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# PICKERING EMULSION LIQUID MEMBRANE STABILIZED BY MAGNETIC NANO-Fe3O4

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***Abstract***

Significant features of the Pickering emulsion liquid membrane (PELM) as innovative trend of the traditional emulsion liquid membrane (ELM) such as simple operation, fast process, high stability and easy de-emulsification process have gained extensive responsiveness in the recent years. PELM consists of an kerosene as the diluent, nano-Fe3O4 particles as a stabilizing agent and NaOH in the internal phase that are used to remove ciprofloxacin (phenol) from wastewater. This paper comprises simultaneous studies of emulsion stability and extraction efficiency through various parameters, including external phase pH, internal phase concentration and extractant concentration. The results confirm that PELM is a very effective technique to extract more than 96% of phenol without significant emulsion breakage after a contact time of 9 mins.

## *Introduction*

Various industrial and manufacturing processes produce multiple types of wastewater that introduce toxic contaminants into water and groundwater. Most of these contaminants are sources of pollution to the environment. This causes serious environmental concern, primarily because these industrial waste contaminants are known to be hazardous. Hydrocarbons such as phenolic compounds of 4-Nitrophenol and other derivatives are often found in wastewater of many industrial processes such as dyes, pesticides, petroleum refinery, and petrochemical, pharmaceuticals, and mineral and mining processes (Wang *et al*., 2006).The United States Environmental Protection Agency (USEPA) has labeled the 4-Nitrophenol among others as toxic aqueous chemicals due to their ability to extinguish the important issues, such as kidneys, central nervous system, liver, and blood cells, in the human and animal body (Meda et al.,2014) Therefore, the wastewater generated from these industries needs efficient treatment before it is discharged to the environment.

The emulsion liquid membrane technique (ELM) is considered an efficient method to separate and recover organic and inorganic contaminants that could otherwise be released into the environment. One important limitation of ELM process concerns the stabilization and destabilization of emulsion globules. To address this, over the last few years a new ELM trend known as the Pickering emulsion liquid membrane (PELM) has been developed. PELM involves nanoparticle concepts to achieve a more stable emulsion for wastewater treatment .Emulsion liquid membrane techniques have been gaining popularity over traditional separation methods, since their development by Norman (Li,1968) who used the method for hydrometallurgical regaining of heavy metals. The earliest researchers who reported the separation of metal-ions from aqueous solutions were (Martin and Davies,1977; Frankenfeld and Li, 1977) . Later in 1986, ELM was effectively used to eliminate zinc ions from wastewaters in the industry of mucilaginous fiber in Lenzing, Austria (Chakraborty *et al*., 2010).

## *2. Chemicals and experimental methods*

### *2.1. Chemicals*

Magnetic nano-iron oxide (Fe3O4) as a stabilizing agent. The diluent kerosene , sodium hydroxide (NaOH), and hydrochloric acid (HCl) were obtained from (Thomas beaker, India). Phenol was obtained from India (ALPHA CHEMIKA), . All the chemicals were used without extra purification. All laboratory experiments were operated at an ambient room temperature of 25 °C.

### *2.2. Experimental methods*

#### *2.2.1. Nano-fluid emulsion preparation*

The membrane phase was prepared by dissolving a desired amount of span 80 as extractant and Fe2O3 nanoparticles as stabilizing agent into the diluent (kerosene), and was homogenized. The same amount of the internal aqueous phase was then added to the membrane phase dropwise, and the system was being emulsified by high speed mixer for appropriate emulsification times and speeds.

#### *2.2.2. Extraction process*

Before creating the emulsion, initial concentration of 100 mg/L in the external phase was formulated by adding certain amounts of phenol into deionized water. The obtained emulsion and the external solution was then poured into a beaker and stirred for certain times to disperse the emulsion into the external phase. A filter syringe (0.22 µm) was used to filtrates all the samples. Stirring speed and external/emulsion volume ratio were constant at 300 rpm and 5/1, respectively.

