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Emulsion Liquid Membrane Extraction of Bisphenol A with Three-dimensional Spiral Plate-type Microchannel

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Authors' contributions

This work was carried out in collaboration among all authors. Authors XC and DH designed the study. Authors DH and YP conducted the experiments. Authors DH and XC performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors DH and ZM managed the analyses of the study. Authors MW and YP managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The extraction of BPA (Bisphenol A) from aqueous solutions was performed using A set of three-dimensional spiral plate-type microchannel (3D-SPM) by emulsion liquid membrane (ELM). In the continuous extraction experiments, the effect of the flow rate ratio of emulsion to external aqueous phase ratios, *Q*e/*Q*a and height of microchannel, H and plate numbers, P, on the BPA extraction was studied. It was found that the less the height of microchannel is, the more extraction efficient it is. By increasing the plate number, the extraction efficiency and the distribution coefficient increase. The optimum performance was investigated by changing the flow rates of *Q*a and *Q*e. When using the flow rate ratio *Q*e/*Q*a of 7:1 in a 3D-SPM with a plate number of 9 and a height of 100 μm, 97% maximum depletion of BPA was obtained in 7.9 Seconds. These results show that 3D-SPM can intensify the ELM extraction process of BPA, which provides an optional technology for the disposal of BPA.

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1. INTRODUCTION

Bisphenol A (BPA, $C_{15}H_{16}O_2$, 2,2-bis (4-hydroxyphenyl)propane), is mainly used as a principle monomer to manufacture epoxy resins, polycarbonate and other plastics [1]. Bisphenol A is added in the plastic to improve the transparency and is widely used in the production of baby bottles, barrels for bottled water, lenses and optical discs, also bisphenol A can be added to acidic fruit containers to protect acid corrosion metal containers. However, BPA is a recognized environmental hormone and may lead to humans and other biological environmental endocrine disorders through its active ingredients. Although the USA, EU, and most areas in the world had banned BPA to be used for baby products from 2010, BPA still may cause serious environmental problems by incorrect disposal into the water from other industry, and the threat to the survival of humans and animals [2].

Usually, BPA can be eliminated through traditional physical, chemical or biological treatments, such as solvent extraction, photochemical degradation, biodegradation, etc [3]. As a pollutant in solution, BPA usually is in low concentration from μg/L to mg/L and it is time-consuming or uneconomical to get rid of BPA with those traditional methods above [4,5]. New techniques should be explored to remove BPA more efficiently from wastewater and water sources.

Emulsion liquid membranes (ELMs) have been used to treat various industrial wastes from aqueous solutions since their invention in 1968, especially when the targeted species is present at low concentrations in the solution. Some researchers [6,7,8] had employ ELMs to extract BPA from aqueous solutions with ppm concentration. Attef Daas and Oualid Hamdaoui [6] employed 0.05N NaOH in Hexane W/O emulsion with 3% w/w SP80 as an emulsifier to extract 5-20 mg/L BPA aqueous solution, and the extraction efficiency can be up to 98% in 10-20 minutes. But in order to get the concentrate BPA in the internal phase after extraction, the chemical demulsification was used for the high emulsifier concentration used. Hongpu Jiao etc [7] used 2-2.5% w/w NaOH in Kerosene W/O emulsion with 4-4.5% w/w OP-4 as an emulsifier to extract 100 mg/L BPA aqueous solution, and the extraction efficiency can be up to 97.5%. The demulsification of emulsion in this research was achieved by heating the emulsion to 80ºC, which is not practicable for other emulsifiers, like SP80.

From these researches [6,7,8], it is obvious that it takes 10-40 minutes for ELMs in batch to remove BPA by above 95% extraction efficiency. Therefore 3-5% w/w emulsifier needed to be used to stabilize the emulsion, which adds difficulty to the demulsification process and makes the whole process hard to be continuous.

Microfluidics has the intrinsic advantage of process intensification for its Micron-scale channel size. In the areas of heat exchange [9], separation [10], reaction [11] and extraction [12], microfluidics shows its high efficiency and shorts the time for these unit operations from hours to minutes or seconds. If the resident time for ELMs extracting BPA was shortened to be seconds, the quantity of emulsifier will be decreased and the process for extraction and demulsification could be simple, which will make all the ELMs extraction process to be more simple, continuous, economical and environmentally-friendly.

