Development of Green Emulsion Liquid Membrane for Removal of Phenol from Aqueous Solution: Extraction and Stability Study

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Abstract. Vegetable oil (rice bran oil; RBO) as an economic, non-toxic green diluent has been used for phenol removal through green emulsion liquid membrane (GELM) process with an aim to reduce environmental glitches triggered by traditional petroleum-based solvents used in ELM processes. GELM is naturally benign and cost-effective as compared to other existing membranes. During this study, novel GELM was composed of a surfactant (Span 80) as stabilizing agent, NaOH as driving force agent, and green solvent (RBO), a diluent as liquid membrane. The study was performed to visualize and analyse the effect of process factors (feed phase pH, treat ratio, phase ratio, stirring time, stirring speed, and NaOH concentration) on both phenol extraction and GELM stability. Extraction efficiency (90±1.5%) and stability of 135±2 min without employing carrier agent have been achieved at optimized experimental conditions viz 450 rpm of agitation speed, pH 0.45 of feed solution, 20 min of extraction time, 0.166 [M] of NaOH concentration, 2:1 (v/v) of treat ratio, 0.45 (v/v) of phase ratio, and 30 ± 1°C of extraction temperature. This study has confirmed that the RBO-based GELM separation technique has the ability to cut the noxious diluents requirement for ELM formulation.

KEYWORDS: Phenol; Rice bran oil; Stability; Extraction; Green process

1. Introduction Since the last few decades, a significant amount of attention has been developed among chemists and environmental researchers to the treatment of polluted water produced by various industrial sectors [1]. This polluted water is harmful to the environment and endangers all types of pollution, hence the inevitability for the treatment of polluted water is increasing day by day [2,3]. Phenol is considered as a water pollutant due to it contaminates potable water even at very small amounts. It is available in the effluent streams of major processing and refining industries [4,5]. It has limited water solubility and acts as a poor base [6,7]. Excessive exposure to phenol not only has many adverse effects on human beings (causes skin-related issues, gastrointestinal uneasiness, and discomfort in the head [8]) but also on other creatures (animals and fish) [9]. The major process industries that contribute to pollution by the presence of phenol are cooking operations, pharmaceuticals, refineries, plastics, and wood products [6,10]. However, phenol is also considered a valuable (used for the production of dyes, adhesives, germicides, and chemical intermediates) chemical compound and plays a key role in industrial chemicals (such as phenolic resin) [6,11]. Therefore, the removal of phenol from the trade effluent streams before their release into nature has become the pertinent need of the present research in the field of wastewater remediation [12]. Nowadays, an assortment of innovative separation methods for handling phenolic amalgams has been established to treat the unwanted phenol from waste industrial effluent streams. Till now, various techniques like steam distillation, membrane pervaporation, extraction, adsorption, and membrane-based solvent extraction have been successfully put into application for the phenol treatment from the waste streams [6]. Each technique has its own pros and cons based on flexibility and simplicity in operations, cost, efficacy, upkeep, and technical glitches. Searching fan economic and potential techniques for phenol removal in the current time is gaining a lot of attention from potential researchers and scientists across the world [13].

Membrane-based various extraction techniques have been recognised as clean and energy-effective techniques for the extraction of various low-concentration pollutants (Co, Cr (VI), Ni, Cu, lead, Uranium, phenol, etc.) in gaseous and liquid systems of the various industries (like chemical and petrochemical) [14,15]. At present, membrane-based separation technologies (ultrafiltration, supported liquid membrane (SLM), and emulsion liquid membrane (ELM)) for phenol removal are very attractive and promising. A comparison has been made among the performance (extraction efficiency) of these membrane-based separation technologies (ultrafiltration (27% - 44.6%), supported liquid membrane (67% - 92.5%), and emulsion liquid membrane (more than 98%)) for the phenol removal. Among all, the ELM has shown better performance for the phenol separation [5,11]. Biological method with respect to the liquid membrane method is not found useful when wastewater (refinery, petrochemical, and pharmaceutical operations) containing a high concentration of phenol [10]. Recently, liquid membrane-based techniques have been considered as a successful separation technique for the remediation of wastewater having contaminated substances in comparison with the solvent extraction method [16]. Among the several liquid membranes (LMs), ELM is the newly introduced separation technique which has found its applications in several fields such as pharmaceuticals, wastewater treatment, environmental, and chemical engineering [15,17]. It is known as one of the most efficient and advantageous categories of LM due to its scope of continuous and simple operation, high efficiency, applicability for the separation of low-concentration solutes, stripping and separation in a single stage, fast extraction, more solute transfer area, and less diffusional resistance [10,15,18]. The wide variety of its applications (removal of phenols [5,19] and other valuable products from wastewater [20-23], extraction of toxic metals [24-27], extraction of organic acids and related products [28-30]) makes ELM processes more promising and attractive. Till date, various research studies [7,10,18] have been reported in the literature regarding the phenol removal using emulsion liquid membrane based on petroleum-based organic solvents (hexane, heptane, and kerosene). All these studies reported better extraction efficiency (90.1% [7], 98.33% [10], and 98.88% [18]) than GELM. On comparing with other green solvent, i.e., palm oil, the green solvent (RBO) used in the present research work has shown better extraction efficiency (83% [5] and 90 % (present work)) in the case of phenol removal. Previously, the maximum ELM separation techniques used only organic solvents, which are categorized as hazardous components to the environment [15]. These have a negative impact on the environment due to their characteristics of harmfulness, non-renewability, poorly biodegradable in nature, flammable, and easily vaporize [5,31]. The key challenge in the industrial application of ELM based separation is the poor ELM stability. The poor ELM stability may be due to the leakage of internal reagent, coalescence of emulsion droplets, dissolution of membranes or may be due to the transport of water-soluble-solutes into the emulsion [14,16].

As an alternative to these organic solvents, the applicability of naturally favourable solvents, i.e., vegetable oils or green solvents, could be developed [32]. Therefore, it has become pertinent need to substitute these conventional extracting agents with the properties of renewable sources, easily available, low cost, and non-toxic, for formulating environment-friendly green emulsion liquid membrane (GELM). Vegetable oils are considered novel and green diluents, which can be applied in the existing membrane phase formulation of ELMs [5,33]. During this study, the feasibility of “Rice Bran Oil” (RBO) along with Span 80 (as an emulsifier) and NaOH (as a driving force agent) in the GELM formulation for phenol removal and its dynamic stability has been searched. RBO (density-910 g/l, refractive index-1.467, absolute viscosity-59.3 cP) has shown better results mainly due to its balanced fatty acid composition, i.e., the ratio of saturated (such as Palmitic (16:0)- 24%), mono-unsaturated (such as Oleic acid (18:2)- 42%, water-insoluble), and poly-unsaturated (such as Linoleic acid (18:1)- 34%, water soluble) fatty acids, which is close to the WHO recommendation of 1:1.5:1 (saturated: mono-unsaturated: polyunsaturated) [30,31]. The application of RBO-based GELM for phenol removal has been studied to reduce the creation of pollutants in nature. In order to get the optimum process conditions, OFAT (one-factor-at-a-time) optimization method was employed. Employing OFAT optimization technique, the effect of various selected process variables (such as speed, external solution pH, contact time, stripping phase concentration, treat ratio, phase ratio, and extraction temperature) for obtaining better phenol removal efficacy as well as better GELM dynamic stability has been examined. Dynamic stability is defined as the stability of the emulsion mainly to maintain its breakage and separation properties over an extraction time during agitation process. It can also be defined as the time of emulsion destabilization after extraction process. Till now, the extraction of phenol using other vegetable oil (such as palm oil)-based ELM has been successfully done but this present research article is using RBO (as a diluent during ELM formulation) first time for the treatment of phenol from the waste aqueous solution. Therefore, application of RBO (economic and environmentally benign) as a green solvent for the phenol separation through GELM without using any carrier agent is the key idea of the present investigation.