### *2.3. Analysis and calculations*

The concentrations of phenol in the external phase were determined by using a ultraviolet spectrophotometer UV (ThermoSpectronic, USA). The standard method and calibration curve were used to determine the concentration of the phenol. Extraction efficiency was calculated as follows:

$$\textbf{Removal efficiency} = \frac{abs_o - absf}{abs_o} \times 100\% \qquad \textbf{(2-1)}$$

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

The emulsion breakage (%ξ) is the percentage ratio of the internal phase volume leaked into the external phase by splitting ($\boldsymbol{V}_{\mathrm{io}}$) to the initial internal phase volume ($\boldsymbol{V}_{\mathrm{i}}$), whereas VS is determined by the mass balance from the external phase measure before and after contact [Salman and Mohammed,2019; Chiha and Hamdaoui,2006; Sabry *et al*., 2007 ).

$$\%\ \xi = \frac{V_{\mathrm{i}}}{V_{\mathrm{io}}} * 100 \qquad \textbf{(2-2)}$$

$$V_{\mathrm{i}} = V_{ext} \frac{10^{pH_{\circ} - 14} - 10^{pH - 14}}{10^{pH} - 14 - C_{OH^-}^{int}} \qquad \textbf{(2-3)}$$

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 $pH_{\circ}$ of the external phase, while pH is the external phase pH after a certain time.

## *3. Results and discussion*

### *3.1. Characterizations of nano-Fe3O4 particles*

#### *3.1.1* SEM Measurement

The XRD diffraction for nanoparticles obviously indicates the hematite structure as depicted by ICDD card. The characteristic peaks of were observed at $2\theta$ =30.11°, 35.50°, 43.3° , 57.14 ° and 62.68°, which correspond to 220, 311, 400, 511, 440 Bragg reflection respectively as shown in Figure(3-1).

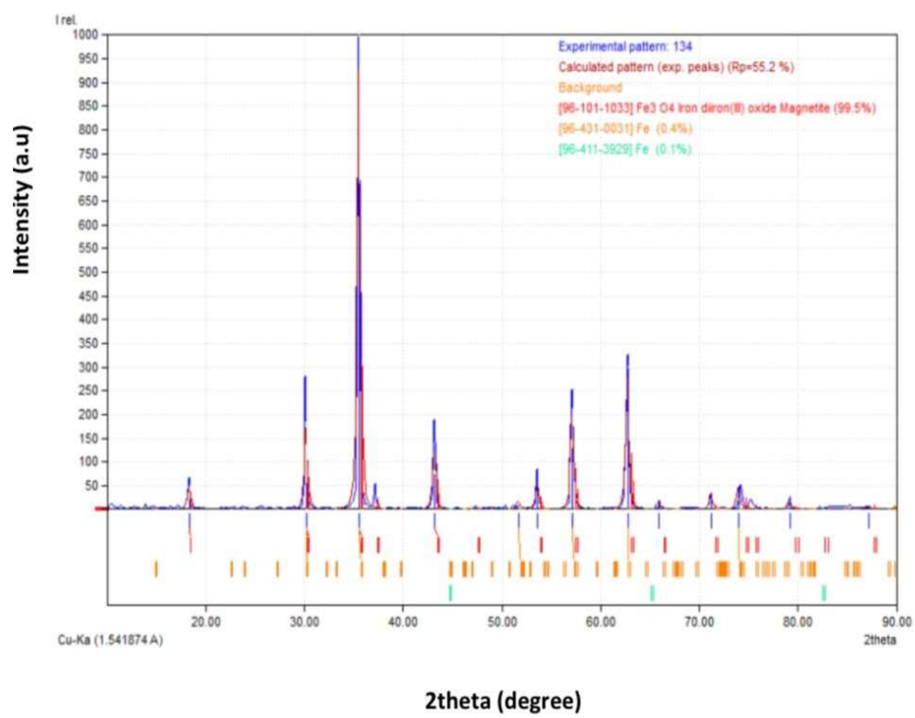



**Figure3-1: XRD diffract graph for Fe3O4 nanoparticles**.

### *3.1.2. SEM Measurement*

**Figure (3-2)** displays the structural characteristics of the hematite nanoparticles, including their shape and particle size, as determined by a scanning electron microscope (SEM).The average hematite particle size ranged from 300 to 900 nm, and the droplet diameter ranged from 20 to 30 nm. All of the particles are spherical in shape.

