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Effects and optimization of operating parameters of anionic dye extraction from an aqueous solution using an emulsified liquid membrane: Application of designs of experiments

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ABSTRACT

To remove Acid Yellow 99 from an aqueous solution, extraction by an emulsified liquid membrane consisting of Aliquat336 as the extractant, Span80 as the surfactant and cyclohexane as the diluent may be used. The process parameters were studied in first using a screening design of Plackett–Burman to study the effects of different operating parameters on the extraction yield. Then, a second experimental Box–Behnken design was applied with the most important parameters determined in the first design. Only a few runs had been necessary and sufficient to optimize eight parameters and to enhance the experimental extraction yield to 99.98%

1. Introduction

Industries such as textile, leather, paper, plastics, *etc.* are some of the principal sources for dye effluents [1,2]. It was estimated that more than 100,000 commercially available dyes with over 7×10^5 tons of dyestuff produced annually [3–5]. Practically, it has been recorded that almost 125–150 L of water must be used for every 1 kg of textile product in the textile processing, including bath residues from preparation, dyeing, washing, soaking and slashing [6]. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons. The presence of dyes in effluents had been a major environmental problem all over the world due to their adverse effects to many forms of life. In industrial water pollution, the color produced by minute amount of organic dyes in water is considered very important because, besides having possible harmful effects, the color in water is aesthetically unpleasant. The treatment of wastewater containing dyes and their removal from water is then necessary [7–11]. There are several methods for dyes removal such as coagulation/flocculation treatments [12–15], chemical oxidization and photocatalytic processes [16–18], electrochemical degradation [19,20], ozone treatment [6,12], membrane processes [21,22], advanced oxidization processes (AOP's) [23–26] and since the last 2 decades, adsorption separation techniques [27–35]. Since their invention, emulsion liquid membranes (ELM's) were demonstrated to have significant potential as effective tools for treatment of various industrial wastes [36]. ELM separation process constitutes an emerging technology with a wide variety of applications such as treatment of industrial wastewater with the aim of removal, recovery and purification of many organic and inorganic compounds from dilute solutions of industrial interest [37–42]. The stability of water–oil–water emulsion depends on the coalescence of the internal aqueous solution as well as oil droplets, the rupture of the internal phase, the swelling of the membrane phase, *etc.*[43–49]. A good stability according to the composition of the membrane has been reported in different studies for the removal of heavy metals [49–52], inorganic and organic compounds [53–55]. Extractions of dyes using ELM had been investigated recently [11,56–61] and stabilities of the membranes were studied before [50,58,60,62]. To develop and design the ELM process, it is important to elucidate the role of the stripping agent (here on referred to as the strippant). The behavior of ELM, like any other process, has some drawbacks, such as the instability of the membrane due to the swelling and the breakage of the emulsion globule. Thus, the selection of a strippant is a key to the success of the ELM process [50].

Experimental design is a very powerful tool for the search of the variables that predominantly affect the extraction process. It is

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a method based on a systematic and a coherent study which allows identification of the factors and their interactions that significantly affect the transport of dyes through the membrane system in the process as well as the determination of the optimal levels of each of these variables [63]. When the run of only one part of the complete full factorial design can give enough information, it is called fractional factorial design. Using this experimental design we can calculate the coefficients for each parameter and express its importance and comportment in relation to the phenomenon studied. We can also calculate the coefficients associated with the interactions between parameters [64].

In this study a first objective of this work was to determine the parameters that influence the extraction of the acid yellow dye (AY99) from an aqueous solution using ELM, applying a fractional factorial design of Plackett–Burman [64,65]. The membrane used for the extraction of AY99 consisted of Aliquat 336 as the extractant, SPAN80 (sorbitan monooleate) as the surfactant and cyclohexane as the thinner. The second objective was to study the effects of most important parameters determined above using response surface methodology [66–68]. Indeed a Box–Behnken design was applied to determine the optimal conditions and to improve the extraction yield [69,70].

2. Experiments

2.1. Reagents and materials

The emulsified liquid membrane used for the extraction of acid yellow 99 consisted of Aliquat 336 (trioctylmethylammonium chloride) as the extractant, SPAN 80 (sorbitan monooleate) as the surfactant, cyclohexane as the thinner and sulfuric acid as the internal phase. Aliquat 336 supplied by Sigma Aldrich, is an excellent carrier of solute in its ionic form. SPAN80 supplied by Sigma Aldrich is a nonionic surfactant type ester with lipophilic character (HLB = 4.3), it was used for the stability of the emulsion. Cyclohexane produced by Riedel-de Haën was used as a thinner, it is a stable product under ordinary conditions and its role was to improve mainly some physicochemical properties of the extractant and the surfactant. The acid yellow 99 is an anionic dye supplied by Sigma Aldrich.

