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# REMOVAL OF PHENOL CONTAMINANTS FROM AQUEOUS SOLUTION USING EMULSION LIQUID MEMBRANE

**Tamara. L. Rasool [a], Ahmed A. Mohammed [b]**
Environmental Engineering Department, University of Baghdad, Baghdad, Iraq.
E-mail: tamara.Luay2111m@coeng.uobaghdad.edu.iq

***Abstract***

The current paper focuses on assessing key parameters affecting the extraction of phenol as well as emulsion stability using the emulsion liquid membrane technology. parameters affecting the extraction have been studied: stripping phase concentration, Effect of Feed Phase pH, Effect of Feed Concentration taking into consideration the emulsion breaking. Experiments proved that using the resulting optimum values will maximize both extraction and stripping efficiencies (92% and 87% respectively), while minimizing the emulsion breakage (increasing the stability of emulsion) to 0.921% with no need to employ a carrier agent. A 4% (v/v) Span 80 as a surfactant, 5800 rpm homogenizer speed, 0.1M NaOH as an internal phase concentration, and 5 min emulsification time are chosen to be the optimum parameters' values. A study of extraction kinetics of this work can be extended to the removal of other types of from water.

## *1.Introduction*

Phenol is a major pollutant in wastewater due to its presence in the effluent of major processing and refining plant. It will cause severe effects on human being (Kalaiarasan.2014).The Environment Protection Agency (EPA) has included phenol as one of primary pollutants that abide to specific regulations in order to protect the environment and human being as their toxicity is high (Othman *et al*., 2017).The methods most frequently employed in phenol removal from aqueous solutions include the following: adsorption (Dehmani *et al*., 2020), advanced oxidation (Jiang and Mao 2012), biological treatment (Jiang et al. 2010), electrocoagulation (Hernández-Francisco et al. 2017), flotation (Wilberg *et al*., 2000) and emulsion liquid membrane, etc. Low efficiency in terms of performance with small concentrations of inorganic and organic contaminants, high operational expenditure incurred, accumulation of secondary sludge, extended treatment and operational times, are some of the factors which pose restrictions on the success of the methods cited above (Mohammed and Selman 2018). In light of the state of the art research works, to date the simplest method of chemical contaminant removal from wastewater is through the use of the emulsion liquid membrane (ELM) technique. On comparison with the ELM, the usage of classical semi-permeable and permeable membranes in reverse osmosis, ultrafiltration and microfiltration displayed limitations induced by sensitivity and difficult operating conditions, besides high maintenance and operating expenditures, heightened power consumption and huge quantities of sludge (Hussein *et al*., 2019). Numerous studies in the literature advocate the ELM technique which has now earned massive popularity (Raji *et al*., 2017, Kusumastuti *et al*., 2018, Seifollahi *et al*., 2019) for its unique features over other conventional methods used in the recovery and removal of

inorganic and organic pollutants from wastewater. These characteristics include simplicity and easy operation process, high degree of efficiency in removal and recovery, simultaneous stripping and extraction, high flux, low operating expenditure and low capital cost (Kohli *et al*., 2019, Mohammed *et al*., 2020). Overall, the ELM is a three-phase dispersion system, which includes an immiscible organic phase (membrane) and a miscible liquid aqueous phase (internal and external). The emulsion is created by homogenization of the internal aqueous phase and organic oil phase via high-speed emulsification, in the presence of a stabilizing agent to help maintain the emulsion stability. This is done by preventing the internal phase droplets from coalescing to produce the water-in-oil (w/o) emulsion. This is then dispersed in an external feed phase to form the water-in-oil-in-water (w/o/w) emulsion (Mohammed *et al*., 2020). The concept of contaminant separation utilizing emulsion liquid membrane involves the dispersal of the emulsion into the aqueous feed phase and the transportation of the constituents across the organic oil phase to arrive at the internal stripping phase as droplets. The principal hurdle in the ELM process is emulsion stability, meaning the breakdown of the emulsion to release the internal phase of the outside emulsion droplet. Therefore, it is necessary to reach the target stability level to overcome the application problems in the ELM system on an industrial scale through the use of the appropriate surfactant. In the literature, the use of many surfactant types has been cited, among which span 80, is extensively employed to produce a milky-white emulsion(Mohammed and Al-Khateeb,2022) .

