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Performance of membrane assisted solvent extraction with homologous solvents for the removal and recovery of phenol

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ABSTRACT

Solvent extraction, an effective separation technique is not normally considered for wastewater treatment due to operational and economic challenges, even though the extracted species can be recovered as value. The current study aims at improving the solvent extraction process using a membrane as interphase. In this context, the performance of three solvents, 1-hexanol, 1-octanol, and 1-decanol, are assessed by both conventional and membrane-assisted solvent extraction using polyvinylidene fluoride-based hollow fiber membrane contactor, particularly to highlight the advantages of membrane assisted solvent extraction. Thermodynamic investigations revealed that the extraction of phenol with all the solvents to be exothermic in nature. Experiments were conducted with the solvent flowing through the shell side of the hollow fiber membrane element. After about six months of use, the shell developed a few cracks indicating the incompatibility of the shell material with the solvent, necessitating the passage of the solvent through the lumens. The experimental results indicated that for conventional solvent extraction, 1-hexanol exhibited 96.24% phenol extraction compared to 95.97% and 92. 87% for 1-octanol and 1-decanol respectively for a solvent to feed ratio of 2.5:1 and for a feed concentration of 500 mg/L phenol. The values for membrane-assisted solvent extraction are 94.82% for 1-hexanol, 91.01% for 1-octanol, and 89.35% for 1-decanol for a solvent to feed ratio of 2:1 and for a feed concentration of 500 mg/L phenol. The comparative assessments indicated that membrane-assisted solvent extraction has the advantages of less solvent inventory, less energy consumption, operational simplicity, and process safety.

Keywords: Membrane-assisted solvent extraction; Polyvinylidene fluoride; Hollow fiber; Phenol; Solvents

1. Introduction

Wastewater containing organic pollutants such as phenolic compounds can be treated by several methods including biological degradation [1], thermal decomposition [2], electrochemical decomposition [3] distillation [4], adsorption [5], solvent extraction [6], and membrane processes such as per-vaporation [7,8], membrane assisted solvent extraction [9], liquid membrane extraction [10], etc. They can be broadly classified into two categories such as destructive and non-destructive methods. Table 1 provides the different methods reported in the literature including process principle, efficiency, merits, and demerits in qualitative terms. Most of these studies have been directed towards improving the process efficiency by destroying the organic species including phenol such as in bioreactors [11,12], Sono-electric Fenton degradation [13], anaerobic stabilization [14], and in a variety of electrochemical reactors [3]. In all these processes, phenol gets destroyed and released into the environment as carbon dioxide, shifting

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Table 1
Destructive and non-destructive methods for the treatment of wastewater containing organic compounds such as phenol

Process	Process principle/Description	Process efficiency	Merits	Demerits	References
Destructive methods					
Bio-degradation (Secondary Treatment)	Microorganisms utilize phenol and other organics present in the wastewater for their growth cycle and finally the dead microorganisms are decomposed to produce methane.	Can remove more than 90% of biodegradable organics.	Simple, economical and efficient. Most widely used in wastewater treatment.	Slow process and requires large foot print. Conducive environment required. Provision of air to sustain the process. May require other chemical treatment/aeration etc.	[12,16]
Advanced oxidation processes (AOP)	Operates through free radical mechanism. Uses chemicals/radiation such as Ozone/UV/Hydrogen peroxide which easily form free radicals.	Highly efficient even for non-biodegradables.	Fast degradation due to radical formation. No sludge.	Successfully tested in lab and not easily scalable due to low through put. Highly energy and cost intensive.	[17]
Electro-chemical decomposition	Use of Fenton along with MnO in advanced electro chemical reactors.	Fast degradation.	Highly efficient.	Highly energy and cost intensive.	[18]
Non-destructive methods					
Distillation	Principle of relative volatility.	Very high	Able to treat high concentration of phenol. Good potential for recovery and reuse.	Highly energy intensive and high cost.	[19]
Chemical precipitation/Coagulation/Flocculation	Conversion of dissolved species in water into solid form.	Low	Simple equipment. Able to treat high concentration of phenol.	Requires chemicals, continuous monitoring. High volume of sludge.	[20]
Adsorption/Ion exchange	Binding of phenol onto solid matrix by physical or physico-chemical interaction.	High	Simple, highly effective with favourable kinetics. Cost-effective.	Not favourable for higher concentration. Not selective and high regeneration cost.	[21]
Liquid–Liquid Extraction or Solvent Extraction	Uses the principle of relative solubility/Chemical affinity.	Very High	Effective removal of phenol and possibility of recovery.	High equipment cost and energy cost. Economically unviable due to high solvent cost, and for low concentrations.	[22]
Pressure Driven Membrane Separation Processes (Reverse Osmosis/Nano-filtration)	Uses high pressure and fine membranes to reject phenols and other compounds.	Low	Cost-effective, reliable, small footprint and scalable.	Complete separation not possible. Limited by osmotic pressure considerations.	[23,24]

the environmental burden from water to air. Some of the processes such as adsorption, chemical precipitation, and ion exchange preserve the organic components but recovery of species from the resultant agglomerates is not techno-economically feasible, due to lack of selectivity and the constraints in handling and processing of the resultant products to recover phenol as value. Despite the fact that conventional solvent extraction is the most effective method to remove and recover organic components from wastewater, it is seldom used in wastewater treatment other than in the nuclear industry [15], because of many operational, safety, and economic challenges. The need for intimate mixing and subsequent phase separation restricts the solvent selection and results in loss of solvent due to emulsification. Most of the solvents used for solvent extraction are costly and the recovery process is cumbersome.

Membranes act as barriers facilitating the transfer of desired species. Membrane processes are mostly rate governed and operate under ambient temperature conditions, enabling the non-dispersive transfer of mass across the contacting phases. Like conventional processes, they can operate under different gradients such as differential pressure, concentration, electrical, and thermal. Passive membrane processes do not require any external energy source to effect the separation as in the case of forward osmosis, diffusion dialysis, membrane distillation, etc., while the active processes such as electrodialysis, reverse osmosis, pervaporation, etc. require external energy to drive the separation [25]. Membrane contactors are essentially microporous passive membrane devices that enable mass transfer across the two contacting phases and are extensively used in many applications as in the secondary treatment of wastewater [26], gaseous absorption [27], and hemodialysis [28].

The emergence of membrane-assisted solvent extraction (MASE) as a unit operation has opened the possibility of its application in wastewater treatment because of its versatility, safety, and low inventory requirements. Membrane contactors are suitable for separation through solvent extraction as the solvent and the aqueous phase can have interfacial contact through a large number of micro-pores present on the membrane surface, dispensing with the need for intimate mixing of the two phases thereby avoiding the problem of emulsification, and consequent solvent loss, besides saving on energy consumption. The solvent selection also becomes easier as post-extraction phase-separation is not required, unlike conventional solvent extraction. MASE, being passive and non-dispersive in nature, offers several advantages in terms of solvent selection, ease of operation including safety, and energy economy [29,30].

