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Study of phenol removal by cloud point extraction: A process optimization using experimental design

Wanessa Paulino Neves Silva [a,*], André Ezequiel Gomes do Nascimento [a], Maria Carlenise Paiva de Alencar Moura [a], Humberto Neves Maia de Oliveira [b], Eduardo Lins de Barros Neto [a]

[a] Universidade Federal do Rio Grande do Norte, Centro de Tecnologia, Departamento de Engenharia Química, Programa de Pós-Graduação em Engenharia Química, Campus Universitário, CEP 59072-970, Natal, RN, Brazil
[b] Universidade Federal do Rio Grande do Norte, Centro de Tecnologia, Departamento de Engenharia Química, Campus Universitário, CEP 59072-970, Natal, RN, Brazil

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ABSTRACT

The use of nonionic surfactants in liquid–liquid extraction consists of a two-phase process without the presence of an organic solvent. The present study aims to optimize the process of phenol removal from an aqueous solution by applying the cloud point extraction technique. A three-level factorial design and response surface methodology were employed to assess the effects of temperature and surfactant concentration on the extraction process. It was evaluated the effects of these factors on the following parameters: percentage of phenol extracted, ratio between phase volumes, and residual amounts of phenol and surfactant in the dilute phase after separation. Mathematical models were developed to predict the effect of each variable and their interactions with the extraction parameters. A comparison between predicted values using model equations and experimental values exhibited correlation coefficients (R^2) greater than 0.98. The models were validated by analysis of variance, significance, and prediction, allowing the estimation of process variables. Response surface methodology allowed the optimization of process variables. The results showed phenol removal of up to 95%.

1. Introduction

Phenol and several of its derivatives are toxic to human beings and aquatic organisms. They are found in the wastewaters of a number of industries, including refineries (6–500 mg/L), coal processing (9–6800 mg/L), and petrochemical (2.8–1220 mg/L). Industries such as the pharmaceutical, plastic, paint, and paper and cellulose also generate wastewater containing phenol (0.1–1600 mg/L) [1]. According to Eksperiandova et al. [2], the maximum permissible concentration for phenol is 0.1 mg/L and 0.001–0.002 mg/L for chlorinated and nonchlorinated water, respectively.

According to González-Muñoz et al. [1] and Earhart et al. [3], liquid–liquid extraction is the most widely process used to recover phenol from wastewater at concentrations above 50 ppm. Liquid–liquid extraction (LLE) consumes little energy, but employs an organic solvent, generally toxic, that requires the energy consumption to be reused.

Surfactants are amphiphilic molecules that exhibit important interfacial properties and can be used in a number of industrial separation processes [4,5]. Nonionic surfactants do not ionize in aqueous solution and, at a certain temperature, promote the separation of two aqueous phases, one rich in surfactant, called coacervate phase, and the other one with a low concentration of surfactant, called diluted phase [5]. This technique can eliminate solvents from the liquid–liquid extraction process. Among the advantages of using surfactants are their non-toxicity, reduced hazard when compared with organic solvents, non-volatility, non-flammability, and small amounts required for the process [6,7].

The phenol extraction technique using nonionic surfactants is considered a environmentally friendly, cost-effective, and safe. It also provides good extraction efficiencies [8]. Studies made by Haddou et al. [9] to remove phenol and benzyl alcohol from aqueous solutions, using the cloud point technique with polyethoxylated alcohols as nonionic surfactants, showed that the process is highly effective, reaching 95% extraction for phenol and 90% for benzyl alcohol. Zain et al. [10] demonstrated that

* Corresponding author.
E-mail addresses: neves_wanessa@yahoo.com.br (W.P.N. Silva), andrenascimento@eq.ufrn.br (A.E.G. Nascimento), carlenise@eq.ufrn.br (M.C.P.A. Moura), humberto@eq.ufrn.br (H.N.M. Oliveira), eduardolbn@yahoo.com.br (E.L. Barros Neto).

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phenol species such as 2,4-dichlorophenol, 2,4,6-trichloroenol, and 4-nitrophenol can be successively removed from water samples by polyethyleneglycol silicone surfactant in the cloud point extraction.

The cloud point extraction (CPE) technique has been applied to remove hydrocarbon from oily wastewaters. Ghouas et al. [11] used alkyl phenol ethoxylate and octyl phenol polyethylene nonionic surfactants to treat real effluents, achieving efficiencies greater than 90%. Hung et al. [12] removed polycyclic aromatic hydrocarbons (PAH) from aqueous solutions using Tergitol 15-S-5, Tergitol 15-S-9, and Neodol 25-7 as nonionic surfactants. Yau et al. [13] studied the removal of PAHs by silicone surfactants. These authors concluded that the use of these surfactants in cloud point technique is a simple and efficient process. The CPE can also be used for pre-concentration and extraction of metallic compounds, including: nickel [14], cadmium [14,15], copper [16], manganese (II) [18], rhodium [19], and zinc [14,17,20].

