (Tlemcen, Algeria), has filed trademarks that give no indication of the structure, but characterize the processes of nuance and application. The fiber–dye affinity is the result of ionic bonds between the sulfonic acid portion of the dye and the amino groups of the textile fibers. Stock dye solutions (200 mg L^{-1}) were prepared by dissolving 2 g of dye in 1 L of distilled water. Experimental solutions of desired concentration were obtained by further dilution. The pH measurements were made by a pH meter Hanna instruments (France). Stirring was provided by a mechanic stirrer type Vortex. Weighs are made with an electronic analytical balance type Carat Series OHAUS Item: PAJ1003. Dosing of the dye and the nickel (II) was carried out using a UV/Visible spectrophotometer, type SPECORD 210/Plus, Tlemcen-Algeria (λ_{max} = 396 nm for Ni^{2+}).

2.2. Procedure

Extraction of the red Bemacid dye in an aqueous medium using CPE (Fig. 1) was carried out in 10 mL graduated tubes in which the nonionic surfactant (Triton X-100) was mixed with the extracting agent ($BMIM^+$, NTf_2^- as an ionic liquid LI) and the salt (sodium sulfate). The mixture was stirred and left to stand in rest for 24 h at room temperature. After this time, the coacervate phase was separated from the diluted phase. The dye present in the diluted phase is then measured using a UV–VIS spectrophotometer. The extraction of dye from the mixture solution "red Bemacid-Nickel" was realized with 4% w ($NiSO_4.7H_2O$). After 24 h, the diluted phase was analyzed (Nickel, Bemacid red).

3. Results and discussion

Factorial experimental design methodology is able to study the effect of each variable (factor) and also to detect the possible interactions between factors with a reasonable number of experiments [20]. In this investigation for quantification of the effects of four variables on the dye removal, a two-level factorial design (low and high) of experiments was adopted. Fig. 2 shows the graphs of surface response of dye extraction and the effects of the different factors on its efficiency.

3.1. Factorial design study

The study of the effects at two levels based of the factorial design of 2^4 experiments of the four factors: pH (P), Triton X-100 (T), sodium sulfate (S) and initial dye concentration (D) is shown in Table 1. Without addition of IL, in Fig. 3 can be seen that in the range of 1%–10% of Triton X-100, the cloud temperature was 63°C. The concentration of IL was fixed at 100 ppm. Beyond this concentration, the cloud point increases (Fig. 4).

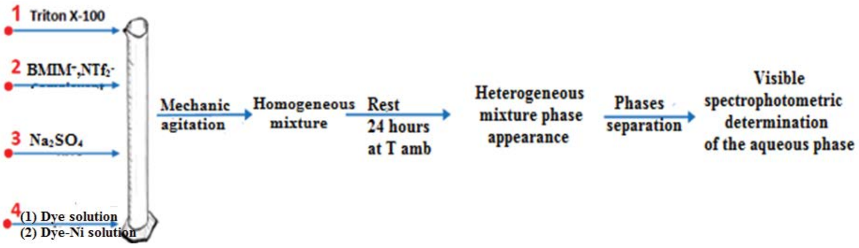
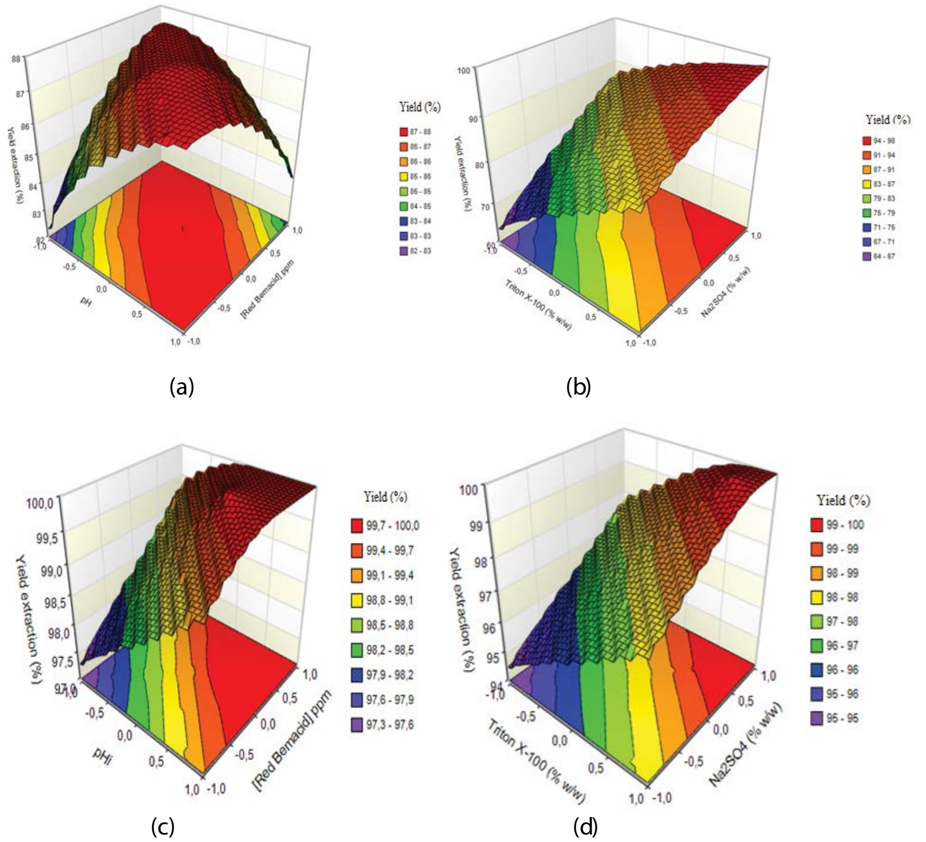