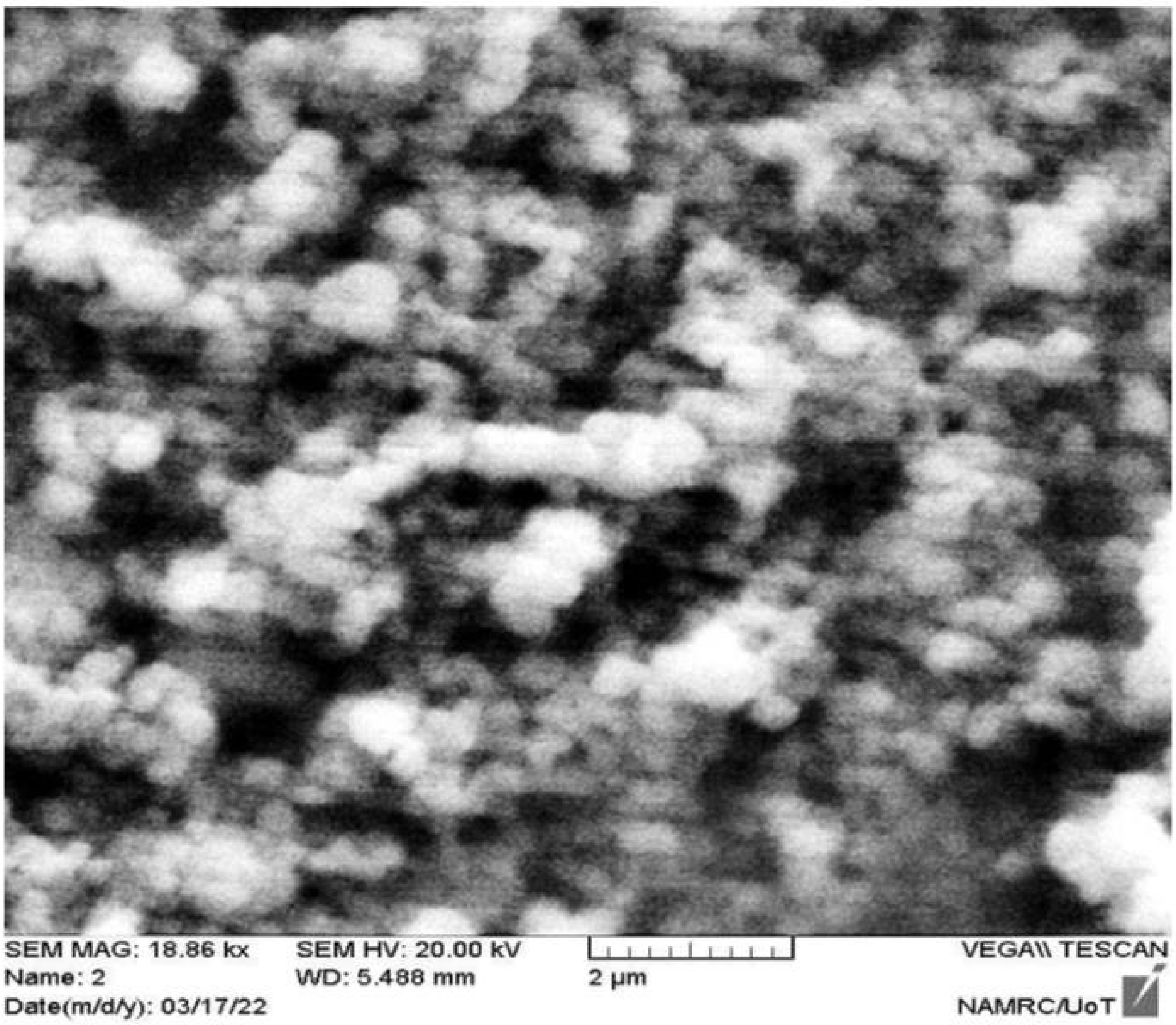
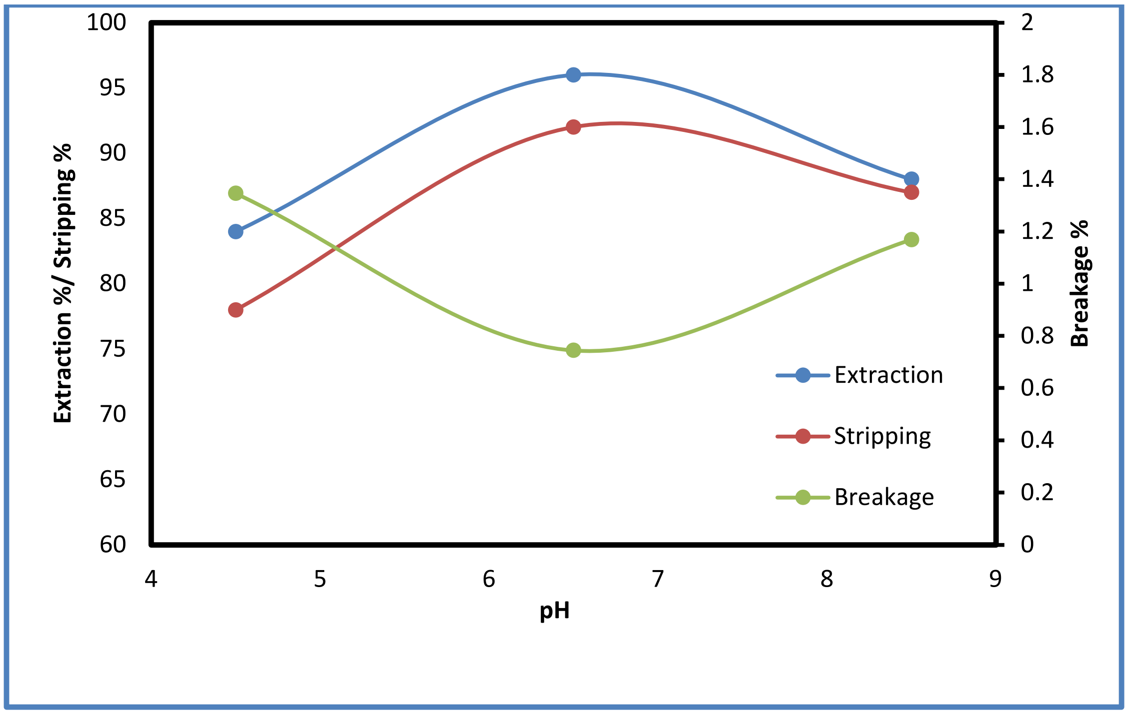