2. Transportation methodology

2.1. Materials and equipment

All materials are of analytical grade and put into application without any additional treatment. Rice bran oil (pure refined) of Ricela Health Foods Ltd. Dhuri, Punjab, India, was purchased from the local market. Span 80, ammonia solution, and chloroform were procured from MERCK. Phenol crystal was supplied by Himedia, Ltd, India. Sodium hydroxide, sulphuric acid, and hexane had been bought from S.D. Fine-Chem. Ltd, India. 4-Aminoantipyrine was procured from Loba Chemie Pvt. Ltd. Potassium ferricyanide was supplied by Ranbaxy Laboratories Ltd. The equipment used during this current investigation includes a UV-Vis spectrophotometer (model DR 5000 HACH, USA), pHTester®30 (Eutech Instruments OAKLON), a magnetic stirrer (Perfit India), and a high-speed agitator (IKA® RW20 Digital).

2.1.1 Environmental health and safety considerations

The green solvent (rice bran oil, 90%) and organic solvent (hexane, 10%) needed per litre treatment is 0.321 litre and 0.0357 litre respectively. Mixing energy required for making a stable emulsion needs application of shear forces to disturb larger droplets of an immiscible liquid (green solvent) into smaller droplets. The estimated power consumption rate per cubic meter of wastewater treated is 0.348 kW. And the estimated power consumption rate per cubic meter of emulsion formation during emulsification is 297 kW. In this present study, a small volume (10%, v/v) of organic solvent i.e., hexane is used during the formulation of GELM organic phase. To avoid hexane losses at higher emulsification speed, hexane was initially mixed into green solvent thoroughly at very minimal speed. Sodium phenolate (formulated in the internal phase of ELM upon stripping of phenol) is an unstable organic reagent as it has tendency to be easily oxidized. Waste handling of sodium phenolate (classified as hazardous waste) can be attained upon adding an appropriate amount of dilute sulfuric acid. First the dilute sulfuric acid is added slowly to the sodium phenolate solution during stirring under controllable reaction temperature. This neutralization reaction then converts it back to phenol. The fume hood is usually used to control any potential phenol vapours.

2.2. Preparation of aqueous solutions

The stock solution of phenol with various desired compositions used during this experimental work was prepared by mixing the desired fraction of phenol crystals in distilled water. The aqueous solution of internal phase (NaOH) reagent of appropriate concentration was made by dissolving NaOH pills into distilled water. The solutions of 4-Aminoantipyine (on each day of use) and Potassium ferricyanide (on each week of use) were prepared in distilled water.

2.3. Green emulsion (W/O) preparation

The ingredients of the emulsion utilized for GELM formulation were organic phase constituents (surfactant and green diluent) and driving force agent (NaOH). The key chemicals of the membrane phase of GELM were: 90% (v/v) RBO, 10% (v/v) hexane, and Span 80 (1.8%, v/v), which were mixed through a magnetic stirrer to gain the GELM organic solution. NaOH solution with an appropriate concentration and phase ratio (internal phase: organic phase) was steadily added to the prepared and formulated organic solution during the emulsification step. It was continuously stirred at 1800 rpm of emulsification speed for 25 min of emulsification time. The fresh green emulsion was made each time before each run during this study of phenol removal through GELM.

2.4. Phenol removal using green emulsion liquid membrane (GELM)

The prepared GELM was added to a 250 ml glass vessel, which contains reagent grade phenol aqueous solution (model wastewater) with the appropriate treat ratio (external feed phase: membrane phase). The whole mixture was then agitated with the help of an overhead stirrer at a stirring speed of 450 rpm for an appropriate agitation time. Thereupon, the whole mixture was put into a separating funnel for an exact phase separation. The bottom layer was analysed for the concentration determination of aqueous feed phase using a UV-Vis Spectrophotometer (model DR 5000 HACH, USA) by the 4-aminoantipyrine (4-AAP) method [34]. UV-Vis Spectro-photometer analysis was done at 510 nm. The volume of the membrane phase (top layer) was analysed and recorded for the determination of dynamic stability and membrane breakage. The dynamic stability was calculated by transporting the emulsion into a measuring cylinder and then left for phase separation. The time was recorded when the water molecules initiated to appear in the cylinder. Various process variables (stirring speed, solution pH, contact time, sodium hydroxide concentration, phase ratio (v/v), treat ratio (v/v), and temperature) were examined through One-factor-at-a-time (OFAT) technique. All of the process variables were ranged within an appropriate range and are shown in Table 1. The extraction efficiency (%) of GELM in terms of phenol removal was measured from the following equation:

$$\text{Phenol removal (\%)} = \frac{\text{Inital concentration} - \text{Samples concentration}}{\text{Initial concentration}} \times 100 \qquad (1)$$

The calculations of values of emulsion swelling (%) and membrane breakage (%) were obtaining using following equations.

$$\text{Swelling/Breakage (\%)} \ = \frac{V_{final} - V_{initial}}{V_{initial}} \times 100 \qquad (2)$$

where, $V_{initial}$ is the green emulsion initial volume before agitation, V_{final} is the green emulsion final volume after agitation. Negative and positive values of difference between V_{final} *and* $V_{initial}$ have been considered as the membrane breakage (%) and emulsion swelling (%) of green emulsion. But the values of emulsion swelling (%) and membrane breakage (%) were found in the manageable range and didn't have any significant effect on the phenol extraction efficiency [17,23].

Additionally, the value of breakage was determined by knowing the initial and final pH of the external aqueous phase and accordingly the magnitude of individual contribution of each factor (swelling (%)/breakage (%)) was determined. After agitation, the external aqueous phase was separated from green emulsion using separating funnel and the pH of external aqueous phase was measured. The magnitude of membrane breakage (%) was found using Eq. (3) and Eq. (4).

$$\text{Membrane breakage (\%)} = \frac{V_s}{V_{int}} \times 100\% \qquad (3)$$

where V_s is internal phase volume leaked into external aqueous phase by splitting and V_{int} is initial volume of internal phase. V_s can be determined by using mass balance.

$$V_s = V_{Ext} \frac{10^{pH_0 - 14} - 10^{pH - 14}}{10^{pH_0 - 14} - C_{OH^-}^{int}} \qquad (4)$$

Where $C_{OH^-}^{int}$ is the initial concentration of OH^- in the internal phase. V_{Ext} is the initial external aqueous phase volume, pH_0 is the initial pH of external aqueous phase, and pH is pH of external aqueous phase after in contacting with emulsion for a certain time of stirring, respectively.

Table 1.