Three types of membrane-enabled solvent extraction methods namely emulsion liquid membrane (ELM), supported liquid membrane (SLM), and membrane assisted solvent extraction have been studied for the removal of organic pollutants from wastewater [31–33]. Liquid membranes both ELM and SLM involve hyphenated contact of feed and strip solutions through the membrane. In ELM the membrane phase is mobile, incorporated into an emulsion stabilized by the surfactant, [34], while in SLM, the solvent is static, impregnated into the pores of the membrane matrix. In ELM, after extraction of the desired species from feed, the emulsion is broken in the strip solution recovering the organic solvent for reuse, while in SLM extraction and stripping takes place in succession seamlessly allowing continuous regeneration of the solvent [35]. Both ELM and SLM exhibit high selectivity and can extract the desired species against the gradient and have been studied extensively for the removal of various pollutants both organic and inorganic species. The major challenges include membrane stability, the high cost of solvents, and scale-up difficulties.

In MASE, the two phases are separated by the membrane, with the interfacial contact being established through the membrane pores. It is simple to operate and is being used albeit in low quantities for the selective extraction of the contaminants. Membranes made of different polymers were used for MASE including polypropylene (PP) [36], polysulfone (PS) [33], and polyethylene (PE) [37] for the study of solvent extraction where mass transfer correlations are discussed with an indication of the possibility of the operation of extraction and stripping steps in a continuous loop enabling instant solvent recovery and reuse. [38]

Phenol is used in several manufacturing processes as a precursor in the production of pharmaceuticals, food preservatives, polymers, resins, and adhesives [4]. Phenol can be present in aqueous streams originating from metabolic waste products of plants, animals, and humans, or in wastewater from many industries including petrochemicals, refineries, and pharmaceuticals. In these streams, the concentrations of phenol may go up to about 7,000 mg/L [39]. Phenol is used as an insecticide and disinfectant but is chemically toxic and also carcinogenic on ingestion and hence classified as a priority pollutant by the US Environmental Protection Agency (USEPA) [4] and the allowed limits for discharge is less than 1 mg/L. The pollution control board in India has specified the limit as 5 ppm for disposal of phenolic effluents into sewers and less than 1 ppm for discharge into running water bodies [40]. Protein degradation, tissue erosion, central nervous system paralysis, kidney, liver, and pancreatic malfunction are all symptoms of drinking phenol-contaminated water [41]. At present, the phenol-containing wastes are subjected to bio-degradation by the micro-organisms in the secondary treatment leading to the loss of value.

Many solvents have been used for the extraction of phenol such as N-octanoyl pyrrolidine, amines, Cyanex 923, diethyl carbonate, methyl isobutyl ketone (MIBK), tributyl phosphate (TBP), ionic liquids, etc. [6]. In our earlier study, the suitability of normal solvents like 1-hexanol was reported to be effective [42]. In this context, it was considered appropriate to examine the substitutability of 1-hexanol with homologous solvents, and assess the relative performance of conventional and membrane-assisted solvent extraction, when the solvent is circulated through the shell side. Accordingly, two similar solvents were chosen, that is, 1-octanol and 1-decanol, considering the relative toxicity, cost of solvents, and low solubility in water. The parameters studied include aqueous feed phenol concentration, pH, temperature, and solvent to feed ratio for conventional solvent extraction (CSE), while MASE was studied with reference to solvent to feed ratio, time at the natural pH of the solution. Stripping of phenol from the solvents was carried out using sodium hydroxide in both cases.

2. Materials and methods

2.1. Materials

Phenol and solvents such as 1-hexanol, 1-octanol, and 1-decanol were of Sigma-Aldrich make and of analytical reagent grade. Sodium hydroxide, hydrochloric acid, potassium hydroxide, sodium chloride, calcium chloride, and magnesium chloride were purchased from M/s Southern India Scientific Corporation, based in Chennai, Tamil Nadu, India.

A stock solution containing 1,000 mg/L phenol in water was made, from where different concentrations of the feed solutions were prepared by appropriate dilution. 1-hexanol, 1-octanol, and 1-decanol were used as organic solvents for extraction. Sodium hydroxide (0.5 N) was used as a stripping solution. Hydrochloric acid and potassium hydroxide were used for pH adjustments, wherever required.

2.2. Methods

2.2.1. Studies on conventional solvent extraction and stripping

Studies were carried out by mixing 50 mL of aqueous phenol feed sample and 50 mL of organic solvent and in a screw-capped Erlenmeyer flask of 250 mL capacity and shaken at 180 rpm for 1 h to ensure thorough mixing and separated using a separating funnel by allowing it to stand for 45 min, to ensure the complete separation of phases. The concentration of phenol in the aqueous phase was estimated at different times during the course of the experimental runs [43]. Fig. 1 depicts the schematic representation of the conventional configuration.

The pH of aqueous phenol solutions was adjusted by the addition of either KOH or HCl solutions depending on the desired value. The effect of temperature was studied in the temperature range of 30°C–50°C using a temperature-controlled orbital shaker Orbitek LT. The concentration of phenol in the aqueous phase was measured using Cary 60 UV-Visible spectrophotometer at 270 nm [44] and the corresponding concentration in the organic phase was estimated by mass balance. Stripping of phenol was carried out similar to extraction except that the organic phase was mixed with 50 mL of 0.5 N NaOH. The concentration of phenol in the aqueous phase was measured using Cary 60 UV-Visible spectrophotometer at 288 nm [45], after stripping with 0.5 N NaOH.

Percentage extraction and stripping, overall recovery percentage of phenol, and distribution coefficient were calculated based on Eqs. (1)–(4) [33] as indicated below.

$$\text{Extraction Percentage}\left(E\%\right)=\frac{\left(C_i-C_f\right)}{C_i}\times 100 \tag{1}$$

$$\text{Stripping Percentage}\left(S\%\right)=\frac{C_s}{C_o}\times 100 \tag{2}$$

$$\text{Overall Recovery Percentage}\left(R\%\right)=\frac{C_s}{C_i}\times 100 \tag{3}$$

$$\text{Distribution Coefficient}\left(D\right)=\frac{C_o}{C_f} \tag{4}$$

where C represents the concentration in mg/L. Suffices i, f, o, s represent initial, final, organic phase, and strip phase, respectively.

2.2.2. Membrane assisted solvent extraction

2.2.2.1. Procurement and specifications of the hollow fiber membrane element

Membrane contactors made of hollow fibers similar to shell and tube heat exchangers are used for the separation of liquids, and gas mixtures [46], where a bundle of porous hollow fibers is assembled inside a shell. It is technically possible to have the aqueous and organic phases flow through the shell side or the lumen (tube) side. The hollow

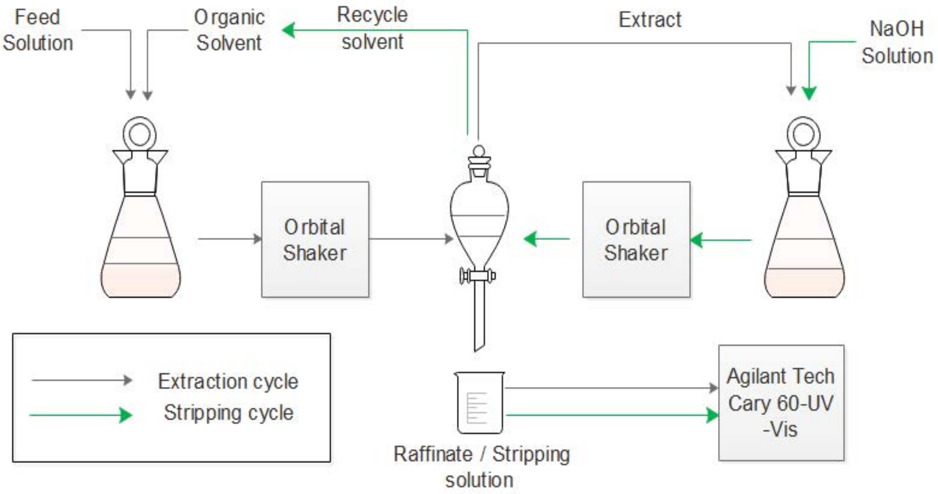

Fig. 1. Schematic representation of CSE experimental setup.

