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Removal of reactive orange 12 by cloud point extraction

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ABSTRACT

Cloud point extraction (CPE) is carried out to extract reactive orange 12 from aqueous solution using non-ionic surfactant, TX-100. The effects of different operating parameters, e.g., concentrations of surfactant, dye and salt, temperature, pH have been studied in details. The developed method may be useful to design a cloud point extractor of a desired efficiency.

KEYWORDS

Cloud point extraction;
Non-ionic surfactant;
TX-100;
Reactive orange 12;
Anionic dye.

INTRODUCTION

The presence of dyes in water is unpleasent, due to toxicity, coloration of natural waters, mutagenic effects, and their carcinogenicity[1-5]. The effluents containing dyes are highly colored making serious environmental problems and therefore need to be treated before disposal.

So, considerable attention has been given for removal of the colored wastes from water. Many investigators have studied different methods for the removal of dyes from wastewater, e.g. (i) membrane separation processes like reverse osmosis[6], nanofiltration[7], adsorption onto solid surfaces such as activated carbon[8], bentonits[9], ozonation[10].

Cloud point extraction (CPE) is another method for removal of dyes from aqueous solution which has initially described by Wtanabe and co-workers[11] for the preconcentration of metal ion using a ligand as a carrier in the presence of an extractant. Later, this method has been applied as an effective method for the removal of dyes from aqueous solution[12].

In the last decade, significant interest on the use of aqueous micellar solution has been found in the field of separation science[13]. At certain temperature, cloud point temperature, aqueous solution of a nonionic surfactant becomes turbid. Above the cloud point temperature, aqueous solution of a nonionic surfactant separate into two phases, namely surfactant rich phase and the other is dilute bulk solution phase containing surfactant concentration slightly above the critical micelle concentration (CMC)[14]. The dye molecules present in aqueous solution of nonionic surfactant are distributed between the two phases above the cloud point temperature[15]. This phenomenon is known as CPE.

In the present study, CPE method was used to remove anionic toxic dye, Reactive orange 12 (RO), from wastewater using TX-100 as nonionic surfactant. The effects of temperature, concentrations of surfactant, salt, pH, incubation time, and interferences on extraction of RO have been studied.

EXPERIMENTAL

Materials

Triton X-100 (Iso-octyl phenoxy polyethoxy ethanol) containing approximately 10 ethoxy units per mol-

TABLE 1 : Effect of interferent ions and dyes the CPE efficiency of RO

Interferences	Ratio interference
Na^+, Ba^{2+}, Cd^{2+}, Ca^{2+}, NH_4^+, I^-, Br^-, F^-, HPO_4^{2-}, CH_3COO^-, Zn^{2+}, NO_2^-, Sr^{2+}, Pb^{+2}, SO_3^{-2}, Bi^{+3}	1000
Ag^+ , Al^{+3}	800
SCN^-, NO_3^-, Mg^{+2}, ClO_4^-, Cu^{+2}	600
Mn^{+2} , Li^+	400
Co^{+2} , Fe^{+2}	200
Direct yellow	150
Direct Red	50

ecule, density at 20°C, 1.06g/mL; mol. Wt, 628; λ_{max}, 226nm, supplied by Merck, has been used as nonionic surfactant. The dye used in this study is G Y which is an anionic dye (mol. Wt, color, yellow; λ_{max}, 426nm) was obtained from Merck. The rest of the chemicals were used as received.

Procedure

Each experiment is carried out using a 50ml volumetric flask containing an aliquot of the RO solution, TX-100, 0.1M; KCl, 0.5M at pH = 1 in a constant temperature bath (65°C) for 40 min. After 10 min cooling in an ice-bath a viscose phase of surfactant was formed and the phase separation completed. The concentration of dye in aqueous solution befor and after extraction was determined spectrophotometrically.

RESULTS AND DISCUSSION

The critical micellar concentration (CMC) of TX-100 is 2.8×10^{-4} at 25×C. The micellar molecular weight is in the range of 60,000-90,000 and a micelle has a radius of about 4.3×10^{-9} m (at 25°C)[16]. The operating temperatures used in this study are in the range of 60-80°C, which ensures the occurrence of the cloud point and phase separation. The efficiency (in percentage) of cloud point extraction is defined as,

Efficiency of extraction of dye = $(1- C_d/C_o)\times100$

where C_o and C_d are the initial concentration and dilute phase concentration of the dye, respectively.

