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Removal of 4-nitrophenol from water by emulsion liquid membrane

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ABSTRACT

In this work, the removal of 4-nitrophenol (4-NP) from water by emulsion liquid membrane (ELM) was investigated. An ELM system is made up of hexane as a diluent, Span 80 as the surfactant, and sodium carbonate as the inner aqueous solution. Effect of volume ratio of emulsion to external phase on the extraction of 4-NP was studied in the range of 5/250–90/250. The influence of 4-NP initial concentration and salt addition on the permeation of the pollutant was also investigated. The obtained results showed that the volume ratio of emulsion to external phase has a significant effect on the removal of 4-NP using ELM. It was found that by appropriate selection of the extraction and stability conditions, a treatment ratio of 30/250 conducted to excellent removal percentage (>99%). The 4-NP transport was influenced by solute initial concentration. The presence of NaCl in the continuous phase had an impact on the removal percentage, especially at high salt concentrations. The ELM treatment process represents a very interesting advanced separation process for the removal of 4-NP from water.

Keywords: 4-nitrophenol; Removal; Emulsion liquid membrane; Wastewater treatment

1. Introduction

A variety of separation difficulties have been tackled by using emulsion liquid membrane (ELM) process over the last two decades. In fact, ELM has some attractive features, compared with conventional processes, such as simple operation, high efficiency, extraction, and stripping in one stage, larger interfacial area, possibility of continuous operation, etc. ELM is known to be one of the most effective methods for the separation and concentration when the material being extracted is present in very low concentration. In addition, the ELM has received special interest for the treatment of industrial wastewaters containing a wide range of toxic contaminants such as 4-nitrophenol (4-NP). This phenolic compound is a toxic and biorefractory pollutant considered priority by the United States Environmental Protection Agency and the European Union [1,2]. It can damage the central nervous system, liver, kidney, and blood of humans and animals [3,4]. It is widely used in the production of pesticides, herbicides, and synthetic dyes. Hence, its removal from industrial effluents is an important practical problem. The treatment times with chemical or biological methods may be quite high and total mineralization of the effluent stream may not be

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possible. Existing wastewater treatment methods such as adsorption on activated carbon and chemical oxidation suffer from limitations, such as limited applicability and low efficiency, thus imparting the need of research into alternative treatment techniques such as extraction by ELM.

The advantage of using ELM process is that the extraction and stripping step can be combined in one stage, which leads to simultaneous purification and concentration of the solute. ELMs consist of an aqueous internal phase stabilized by a surfactant and dispersed as very fine droplets inside a membrane (organic) phase. The resulting liquid membrane, or water-in-oil (W/O) emulsion, is further dispersed as emulsion globules in external feed phase (a second aqueous phase). Target solute in the external feed phase is transferred across the membrane phase into the internal phase during an extraction process. In this water-in-oil-in-water (W/O/W) ELM, the organic phase functions as a membrane. The solute mass transfer is driven by the concentration difference between the external feed phase and the internal phase. After the subsequent separation of the external phase from the W/O emulsion by gravity (settling), splitting of the emulsion (demulsification) is carried out. Demulsification is performed in order to separate the phases that makeup the emulsion, the internal aqueous phase, and the organic membrane phase. At the end of the process, the membrane phase can be reused and the receiving phase (enriched in the recovered solute) can be recycled or recovered for solute [5].

Despite the fact that numerous investigations have been carried out on the extraction of phenols from water by ELM [6–17], comprehensive studies on the influence of process parameters are yet to be conducted. The aim of this work was to investigate the removal of 4-NP from water by ELM. The influence of volume ratio of emulsion to external phase on the extraction of 4-NP was examined. Effect of 4-NP initial concentration and salt addition on the removal of the pollutant was also studied.

2. Materials and methods

4-NP stock solutions were prepared by dissolving analytical grade 4-NP, purchased from Sigma–Aldrich, in distilled water. Feed solutions were prepared by addition of an acid solution into aqueous solution containing appropriate amount of 4-NP. 4-NP feed solutions from a known amount of 4-NP stock solution were diluted with distilled water to a given concentration. All other chemicals used were of the highest available purity and were purchased from Sigma–Aldrich.