## *2.Materials and Methods*

### *2.1. Materials*

Analytical reagent-grade chemicals, along with distilled water were employed in this work. Chemicals used phenol, purchased from the local market (ALPHA CHEMIKA made in India). The chemical formula of phenol ($C_6H_6O$) is shown in Figure (2-1). Molar mass (94.11 g/mol), Wavelength (270 nm), Assay=99.5%. Both hydrochloric acid (HCl) and sodium hydroxide are acquired from (Thomas beaker, India). The liquid membrane phase consists of a surfactant and a diluent, the nonionic surfactant engaged was sorbitan monooleate, commonly recognized as Span 80, which was obtained from (Merck; Darmstadt; Germany), while kerosene(diluent) was obtained from (Iraq southren oil company) . All laboratory tests were carried out at room temperature of 25 °C. The equipment used in this research are homogenizer (Mtops, SR 30), compact digital mixer system (Heidolph, RZR 2021), quartz cells, UV Spectrophotometer (UV-1800 24v, made in Japan), centrifuge (Isolab), pH meter (ATC) and a magnetic stirrer with temperature controller (Isolab).

### *2.2. Experimental work*

The experimental structure was confined into two main sections. The first one is the ELM formulation, and determining the membrane stability via diverse operating parameters. The second section concerns investigating the ELM performance on the extraction of phenol (feed phase). For the first part, a water-in-oil emulsion was formed by the addition of internal phase (NaOH)

dropwise into the membrane phase (Span 80 and kerosene) while using a homogenizer (high speed mixer) for a specified time. The membrane phase was formed via dissolving a specific amount of surfactant (Span 80) in kerosene by gently stirring via magnetic stirrer. While the internal aqueous solution was formed by taking the required amount of acid solution (NaOH) in the allocated amount of distilled water. The emulsion is poured to external aqueous solution while mixing continuously, causing globule formation. Each globule is made of droplets of stripping solution encased in the membrane solution that contains the surfactant. A flow diagram of ELM process is outlined in Figure( 2-1) Samples were taken from the mixture at certain time intervals using syringes and pH values were recorded. By the completion of each experiment, the resulting double emulsion is allowed to be naturally separated from feed solution due to gravitational force, then a de-emulsification process was achieved by applying centrifugal force on the emulsion to segregate the phases making up the emulsion resulting in the capability of reusing membrane solution while the contaminant would be extracted as a concentrated solution. Samples are filtered using syringe filters (pore diameter 0.22 μm). phenol concentration in the separated external phase and in filtered samples is measured using an ultraviolet spectrophotometer (UV) corresponding to a 270 nm wavelength to evaluate the stripping and extraction capacity of phenol.