Fig. 1. Procedure adopted for the study of the extraction of dye without Ni^{2+} and with Ni^{2+} by coacervate.



(a) (b)

(c) (d)

Fig. 2. Three-dimensional isometric response curves smoothed by a simple mathematical model (Eqs. (3) and (4)): (a)and (b) red Bemacid without Ni^{2+}/(c) and (d) red Bemacid in presence of Ni^{2+}.

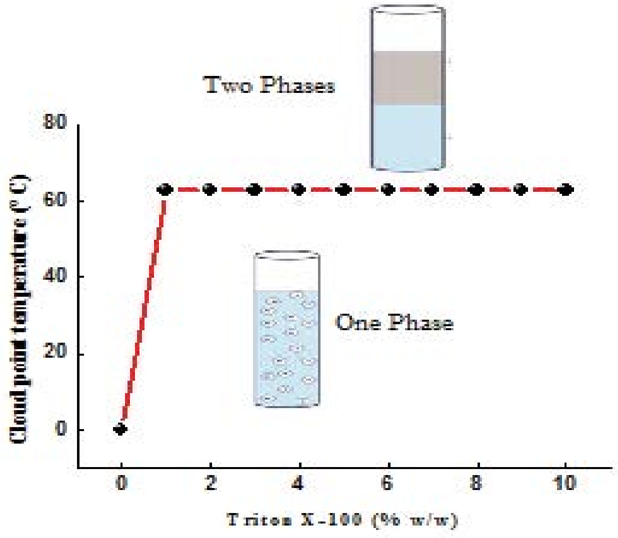


Fig. 3. Influence of the nonionic surfactant (Triton X-100) on the cloud point temperature.

Table 1
Basis of the factorial design of 2^4 experiments

Settings	Reduced variable	Value of the actual variable		
		Minimum	Average	Maximum
pH (*P*)	X_1	4	6	8
Triton X-100 (*T*)	X_2	2	6	10
Na_2SO_4 (*S*)	X_3	8	9	10
Initial dye concentration (*D*)	X_4	10	55	100

The sample solutions used for the cloud point determination were prepared by directly mixing 2% Triton X-100 and different concentrations of the ionic liquid in graduated tubes with a total volume of 10 mL, then homogenized and placed in a bath thermostatic by varying the temperature of 5°C every 30 min. When the solution has become cloudy, the temperature T_c increases sharply with the increase in ionic liquid concentrations. In the range 0–500 ppm of IL, the T_c increases from 63°C to 90°C.

Fig. 4 indicates that the cloud point of Triton X-100 increased by addition of the ionic liquid. It is known that turbidity is obtained around the CMC so that its addition can alter/modify favorably the physicochemical properties of such systems [21].