fiber membrane contactor element made of polyvinylidene fluoride (PVDF) used in this experiment was purchased from TECH INC Chennai, Tamil Nadu, India, and the exact specifications are listed in our previous paper [42]. The basic specifications of the membrane element consisted of 500 lumens of 0.25 m length with a net porosity of 0.6 accommodated in a shell of 0.036 m (36 cm) internal diameter. The lumen inner diameter was 0.0005 m (0.5 mm) and the outer diameter 0.001 m (1 mm).

2.2.2.2. Experimental studies on membrane assisted solvent extraction

A schematic diagram of the experimental setup is depicted in Fig. 2 along with its photograph in Fig. 3 of the unit in operation. For the experiments, following the methodology adopted in literature [9] phases aqueous and organic were passed between the lumens and shell respectively. 250 mL of the aqueous phase and 250 mL of organic phase were continuously circulated through the tube side and shell side of the hollow fiber membrane element respectively.

The flowrate on the tube side (aqueous phase) was maintained constant at 25 mL/min while that of the shell side (organic phase) was varied from 12.5 to 75 mL/min using a peristaltic pump. The samples were collected from the tube side at regular time intervals and analyzed for the phenol content using a UV-Visible spectrophotometer. All the experiments were carried out thrice to ensure reproducibility and the error was found to be less than 2%.

2.3. Estimation of overall mass transfer coefficient using membrane contactors

As CSE is a bulk phenomenon, the analysis of mass transfer is confined to MASE. Mass transfer coefficients are calculated based on the experimental data and using the empirical correlations published in the literature as a function of the organic phase Reynolds number for the shell side flow of solvent.

2.3.1. Empirical estimation of overall mass transfer coefficient

Empirical values are based on correlations using various dimensionless numbers which include fluid properties and hydrodynamic properties. The overall mass transfer coefficient through a membrane contactor was estimated using resistance in series model which includes resistance offered by the aqueous phase (tube side), membrane, and finally the organic phase (shell side).

$$\frac{1}{K_{\text{aq}}} = \frac{1}{k_t} + \frac{d_i}{Dk_m d_{\text{lm}}} + \frac{d_i}{Dk_s d_o} \tag{5}$$

where k_t, k_m, and k_s are the local mass transfer coefficients of tube side, membrane pore, and shell side, respectively. D is the distribution coefficient. d_i, d_o and d_{lm} are the inner, outer, and log mean diameters of the hollow fibre, respectively.

2.3.1.1. Estimation of tube side mass transfer coefficient

The tube side mass transfer coefficient is calculated using the Leveque correlation for Sherwood number (Sh) based on Graetz number (Gz) where $\text{Gz} = \text{Re}\cdot\text{Sc}\cdot(d_i/L)$.

$$\text{Sh}_t = \frac{k_t d_i}{D_{\text{aq}}} = 1.62(\text{Re})^{1/3}(\text{Sc})^{1/3}\left(\frac{d_i}{L}\right)^{1/3} = 1.62(\text{Gz})^{1/3} \quad \text{Gz} > 6 \tag{6}$$

$$\text{Sh}_t = \frac{k_t d_i}{D_{\text{aq}}} = 0.5(\text{Re})(\text{Sc})\left(\frac{d_i}{L}\right) = 0.5\text{Gz} \qquad \text{Gz} < 6 \tag{7}$$

where Gz is 0.8 for this study. The diffusivity of phenol in the aqueous and in the organic phase was estimated using the Wilke–Chang correlation.

2.3.1.2. Estimation of shell side Reynolds number and mass transfer coefficient

Reynolds number for shell side is calculated using the equation:

$$\text{Re} = \frac{D_H \upsilon\, \rho}{\mu} \tag{8}$$

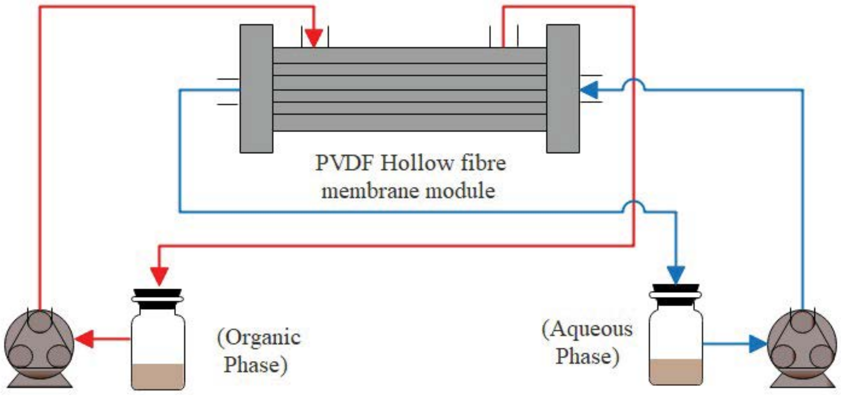

Fig. 2. Schematic diagram of experimental setup.

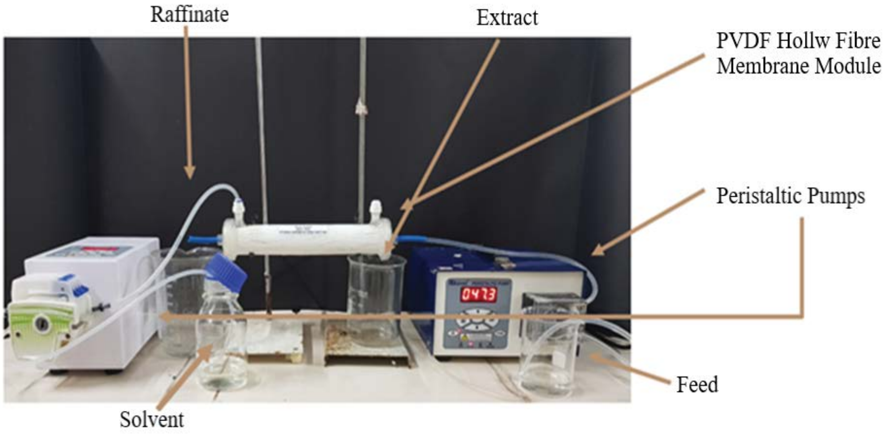

Fig. 3. Photograph of experimental setup.

where Re is the Reynolds number, D_H is the shell hydraulic diameter, v the average linear velocity, ρ and μ are the density and viscosity of the fluids.

$$D_H = \frac{4X\left(\text{cross-sectional area of flow}\right)}{\text{wetted perimeter}} = \frac{D_s^2 - N_t d_o^2}{D_s + N_t d_o} \quad (9)$$

$$v = \frac{Q_{\text{org}}}{A_s} \quad (10)$$

$$A_s = \frac{\pi}{4}\left(D_s^2 - N_t d_o^2\right) \quad (11)$$

where D_s is the inner diameter of the shell, N_t is the number of fibers, Q_{org} is the solvent flow rate through the shell side, and A_s is the cross-sectional flow area.