The extraction of 4-NP using ELM involves three steps, namely preparation of liquid membrane emulsion, extraction of the solute from feed by contacting the emulsion, and separation of liquid emulsion from the external phase by settling (Fig. 1).

Internal aqueous standard solutions were prepared by taking the required amount of Na_2CO_3 in distilled water. The organic membrane phase was prepared by dissolving the appropriate amount (3% w/w) of Span 80 as a surfactant in hexane under a gentle mixing by a magnetic stirrer. The emulsion was prepared by mixing the internal aqueous solution with the organic membrane phase using a high-speed disperser for a fixed mixing time.

The three-phase dispersion W/O/W was stirred with a mechanic stirrer at 300 rpm. A volume (30 mL, except when the effect of treatment ratio was examined) of the prepared W/O emulsion was added to 250 mL of external aqueous solution in a cylindrical thermostated vessel that was attached to an overhead mechanical stirrer. The agitator used was a 45° pitch four blades down pumping impeller (diameter 5 cm). The content of the vessel was stirred in order to disperse the W/O emulsion in the external phase at a fixed speed (300 rpm) for different contact times to make the W/O/W double emulsions. The external phase solution was periodically sampled at various time intervals. The concentration of pollutant in the solutions was determined by a UV–Visible spectrophotometer set at the wavelength corresponding to maximum absorbance of the studied pollutant (318 nm). Each experiment was performed twice at

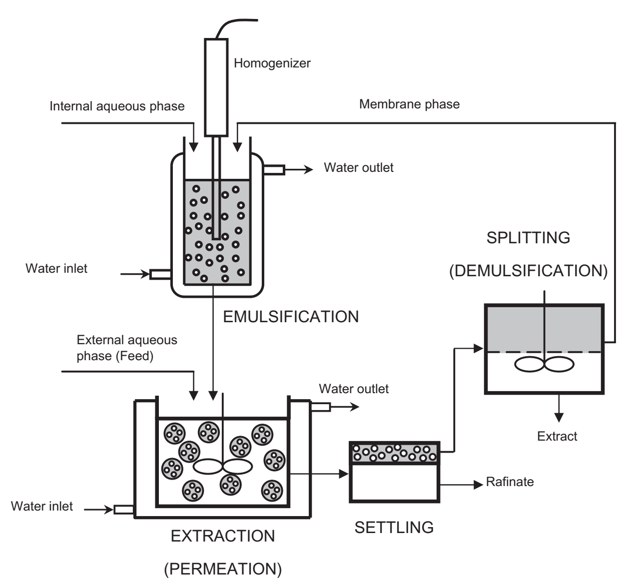

Fig. 1. The ELM process.

least and the mean values were presented. The maximum standard deviation was about 2%.

3. Results and discussion

The 4-NP in the external phase penetrates from the external phase to the internal phase through the membrane in molecular state. It reaches the surface between membrane and internal phase and reacts with Na_2CO_3 to form sodium 4-nitrophenolate. The latter compound, that is charged specie in basic aqueous phase, could not diffuse back to the external phase, and thus was retained in the internal aqueous phase. The reaction maintains a low solute concentration in the internal phase, providing a high driving force. The internal aqueous phase, rich in pollutant 4-NP, was separated from the liquid membrane, where the membrane phase is recycled for other uses.