3. Reaction mechanism and transport methodology of the phenol removal process

GELM used in this investigation was a water-in-oil (W/O) type. The formulation of the GELM organic phase can be changed based on its operation and the type of solutes to be treated [15]. The W/O type emulsion splits both phases (external and internal phases) by creating the two aqueous-organic interfaces, i.e., outer interface (between feed phase and membrane phase) and inner interface (between membrane and internal phase). The transportation of phenol molecules from the feed side through the membrane phase side is a simple permeation through the mixture of rice bran oil and hexane (as shown in Figure 1). In case of rice bran oil (which acts as a liquid membrane), the reaction between total phenol (molecular, undissociated, and dissociated phenol) and triglyceride (available in the membrane phase) took place to form a complex (i.e. total phenol – triglyceride (TG) complex) through hydrogen bonding or intermolecular interactions between them as discussed through Eq. 3.

$$\underbrace{[(\mathrm{C_6H_5OH})_{\mathrm{total}}]}_{\text{Total phenol}} + \underbrace{[\mathrm{TG}]}_{\text{Triglyceride}} \leftrightarrow \underbrace{[(\mathrm{C_6H_5OH})_{\mathrm{total}}:\mathrm{TG}]}_{\text{Total phenol: Triglyceride complex}} \tag{3}$$

Then this formed complex reacted with the NaOH (act as internal phase reagent) to form sodium phenolate and the triglyceride molecules, which returned back to form new complexes again with the total phenol molecules available in the feed phase side [5,35]. And the transportation of phenol molecules in the case of hexane occurred through the process of diffusion in the membrane phase. And after this, these total phenol molecules were stripped out in the internal solution owing to the driving force and their solubility in hexane. At the end, these extracted total phenol molecules have been regained from the organic solvent through the stripping agent, i.e., sodium hydroxide as shown in Eq.4 (an irreversible and instantaneous reaction) [5, 36]. The formed sodium phenolate (as elucidated in Eq.4) can't diffuse back to the aqueous phase side since they are not soluble in the membrane side. Hence, these two liquid membranes constitute (RBO and hexane) have shown a significant contribution towards facilitating the passage of total phenol molecules from the aqueous solution to the stripping side.

$$\underbrace{[(\mathrm{C_6H_5OH})_{\mathrm{total}}:\mathrm{TG}]}_{\text{Total phenol:Triglyceride complex}} + \underbrace{\mathrm{NaOH}}_{\text{Stripping phase}} \rightarrow \underbrace{[(\mathrm{C_6H_5OH})_{\mathrm{total}}\mathrm{Na}]}_{\text{Sodium Phenolate}} + \underbrace{\mathrm{TG}}_{\text{Triglyceride}} + \underbrace{\mathrm{H_2O}}_{\text{Water}} \tag{4}$$

Figure 1.

4. Results and discussion

4.1. The effect of aqueous solution pH

Aqueous solution pH plays a very big role during the phenol removal process through GELM. The outcome of aqueous solution pH related to the phenol removal and dynamic stability has been discussed and shown in Figure 2. Phenol is known as a weak acid [5]. It dissociates in the feed phase to give ionic components ($\mathrm{Ph-\ O^- + H^+}$) as expressed by the following equation:

$$\mathrm{Ph-OH}\ \leftrightarrow \mathrm{Ph-\ O^- + H^+} \tag{5}$$

The molecular form ($\mathrm{Ph-OH}$) of phenol is oil soluble while the ionic form ($\mathrm{Ph-\ O^- + H^+}$) is oil insoluble. An increment in $\mathrm{H^+}$ concentration (or a reduction in pH value) reverses the direction of this dissociation reaction and helps phenol to remain in its molecular form and in oil-soluble state, which is desirable for the phenol removal through vegetable oil/green solvent based GELM [7].

Figure 2.

It can be seen from Figure 2 that the enhanced pH value from pH 0.3 to 0.9 has a significant effect on the phenol extraction and dynamic stability. It is well explained that the feed solution pH during the GELM-based separation process influences the inter-phase mass transfer process as it acts as a driving force between the phases (external and internal phase) during the phenol removal system [20]. It is evident from the Figure 2 that the extraction efficiency (%) increases with the decrease in the external solution pH (from 0.9 to 0.3) since with the increment in $\mathrm{H^+}$ concentration (or a reduction in pH value), the availability of phenol molecules in solution in molecular form increases which further rises the rate of complex formation and finally the removal efficiency (%). The phenol extraction efficiency and GELM dynamic stability decrease with an increase in aqueous solution pH. The other plausible reason is the emulsion breakage, which is not preventable for highly stable emulsions (due to applied shear forces by impeller on the globules), and further, this breakage increases solution pH through the movement of internal phase reagent (sodium hydroxide) molecules [38,39]. This breakage also contributes to the introduction of phenolate ions back to the aqueous solution side which further reduces the removal efficiency [40]. However, the lowest pH value (0.3) gives the highest removal efficiency than the selected value of pH (0.45) but it needed more amount of sulphuric acid to maintain the pH value at 0.3 for just 2.6 % increment in phenol removal efficiency [7]. Hence, during this phenol removal operation, the pH (aqueous solution)

= 0.45 has been selected as the optimum pH value for gaining good extraction and GELM dynamic stability.

4.2. The effect of internal phase concentration

To examine the stripping efficiency (phenol removal efficiency (%)), the effect of stripping agent (sodium hydroxide) concentration (0.10, 0.125, 0.166, 0.25, 0.50 [M]) was examined, and the findings have been elucidated in Figure 3. The strength of the stripping phase affects the solute permeability during the GELM-based separation process as well as GELM dynamic stability. The amount of internal agent in the emulsion is a key variable in selecting the transportation efficiency of phenol molecules from the feed to the internal solution [37]. From the previous literature studies, it was noticed that with an increase of internal phase concentration, the separation efficiency was also raised to a certain concentration, but beyond that certain concentration, it started reducing [20,30,41]. It can be described from the Figure 3 that with the raise in the amount of stripping phase concentration (from 0.1 [M] to 0.166 [M]), the phenol removal efficiency (%) and dynamic stability (min) of GELM was improved because of the large availability of stripping agent in GELM and as a result more driving force for the removal of phenol from aqueous side to inner side by making more complexes at the inner interface was present. This could be attributed to the large internal agent concentration that tends to raise the concentration gradient between phases, subsequently inducing the transportation of phenol molecules [41,42]. Another plausible reason is the increased stripping phase capability, which increases the rate of complex formation in the membrane phase/stripping phase interphase. This internal phase concentration also strongly influences the GELM dynamic stability. When NaOH concentration was raised beyond a certain limit (0.166 [M]), the GELM dynamic stability dropped very drastically (up to 38 min). It is because of the initiation of the reaction between the sodium hydroxide molecules and the span 80 (acts as an emulsifying agent) molecules, which further reduces the stabilization properties of the surfactant [43, 27]. Poor dynamic stability of GELM for higher concentration may be due to the enhanced movement of water molecules towards the feed phase side which makes GELM unstable and further responsible for poor phenol removal efficiency [5,10,30]. During the current experimental study, 0.166 [M] concentration of NaOH with 92.75% phenol removal efficiency was found to be the optimum concentration.

Figure 3.