Mass transfer coefficient for the shell side is determined using the correlation:

$$\text{Sh}_s = \frac{k_s D_H}{D_{\text{org}}} = \beta\left(1-\Psi\right)\left(\frac{D_H}{L}\right)\text{Re}^{0.6}\text{Sc}^{0.33} \quad (12)$$

where β is a constant depending on nature of the membrane (5.85 – hydrophobic, 6.1 – hydrophilic), $0 < \text{Re} < 500$, $0.04 < \Psi < 0.4$, L is the length of the fibre [47].

2.3.1.3. Estimation of membrane mass transfer coefficient

The mass transfer coefficient within the membrane is estimated using equation:

$$k_m = \frac{2\varepsilon D_{\text{org}}}{\tau\left(d_o - d_i\right)} \quad (13)$$

where τ is the tortuosity, ε is the porosity and D_{org} is the solute diffusivity in the organic phase.

2.3.2. Experimental estimation of mass transfer coefficient

The overall mass transfer coefficient for phenol transfer in the extraction process is calculated using the following equation:

$$K_{\text{aq}} = \frac{J_{\text{sol}}}{\dfrac{\left(C_{\text{aq}} - C_{\text{aq}}^*\right)}{\ln\left(\dfrac{C_{\text{aq}}}{C_{\text{aq}}^*}\right)}} \quad (14)$$

where J_{sol} is the solute flux (kg/m^2 s) and C is the concentration (mg/L)

Suffices aq and aq* represent the aqueous phase and aqueous phase in equilibrium with the organic phase respectively.

3. Results and discussion

3.1. Conventional solvent extraction

3.1.1. Solvent selection

The objective of the current study is to intensify the solvent extraction process to make it a simple, cost-effective, and safe method for recovering phenol from wastewater streams. Even though literature reports several solvents such as ethyl acetate, methyl isobutyl ketone, etc., with high extraction efficiency, 1-hexanol, 1-octanol, and 1-decanol have been chosen for initial assessment based on the parameters including solubility of the solvent in water, reasonable distribution coefficient, compatibility with the chosen membrane material, viscosity, and specific cost of the solvent. Further, the selection is guided by the consideration that phenol is often more soluble in organic solvents less polar than water with reasonably lower viscosities.

3.1.2. Effect of initial feed concentration

Fig. 4 presents the observed variation of percentage extraction of phenol as a function of feed concentration from 100 to 500 mg/L for all the three solvents 1-hexanol, 1-octanol, and 1-decanol. The percentage extraction of phenol increases with initial concentration for all the solvents albeit to different extents. Amongst the solvents,1-hexanol shows better extraction of about 94.7% at 500 mg/L initial concentration, while for 1-octanol and 1-decanol the corresponding values are 93.2% and 91.7%, respectively.

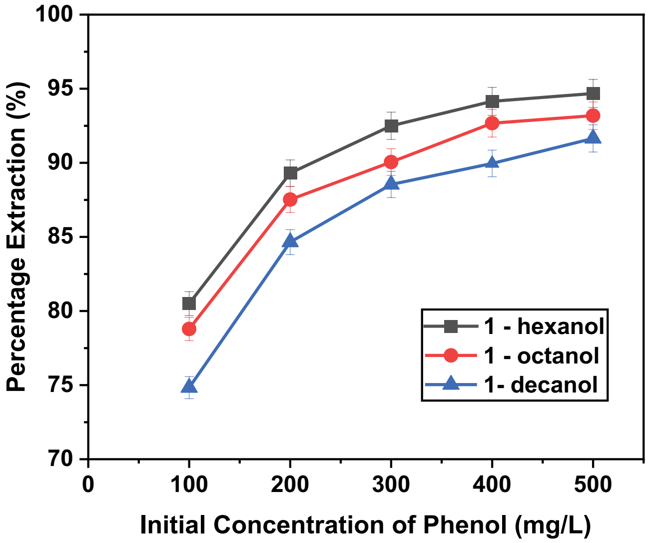

Fig. 4. Influence of feed concentration on percentage extraction of phenol.

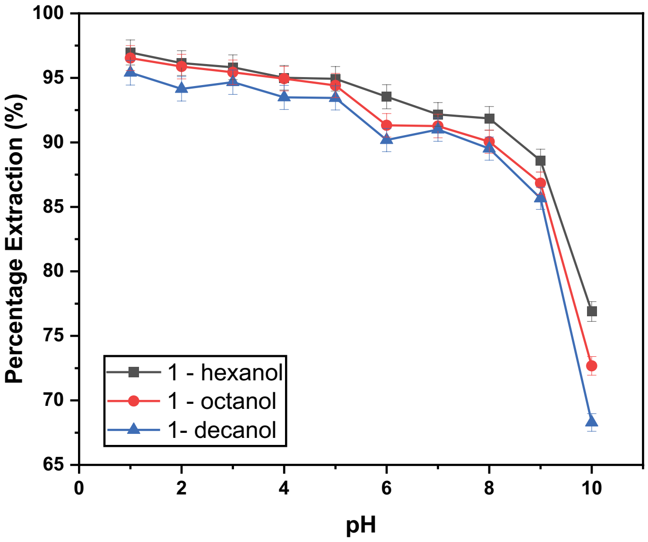

Fig. 5. Influence of pH on percentage extraction of phenol (Initial concentration of feed solution: 500 mg/L of phenol).

The relative values are maintained in the same order for the entire concentrations studied and in keeping with the expectation that the lesser the polarity of the solvents, the higher would be the extraction.

The change in percentage extraction of phenol with concentration shows two distinct trends. At lower concentrations, that is, up to about 300 mg/L, there is a sharp increase beyond which the increase is less pronounced tending to reach a constant value, for all the solvents. The percentage extraction of phenol is also observed to be high for 1-hexanol compared to other solvents throughout the concentrations studied. All of them follow the same trend, maintaining almost constant differences and attaining nearly a constant value beyond 400 mg/L. Relatively significant solubility of water and low polarity of 1-hexanol, compared to other solvents, accounts for higher percentage extraction. The dissociation of phenol in the aqueous phase is responsible for lower percentage extractions at lower concentrations indicating that phenol is getting extracted as undissociated species. Probably, the net extraction appears to be the result of phenol solubility in the solvent in addition to the water present. For further experiments, a feed concentration of 500 mg/L has been chosen.

3.1.3. Effect of pH of aqueous phase

pH is an important chemical parameter as lower pH values tend to keep the phenol species mostly in the undissociated state. Fig. 5 presents the percentage extraction of phenol as a function of feed pH at a fixed feed concentration of 500 mg/L at room temperature (30°C ± 2°C). The percentage extraction of phenol is more than 95% for all the solvents at pH 1, decreasing marginally till pH 6, the natural pH of the aqueous solution of 500 mg/L phenol to a value of about 90% and thereafter drastically declines with increasing pH in agreement with the reported observations [48].