3.1. Effect of treatment ratio

The treatment ratio is the volume ratio of the emulsion to the external solution and it is identical to solvent to feed ratio in conventional solvent extraction. The treatment ratio plays an important role in determining effectiveness of ELMs [13,18]. The effect of the volume ratio of emulsion to the external phase on the extraction efficiency was studied. Experiments were carried out using the following experimental conditions [19,20]: initial 4-NP concentration of 25 mg/L; external phase (4-NP solution) volume of 250 mL; volume ratio of internal phase to organic phase of 1/1; emulsification time of 4 min; stirring speed of 300 rpm; Span 80 concentration of 3% (w/w); internal phase concentration (Na_2CO_3) of 0.1 N; sulfuric acid concentration in the feed phase of 0.1 N; and hexane as diluent. The obtained results are shown in Fig. 2. It was observed that the removal percentage increased from 10.5 to 99.7% with increasing treatment ratio from 5/250 to 30/250. The highest extraction performance of 4-NP from external feed phase was obtained at a treatment ratio of 30/250. Further increase in treatment ratio above 30/250 slightly decreased the removal percentage. This was due to improper mixing of phases because of higher proportion of the more viscous emulsion phase [21]. The lower treatment ratio means less emulsion is required to extract the solute that is desirable from a processing point of view to ensure maximum enrichment with respect to the external phase [22]. In general, a larger treatment ratio value translates to a larger contact area of ELM with the solution to be treated, resulting in a greater mass transfer ratio, but at the expense of higher emulsion volume. Therefore, in order to ensure a good dispersion of emulsion in the external phase solution and to increase the concentration of the solute in the stripping phase, volume ratio of emulsion to external feed solution of 30/250 was selected as the best treatment ratio.

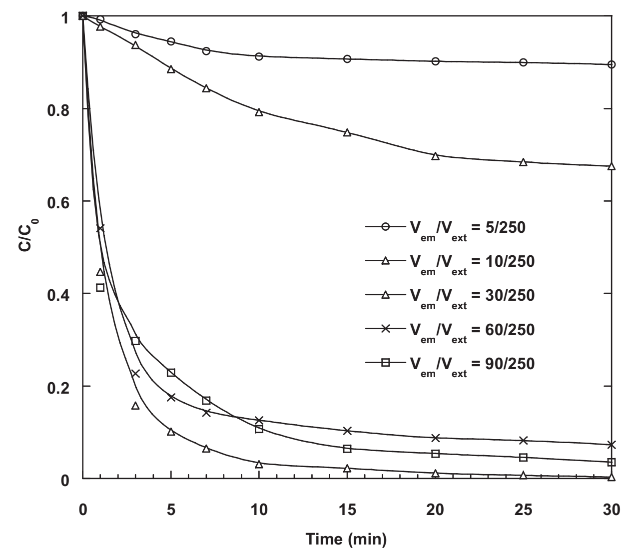

Fig. 2. Effect of volume ratio of emulsion to external phase on the extraction of 4-NP (25 mg/L) by ELM (experimental conditions—External phase (4-NP solution) volume: 250 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 4 min; stirring speed: 300 rpm; concentration of Span 80: 3% (w/w); internal phase concentration (Na_2CO_3): 0.1 N; sulfuric acid concentration in the feed phase: 0.1 N; and diluent: hexane).

3.2. Effect of initial 4-NP concentration

The effect of initial concentration of 4-NP ranging from 5 to 80 mg/L on the degree of extraction was studied and the obtained results are shown in Fig. 3. The removal efficiency increases with the increase of 4-NP concentration from 5 to 25 mg/L. This may be attributed to an increase in the driving force, the concentration gradient, with the increase in the initial solute concentration [23]. When initial 4-NP concentration is low, most of the solute diffusing within the emulsion globule is stripped by the internal aqueous phase droplets, which are situated in the peripheral regions of the emulsion globule. For substrate concentrations higher than 25 mg/L, the extraction percentage decreased. The saturation of the internal droplets in the peripheral region of the emulsion is attained more