In this research, to further improve the extraction efficiency of BPA with ELMs, we used 100-200 μm 3D-PSM as a contactor for ELMs extracting BPA from aqueous solutions, and explore the optimization condition to short the resident time for extraction. The 3D-PSM had been reported [13,14] to demulsify the W/O emulsion efficiently by adding a DC electric field. And with this research, we focus on the effect of flow rate ratios, Q_a/Q_e the height of microchannel H, and plate numbers P, on the BPA extraction η, and try to find a simple continuous process for ELMs extraction.

2. EXPERIMENTAL SECTION

2.1 Materials

Kerosene was purchased from China Petrochemical Group Co., Ltd. (Chengdu, China); BPA, Span80, sodium hydroxide (NaOH), methanol and anhydrous ethanol were all purchased from Kelong Chemicals Co., Ltd. (Chengdu, China). BPA, Span80, NaOH, methanol and anhydrous ethanol were all of the analytical grades and used as received. All the water used was RO water obtained by the pure water machine (DZG-303A, AiKe, Shanghai, China).

2.2 Experimental Setup

The experimental apparatus is shown in Fig. 1, which is composed of two conical flasks, two medium pressure piston pumps (Flash100 & TBP5002, Tong Tian Biotech, Shanghai, China), three-dimensional spiral plate-type microchannel (3D-SPM) and an effluent collection separatory funnel.

The structure of 3D-SPM was illustrated in Fig. 2. Fig. 2A and 2B show the external and internal structure of 3D-SPM, alternatively. Fig. 2C shows the arrangement of plates composing this plate-type microchannel. The 3D-SPM was composed of an alternating arrangement of hollow copper plates (100 μm, 150 μm and 200 μm, Golden Dragon, Chengdu, China) and polytetrafluoro ethylene (PTFE) plates (100 μm, Resistance Sealing Material, Chengdu, China) and two stainless steel end-plates. A semicircle arch with radian of 180° was etched onto each hollow Cu plate, and one orifice corresponding to the end of the arc was pierced onto the adjacent PTFE sheets. At both ends along the arrangement line, there were two pieces of stainless steel end-plates, which were 5 mm in-depth and with two orifices of entrance and exit. For the manufacturing details of 3D-SPM, please refer to our previous article [10,13,14].

2.3 Feed Solution Preparation

100 mg·L^{-1} BPA aqueous solution was used as the to-be-extracted external aqueous phase. It was prepared by dissolving 0.05 g analytical grade BPA in 5mL of methanol and then diluting with RO water to the volume of 500 mL. BPA concentrations were analyzed by a UV-visible spectrophotometer (TU-1950, PuXi, Beijing, China).

2.4 Preparation of W/O Emulsion

The W/O emulsion was prepared as follows: Firstly, 0.25M NaOH aqueous solution and 100 g·L^{-1} Span80 kerosene solution were pre-prepared. Then, 47 mL kerosene, 3 mL Span80 emulsifier, and 40 mL NaOH solution were added in sequence and then mixed. At last, the mixed solution was stirred with a high-speed homogenizer (FJ200, Specimen & Model, Shanghai, China) at the speed of 14,000 rpm for two minutes. The stability of emulsion prepared was evaluated according to Equation (1):

$$J = \frac{V_{\text{emulsion}}}{V_{\text{total}}} = \frac{V_{\text{total}} - V_{\text{water}} - V_{\text{kerosene}}}{V_{\text{total}}} \quad (1)$$

Where J is the stability of the emulsion, V_{emulsion} (mL) is the volume of the residual emulsion after standing, V_{total} (mL) is the total volume of emulsion collected before standing, V_{water} (mL) is the volume of water phase after standing, V_{kerosene} (mL) is the volume of oil phase after standing. The emulsion prepared with this method can be stable for at least 2 hours with stability over 90% [13,14].

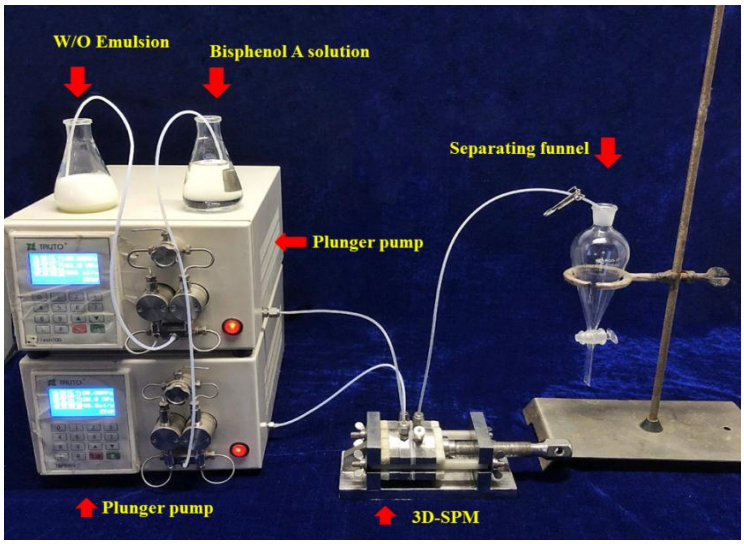

Fig. 1. Photograph of the three-dimensional spiral plate-type microchannel (3D-SPM) experimental setup