Based on the experimental studies, it can be inferred that at low pH, the percentage extraction is maximum around 95% or more and at normal pH of phenolic solutions, the percentage extraction is high around 90%. Even at higher pH, the percentage extraction is appreciable around 70%. Among the three solvents, the percentage extraction of phenol, is maximum for 1-hexanol (97.5%) at pH 1, while 1-octanol (97%) and 1-decanol (96%), exhibited lower percentage extraction. The relative performance of the solvents was found to be the same at all the pH values.

3.1.4. Effect of solvent to feed ratio

Experiments were carried out by varying the organic phase to aqueous phase volume ratios at natural pH (5.5) and room temperature (30°C ± 2°C). The results as seen in Fig. 6 show a significant increase in percentage extraction from a solvent to feed ratio of 0.5 to 2, but the improvement thereafter is minimal, indicating the best performance around the solvent to feed ratio of about 2.5. The relative extraction by the three solvents remains like the earlier observations, with 1-hexanol showing better performance at about 96% followed by 1-octanol (about 94%) and 1-decanol (about 92%) at a solvent to feed ratio of about 2.5:1.

3.1.5. Effect of feed temperature

The percentage extraction of phenol has been found to decrease with increasing temperature as shown in Fig. 7 which is in line with those reported in the literature [22,49–51]. The behavior of all three solvents is similar with percentage extraction decreasing with temperature. Based on the estimated distribution coefficient for all the three solvents at different temperatures, the enthalpies of solvent extraction were calculated using the Van't Hoff plot as shown in Fig. 8. Based on the slopes obtained in the plot of ln$D$ vs. (1/T), (Fig. 8), the enthalpies were estimated as shown in Table 2.

The studies with reference to temperature indicate that the extraction of phenol by any of the three solvents is exothermic in nature and could lead to better performance at

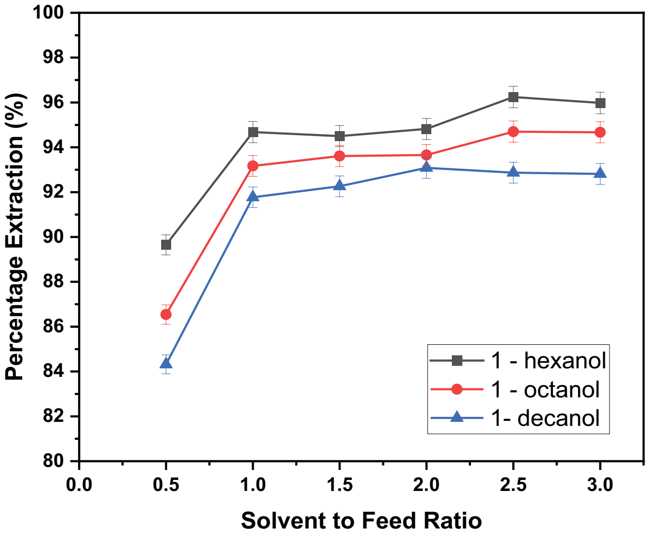

Fig. 6. Effect of varying solvent to feed ratio on percentage extraction of phenol (Initial feed phase concentration 500 mg/L of phenol).

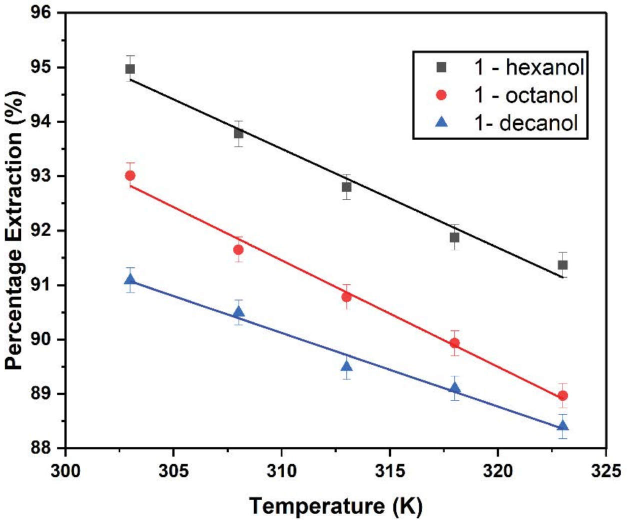

Fig. 7. Effect of temperature on percentage extraction of phenol (Initial concentration of feed 500 mg/L).

Table 2
Enthalpy of extraction

System	Δ*H*° for phenol extraction (kJ/kmol)
Phenol – 1-hexanol	–23,612
Phenol – 1-octanol	–22,997
Phenol – 1-decanol	–15,323

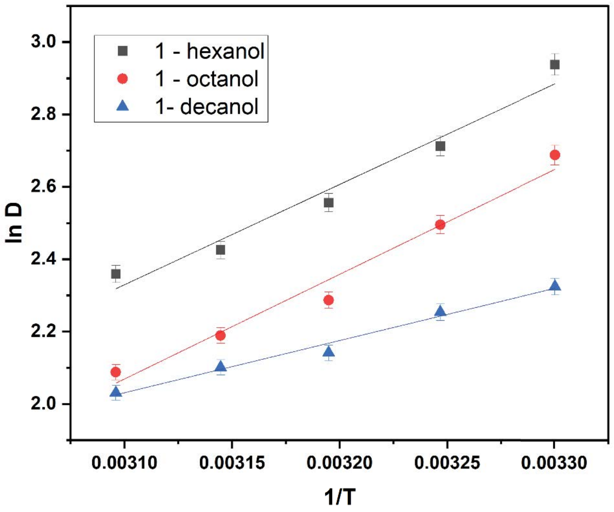

Fig. 8. Van't Hoff equation plot for phenol extraction.

lower temperatures. The relative values of the enthalpies of extraction are in the same order as observed percentage extraction within the experimental errors. The higher percentage extraction at low temperature can be attributed to both the factors namely higher dissociation with temperature and the exothermic nature of the solvation process [52].

3.1.6. Effect of dissolved salts in the aqueous phase

Normally the effluent streams contain dissolved ionic solutes. In order to assess the performance of solvent extraction, experiments were conducted by the deliberate addition of commonly used solutes such as chlorides of sodium, calcium, and magnesium. As seen in Fig. 9, the percentage extraction of phenol increases with the increasing concentration of dissolved solutes in the aqueous phase. The effect is more pronounced for 1-hexanol compared to 1-octanol, and 1-decanol in that order.

The increased percentage extraction of phenol can be related to decreased solubility in the aqueous phase due to the salting-out effect. The improvement in percentage extraction is quite significant with an addition of 0.2% salts for all the solvents, although to a different extent for each of the solvents. Any further addition of salt only results in a slight improvement. The effect appears to be significant for sodium chloride compared to salts of calcium and magnesium which are considered to be weak basic salts. The improvement in percentage extraction is relatively less with respect to calcium and magnesium salts and can be related to the hydrolysis of these salts, impeding the extraction, as can be seen from Table 3 and Fig. 9.