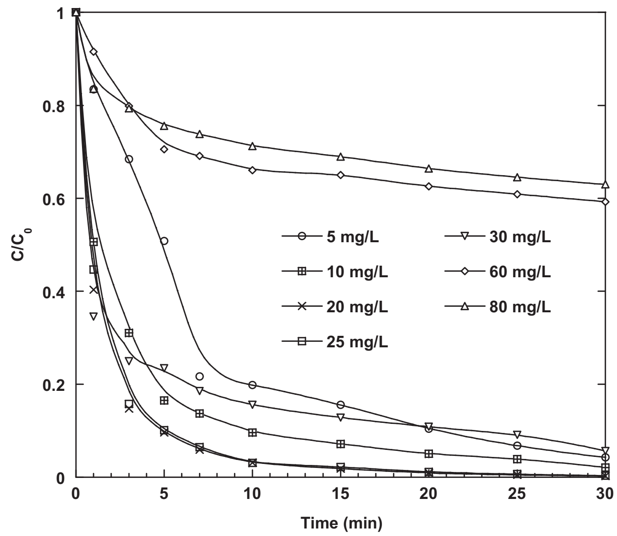

Fig. 3. Effect of 4-NP concentration on the extraction efficiency (experimental conditions—Emulsion volume: 30 mL; external phase (4-NP solution) volume: 250 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 4 min; stirring speed: 300 rpm; concentration of Span 80: 3% (w/w); volume ratio of W/O emulsion to external phase: 30/250; internal phase concentration (Na_2CO_3): 0.1 N; sulfuric acid concentration in the external phase: 0.1 N; and diluent: hexane).

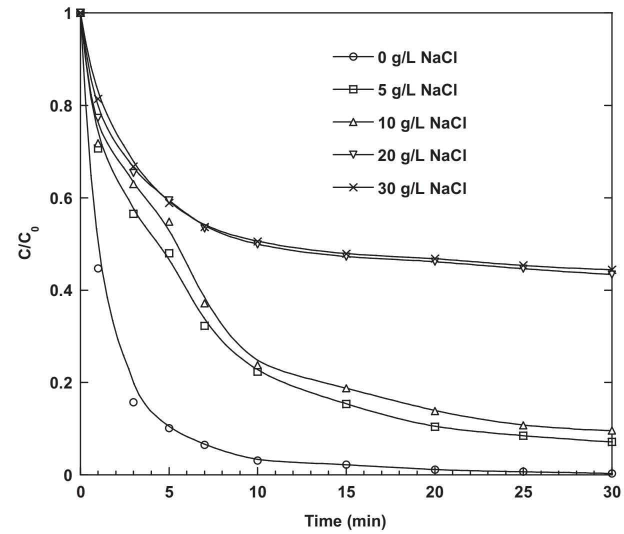

Fig. 4. Effect of salt on the extraction of 4-NP (25 mg/L) by ELM (experimental conditions—Emulsion volume: 30 mL; external phase (4-NP solution) volume: 250 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 4 min; stirring speed: 300 rpm; concentration of Span 80: 3% (w/w); volume ratio of W/O emulsion to external phase: 30/250; internal phase concentration (Na_2CO_3): 0.1 N sulfuric acid concentration in the external phase: 0.1 N; and diluent: hexane).

rapidly for high 4-NP concentrations in the feed phase. When initial 4-NP concentration increases, the peripheral droplets are rapidly exhausted, requiring the solute to permeate deeper within the globule prior to being stripped. Therefore, an increase in initial 4-NP concentration also corresponds to an increase in diffusional path lengths.

3.3. *Effect of salt*

Salt could be present in a various range of concentration in wastewater and influence the ELM process by changing the ionic strength in the external phase, which affects the membrane stability [24]. To understand the influence of salt (sodium chloride) on 4-NP extraction, feed solution with different concentrations of sodium chloride were prepared and tested. Experiments were conducted in the same operating conditions as mentioned previously. The effect of salt concentration in the external feed phase on the degree of 4-NP removal was analyzed over NaCl concentration range from 0 to 30 g/L. The influence of sodium chloride concentration on the extraction of 4-NP is illustrated in Fig. 4. As observed, both the rate and efficiency of extraction were gradually affected by the increase in sodium chloride concentration.

4. Conclusion

In this study, it was clearly indicated that the treatment ratio controls the interfacial mass transfer across ELMs and the separation efficiency. Consequently, in order to ensure a good dispersion of emulsion in the external phase solution and to increase the concentration of the solute in the stripping phase, volume ratio of emulsion to external feed solution of 30/250 was selected as the best treatment ratio. By using the optimal operating parameters, it was possible to wholly remove all of 4-NP molecules from the external feed solution. The 4-NP transport was influenced by solute initial concentration. The presence of NaCl in the continuous phase had an impact on the removal percentage, particularly at high salt concentrations. ELM technique is a promising alternative to conventional methods and should increase awareness of the potential for recovery of 4-NP.

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