**Figure (3-2): SEM image ofFe3O4 nanoparticles**.

### *3.2 Effect of external phase pH*

The pH of the external phase plays an essential role in the phenol extraction process, and it can also influence the stability of the membrane phase, since high or low pH values can accelerate the de-emulsification process of droplets. Experiments were carried out at acidic, neutral and basic pH values in the range of 4.5 to 8.5 and the results are showm in figure (3-3). It is obviously that phenol extraction is highly affected by the pH of the external phase (Mohammed and Hussein, 2020). At high acidity (pH= 4.5), the extraction efficiency was only about 84%, while the breakage percentage was at its highest about 1.346%. This might be due to higher H+ concentrations (lower pH) causing a destabilization process to the PE, while the dropping in the extraction efficiency is due to the neutral extractant which cannot sufficiently make a complex with phenol molecule at this pH region. While in the case of pH=6.5, phenol extraction efficiency reached the optimal value of 96% and the emulsion breakage remained unaffected. Moreover, at a pH of 8.5 the extraction efficiency began to reduce slightly to about 88% and the breakage increased to 1.169%. This can be explained by the protons being released as a result of anion exchange reaction (Mohammed and Hussein, 2018), and also an increasing pH causes a formation of other species. For further experiments, it was very suitable to maintain the external phase pH at 6.5 this applies to the process of ELM.