The hydrophobicity deficiency leaves the ionic liquid close to the micelle–water interface while preventing penetration into the Triton X-100 micelle and replacement of the

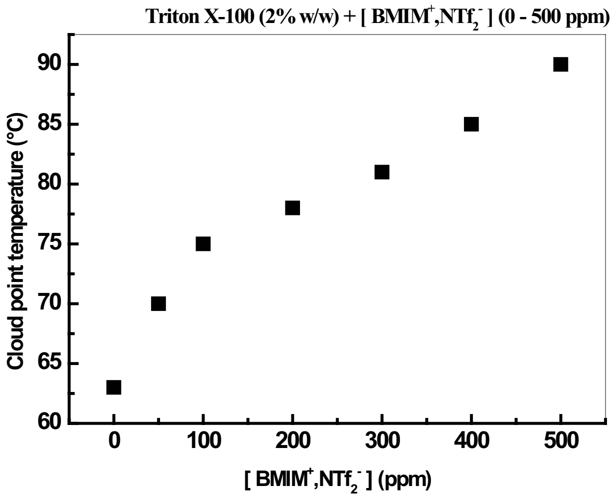


Fig. 4. Effect of IL on the cloud point temperature.

nonionic surfactant monomers. Nevertheless, an increase in the cloud point caused by the hydrogen bond between H of the imidazolium ring and O of the oxyethylene chain of Triton X-100 cannot be neglected [22,23].

CMC, micelle size, aggregation numbers are the key physicochemical properties of aqueous surfactant solutions [24]. Aggregate size is significantly affected by hydrophobic and hydrophilic ionic liquids while affecting the cloud point [24,25].

Thus, 16 experiments with all possible combinations of variables were performed at room temperature (T = 25°C) and a matrix was established according to their high (+1) and low (–1) levels, to which three central points (0) were added to estimate the experimental error. The results of the dye extraction were expressed in terms of extraction yield (Table 2).

Extraction yield is calculated according to Eq. (1):

$$Y(\%) = \frac{C_i - C_a}{C_i} \times 100 \tag{1}$$

where C_i is the initial concentration and C_a is the concentration in aqueous phase after extraction.

The coded model used for 2^4 factorial designs was as follows:

$$Y(\%) = a_0 + \sum_{1}^{4} a_i X_i + \sum_{i=1,j=2}^{i=3,j=4} a_{ij} X_i X_j + \sum_{i=1,j=2,k=3}^{i=2,j=3,k=4} a_{ijk} X_i X_j X_k + a_{1234} X_1 X_2 X_3 X_4 \tag{2}$$

where a_0 represents the overall mean and a_i represents the regression coefficient corresponding to the main interactions and effects of the factors.

For reasons of reproducibility, it is necessary to check whether this model accurately describes the process studied by determining which coefficients could be neglected, by means of Student's t-test and Fisher's test. The adequacy

Table 2
Experimental data

Testing	Settings				Reduced variable				Replies	
	pH	Triton X-100 (% p/p)	Na_2SO_4 (% p/p)	[Dye] ppm	X_1	X_2	X_3	X_4	Yield %	
									Dye	Dye + Ni^{2+}
1	4.0	2	8	10	–	–	–	–	75.6	95.6
2	8.0	2	8	10	+	–	–	–	63.4	100
3	4.0	10	8	10	–	+	–	–	95.1	95.1
4	8.0	10	8	10	+	+	–	–	100	100
5	4.0	2	10	10	–	–	+	–	100	100
6	8.0	2	10	10	+	–	+	–	100	100
7	4.0	10	10	10	–	+	+	–	100	100
8	8.0	10	10	10	+	+	+	–	100	100
9	4.0	2	8	100	–	–	–	+	95.1	95.1
10	8.0	2	8	100	+	–	–	+	54.0	100
11	4.0	10	8	100	–	+	–	+	54.6	95.1
12	8.0	10	8	100	+	+	–	+	87.8	100
13	4.0	2	10	100	–	–	+	+	90.24	100
14	8.0	2	10	100	+	–	+	+	90.24	96.24
15	4.0	10	10	100	–	+	+	+	100	100
16	8.0	10	10	100	+	+	+	+	100	100
17[a]	6.0	6	9	55	0	0	0	0	100	100
18[a]	6.0	6	9	55	0	0	0	0	99.6	99.8
19[a]	6.0	6	9	55	0	0	0	0	98.9	98.9

[a] Three additional central point tests (0,0,0) for calculating student and Fisher tests, using the normal variance rule.

of the model strongly depends on the accuracy of the experiment.