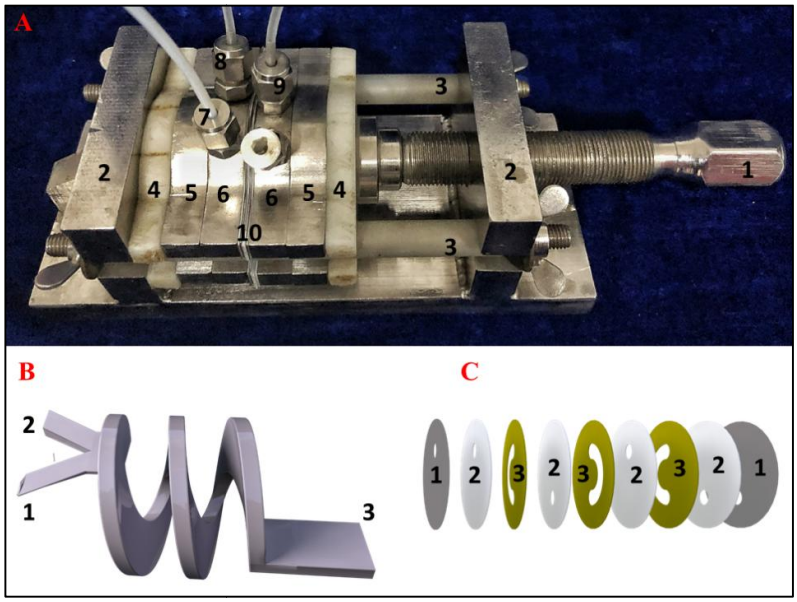

Fig. 2. Schematic diagram of the 3D-SPM

A. Assembled diagram (1: screw; 2: stainless steel bracket; 3: PTFE coated stainless steel pull rod; 4: 10 mm thick PTFE plate; 5: stainless steel pressure plate; 6: stainless steel end plate; 7, 8: inlet; 9: outlet; 10: microchannel); B. Perspective diagram (1, 2: inlet; 3: outlet); C. Assembly diagram (1: stainless steel end plates; 2: PTFE plates; 3: hollow copper plates)

2.5 BPA Extraction

The W/O emulsion and BPA external aqueous solution were pumped to the two inlets of 3D-SPM simultaneously, the extraction process was carried out by the multiphase fluid passing through the 3D-SPM and from the outlet a segmented flow of the extracted raffinate and the extract emulsion flow out into the separatory funnel. After 10 minutes of standing by gravity, the external aqueous phase was separated from the emulsion. Then the emulsion was demulsified by centrifugated at 4000 rpm for 30 minutes and the internal aqueous phase was separated from the kerosene oil phase. For the external and internal aqueous phases, the BPA concentrations were measured by the ultraviolet spectrophotometry as shown in 2.6. Then the extraction efficiency was calculated according to Equation (2).

$$\eta = \frac{c_{e,0} - c_{e,1}}{c_{e,0}} \quad (2)$$

where η is the extraction efficiency, $c_{e,0}$ (mg/L) is the initial BPA concentration, $c_{e,1}$ (mg/L) is the final BPA concentration in the external aqueous phase. Each experiment was performed twice at least and the mean values were presented.

2.6 Analysis

The BPA concentrations were analyzed with a well-known procedure based on Lambert-Beer law by using a UV-visible spectrophotometer (TU-1950, PuXi, Beijing, China). The wavelength resolution and the bandwidth were, respectively, 0.3 and 0.1 nm. The length of the optical path in the quartz cell was 1 cm. The maximum absorption wavelength was determined at 278 nm for the non-ionic form of BPA at the pH values of 7-8. The Calibration plot was constructed by the standard BPA solution of 1, 2, 5, 10, 15, 20, 25, 30 $mg \cdot L^{-1}$. The ambient temperature was stabilized at 20ºC for all the experiments. The calibration was repeated five times during the period of measurements. The linearization of this plot usually provided the determination coefficient above 99.95%.