3.1.7. Stripping of extracted phenol

It is well known that phenol can be effectively stripped by using a basic solution. Experiments were conducted for optimizing the concentration of NaOH for maximum stripping of the phenol from the organic phase. Since extraction of phenol is dependent on the pH of the aqueous phase and as low pH favors extraction, stripping of phenol from the organic phase can be done using alkaline solutions like NaOH. Fig. 10 illustrates the effect of NaOH concentration on percentage stripping.

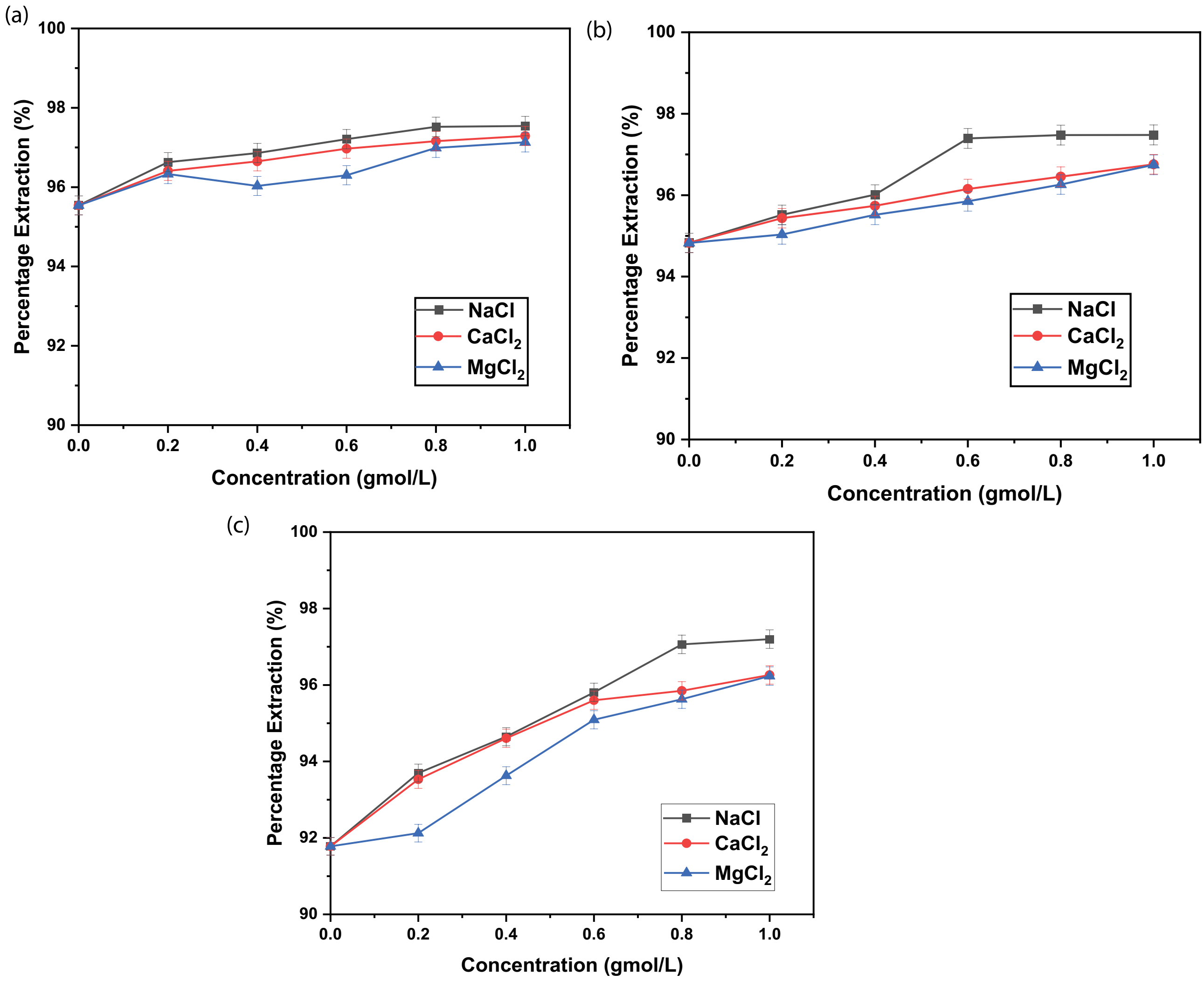

Fig. 9. Effect of salt concentration on percentage extraction of phenol using different solvents (a) 1-hexanol, (b) 1-octanol and (c) 1-decanol.

Table 3
Effect of salt concentration

Concentration (gmol/L)	Percentage recovery (%)								
	1-hexanol			1-octanol			1-decanol		
	NaCl	$CaCl_2$	$MgCl_2$	NaCl	$CaCl_2$	$MgCl_2$	NaCl	$CaCl_2$	$MgCl_2$
0	95.54	95.54	95.54	94.83	94.83	94.83	91.78	91.78	91.78
0.2	96.63	96.41	96.33	95.52	95.43	95.03	93.70	93.53	92.12
0.4	96.86	96.65	96.03	96.01	95.74	95.52	94.65	94.61	93.63
0.6	97.21	96.97	96.30	97.39	96.15	95.85	95.81	95.60	95.09
0.8	97.52	97.16	96.99	97.48	96.46	96.26	97.06	95.85	95.63
1	97.54	97.29	97.13	97.48	96.76	96.74	97.20	96.26	96.23

Stripping percentage increases from 63% for 0.1 N NaOH to 97% for 0.5 N NaOH. Upon further increase of NaOH concentration, the stripping percentage does not improve any further [48]. The results indicate that 0.5 N NaOH [22], could effectively be used for the recovery of phenol from the loaded organic phase. It is also observed that the stripping percentage of phenol from 1-hexanol and 1-octanol are nearly the same while for 1-decanol it is significantly less.

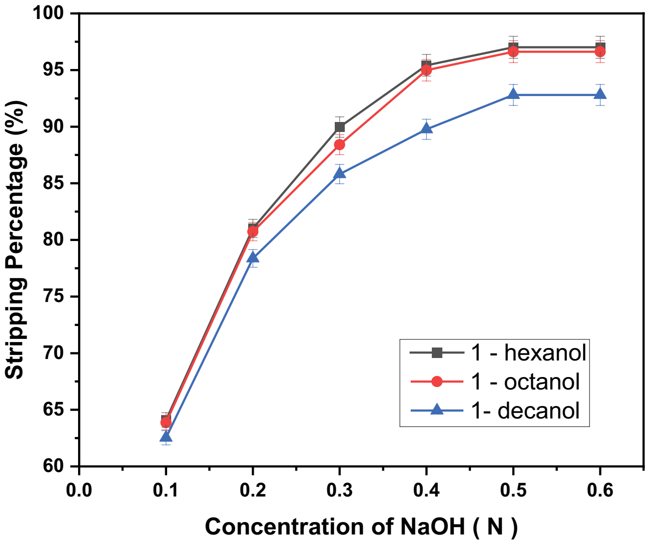

Fig. 10. Effect of NaOH concentration on stripping percentage of phenol.