For the current experiment, measurements of volume, weight and dye analysis are the main causes of errors. For this purpose, three additional central point attempts (0,0,0) are required to estimate the average error in the value of each coefficient, based on the random variance. Calculations are summarized in Table 3. Thus, with 95% confidence ($\alpha = 0.05$), and for two variances (three attempts at the central point), the value of $t_{\nu,1-\alpha/2}$ was calculated as 2.92. Therefore, and at $(1 - \alpha)$, the confidence interval for all the estimated coefficients, using 19 tests ($N = 19$), were $\Delta a_i = \pm 0.293$ and $\Delta a_i = \pm 0.2652$, for red Bemacid, with and without Ni^{2+} addition, respectively, with a confidence level of 95% according to the Student's test. The final forms of polynomial models that describe the extraction of red Bemacid were as follows:

Bemacid red solution without nickel:

$$\begin{aligned} Y = {} & 87.58 - 0.54X_1 + 3.37X_2 + 3.62X_3 + 1.25X_4 + 5.06X_1X_2 \\ & + 5.32X_1X_3 - 4.55X_1X_4 - 6.09X_2X_3 + 2.24X_2X_4 + 1.28X_3X_4 \\ & - 1.50X_1X_2X_4 + 4.58X_2X_3X_4 - 3.26X_1X_2X_3X_4 \end{aligned} \tag{3}$$

Bemacid red solution in the presence of nickel:

$$Y(\%) = 98.57 + 0.8X_1 + 0.8X_3 - 1.19X_1X_2 + 1.28X_3X_4 \tag{4}$$

The three-dimensional isometric response curves (Fig. 2) are smoothed by the mathematical model (Eqs. (3) and (4)): (a) and (b) red Bemacid without Ni^{2+}/(c) and (d) red Bemacid in the presence of Ni^{2+}.

3.2. Effect of pH

pH is the most important factor for CPE because it regulates the partition of the target micellar phase for organic molecules [26]. It increases the partition coefficient of the analyte between the coacervate and the aqueous phase. Its effect depends on the characteristics of the surfactants and the analytes [27]. Note that the percentage of recovery of the dye is lower in acidic medium and increases with the pH [28], it is 80% for the pH = 4.0 and 90% for pH = 8.0 (Fig. 2(a)).

These results can be explained by the characteristics of the dye molecules in solution. The pH affects the mechanism of reactivity and the formation of micelles [29].

At acidic pH, the efficiency is not quantitative, due to the incomplete formation of the complexes [30] and to the increasing ionic character of the oxy group of the nonionic surfactant, favoring the CMC and leading to the decrease of solubility of the dyes in the micelles [31]. On the other hand, at a basic pH, the CMC is lowered because of the cracking hydrophobicity of the oxy groups which increases the size of the micelles as well as the number of agragation and the dyes are deprotonated and behave similar to a hydrophobic molecule. Consequently, their solubilization increases leading to an increase in extraction [30,31].

3.3. Effect of Na_2SO_4 salt

The cloud point temperature of nonionic surfactants can be affected by the system environment. The addition of salts has the effect of salting out, moreover it facilitates the phase separation process [30,31]. In this concept, Na_2SO_4 was investigated as an electrolyte in the range of 1%–10%. From Fig. 2(b), it can be noticed that the yield increases from 83% to 98% by adding more Na_2SO_4. The dehydration of the ethoxy groups on the outer surface of the micelles is favored in the presence of the salts leading to the increase of the aggregates and consequently to solubilize more quantity of dyes [32,33]. The anion SO_4^{2-} is common between $NiSO_4.7H_2O$ and Na_2SO_4 used in this study. Sodium sulfate has the most negative effect. Thus, addition of a small amount of this salt can reduce the cloud point to less than 20°C. The cloud temperature in the presence of Na_2SO_4 is lower than those in the presence of NaCl, $Na_2S_2O_3$, KI, KBr and KNO_3 salts [34]. The phenomenon obeys the arrangement of anions in the lyotropic Hofmeister's series [35]. SO_4^{2-} is a strongly hydrated anion (salting out).