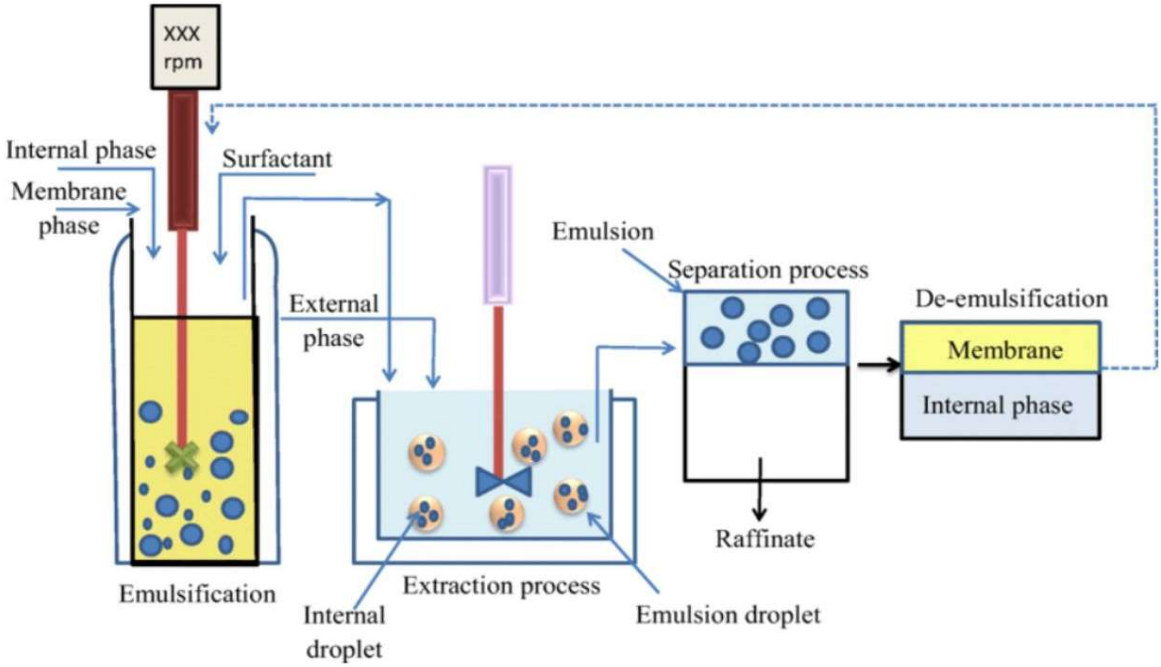


**figure:(2-1) flow diagram of ELM process.**

### *3. Analysis and Calculations*

### *3.1. Extraction process of phenol*

The concentration of phenol in the external and internal phase were by using the was measured by UV visible spectrophotometer at the maximum wavelength (270nm) .According Eq. (3-1) gotten the removal efficiency of phenol solution.

$$\textbf{Removal efficiency} = \frac{abs_o - absf}{abs_o} \times 100\% \quad \textbf{(3-1)}$$

Where absf is the absorbance at requested time and $abs_o$. is the initial absorbance of solution.

### *3.2. Stripping*

The stripping process was conducted after the extraction processes, in which the double water-in-oil emulsion is de-emulsified and broken into oil and internal water phases. The concentration of phenol re-extracted from the membrane phase was determined according to equation (3-2):

$$\%S = \frac{C_{iF}}{C_{eo} - C_{eF}} * 100 \quad \textbf{(3-2)}$$

Where Cir and are $C_{iF}$ the final concentrations of solute in the internal and external phases, respectively.

### 3.3. Membrane leakage/breakage

The emulsion breakage (%ξ) can be defined as the percentage ratio of the internal phase volume leaked into the external phase ($V_i$) to the initial internal phase volume ($V_{io}$), whereas $V_i$, is determined by the mass balance from the pH of external solute before and after the extraction process as described in equation (3-3) and equation (3-4).

$$\% \xi = \frac{V_i}{V_{io}} * 100 \quad \textbf{(3-3)}$$

$$V_i = Vext \frac{10^{pH_o - 14} - 10^{pH - 14}}{10^{pH - 14} - C_{OH^-}^{int}} \quad \textbf{(3-4)}$$

Where Vext is the initial external phase volume, $c_{oH^-}^{int}$int is the initial $o\bar{H}$ concentration in the internal phase, pH is the initial $pH_o$ of the external phase, while pH is the external phase pH after a certain time.

## *4. Results and Discussion*

### *4.1. Effect of Feed Phase pH*

The pH of external solution plays an essential role in the extraction process, and it can also influence the stability of the membrane phase since high or low pH can accelerate the de-emulsification process of emulsion droplets (Mohammed and Hussein,2020). Fig.( 4-1) shows the effect of external phase pH on emulsion leakage and removal of phenol from aqueous solutions and its influence has been studied experimentally by varying the pH range limit 4.5-8.5, it is observed that as the external phase pH decreased from unadjusted value of 6.5 to 4.5, the removal and stripping of phenol is decreased from 92to 80% and from 75 to 87% in 9 min time .While, the

breakage increase from 0.921 to1.8%. This is due to the emulsion containing 4% Span 80, with 0.1N NaOH concentration is not capable of withstanding the higher acidic nature of external phase containing phenol. Beyond 9 min, no phenol was detected in external phase due to membrane leakage. As the external phase pH increased to 8.5 , all phenols were converted to sodium phenoxide by reaction with leaked NaOH in external phase. No removal of phenol was found. This was mainly due to negligible pH difference between external phase and internal phase. As from the literature (Nosrati et al., 2011), neutral form of (pH=6.5) phenol in the external phase favors the more extraction. Hence, the experiments were carried out using unadjusted pH of 6.5 for removal of phenol(Balasubramanian and Venkatesan, 2012).