3.1.8. Overall observations related to CSE

Conventional solvent extraction studies have indicated that 1-hexanol to be more efficient compared to the other solvents studied. Under equilibrium conditions, the percentage extraction of phenol appears to be a maximum of around 94.5%, for an initial feed concentration of 500 mg/L and a solvent to feed ratio of above 1:1 indicating a value of around 20 for the distribution coefficient. Adjustment of the feed pH towards acidic conditions has shown improvement with a maximum percentage extraction of around 97%. However, the percentage extraction at native pH (5.5–6) of phenol is around 90%, indicating that the pH conditioning, does not result in significant improvement, particularly considering the cost and logistics of adding the acid. The exothermic nature of the extraction leads to the inference that better results could be achieved at lower temperatures. It is established that the presence of dissolved solutes in the aqueous streams leads to better extraction. 0.5 N NaOH was found to be the optimum concentration for effective stripping of phenol from the solvent and could be effectively used for stripping.

3.2. Membrane assisted solvent extraction

3.2.1. Selection of membrane and configuration

Membrane-based solvent extraction has several advantages over the conventional ones [30], as being non-dispersive without the need for intimate mixing of the organic and aqueous phases. Out of the three membrane processes, membrane-assisted solvent extraction is more suitable in capillary configuration, as it provides more interfacial contact area in a controlled environment and is more compact compared to all other commercially available membrane configurations. The membranes for use in MASE have to be hydrophobic in nature, besides being solvent resistant. In literature, experiments were conducted with polypropylene [9] module mostly used for solvent extraction studies. The selection criteria of the membrane material, akin to the solvent selection is guided by solvent compatibility, hydrophobicity, availability, and cost-effectiveness.

Among the membrane materials polyethersulphone (PES) and polysulphone (PS) being more hydrophilic are not considered suitable. Poly-vinylidene fluoride (PVDF), a fluorinated polymer with its native hydrophobicity is easily available in the market. A few strands of PVDF membranes, obtained from the suppliers were immersed in all three solvents and aqueous phenol solution for about a week, and its integrity was tested. Having withstood the test and considering its easy availability, affordable cost, and hydrophobicity, the PVDF membrane element has been chosen for detailed experimental investigations.

3.2.2. Experimental investigations on membrane assisted solvent extraction

Aqueous phenol solution was introduced through the lumens (tube side) of the hollow fiber PVDF membrane element and the organic phase through the shell side following the methodology adopted in many reported studies [9,33,53]. Since the solvent is hydrophobic and more viscous compared to the aqueous phase, will fill the pores of the hydrophobic membrane. The only precaution is to ensure that the solvent is circulated well below the liquid entry pressure (LEP) so that it is not forced out of the pores into the aqueous phase. As the contacting volumes of the interphase are dependent on the flow rates, both the solvent and the aqueous phase flow rates represent relative volumes or solvent to feed ratios.

Mixing and settling are not relevant in MASE but the time of contact determines the extent of extraction. Following the studies reported in the literature, the solvent was circulated through the shell side of the membrane element while the aqueous phase was circulated through the tube side. The progressive experimental observations of the percentage extraction of phenol for all the three solvents with respect to feed flowrates (representing varying solvent to feed ratios) and time are shown in Fig. 11. The duration of the experiment was fixed for 300 min after observing the consistency of the percentage extraction in the last few readings.

The experimental studies as shown in Fig. 11a–c, have indicated that all the solvents can achieve more than 90% phenol removal around 4–5 h, in membrane-assisted solvent extraction for all solvent to feed ratios varying from 1:1 to 3:1. Further, 1-hexanol has been found to be the best of the three solvents studied, indicating a maximum percentage extraction of about 96% phenol, compared to around 91% for 1-octanol and 91% 1-decanol. Solvent to feed ratio has a significant effect in terms of percentage extraction during the initial period of contact, but later with further progression of time, the percentage extraction values converge towards the maximum percent removal, irrespective of the solvent to feed ratios for 1-hexanol. For the other two solvents, the performance has shown observable differences particularly for 1-decanol for the entire duration of the experiment. The optimum solvent to feed ratio is 2:1 for all the solvents indicating that relative fluid velocities which indirectly indicate the optimum contact time between the organic and

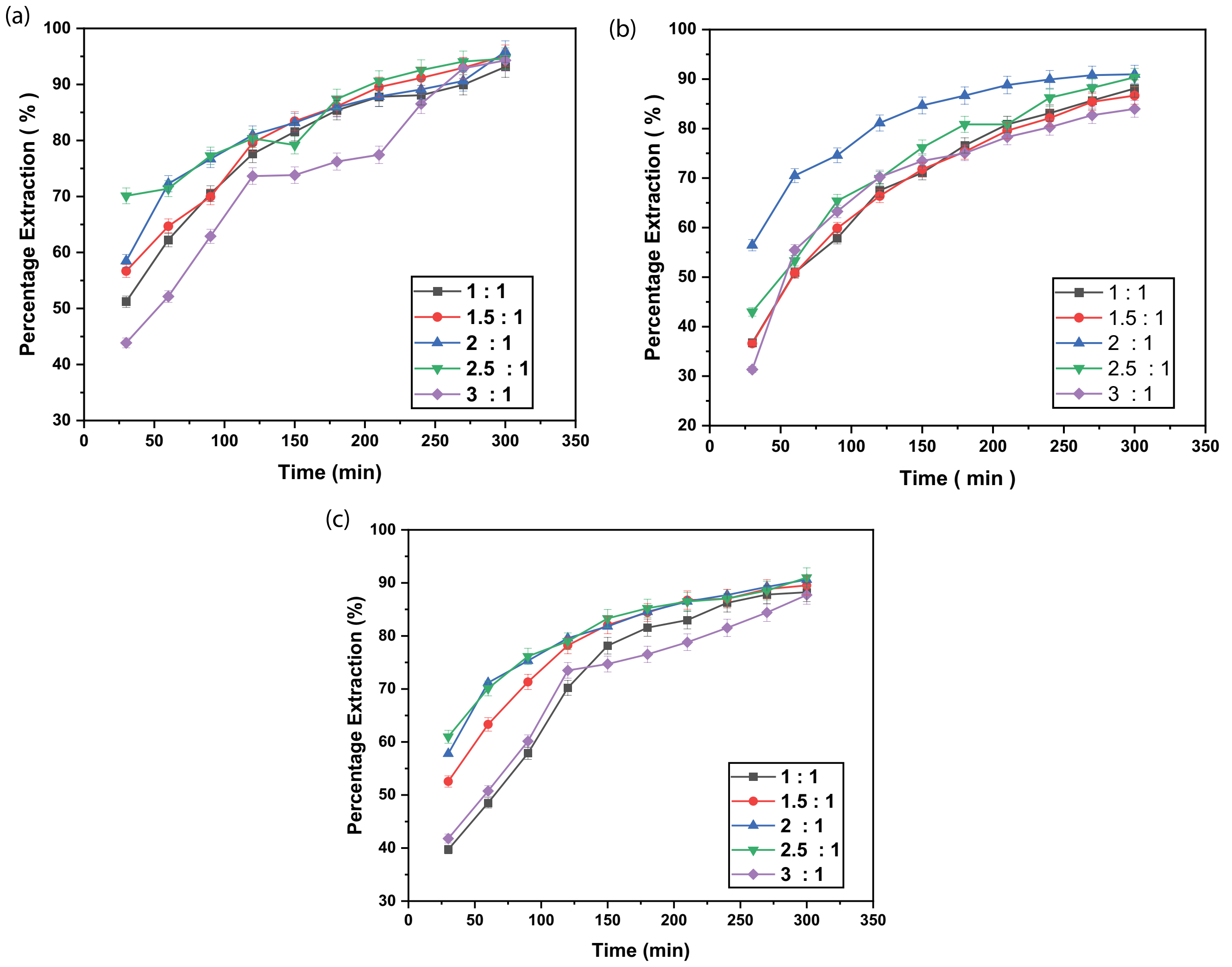

Fig. 11. Percentage extraction of phenol with time in MASE for varying solvent to feed ratios (a) 1-hexanol, (b) 1-octanol and (c) 1-decanol.

aqueous phase. From the experimental studies, it is evident that within a maximum time of 300 min, the maximum removal can be achieved.