The homogenizer Ultra-Turrax T8 is a mechanical agitator type RW20Junk & Kunkel, with a marine propeller; it is used to make a double emulsion W/O/W (water/oil/water). At high speed the rotating rotor sucks in the solution to the head axially and then disperses through the rejects of the rotor stator slots laterally.

2.2. Experimental procedures

Emulsions were made using the homogenizer Ultra-Turrax T8; a certain volume of H_2SO_4 as an internal aqueous phase was added to an organic phase composed of cyclohexane as thinner, this solution was characterized by O/A ratio (Organic/Aqueous), Aliquat 336 as extractant and Span 80 as surfactant were then added. The mixture was emulsified at 5000 rpm into a tall beaker within 5 min. This emulsified membrane obtained, was then dispersed into a beaker containing 150 mL of an external solution with a known initial concentration of AY99. The new mixture characterized by a V_{ex}/V_{em} ratio ($V_{external}/V_{emulsion}$) was agitated at150 rpm using a mechanical stirrer type RW20 Kjank & Kunkel. The pH variation of the external phase was monitored using a pH-meter type HANA Hi 8519 N.

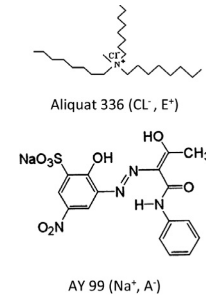
Initially, the dye and the extractant (Schema 1) were in the external phase and the membrane respectively. At the interface, anion exchange was performed, the (CL^-) accompanying the extractant (E^+) was attracted by the Na^+ and passed into the external phase to form (Na^+, CL^-). In exchange, the anionic dye (A^-) passed into the membrane to form the complex (E^+, A^-).

The concentration of the residual complex AY99 at equilibrium time was determined by taking up a sample of 2 mL from the external solution and measuring the absorption intensity using a Jenway (6705UV/VIS) spectrophotometer. The wavelength was determined experimentally and was used in the same conditions. The sample was analyzed to determine the concentration of the residual complex AY99 from the calibration curve carried out also in the same operating conditions and at ordinary temperature.

The extraction efficiency was calculated by the Eq. 1.

$$Y(\%) = \left[1 - \left[(C_{fext} \times V_{fext})/(C_{0ext} \times V_{0ext})\right]\right] \times 100 \quad (1)$$

V_{0ext}: initial volume of the external phase.
V_{extf}: final volume of the external phase.
C_{0ext}: initial concentration of AY99 in the external phase.
C_{fext}: final concentration of AY99 in the external phase.
$\boldsymbol{Y}_{ext}$: extraction yield.



Schema 1. Chemical structures of Aliquat 336 and AY 99.

Table 1
Parameters and levels.

N° run	Parameter	Unit	Level	
			Low (−1)	High (+1)
1	SPAN 80	%	8	11
2	Aliquat336	%	3	5
3	Stirring velocity (SV)	rpm	100	150
4	[H_2SO_4] internal	mol/L	0.5	1
5	Organic/Aqueous	–	1	3
6	$V_{external}/V_{emulsion}$	–	5	7
7	$[AY99]_0$ (initial)	ppm	10	50
8	[H_2SO_4] external	mol/L	0.1	0.5

3. Results and discussion

3.1. Screening design

3.1.1. Experimental results

The extraction of AY99 was conducted by varying eight factors simultaneously listed in the Table 1. The minimum and maximum of levels for each factor were chosen after a literature review and especially after performing preliminary tests. The Table 2 summarizes the different operating conditions of extractions using an emulsified liquid membrane according to a Plackett–Burman experiments design. The experimental results of extraction yields are also presented.

3.1.2. Discussion

The Pareto chart of effects is a useful field to identify the most important factors (Fig. 1). It shows the estimated main plot against the horizontal effect. From Fig. 1 we can see that the most important factors are the acidity of the internal phase and the proportion of the emulsion represented by the V_{ex}/V_{em} ratio. The O/A ratios, the acidity of the external phase are also important, the initial concentration of dye, the extractant and the surfactant are less important. The stirring velocity has a low effect.

The main effects plot is the most useful when there are several factors (Fig. 2). From level changes, we can deduce the influence of all factors. These effects may be positive or negative.