4.3. The Effect of the internal phase to organic phase ratio

Phase ratio is defined as the volume ratio of the internal phase to the organic phase. Phase ratio has an important role during the various GELM-based separation processes (phenol removal) [41]. The outcomes of the phase ratio (internal phase: organic phase) on the phenol removal process as well as on the GELM dynamic stability are elucidated in Figure 4. During experimental study for investigating the phase ratio effect, the volume of sodium hydroxide solution (acting as a stripping agent) was varied within the desired range but the volume of the organic phase constituents was fixed. Phase ratio was changed from 0.30 to 0.50 (v/v) to gain the maximum phenol removal efficiency (%) and better dynamic stability (min). At a phase ratio of 0.45 (v/v), the highest efficiency (89.12%) was achieved. With the rise of the phase ratio, the phenol removal efficiency was also increased, but up to a phase ratio of 0.45, (v/v) but beyond that it was reduced. This reduction in performance may be owing to the improved volume of internal reagent solution in w/o membrane, which further increases the viscosity of the emulsion and, as a consequence, the process of interfacial mass transfer becomes much difficult [44,45]. This is similar to inference drawn by Yildirim et al. [46] who explains that the large volume of stripping agent in membrane phase results in breakage of membrane and the phenomenon of phase inversion was also noticed [46].

Figure 4.

It may also be due to the minimum ability of the organic phase for the high values of phase ratios, which is further responsible for the poor dispersion of larger emulsion droplets and as a result, it affects the GELM dynamic stability [42]. With the rise of phase ratio from 0.30 to 0.45, the extraction (phenol removal) efficiency (%) and dynamic stability (min) were observed to be increased. It is notable that the increase phase ratio also increases the number of NaOH (internal agent) molecules per unit volume which additionally supports an increment in the stripping of phenol molecules (i.e., $\mathrm{Ph-OH}$) in internal phase at the inner interface (between membrane phase and internal phase) [5,10]. Because of the effect of increasing viscosity in the membrane solution, higher values of phase ratios are not selected since it creates hindrance during the removal of phenol molecules.

4.4. The effect of the external phase to the emulsion phase ratio

The influence of the treat ratio (volume ratio of external phase: to membrane phase) on the phenol extraction process through GELM has been shown in Figure 5. The treatment ratio not only affects the GELM extraction efficiency (%) and the emulsion stability but also influences the operating expenses (i.e., GELM process cost during phenol removal process) of the process, which increases with the rise in the treatment ratio [37,41]. The minimum requirement of emulsion volume for the phenol removal process would earn cost-effective advantages over the existing LLE (liquid-liquid extraction) technique [47]. It controls the interfacial mass transfer of the phenol transportation process at the outer interface (feed side and membrane side) [41].

Figure 5.

During this study, the GELM volume was kept constant (21 mL), and the volume of feed solution was varied. For the large values of treat ratio, the available interfacial mass transfer area (less contact area) at outer interface for phenol molecules to form complexes is very less which is further in turn responsible for poor mass transfer rate and consequently for poor phenol removal efficiency (%) [5,27]. Another plausible reason of getting poor phenol removal at high treat ratio could be owing to emulsion swelling and improved ionic phase internal strength and reverse osmosis process, leading to poor mass transfer rate as well as poor GELM dynamic stability [41]. The GELM dynamic stability also decreases with the increase in the treat ratio. Accordingly, the lower treat ratio value (2:1, v/v) was decided for obtaining maximum phenol removal efficiency (91.23 %) and better GELM dynamic stability. For the higher values of the volume ratio (4:1, v/v), the phenol removal efficiency (%) was reduced up to 35.90%. Accordingly, in later phenol removal experiments, the treat ratio of 2:1 was considered.

4.5. The effect of stirring speed in GELM extraction

One of the important variables during the GELM mass transfer-based separation process is the rate of stirring and turbulence in the external feed phase, having an emulsion liquid membrane [5]. The consequence of stirring speed (400-600 rpm) on the phenol removal efficiency (%) and GELM dynamic stability is depicted in Figure 6. The best performance has been attained at an optimum value of agitation speed (450 rpm) with 88.68 % removal efficiency of phenol through GELM and 135 min of dynamic stability. With the rise in speed, the diameter of the emulsion micelles was found to be reduced, which further helps in enhancing the transfer area for the transport of phenol molecules through the GELM membrane layer into the stripping side [37,42].

Figure 6.

The findings of the present research work (as shown in Figure 6) on the phenol removal are also in parallel with the previous results of the other researchers' work [5,7,10]. It was observed that the excessive increment in stirring speed does not increase extraction efficiency (%). Moreover, a further rise in stirring speed disturbs the emulsion dynamic stability, which has supplementary consequences in emulsion breakdown and subsequently, in poor extraction [41,48,49]. Another possible reason for getting poor extraction efficiency (%) for higher agitation speeds is the introduction larger amount of energy to rupture the fine drops of sodium hydroxide solution acting as stripping agent [50,51]. Hence, 450 rpm was selected as an optimum agitation speed for providing a good dispersion of fine droplets of stripping reagent in aqueous solution as well as minimum breakage with the desirable phenol removal efficiency (88.68 %).

4.6. The effect of contact time

The effect of extraction time (10-30 min) on the phenol extraction (%) and GELM dynamic stability (min) is illustrated in Figure 7. It can be elucidated from Figure 7 that with an increase of contact time from 10 to 20 min, both phenol removal efficiency and dynamic stability were found to be increased owing to the formation of smaller droplets of internal phase, which further resulted in enhanced surface area for the phenol removal process through GELM from the feed phase [5]. The 90 % removal of phenol using GELM was obtained within 20 min of contact time. After 20 min of extraction time, both phenol removal efficiency as well as GELM dynamic stability got reduced.

Figure 7.

This reduction in both parameters (phenol removal efficiency and dynamic stability) is mainly due to osmotic swelling of GELM, which has been developed due to the longer exposure time (means large contact time) of internal phase droplets, which further may have resulted an increment in the leakage process of the stripping phase into feed solution [20]. It may also be due to more entrainment of water molecules to the stripping phase, leading to dilution of the stripping phase and consequently a reduction in driving force [52]. Research work of Kulkarni et al. [53] has also reported that more contact time causes the membrane to swell due to transportation of large water molecules from the feed side to the internal side, which further breaks the emulsion (causes back transfer of the solute molecules to the feed phase from stripping phase) [53]. So, it is imperative to choose the appropriate amount of contact time that gives high extraction of phenol and good dynamic stability. Here, 20 min of duration is selected as the most favourable time for uniform distribution of droplets in the feed solution.

4.7. The effect of feed phase temperature

The membrane phase of the GELM acts as a partition between the feed phase and internal stripping phase, and passage of the phenol molecules from the feed phase to the internal phase (sodium hydroxide (NaOH)) droplets is usually done through the GELM. Feed phase temperature was observed as one of the key parameters during the phenol removal process through GELM due to its strongly effects on the phenol removal efficiency and the dynamic stability [7,27]. The influence of temperatures (20, 25, 30, 35, and 40 ºC) on the phenol separation efficiency and dynamic stability of GELM has been experimentally determined and elucidated in Figure 8.

Figure 8.