One at the time method was applied to optimize some important CPE parameters such as pH, surfactant concentration, salt concentration, equilibrium temperature and time.

TABLE 2 : Removal of RO in water samples

Sample	RO added (mg L^{-1})	Extraction efficiency (%)
Domestic waste warer (20mL)	10	96.58%±1.2
	15	96.48%±1.16
	20	95.51%±1.19
Domestic waste water (12 ml)	10	97.18%±1.32
	15	96.20%±1.35
	20	95.92%±1.23
River water (20 ml)	10	97.45%±1.03
	15	96.52%±1.27
	20	96.35%±0.30
River water (10 ml)	10	97.14%±1.38
	15	96.11%±1.29
	20	95.67%±1.18

Effect of surfactant concentration

For successful CPE of dye, it is desirable to use minimum amount of surfactant for maximum extraction of dye. Figure 1 shows the effect of the concentration of TX-100 on the extraction of dye at 65C. It was observed from figure1 that at a fixed temperature and dye concentration, the extraction efficiency of dye increases with surfactant concentration. The concentration of the micelles increases with surfactant concentration, resulting in more solubilization of dyes in the micelles. Therefore, the extraction efficiency of dye increases with surfactant concentration.

Effect of temperature

The effect of the operating temperature on the extraction efficiency of dye is clear from figure 2. The exctraction efficiency of dye increases with temperature up to maximum amount at cloud point of TX-100 (65°C), and beyond this temperature the efficiency decreases gradually.

Effect of pH

Since the efficiency of extraction process is strongly dependent on pH, which affects the degree of ionization of the dye, comparative experiments were carried out over the pH range 1-10 at 80°C and contact time of 10 min in a water bath. The pH in fluences the ionization state of ionizable organic molecules and since this dye exposes negatively charged group, it is con-