Table 3
Model adequacy tests and analysis of variance

Characteristics	Symbols	Values	
		Red	Red-Ni^{2+}
Average yield at point (0,0,0)	Y_0	87.58	98.57
Random variance	$S^2 = \sigma$	0.1922	0.1568
Square root of variance	S	0.4384	0.3959
Risk factor (arbitrarily chosen)	α	0.05	0.05
Average error on coefficient value	Δa_i	0.2936	0.2652
Remaining coefficients	R	14	5
Model response to point (0,0,0)	$a_0(y_{0,0,0})$	87.58	98.57
Divergence of average return	D	11.9193	0.9243
Error on the divergence of the average return	Δd	5.6287	5.0840
Average yield of the 16 experiments	Y_m	89.46	98.73
Residual variance	Sr^2	177,922.46	11,807.99
Fisher's test	F	3.81	6.94

[a] $\alpha = 0.05$ was arbitrarily chosen. In this case, it was considered that 95% confidence can be satisfactory.

3.4. Effect of dye concentration

Fig. 2(a) indicates that extraction decreases with increasing of red Bemacid concentration. By working in a basic medium, a removal yield of 88% is obtained for a concentration of 10 ppm, when the latter increases to 100 ppm, the percentage of recovery decreases to 82%. It can be assumed that the CMC of the nonionic surfactant increases in the presence of dye. It also implies that the number of micelles decreases with the concentration of the dye. Declining the extraction efficiency with increasing concentration of the feed dye is due to the increase of non-solubilized dye molecules in the diluted phase [2].

3.5. Effect of Triton X-100

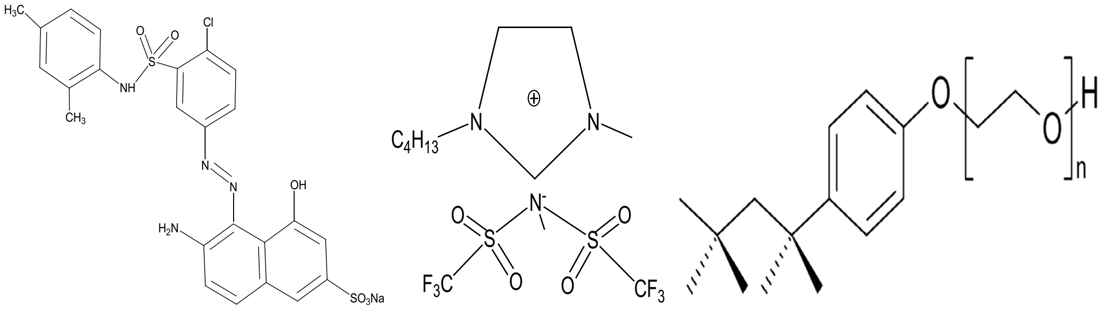
The extraction variation as a function of mass percentages in Triton X-100 was followed in the range of 2%–10%, as shown in Fig. 2(b). Respectively, at 2% and 10% of the Triton X-100, yields extraction of 64% and 83% were obtained. For small percentages of the nonionic surfactant, recovery by extraction of the complex is likely due to the inadequacy of the assemblies to trap the hydrophobic complex quantitatively [27,36]. The extraction percentages increase progressively with the percentage of Triton X-100, this may be due to the increasing in the viscosity of the coacervate phase [34] containing "Triton X-100 + IL". Triton X-100 has a viscosity of 27 Cp at 25°C, which of the mixture "Triton X-100 2% + IL 100 ppm" is 390 Cp. More Triton X-100 is added to the IL and the higher the viscosity increases. The increase in the viscosity may be due to the decreased water phase volume [37] and increased surfactant phase volume in coacervate phase at higher Triton X-100 concentrations. The concentration of micelles in the solution varies proportionally with the concentration of the surfactant, the higher the latter, the greater the solubilization of the dyes in the coacervate phase will be. As a result, extraction efficiency increases [38–41].