During experimentation, it was observed that the phenol removal efficiency and GELM dynamic stability were raised with an increment in temperature, but up to a certain limit (20 to 30 ºC), but after that they were reduced with further rise in extraction temperature (beyond 30 ºC). It may be due to the reason that with the rise in extraction temperature, the membrane phase viscosity decreased which further helped in increasing the diffusion process and consequently the rate of interfacial mass transfer during phenol removal through GELM [54]. Although at larger extraction temperatures (such as 35 and 40 ºC), the reduction in viscosity was found to be very large, which has further decreased the GELM dynamic stability, and as a result, the extraction efficiency was decreased. Performing the phenol removal experiment through GELM at 40 ºC was also unsuccessful. The variation in extraction temperature does not affect the impact of reaction rate on the extraction rate through GELM due to the reaction (between phenol ($\mathrm{Ph}-\mathrm{OH}$) and NaOH) is assumed to be very fast and instantaneous [7]. Hence in the experiments, 30±1°C extraction temperature with 92.50±1.95% phenol extraction efficiency (%) was selected as the most appropriate extraction temperature for phenol removal through GELM and also for providing optimum GELM dynamic stability. A comparison had been made between green emulsion liquid membranes (GELMs) based on green solvents (rice bran oil and palm oil) for the removal of phenol which are categorized in Table 2.

Table 2.

5. Conclusion

This current research work has been undertaken to explore the feasibility of using low-cost green diluent, i.e., Rice bran oil (RBO), in the GELM process for the removal of phenol from feed solution. The most appropriate value of ratio (90:10; v/v) of RBO to hexane has been selected as a liquid membrane during this process, as this proportion was found stable enough for the GELM extraction process. In order to get the optimum process conditions, OFAT (one-factor-at-a-time) optimization method was employed. Employing OFAT optimization technique, the optimization of the selected process factors was eventuated as 450 rpm of stirring speed, pH 0.45 of feed solution, 20 min of extraction time, 0.166 [M] of NaOH concentration, 2:1 (v/v) of treat ratio, 0.45 (v/v) of phase ratio, and 30±1°C of extraction temperature. The maximum obtainable phenol removal efficiency was found to be 90±1.5% with the dynamic stability of 135±2 under the optimized conditions and without employing any carrier reagent. The experimental outcomes of this research work disclosed that the RBO-based GELM is very promising and economical for the removal of phenol from the feed phase. Finally, it could be concluded that the vegetable oils as green solvents can be brought up as a treating substance for the treatment of contaminants via the GELM-based separation technique. The emergent future research challenges of this technique like scale-up (from lab scale to pilot plant scale and thereon to the industrial scale) and process intensification, still remain the key challenge for its commercial/industrial scale applications.

Declaration for conflicts of interests

The authors declare that they have no known competing interests with respect to the work reported in this paper.

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FIGURES CAPTIONS

Figure 1. Schematic representation of mechanism of mass transportation of phenol through green emulsion liquid membrane (GELM) [process conditions: NaOH concentration: 0.166 [M], treat ratio: 2:1 (v/v), phase ratio: 0.45 (v/v), pH of feed phase: 0.45, stirring speed: 450 (rpm), contact time: 20 (min), and temperature of feed phase: 30 ±1 (°C)]

Figure 2. Effect of feed solution pH on the extraction efficiency (%) and dynamic stability (min) [Process conditions: NaOH concentration: 0.166 [M], phase ratio: 0.45 (v/v), treat ratio: 2:1 (v/v), temperature of feed phase: 30 ±1 (°C), contact time: 20 min, and stirring speed: 450 (rpm)]

Figure 3. Effect of NaOH concentration on the extraction efficiency (%) and dynamic stability (min) [process conditions: phase ratio: 0.45 (v/v), treat ratio: 2:1 (v/v), pH of feed phase: 0.45, contact time: 20 min, stirring speed: 450 (rpm), and temperature of feed phase: 30 ±1 (°C)]

Figure 4. Effect of phase ratio on the extraction efficiency (%) and dynamic stability (min) [process conditions: NaOH concentration: 0.166 [M], pH of feed phase: 0.45, treat ratio: 2:1 (v/v), temperature of feed phase: 30 ±1 (°C), contact time: 20 min, and stirring speed: 450 (rpm)]

Figure 5. Effect of treat ratio on the extraction efficiency (%) and dynamic stability (min) [process conditions: NaOH concentration: 0.166 [M], phase ratio: 0.45 (v/v), pH of feed phase: 0.45, temperature of feed phase: 30 ±1 (°C), contact time: 20 min, and stirring speed: 450 (rpm)]

Figure 6. Effect of stirring speed on the extraction efficiency (%) and dynamic stability (min) [Process conditions: NaOH concentration: 0.166 [M], phase ratio: 0.45 (v/v), pH of feed phase: 0.45, treat ratio: 2:1 (v/v), temperature of feed phase: 30 ±1 (°C), and contact time: 20 (min)]

Figure 7. Effect of contact time on the extraction efficiency (%) and dynamic stability (min) [process conditions: NaOH concentration: 0.166 [M], phase ratio: 0.45 (v/v), pH of feed phase: 0.45, treat ratio: 2:1 (v/v), temperature of feed phase: 30 ±1 (°C), and stirring speed: 450 (rpm)]

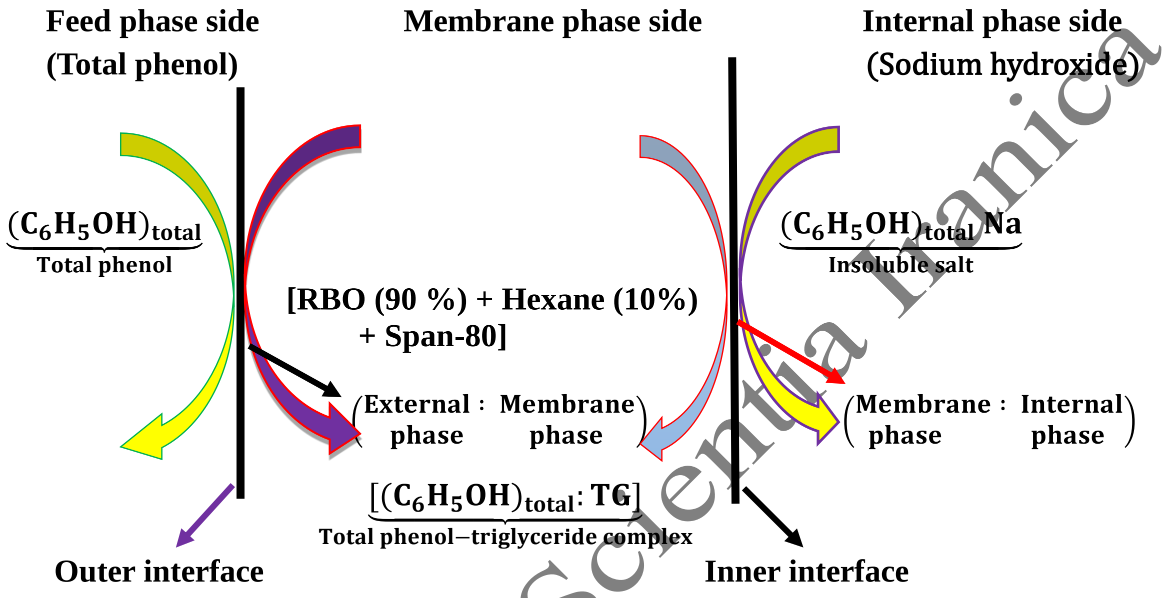
Figure 8. Effect of feed phase temperature on the extraction efficiency (%) and dynamic stability (min) [process conditions: NaOH concentration: 0.166 [M], phase ratio: 0.45 (v/v), pH of feed phase: 0.45, treat ratio: 2:1 (v/v), contact time: 20 min, and stirring speed: 450 (rpm)]