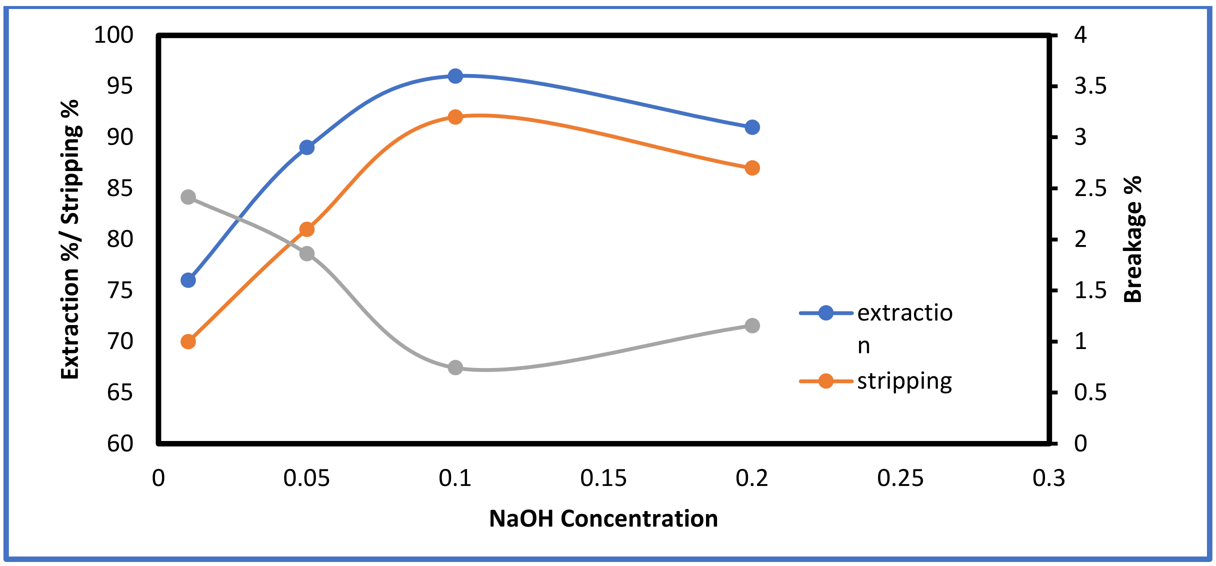



**Figure(3-3):Effect of external phase pH on removal efficiency (phenol concentration =100ppm, speed of homogenizer:5800 rpm, concentration of span80: 3% (v/v), ET: 5min., stirrer speed: 300rpm, 0.1M NaOH, Fe3O4 concentration= 0.2% ).**

### *3.3 Effect of NaOH concentration*

As the extraction step take place in the interface between the liquid membrane and the feed phase solution, the extraction of species necessarily requires a simultaneous stripping step at the opposite side of the membrane (Kumbasar, 2008). In this study, investigation was also done on the influence exerted by the NaOH concentration on the degree of extraction so as to boost the regeneration of the membrane and increase the phenol concentration in the stripping phase. In

Figure (3-4) it is evident that when the NaOH concentration was raised from 0.01 to 0.1 M, the percentage of breakage reduced from 2.415 to 0.745%. On further increasing the NaOH concentration to 0.2 M the breakage percent escalated. Besides, the phenol extraction and stripping efficiency intensified from 76 to 96% and from 70 to 92%, respectively, when the NaOH concentration was boosted in the internal phase, from 0.01 to 0.1 M. Therefore, when the NaOH concentration was raised beyond 0.1 M, the phenol extraction and stripping efficiency were seen to decline. This was possibly because the increase in the NaOH concentration in the stripping phase reduced the difference in densities and built up the emulsion viscosity, which was reflected in the enhanced droplet sizes. Further, at the higher concentration of the sodium hydroxide, the emulsion stability declined, a reaction induced by the NaOH-surfactant interaction. This also caused the partial loss of its surfactant properties resulting in the de-stabilization of the emulsion and lowered extraction efficiency (Dâas and Hamdaoui 2010). Therefore, in this study, the 0.1 M NaOH concentration was selected as it induced a higher extraction percentage and lower degree of breakage (Mohammed and AL-khateeb, 2022)