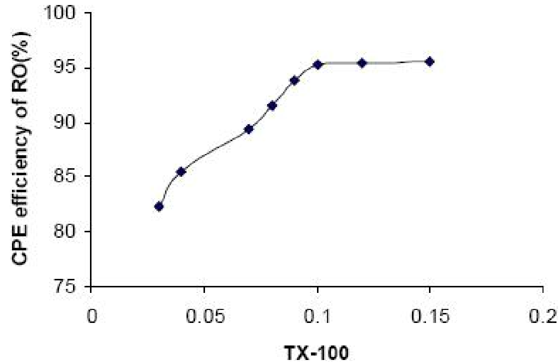

Figure 1 : Effect of concentration TX-100 on the CPE efficiency of RO

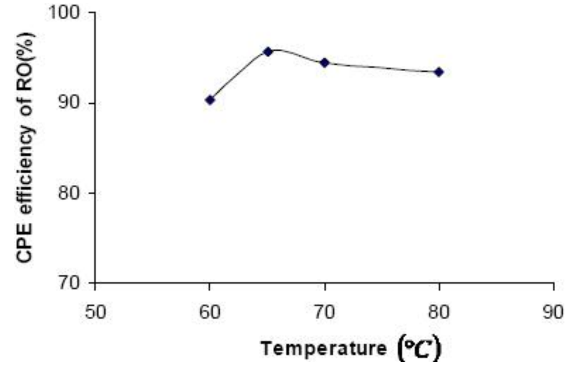

Figure 2 : Effect of temperature on the CPE efficiency of RO

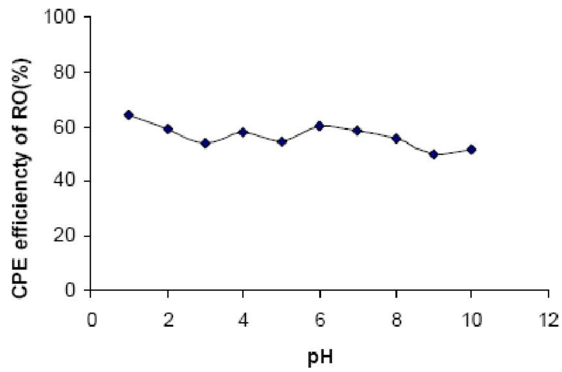

Figure 3 : Effect of pH on the CPE efficiency of RO

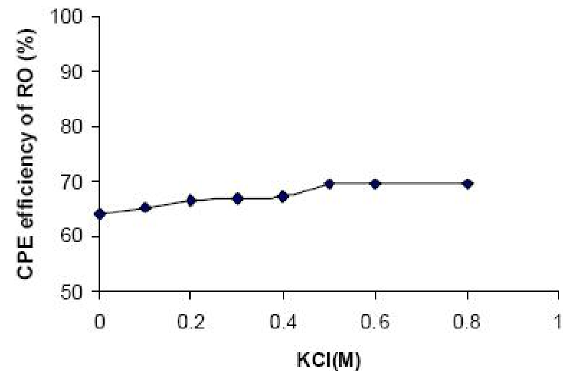

Figure 4 : Effect of salt concentration KCl on the CPE efficiency of RO

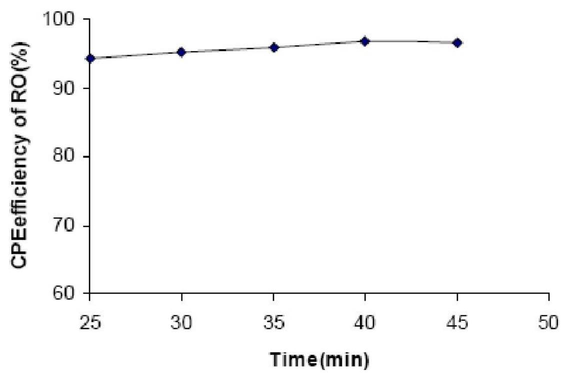

Figure 5 : Effect of equilibrium time on the CPE efficiency of RO

ceivable that at low pHs, its extraction is favored. It was observed that the maximum uptake of dye takes at pH = 1.0 (Figure 3).

Effect of salt concentration

The effect of electrolyte (postassuim chloride, KCl) on the extraction efficiency of dye is summarized in figure 4. It is absorved from the figure 4. The extraction efficiency of dye increases when KCL concentration increases from 0.0 to 0.5M and beyond this concentration the efficiency of extraction will be constant.

It is well known that due to its salting-out effect, potassium chloride decreases the cloud point of the surfactant and it promotes the dehydration of ethoxy group on the outer surface of the micelles[17]. Therefore, addition of KCL increases phase separation, enhancing.

The micellar concentration in the coacerrate phase as well as the concentration of the solubilized dyes. Hence, the extraction efficiency of both the dye and surfactant increase with the salt concentration.

However, this salting out effect of KCL reaches a limit at about 0.5M, beyond which the extraction profiles remain un altered.

Effect of equlibrium time

The effect of the equilibrium time was also studied which is shown in figure 5. Maximum extraction efficiency was abserved at 65°C after 45 min.

Interference studies

The influence of some ions and dyes on the determination of RO was studied. Various amounts of other species were added to a solution containing RO and the recommended procedure was applied. An error of less than or equal to ±5% in the absorbance reading was considered tolerateable. The results presented in

TABLE 1 show the good selectivity of the procedure. The interference effects of the two dyes (Direct red and Direct yellow) in solution of RO were studied.

Application to real samples

In order to test the reliability of the proposed methodology, it was applied to the removal of concentrations of RO in domestic wastewater and Maroon river samples. For this purpose, various amounts of RO (10 or 12 or 20mg L^{-1}) were spiked to the sample. Then, spiked samples were treated under the general procedure. The results presented in Table 2 show that good extraction efficiency are obtained and confirm the validity of the proposed method for real samples.

CONCLUSION

A method is proposed for cloud point extraction of RO, an anionic dye, using TX-100 as non-ionic surfactant. The method can be successfully used to remove RO from wastewater. It is observed the some parmeters (temperation, pH, salt concentration) are effective on extraction efficiency.

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