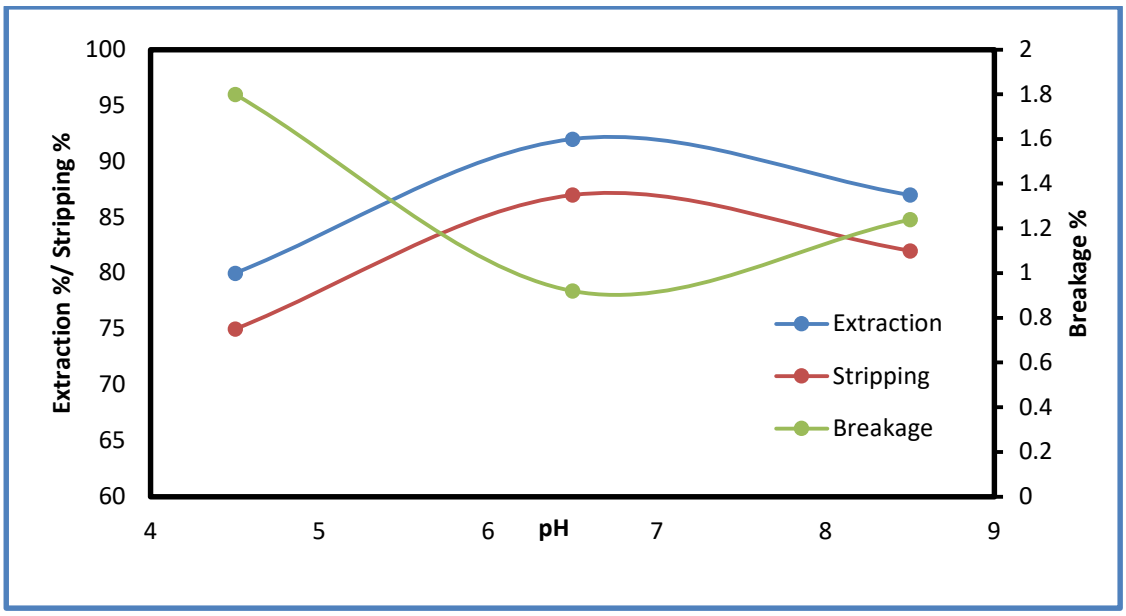


**Figure:(4-1)effect of external phase pH on removal efficiency (phenol concentration =100ppm, speed of homogenizer:5800 rpm, concentration of span80: 4% (v/v), ET: 5min., stirrer speed: 300rpm, 0.1M NaOH), temperature 25℃.**

### 4.2 *Effect of Feed Concentration*

The effect of the feed phase phenol concentration on membrane stability, extraction and stripping efficiencies in the range from 25 to 200 mg/L (ppm) was investigated and displayed in Figure(4-2). At increasing feed concentration from 25mg/L to 100 mg/L lead to increase the extraction and stripping efficiencies from 65% to 92% and from 52% to 87% respectively and decreased the breakage percent from 3.042% to 0.921%, while increasing the concentration of phenol above the critical value to 200 mg/L caused to reduction in extraction and stripping efficiencies to 90%% and to 85% respectively, but observed rising in the breakage percent to 1.273%. This behavior occur because of the quickly saturation of the internal droplets that led to a longer diffusion path and lower yield of phenol removal (Seifollahi and Rahbar-Kelishami,

2017). Feed phenol concentration of 100 ppm was indicated the optimal concentration(Mohamed and Al-Khateeb, 2022).

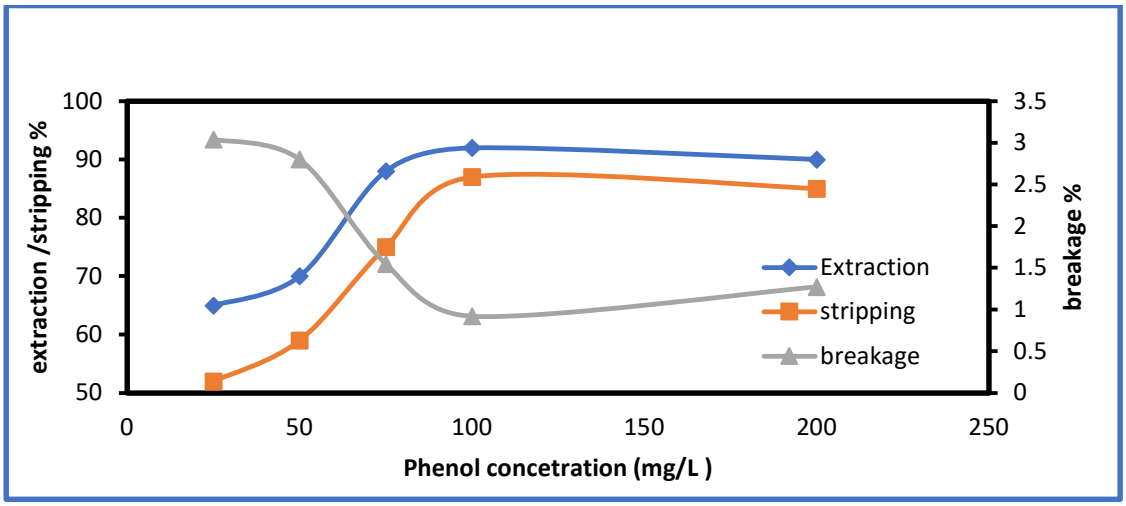


**Figure:(4-2)Extrernal effect phenol concentration on the breakage, stripping and extraction of membrane (speed of homogenizer:5800 rpm, concentration of span80: 4%(v/v), ET: 5min, speed of stirrer: 300rpm, 0.1M NaOH, temperature 25℃ .**