3. RESULTS AND DISCUSSION

3.1 Membrane Stability

For ELMs extraction, the emulsion must be stable during extraction, which gives the requirement for the quantity of emulsifier used in the preparation of emulsions. For the 3D-SPM extraction process, the W/O emulsion is pump

through the microchannel together with the target BPA solution. The resident time of W/O emulsion touching with BPA solution in the 3D-SPM is less than 10 seconds, which is much less than the resident time of 10-40 minutes [6,7,8] for ELMs extraction in Batch. Therefore, the membrane, oil phase between external and internal water phase, should be stable in this short period, and less quantity of emulsifier SP80 was used to stable the W/O emulsion. In our experiments, only 33.33 mg/L SP80 was used, and the detailed emulsion preparation method could refer to our former work [13,14]. The W/O emulsions prepared were pumped through the 3D-SPM, and no significant demulsification was observed. Also, we had reported [14] that the 3D-SPM could demulsify the W/O emulsion only by adding a 40-100 $V \cdot cm^{-1}$ DC electric field. So, the emulsifier dosage for the emulsion used in the 3D-SPM extraction process could be decreased by 90%, which is easy for recycling the emulsion and friendly for the environment.

3.2 BPA Extraction

Keeping BPA concentration at 100 $mg \cdot L^{-1}$ in the external aqueous phase, NaOH concentration at 10 $g \cdot L^{-1}$ in internal aqueous phase and volume ratio of W/O emulsion at 40%, a series of experiments was conducted to obtain adequate hydrodynamic and microchannel structure conditions.

3.2.1 Effect of flow rate ratio *Q*e/*Q*a

For this continuous extraction process, the flow rates of BPA feeding solution and W/O emulsion were controlled to control the phase ratio between the external phase and the emulsion phase. The flow rate ratios *Q*e/*Q*a were 1:7, 2:6, 4:4, 6:2, 7:1 and the total flow rate is controlled at 8 $mL \cdot min^{-1}$ to keep the total resident time of fluid to be constant. The effect of the flow rate ratio on the extraction efficiency was shown in Fig. 3.

From Fig. 3, the extraction efficiency increases from 44.38% to 97.79% with the flow rate ratios *Q*e/*Q*a increase from 1:7 to 7:1. Based on the distribution nature, the BPA will transfer from the external aqueous phase through the membrane phase to the internal phase. The more the flow rate ratio *Q*e/*Q*a is, the more emulsion is used to extract the BPA solution, and the more BPA is transferred. To be mentioned is the resident time for the 97.79% extraction efficiency is only 7.9 seconds, and it shows a high efficiency compared with traditional extraction processes [15,16].

3.2.2 Effect of plate number

3D-SPM is a kind of compact microchannel and the length of microchannel can be easily enlarged by adding the plate number. The plate numbers of 5, 7 and 9 were investigated by fixing the flow rate ratio *Q*e/*Q*a to be 7:1 and the height of microchannel to be 100 μm. The result is shown in Fig. 4.

From Fig. 4, it is obvious that the extraction efficiency increases by adding the plate number from 5 to 9. The increased plate number leads to a bigger length of the microchannel and the resident time of extraction will be longer. The resident time rises from 4.4 seconds to 7.9 seconds. By increasing the resident time, more BPA in the external solution will be transferred through the membrane phase to the internal