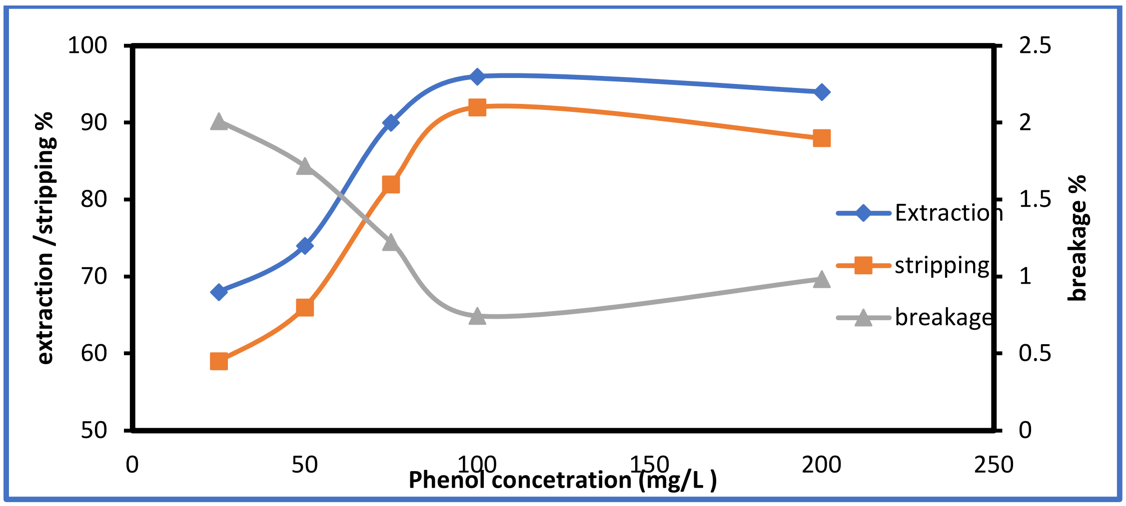



**Figure(3-4):NaOH concentration effect on the breakage, stripping and extraction of membrane (external phase pH=6.5, speed of homogenizer:5800 rpm, concentration of span80: 3%(v/v), ET: 5min., stirrer speed: 300rpm Fe3O4 concentration= 0.2%).**

### *3.1.5Effect of phenol concentrations*

The present study investigated the optimum parameter values for the extraction of phenols by Pickering emulsion liquid membranes stabilized by both a surfactant. Magnetic Fe3O4 nanoparticles were selected as Pickering emulsions stabilizers due to their low-cost, environmental friendliness, and low-toxicity (Al-Ani and Al-Dahhan, 2021). The rates of phenol extraction were examined at different concentrations (i.e., 25; 50; 75;100 and 200 ppm). The effect of phenol concentration on extraction efficiency was shown in figure (3-5) . The extraction efficiency of phenol was high at concentration of 100 mg/L in the feed phase of the solution , whereas above

100 mg/L of concentration, the decrease in phenol extraction efficiency occurs. The reduction in extraction efficiency of phenol was because of the region of interface between external feed phase and liquid membrane phase becomes saturated rapidly with phenol ions. Therefore, the phenol complex compounds permeate very slowly through the membrane phase and this happens because of mass transfer resistance created by high phenol ion concentration (Rajamohan *et al*., 2019) . A maximum removal efficiency of phenol ion of 96% was obtained for 100 mg/L of concentration of phenol in the external feed phase. While a minimum extraction efficiency of 59% obtained was obtained for 25 mg/L of initial concentration of phenol in the external feed. Removal of phenol decreases with the increase in the concentration range of 200 mg/L. The saturation achieved at concentration 100ppm (Sujatha et al., 2021).




**Figure(3-5):phenol concentration effect on the breakage, stripping and extraction of membrane (external phase pH=6.5, speed of homogenizer:5800 rpm, concentration of span80: 3%(v/v), ET: 5min., stirrer speed: 300rpm Fe3O4 concentration= 0.2%).**

## *4.Conclusions*

The experimental results of the current study show that emulsion and Pickering emulsion liquid membrane are extremely efficient techniques for removing phenol contaminated aqueous solutions. The best conditions to obtain the highest stability and extraction efficiency in PELM are: 5800 rpm homogenizer speed, 5 min emulsification time, 0.2% (w/v) nanoparticle concentration, 3% (v/v) Span 80, 0.1 M NaOH as the internal phase and external phase pH of 6.5, also without use carrier. At this conditions obtained the highest extraction and stripping efficiencies of phenol 96% and 92% respectively, with the lowest breakage percent of 0.745% at a contact time of 9min.

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