### 4.3. *Effect of Stripping Agent Concentration*

The effect of stripping agent concentration on phenol removal was determined as shown in Figure (4-3)., which was the lowest alkaline level that is close to the neutral phase. The phenol removal and stripping efficiency increased from 73% to 92% and from 68% to 87 % with an increase of stripping concentration from 0.01M 0.1M. The increase of NaOH concentration may cause the surfactant to hydrolyze, resulting in a reduction in emulsion stability. As a result, it is necessary to determine the optimal concentration . Where the extraction efficiency was very little affected while changing the stripping agent concentration after the sufficient amount of 0.1 M for the stripping process. Moreover, there was a declining trend in the removal and swelling percentage when the NaOH concentration was increased beyond 0.1M. Excess NaOH could be responsible for hydrolyzing the number of surfactant molecules(N.Othman *et al*., 2017), which would transport more water into the internal phase Thus, 0.1 of NaOH was chosen (N.Othman *et al*., 2017, Rosly *et al*., 2020).

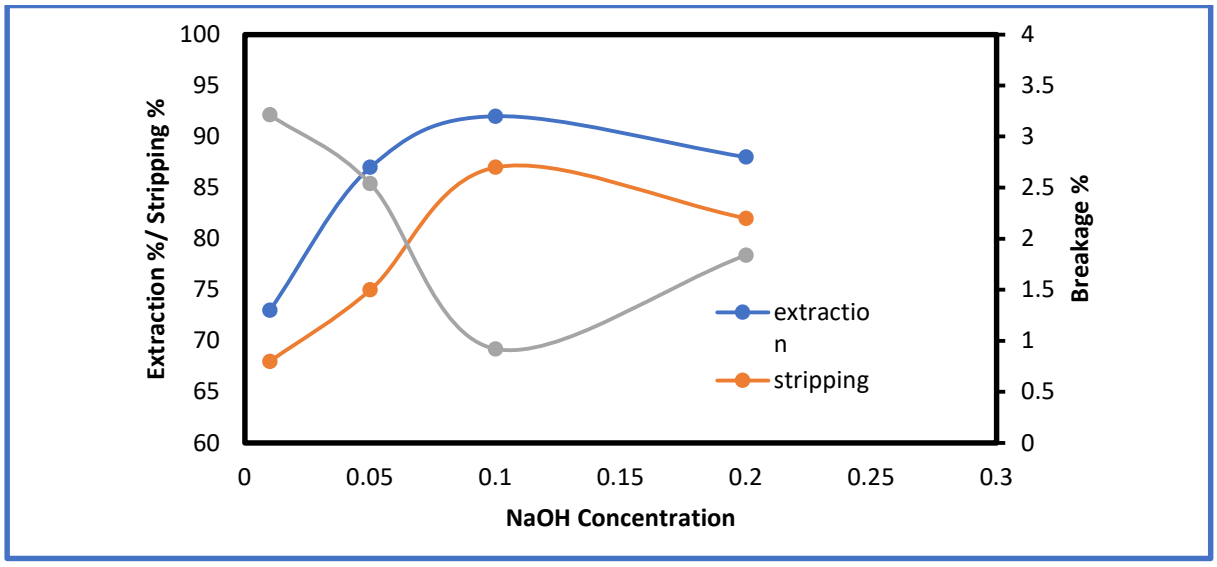


**Figure:(4-3) NaOH concentration effect on the breakage, stripping and extraction of membrane (external phase pH=6.5, speed of homogenizer:5800 rpm, concentration of span80: 4%(v/v), ET: 5min., stirrer speed: 300rpm).**

### *5. Conclusions*

Various factors that have an impact on phenol extraction and on the stability of the emulsion were carefully studied, and the optimal conditions were found. For ELM process when the experiments done were under optimal condition, it was observed that about 92% and 87% extraction and stripping efficiencies of phenol respectively, at 9 minutes mixing time, with lower breakage percent of 0.921%. At homogenizer speed of 5800 rpm, Span 80 concentration of 4% (v/v), (I/O) ratio of 1:1, external to emulsion phase volume ratio of 5:1, mixing speed of 250 rpm at 8 min emulsification time, internal phase of 0.1 M NaOH, external phase pH of 6.5 and temperature 25℃.

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