TABLE CAPTIONS

Table 1. Operating conditions for the phenol removal through GELM

Table 2. Comparison of phenol removal using GELM based on green solvents

LIST OF FIGURES



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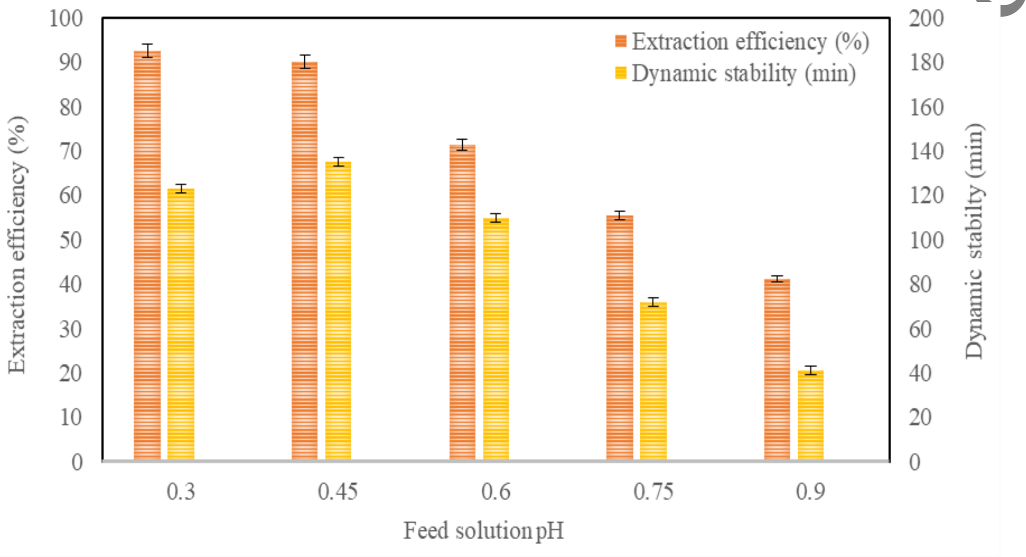

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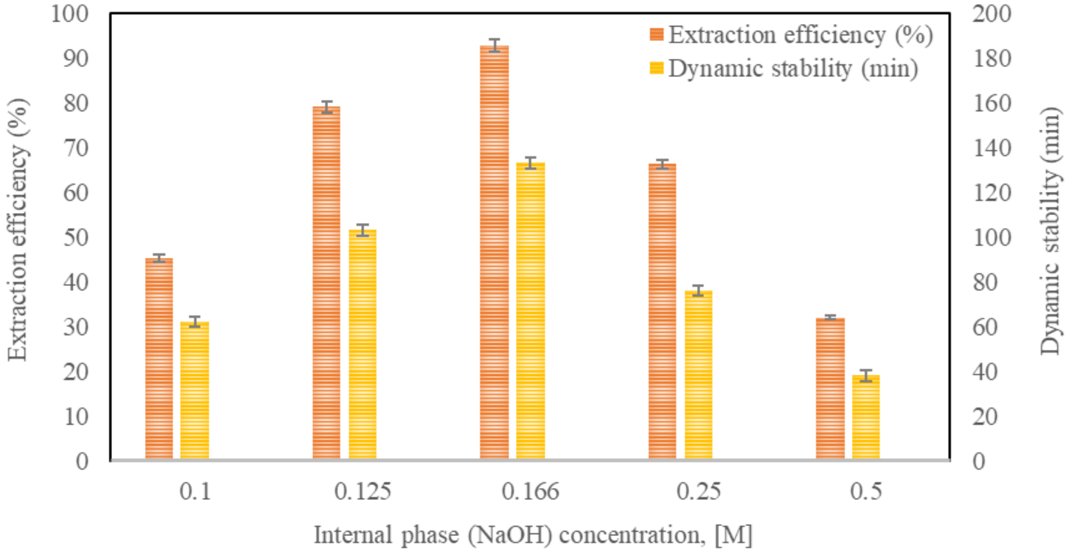

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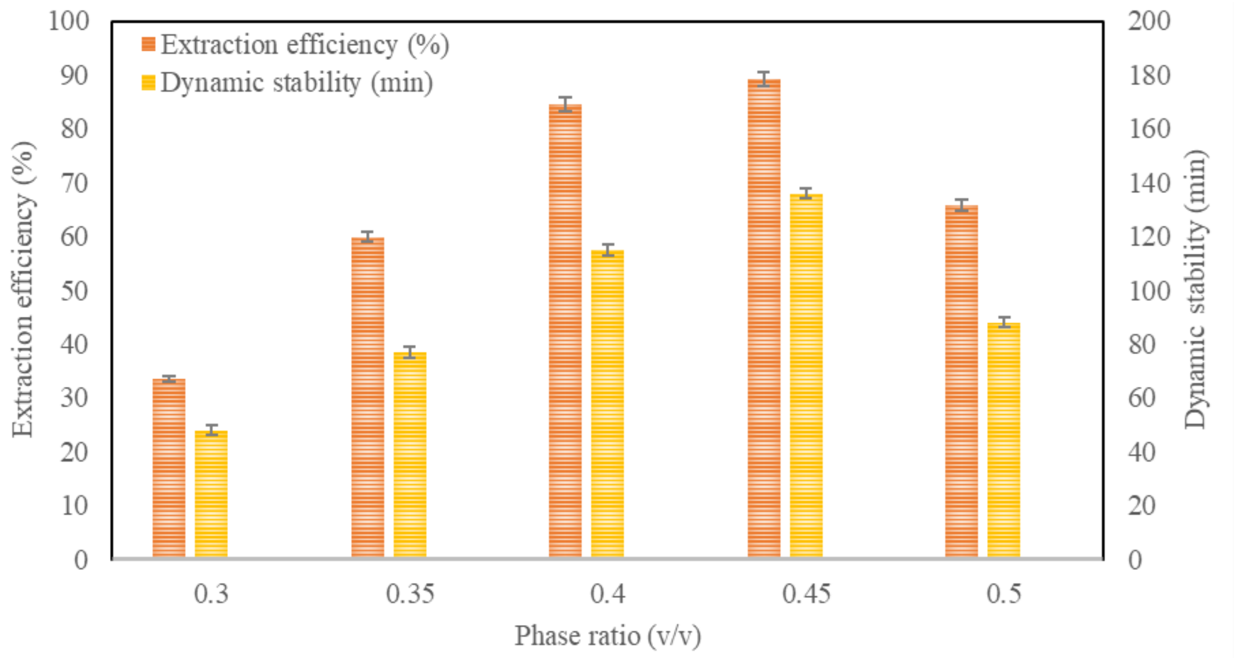

