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Extraction performance of bisphenol A from aqueous solutions by emulsion liquid membrane using response surface methodology

Hongpu Jiao, Wei Peng, Juntong Zhao, Chunjian Xu *

State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

HIGHLIGHTS

► Process variables were optimized through response surface methodology.
► Membrane leakage analyzed by detecting the pH of external phase was very low.
► BPA extraction efficiency by emulsion liquid membrane with OP-4 as surfactant can reach 97.52%.
► Heat-induced demulsification was proved to be effective.

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ABSTRACT

In this work, the extraction of bisphenol A (BPA) from aqueous solutions by emulsion liquid membrane (ELM) was investigated using response surface methodology (RSM). The organic membrane phase of the ELM consisted of a solvent (kerosene) and a surfactant (OP-4). The internal phase was sodium hydroxide (NaOH) solution with varying concentrations. Optimum conditions for stable emulsion were found out experimentally. The effects of the important operating variables on the BPA extraction were investigated and the values of these variables were optimized using the Central Composition Design (CCD) of RSM. These variables are the concentration of surfactant OP-4 in organic membrane phase, the treatment ratio (volume ratio of external phase to ELM phase, R_{we}), the concentration of NaOH in internal phase and the volume ratio of organic membrane phase to internal phase (R_{oi}). The 3D response surfaces of BPA extraction efficiency were obtained. The result shows that, under the optimum conditions, the observed BPA extraction efficiency of 97.52% can be achieved. Heat-induced demulsification was successfully conducted and the recycled membrane phase was proved to be effective.

1. Introduction

Bisphenol A (BPA: 2, 2-bis (4-hydroxyphenyl) propane) is primarily used as a small monomer to make polycarbonate plastic and epoxy resins. By adding BPA, many properties of the plastic such as transparence, durability and weight can be improved significantly. Thus BPA is widely used in the manufacturing of feeding bottles, glasses, CDs, dental sealants and so on. Especially, in the canned foods industry, BPA can prevent acidic vegetables and fruits from eroding the canister from the inside, therefore it is also widely used as surface coatings for beverage containers and metal food cans [1]. However, under acidic or basic conditions, BPA can infiltrate out of these products by the hydrolysis of ester bonds which link BPA monomers [2]. Recognized as an environmental hormone, BPA is also an endocrine disrupting compound which contributes to the daily exogenous burden of humans and wildlife with hormonally active agents [3]. Studies have found that BPA is even contained in some paper products, particularly thermal receipt papers [4]. Moreover, BPA significantly contributes to the environmental problem, as it is released to environmental water through the discharge of municipal effluent and as a result of leaching from polycarbonate plastics and epoxy resins [5,6]. Thus it presents a risk to humans and animals [7–11].

Methods for the removal of BPA from aqueous solutions include biological treatment [12–14], oxidative removal [15] and adsorption [16–18]. Since emulsion liquid membrane (ELM) as an improved solvent extraction technique was initially proposed by Li [19], ELM technology has been developing rapidly. It has been applied to the separation of dyes [20–22], phenols [23,24] and metal ions [25,26] from aqueous solutions. Usually, under optimum conditions, the recovery rates for dyes are within the range of 90–99% [20]. The reported extraction rate for phenol can be 98–99% [23,24] while for aniline removal, the recovery rate is up to 99.5% [27] and for chromium extraction, the highest recovery rate can be 97.5–99.6% [26,28]. The emulsion is made by dispersing the internal phase in membrane phase under high emulsification speed in the presence of a surfactant, which helps to keep the emulsion stable by preventing the droplets of internal phase from coalescing. Typically, the size distribution of the

* Corresponding author. Tel.: +86 22 27892145; fax: +86 22 27404440.
E-mail address: cjxu@tju.edu.cn (C. Xu).

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dispersed internal phase droplets is about 1 to 100 μm [27]. Compared to liquid–liquid extraction, ELM holds many advantages such as simplicity, improved kinetics and good selectivity. Moreover, ELM processes allow very high mass transfer rate due to its large surface area within the emulsion globules and internal droplets [28] and allow both extraction and stripping simultaneously in only one step. Thus it is gaining more and more importance in areas like metallurgy, medicine, biochemistry and environmental protection.

The application of ELM in the BPA extraction from aqueous phase is scarce in the literature. Although Attef Dâas and Oualid Hamdaoui [29] studied the effects of different factors on the BPA extraction, comprehensive studies on the interaction between process variables are yet to be carried out. In most of the ELM applications, the commonly used surfactant was Span 80. Whereas heat-induced demulsification is simple and easy to be industrialized, the demulsification efficiency is not desirable with Span-80 as surfactant [30], which would inevitably exert a negative effect on membrane recycle. OP-4, as a lipophilic surfactant with four ethyoxyls, can form hydrogen bonds with water, which would be easily broken when heat is introduced. So in our work, commercial kerosene as an inexpensive and common industrial chemical was chosen as membrane solvent and the relatively new surfactant OP-4 for ELM was selected in the extraction of BPA from aqueous solutions.

In traditional approach, experiments are conducted by changing one factor at a time and examine the corresponding result of interest, which is both material-wasting and time-consuming. While response surface methodology (RSM), as an advanced tool, now is commonly applied to explore the relationships between test variables and their effect on one or more response variables, which decreases the number of required experiments considerably without overlooking the interactions among the test variables. The optimum conditions can be found through the statistical response analysis of designed experiments. Central Composite Design (CCD), known as a standard RSM design, is well suited for fitting a quadratic surface, which usually works well for process optimization.