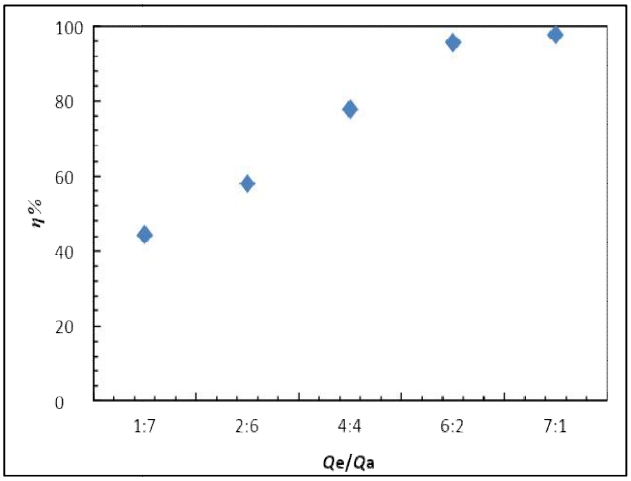

Fig. 3. Effect of flow rate ratio *Q*e/*Q*a on the extraction efficiency

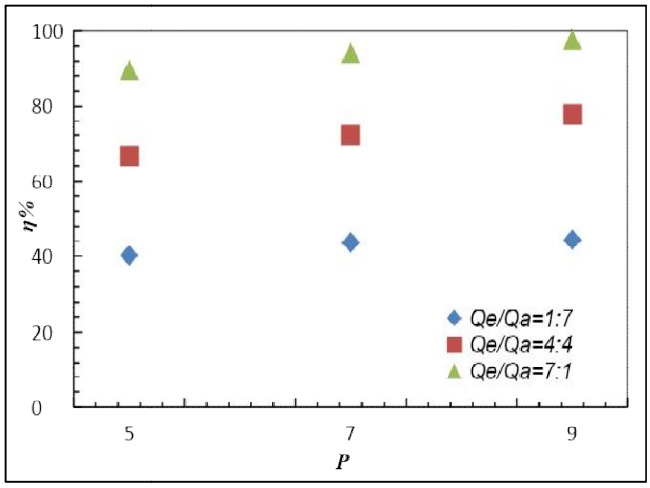

Fig. 4. Effect of plate number of microchannel on the extraction efficiency

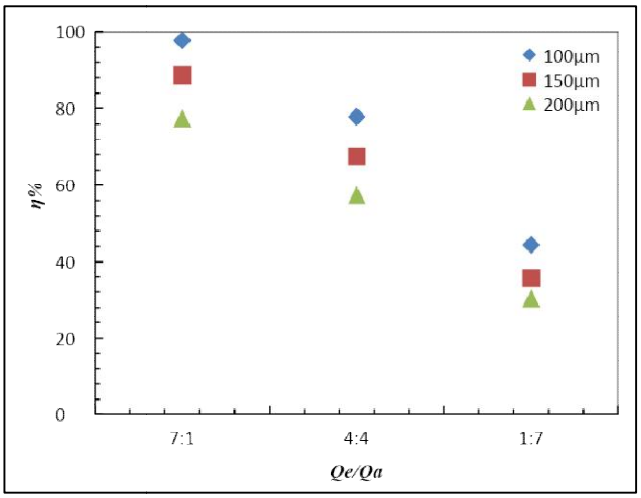

Fig. 5. Effect of microchannel height on the extraction efficiency

aqueous phase. It is important to note that even the 3D-SPM with 5 plates could reach 89.66% extraction efficiency and the resident time is only 4.4 seconds.

3.2.3 Effect of msicrochannel height

By changing the hollow copper plates with a depth of 100, 150 and 200 μm, the microchannel height could be adjusted and the effect of microchannel height on the extraction was investigated. The result is shown in Fig. 5.

Fig. 5 shows that the extraction efficiency increase by lowing the height of the microchannel. For the height of 100 μm at the same flow rate, the resident time of BPA solution and the emulsion is only half of that of microchannel with height of 200 μm, however, the extraction efficiency of the former is 97.79% when *Qe/Qa* equal to 7:1, and that of the latter is only 77.46%. This result suggests that the microchannel with lower height could intensify the mass transfer in the ELMs extraction. According to references [17,18,19], by lowing the channel height, the confinement of multiphase fluid in the microchannel will be increased. It is obvious that confined flow of multiphase slug flow, which is observed at the outlet of 3D-SPM, would help the mass transfer in the microchannel.

3.3 Demulsification

After the extraction process, the emulsion was separated with an external aqueous phase in the

separatory funnel and demulsified with 3D-SPM adding a 250 $V \cdot cm^{-1}$ DC electric field to collect the inner phase and recycle the emulsion. The demulsification efficiency is 90.3% when employing the 3D-SPM with a height of 200 μm and a plate number of 18 at an emulsion flow rate of 2 $mL \cdot min^{-1}$. The result of the demulsification of W/O emulsion with 3D-ESPM could be referred to as our work [13,14]. This means the maximum recovery of BPA by 88.3%. Regarding the demulsification step is also a continuous process, the ELMs extraction with 3D-SPM is a feasible technology to be applied in the industry by the advantage of continuous operation and high efficiency.

4. CONCLUSION

BPA in aqueous solution was continuously extracted by ELMs with three-dimensional spiral plate-type microchannel (3D-SPM). High extraction efficiency 97.79% was achieved in the 3D-SPM with a height of 100 μm and a plate number of 9 and continuous demulsification of the emulsion after extraction was achieved by the efficiency of 90.3% with a 3D-SPM adding 250 $V \cdot cm^{-1}$ DC electric field. An important finding is the microchannel with lower height shows higher extraction efficiency, which implies that confined multiphase flow will intensify the ELMs extraction process.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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