3.6. Extraction mechanism

The ionic liquid demonstrates a multiple hydrogen bonding interaction with TX-100. Due to the interactions between the hydrogen bonds, solvation of the surfactant around the Triton X-100 chain occurs, which must be the beginning of the solvophilic character of the Triton X-100 chain in the "$BMIM^+$, NTf_2^-" solution (See Fig. 6). The strength of a hydrogen bonding interaction decreases with increasing temperature. Thus, the desolvation of the Triton X-100 chain would occur at a high temperature, which would lead to reduced solubility of the surfactant molecules and thus induce phase separation. Therefore, the addition of IL increases the phase separation, increasing the concentration of micelles in the coacervate phase, leading to the solubilization of more Bemacid red.

3.7. Effect of Ni^{2+} on the extraction of Bemacid red textile dye

According to Figs. 2(c) and (d), the presence of Ni^{2+} enhances the extraction of dye, keeping the same effect of the four factors pH, TX-100, Na_2SO_4 and dye concentration. The minimum yield is 96% in the presence of Ni^{2+}. In the same conditions, in absence of Ni^{2+} (dye alone) its value is only 83%. The presence of nickel yields the yield per unit (100%) under the two effects, the pH and that of the concentration of the dye. In the effect study of TX-100 and Na_2SO_4, the yield improves from 60% to 98% in the absence of Ni^{2+}. In its presence, it goes from 94% to 100%. The study of the mixture "Bemacid red + Ni^{2+}" shows that the extraction selectivity was



(a) **(b)** **(c)**

Fig. 5. Molecular structures of (a) red Bemacid dye, (b) ionic liquid $BMIM^+$, NTF_2^- and (c) Triton X-100.

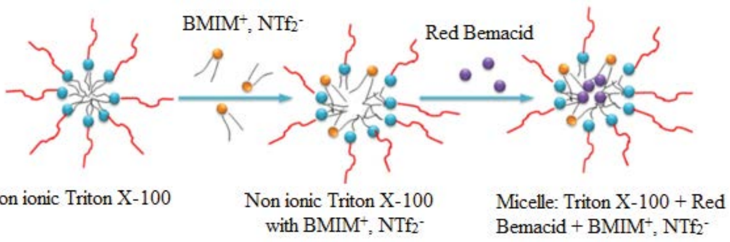


Fig. 6. Mechanism of extraction of Bemacid red.

quantitative for the dye (100%) and 0% for Ni^{2+} in the field studied. In Pearson's classification [42] Na^+ is a hard acid, red Bemacid is a soft base and Ni^{2+} is a soft acid. As a result, Ni^{2+} cannot be exchanged with Na^+ linked to the red Bemacid ligand (Fig. 5). A reaction carried out between red Bemacid and Ni^{2+} did not allow under reflux to form nickel complex (red Bemacid-Ni). In the aqueous mixture containing the red Bemacid, the nickel remains free after analysis.

4. Conclusion

Cloud point extraction can be successfully used to extract and separate the azo dye named red Bemacid alone and in the presence of Nickel (II) using Triton X-100 as a nonionic surfactant. The effects of pH (4.0–8.0), percentages of Triton X-100 (2%–10%w), Na_2SO_4 (8%–10%w), initial dye concentration (10–100 ppm) and IL concentration (100 ppm) on extraction efficiency were studied in detail. Without addition of nickel, the maximum pH is used, Triton X100 (% w) and Na_2SO_4 (w %), and minima of dye (100 ppm). With the addition of nickel, at lower pH is used, Triton X-100 (% w), Na_2SO_4 (w %), and minimum concentration of dye (100 ppm). pH is a critical parameter and can be observed that the extraction efficiency increases with the pH, the percentage of Triton X-100 and Na_2SO_4 but decreases with the initial concentration of red Bemacid. Responses showed elimination of red Bemacid alone with an efficiency of 96%. The study of the mixture "red Bemacid + Ni^{2+}" shows that the extraction selectivity was quantitative for the red Bemacid (100%) and 0% for Ni^{2+} in the field studied.

Cloud point extraction is a promising method for separating compounds in a complex matrix.

Conflict of interest

The authors confirm that this article content has no conflict of interest.

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