The purpose of this study is to determine the optimum conditions of operating variables for the extraction of BPA from aqueous solutions by ELM through examining the effects of these variables on BPA extraction using RSM and explore the effectiveness of heat-induced demulsification with OP-4 as surfactant. Emulsion stability has always been a major concern in the application of ELM, so optimum conditions for stable emulsion were found out experimentally. The success of this work will make it possible to extract BPA from aqueous solutions by ELM using a cheap raw material, i.e. the kerosene and recycle membrane phase through an easy and effective way, i.e. the heat-induced demulsification. This study will also provide important data for the treatment of BPA wastewaters.

2. Experimental procedures

2.1. Materials

The organic membrane phase was composed of a surfactant and a solvent. The surfactant was chemical grade OP-4 and the solvent was commercial kerosene. Sulfuric acid, sodium hydroxide and BPA used in this work were all analytical grade. Purified water was used throughout this study.

2.2. Experimental design

Design-Expert 7.1.3 software was employed for the statistical design and data analysis. Four variables: the concentration of OP-4 in membrane phase, the treatment ratio (R_{we}), the concentration of NaOH in the internal phase and the volume ratio of membrane phase to internal phase (R_{oi}) were considered as important process parameters for the extraction of BPA from aqueous solutions. Therefore they were chosen as the independent variables and designated as factors A, B, C and D, respectively. Each numeric factor is varied over 5 levels: plus and minus α (α = 2), plus and minus 1 and the center point respectively, which are presented in Table 1. The results for this design are shown in Table 2. The response of the experiments was measured in terms of extraction efficiency which is defined by Eq. (1):

$$\text{Extraction Efficiency} = \frac{C_0 - C_1}{C_0} \times 100\% \tag{1}$$

where C_0 is the initial BPA concentration and C_1 is the final BPA concentration in the external aqueous phase.

The regression analysis was performed to estimate the response function. The extraction efficiency can be predicted by the quadratic model as shown by Eq. (2):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{j=1}^{k} \beta_j X_j^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \tag{2}$$

where β_i is the linear coefficient, β_j is the quadratic coefficient, β_{ij} is the cross coefficient, k is the number of factors studied in the experiment, X_i, X_j represent the coded value of each factor(A, B, C, D) and Y is the predicted response (Extraction Efficiency). In developing this regression equation, the factors were coded according to Eq. (3):

$$X_i = \left(x_i - x_i^*\right) / \Delta x_i \tag{3}$$

Table 1
Experimental range and levels of independent variables in coded and un-coded forms.

Variables	Range and levels				
	−α	−1	0	1	α
OP-4 concentration in membrane phase, %(w/v), A	2	3	4	5	6
Ratio of external phase to emulsion phase, R_{we}, B	4	8	12	16	20
NaOH concentration in internal phase, %(w/w), C	1	1.5	2	2.5	3
Ratio of membrane phase to internal phase, R_{oi}, D	0.5	0.75	1	1.25	1.5

Table 2
Central composite design matrix of four variables in coded and un-coded forms along with the observed response.

Run	A	B	C	D	OP-4% (w/v)	R_{we}	NaOH %(w/w)	R_{oi}	Extraction efficiency
1	0	0	0	0	4	12	2	1	0.9463
2	−1	1	1	−1	3	16	2.5	0.75	0.8433
3	−1	−1	1	1	3	8	2.5	1.25	0.8904
4	0	2	0	0	4	20	2	1	0.6658
5	0	0	0	0	4	12	2	1	0.9447
6	1	−1	1	−1	5	8	2.5	0.75	0.9400
7	−1	1	1	1	3	16	2.5	1.25	0.8151
8	−1	1	−1	−1	3	16	1.5	0.75	0.7754
9	1	1	1	−1	5	16	2.5	0.75	0.8737
10	0	0	0	0	4	12	2	1	0.9477
11	2	0	0	0	6	12	2	1	0.8739
12	−1	−1	−1	1	3	8	1.5	1.25	0.9220
13	1	1	−1	1	5	16	1.5	1.25	0.7995
14	1	−1	−1	1	5	8	1.5	1.25	0.9195
15	1	1	1	1	5	16	2.5	1.25	0.8701
16	−1	−1	−1	−1	3	8	1.5	0.75	0.9378
17	0	0	0	2	4	12	2	1.5	0.9053
18	0	0	−2	0	4	12	1	1	0.8987
19	−1	1	−1	1	3	16	1.5	1.25	0.7583
20	0	0	2	0	4	12	3	1	0.9330
21	0	0	0	0	4	12	2	1	0.9600
22	1	−1	1	1	5	8	2.5	1.25	0.9383
23	0	0	0	0	4	12	2	1	0.9510
24	1	−1	−1	−1	5	8	1.5	0.75	0.9376
25	0	0	0	−2	4	12	2	0.5	0.9350
26	−2	0	0	0	2	12	2	1	0.7936
27	−1	−1	1	−1	3	8	2.5	0.75	0.9333
28	0	0	0	0	4	12	2	1	0.9472
29	1	1	−1	−1	5	16	1.5	0.75	0.7639
30	0	−2	0	0	4	4	2	1	0.8798