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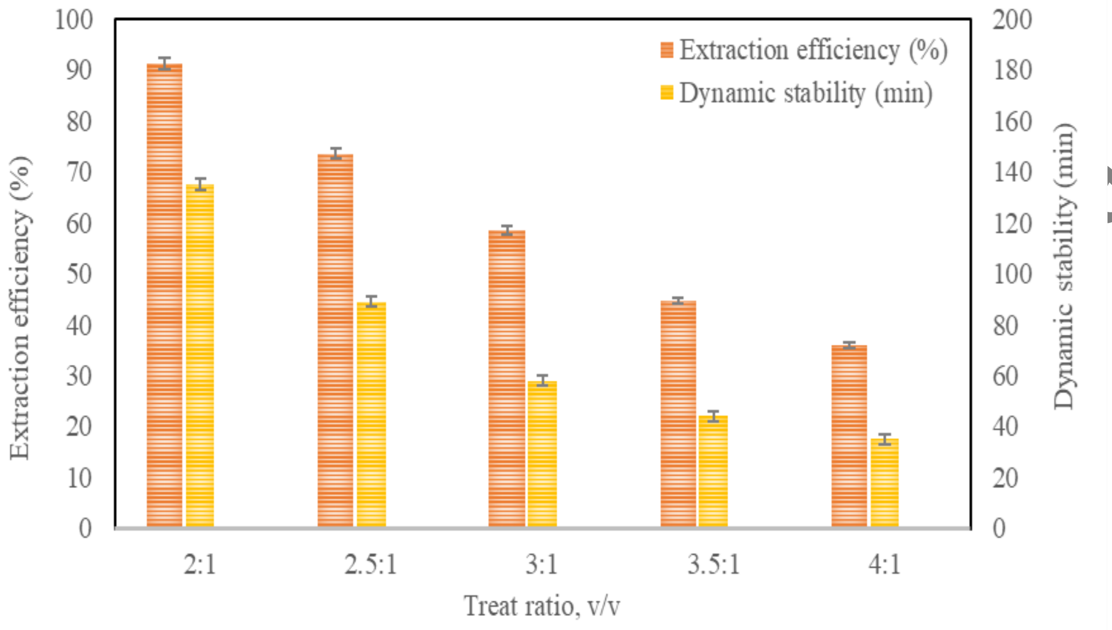

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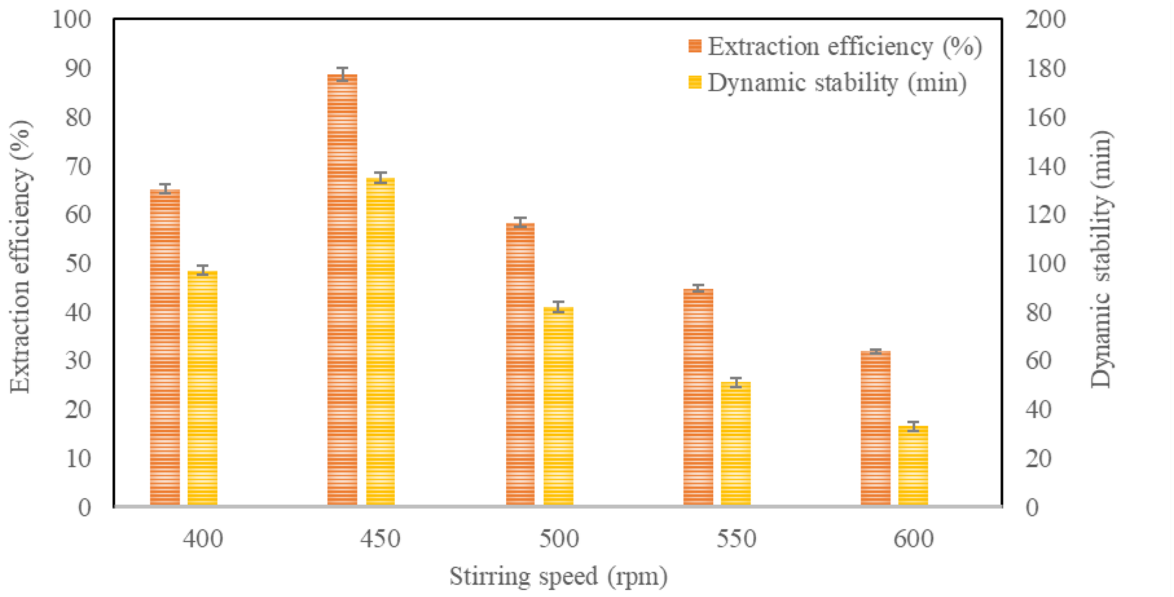

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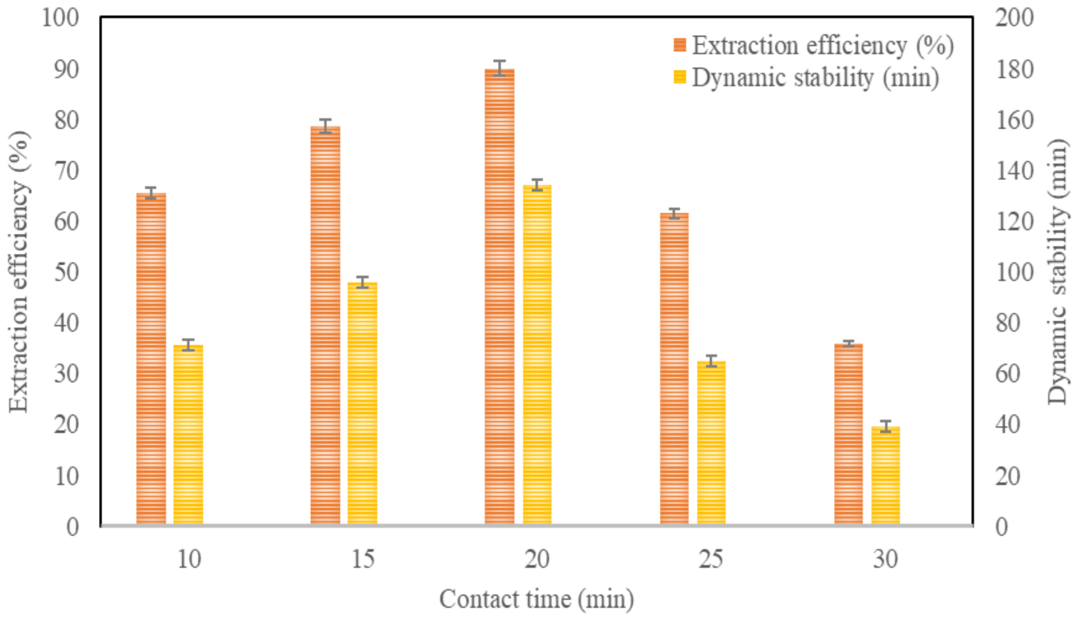

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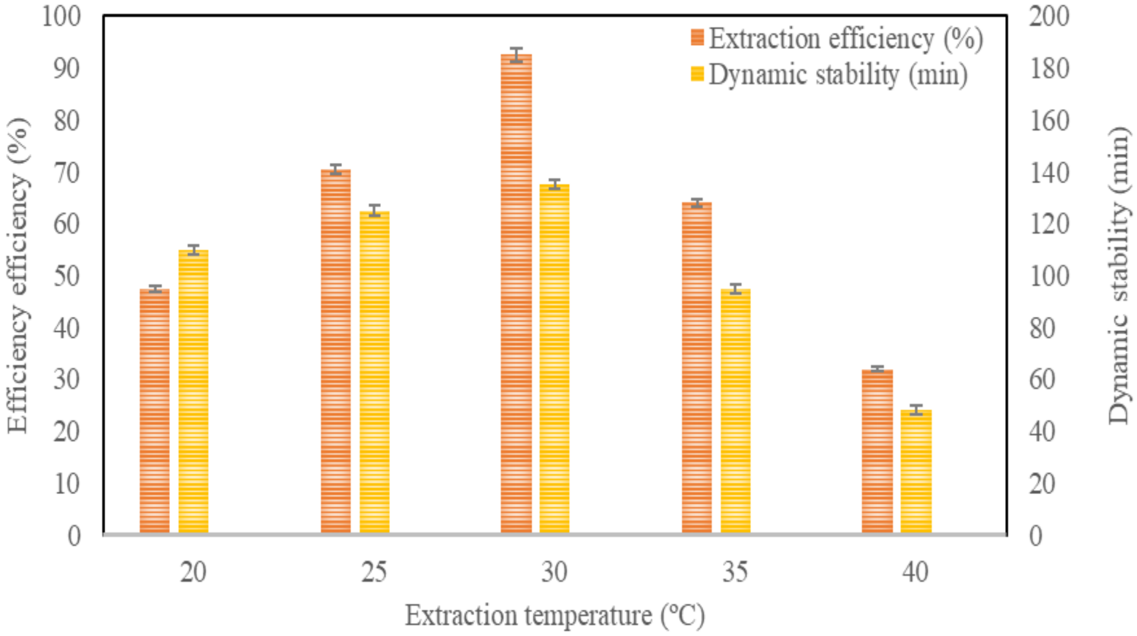