The use of experimental design to assess a wide range of studies has produced important results, including the optimization of the mechanical properties of cement containing residue of boron (PN) and rice husk ash (RHA) [21]. It has also impacted positively the study of phenol and flavonoid extraction and antioxidant recovery from palm kernel by-product [22]; the analysis of the main and interaction effects of operational parameters on photocatalytic degradation of oxalic acid in a batch photoreactor using TiO_2 aqueous suspension [23]; the optimization of cobalt aluminate synthesis [24]; and the study of oxidative thermal decomposition of low-density polyethylene residue [25].

It is well known that CPE is influenced by surfactant concentration and temperature because the cloud point of nonionic surfactants changes with surfactant solution concentration. In light of this, there is a need to obtain a model that represents phenol removal considering the effects of temperature and surfactant concentration, which interfere directly on extraction efficiency. In the present study, phenol, a universal pollutant, was extracted using octyl phenol ethoxylated in CPE. The following parameters were assessed: phase volume, phenol and surfactant concentration in the dilute phase after separation, and extraction efficiency.

2. Materials and methods

2.1. Materials

The extracting agent used in this study was Triton X114, a polyethoxylated t-octylphenol with an average of 7.5 ethylene oxide units. Its properties are presented in Table 1. Cromoline Quimica Fina LTDA provided the phenol used in all experimental procedures (99%). Solutions were prepared using deionized water, and all chemicals were of analytical grade.

2.2. Cloud point extraction experiments

A stand stock solution of phenol (5 wt.%) was prepared by dissolving the required amount of phenol in deionized water. The CPEs were made by adding the surfactant concentration, as established by experimental planning, and the phenol solution, with concentrations adjusted by dilution of the stock solution to obtain a final concentration of 0.15 wt.%, into a 10-mL measuring cylinder. The samples were kept under stirring during 5 min (100 rpm). Following, the samples were kept in rest in a thermostatic water bath to allow phase separation (1 h). The temperature was adjusted in accordance with the experimental design matrix.

After the complete phase separation, the phase volumes were measured to establish the volumetric ratio, followed by mass balance, to determine solute concentrations in both phases. Next, a sample of the dilute phase was removed carefully from the solution using a precision syringe. Phenol and surfactant concentrations in the dilute phase were measured by liquid chromatography (Variable Wavelength UV–Vis Detector, VARIAN 9050) using acetonitrile/methanol/water as eluent at a ratio of 3/2/1, respectively.

2.3. Experimental design

There are two types of variables in the multivariate optimization procedure: responses and factors. Responses are dependent variables; their values depend on the levels of the factors [26,27].

Factorial design was used at three levels: low, medium, and high. The graphs, analysis of variance, and calculations of the effects were obtained with STATISTICA 7.0 software.

Surfactant concentration (X_1) and temperature (X_2) were used as factors, both at three levels (Table 2). The assays were conducted in duplicate and the mean value was used as the experimental response. A total of 10 assays were performed, 9 related to the experimental design matrix and one a repetition at the central point (0,0). The design matrix and the experimental results are shown in Table 3.

Temperatures and surfactant concentrations were selected for being above the turbidity curve of the surfactant under study, as shown in Fig. 1. The cloud point was determined by visual observation. It is important to observe that the plot with phenol showed lower cloud point values. This is due to the interaction of the organic molecules with the polar head group of surfactant.

3. Results

3.1. Cloud point extraction

The experimental results obtained are shown in Table 3. It was determined phenol extraction (E); phenol concentration ($X_{s,w}$) in the dilute phase; surfactant concentration ($X_{t,w}$) in the dilute phase; and the coacervate phase volume fraction (f_c).

3.2. Regression analysis

Regression analysis was applied to obtain the mathematical models, resulting in second-order polynomial equations that express the relationship between each response and the significant factors and iterations. The following models were obtained by the experimental design:

Percentage of phenol extracted (%):

$$\%E = 82.219 + 30.583X_1 - 18.962X_1^2 - 1.475X_2 + 1.524X_2^2 - 1.878X_1X_2$$

Table 1
Surfactant properties.

Surfactant	Molar mass (g/mol)	HBL[a]	Viscosity (cP, at 25 °C)	Density (g/mL)
Triton X114	536	12.4	260	1.055

[a] Hydrophilic–lipophilic balance.

Table 2
Factors and levels used in experimental design.

Factor	Symbol	Level		
		−1	0	1
Surfactant concentration (wt.%)	X_1	1	7	13
Temperature (°C)	X_2	29	33.5	38