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Table 1. Operating conditions for the phenol removal through GELM

S. No.	Parameters	Range
		Process conditions
1	Aqueous solution pH	0.15, 0.3, 0.45, 0.6, 0.75
2	NaOH concentration, [M]	0.10, 0.125, 0.166, 0.25, 0.50
3	Phase ratio, (v/v)	0.30, 0.35, 0.40, 0.45, 0.50
4	Treat ratio, (v/v)	2:1, 2.5:1, 3:1, 3.5:1, 4:1
5	Agitation speed, (rpm)	400, 450, 500, 550, 600
6	Extraction time, (min)	10, 15, 20, 25, 30
7	Extraction Temperature (ºC)	20, 25, 30, 35, 40
		Hold values
8	Diluent ratio (RBO: hexane)	9:1
9	Phenol concentration, (ppm)	100
10	Emulsification time, (min)	25
11	Emulsification speed, (rpm)	1800
12	Span-80 concentration, (%, v/v)	1.8

Table 2. Comparison of phenol removal using GELM based on green solvents

Comparable conditions/factors	**Rice bran oil (RBO)**	**Palm oil**
Solute treated	Phenol	Phenol
Organic solvent	Hexane	Kerosene
Organic solvent volume, %	10%	30%
Surfactant	Span 80	Span 80
Surfactant concentration	1.8 %	3 %
Stripping agent	NaOH	NaOH
Stripping agent concentration	0.166 [M]	0.1 [M]
pH of external phase solution	0.45	8
Phase ratio (Internal: Organic)	0.45 v/v	0.33 v/v
Treat ratio (Emulsion: External)	1:2	1:10
Emulsification	25 min and 1800 rpm	5 min and 1300 rpm
Extraction	20 min and 450 rpm	5 min and 500 rpm
Efficiency	90±1.5%	83%

A Brief on Technical Biography of Authors

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Dr. Anil Kumar is working as a guest faculty in the Department of Chemical Engineering, Sant Longowal Institute of Engineering and Technology (Deemed to be University, Under MHRD, Govt. of India), Longowal-148106, Sangrur since 24 January, 2020. He has more than 4.5 years of teaching experience. He has published 17 articles in the peer-reviewed journals (such as Journal of Cleaner Production, Separation and Purification Technology, Journal of Industrial and Engineering Chemistry, Reviews in Environmental Science and Bio/Technology, Journal of Dispersion Science and Technology, etc.) with the total impact factor (TIF) of 81.541. He also got one Indian patent granted. He has 685 Citations with h-index 12. He got SLIET Quality Publication Award 6 times with the cash prize of 30,000. He visited 3 International conferences, various national conferences, and participated in many more short-term courses and other academic activities. He is also a life member of Biotechnology Research Society of India (BRSI) and Indian institute of Chemical Engineers (IIChE). His research is based on Green Chemical Engineering (GCHE). During doctorate work, he explored the potential applications of "Green Solvents" for the formulation and preparation of Emulsion Liquid Membrane (ELM). He has discovered "Rice Bran Oil" as a Green Solvent for successful application in Emulsion Liquid Membrane Technology in place of toxic and costly petroleum based organic solvents. He has developed a stable GELM and applied for LA extraction application. His areas of interest are Green chemical Engineering, Liquid membrane technology, Sustainable separation processes, Wastewater engineering, waste to waste technology, mathematical modeling, and process optimization.

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Dr. Avinash Thakur is presently working as Professor in the Department of Chemical Engineering at Sant Longowal Institute of Engineering and Technology (Deemed to be University: Established by Govt. of India), Longowal-148106, Punjab. India. He has also served as Head of the Department. He has 28 years of experience in teaching and research. Dr. Avinash Thakur has supervised 02 Ph.D. Scholar, and 10 M. Tech. projects and currently supervising 07 Ph.D. scholars. He has one process and two design patents to his credit. Two no of externally funded research projects by Govt. agencies has been successfully looked after by him. He is life member of Biotechnology Research Society of India, Indian Society for Technical Education etc. His articles have appeared in journals such as Waste and Biomass Valorization, Journal of Cleaner Production, International Journal of Food Engineering, Separation and Purification Technology, Journal of Industrial and Engineering Chemistry, Biomass Conversion and Biorefinery, Reviews in Environmental Science and Bio/Technology, Journal of Dispersion Science and Technology etc. His research is focused in Biochemical Engineering and downstream separation processes especially green solvent extraction and value addition of agro-industrial wastes. Prof. Thakur has h-index of 18 (Google scholar) and more than 1000 citations. He has visited countries such as UK, Switzerland, New Zealand, Australia for academic assignments.

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Prof. Parmjit S. Panesar is currently working as Professor, Department of Food Engineering & Technology, Sant Longowal Institute of Engineering and Technology. Prof. Panesar has more than 28 years of teaching & research experience and also served in administrative positions. In 2005, he has been awarded BOYSCAST fellowship by Department of Science & Technology (DST), Govt. of India, to carry out advance research at Chembiotech labs, University of Birmingham Research Park, UK. In 1999, Prof. Panesar was awarded Young Scientist Fellowship. He has published 207 international/national scientific papers, 50 book reviews in peer-reviewed journals, 50 chapters and has authored/edited 10 books. He has supervised 20 Ph.D. students & more than 30 M. Tech students. He is a member of the editorial advisory boards of various national/international journals. He is now serving as a member of the National level Scientific Panel on “Alcoholic Beverages” constituted by FSSAI, India. In recognition of his work, Prof. Panesar was elected as ‘Fellow 2018’ by The Biotech Research Society of India (BRSI), ‘Fellow 2019’ of ‘National Academy of Dairy Sciences’, ‘Fellow 2021’ by the ‘International Society for Energy, Environment & Sustainability (ISEES)’ and ‘Fellow 2021’ of ‘Academy of Microbiological Sciences’. Prof. Panesar was also listed consequently four times in the most coveted list (2020, 2021, 2022, 2023, 2024) of "World Ranking of Top 2% Scientists" published by Stanford University, USA. His research is focused in the area of value addition of food industry by products, circular economy, green extraction of bioactives, nanoencapsulation, functional food products. Prof. Panesar has h-index of 54 and more than 10420 citations (Google scholar).