Since solvent to feed ratio is an important criterion, which represents the solvent inventory requirements, the performance of different solvents is shown separately in Fig. 12. The percentage extraction exhibited by 1-hexanol is higher compared to 1-octanol, and 1-decanol, in that order. The optimal ratio becomes less pronounced as the solvent is changed from 1-hexanol to 1-decanol through 1-octanol. Since the inherent viscosities of these three solvents increase in the same order, the observations can be related to the viscosity, as the entrainment rate increases with viscosity.

Accordingly, the superior performance of 1-hexanol with respect to percentage extraction is evident compared to the other two solvents. The maximum percentage extraction for 1-hexanol is above 95% while those for 1-octanol and 1-decanol are significantly less at 91% and 87% respectively throughout the entire duration of the experiments. It is also evident that the percentage extraction is maximum at a solvent to feed ratio of about 2:1, for a feed concentration of 500 mg/L.

In contrast, the percentage extraction of phenol observed for CSE (Fig. 6) shows significantly lower values. Since CSE is equilibrium controlled, the extraction is limited by the partition/distribution coefficient for the system as a bulk. In the case of MASE, the process is akin to multi-stage operation, where the equilibrium value shifts constantly towards better separation. Accordingly, MASE shows better percentage extraction compared to CSE.

In all the experiments, the volumes of the feed and solvents were the same while the circulation (flow) rates were adjusted corresponding to the chosen solvent to feed ratio. In real-time applications, a few membrane elements may have to be assembled in series as modules to achieve the desired percentage extraction of phenol, when needed. The above observations indicate that MASE can give percentage extraction better than conventional solvent extraction. Since the flow rates and not the volume determines the

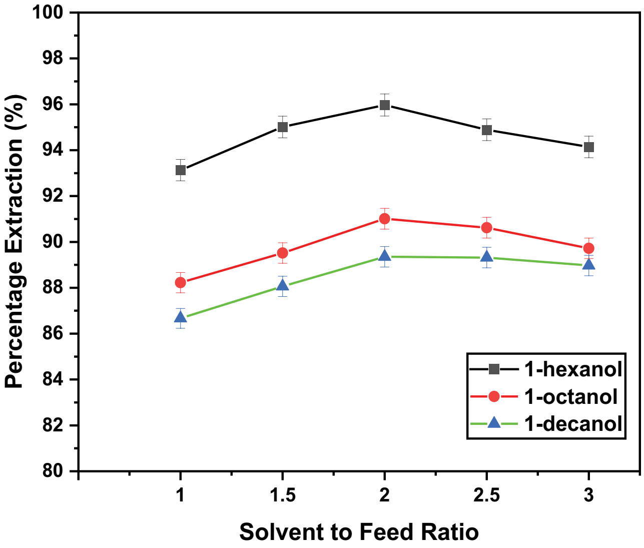

Fig. 12. Percentage extraction of phenol for varying solvent to feed ratios (Feed concentration: 500 mg/L of phenol, Time: 300 min).

percentage extraction, the solvent inventories to be maintained may not be high, under these conditions.

3.2.3. Challenges faced

During the literature review, it was observed that most of the studies use solvent in the shell side to study the mass transfer effects of MASE [33]. Accordingly, initial experiments were carried out with aqueous phenol solution on the tube side and solvent on the shell side.

The tubes in the tube bundle, unlike a regular shell and tube exchanger, are not rigid and not always parallel to each other with a uniform gap amongst them. To achieve compactness (more surface area per unit volume), more fibers are packed within the available volume. The fibers being small in diameter and flexible in nature are closely spaced sometimes even touching each other depriving the free flow of the fluid. Under these conditions, the possibility of channeling does exist, depriving the efficient contact of the solvent for extraction. Further, the membrane elements consist of fibers, which are tightly packed leading to non-uniform solvent flow. It is challenging to make the strands parallel while accommodating a large surface area, as membranes are twisted when a large number of fibers are assembled because of low thickness and small diameters.

The solvent passage through the shell side of the membrane requires the shell material not only to be chemically stable with the solvent and possess thermal stability to withstand the heat of extraction, notwithstanding the fact that the membrane should be equally stable. Further, the possibility of stagnancy should be minimum with quick dispersal of the heat of extraction. This may require either a metallic shell or high solvent velocities. Even though the membrane was compatible with solvent and feed solution, the shell material was not. After prolonged use of the membrane element, a few cracks started developing on the shell side surface as shown in Fig. 13 whose material of construction is acrylic. These membrane elements are normally used for water treatment applications. Exothermicity of the extraction process combined with heat-sensitive shell material is responsible for the development of cracks possibly attributable to differential thermal expansion and possible stagnation due to higher solvent viscosity.

Fig. 13. Photograph of cracked shell.

Since the membrane material is resistant to solvent, based on the integrity tests it is thought prudent to ensure that solvent after extraction is not in contact with the shell material. Further, the solution should be such that the possibility of stagnation be minimized or eliminated to avoid any thermal effects and to ensure efficient contact of the solvent with the aqueous phase so that there is no compromise on availability or cost.

3.3. Determination of overall mass transfer coefficient

Overall mass transfer coefficients are estimated based on the experimental data and empirical correlations published in the literature as a function of the organic phase Reynold's number.

It is noted that because of the differing kinematic viscosities of the solvents as indicated in Table 4, the Reynolds number values are different for the same flow rate of the solvents. The mass transfer coefficients estimated based on experimental values and through empirical equations are presented in Table 5 and Fig. 14 for all three solvents. In both the methods of estimation, the mass transfer coefficients for the shell side solvent flow are in the same order, and relative variations are within a small range and are in agreement with the reported range of values [9]. With the increase in Reynolds number of the organic phase, the overall mass transfer coefficient increases up to a critical value beyond which there is a drop in the value.

1-hexanol, whose kinematic viscosity (Table 4) is the lowest, exhibits the maximum mass transfer coefficient while the mass transfer coefficients of 1-octanol and 1-decanol is relatively less in the same order both with respect to experimental values and empirical correlations indicating that kinematic viscosity has a role to play in the mass transfer during the extraction process. Further, it can be noticed that the mass transfer coefficient has a maximum value as a function of Reynold's number both for experimental values and empirical estimations except for the fact that it is more pronounced in empirical estimations than in experimental observations. Reynolds number where the maximum percentage extraction occurs shifts to lower values as the solvent is changed from 1-hexanol to 1-octanol and 1-decanol in that order.

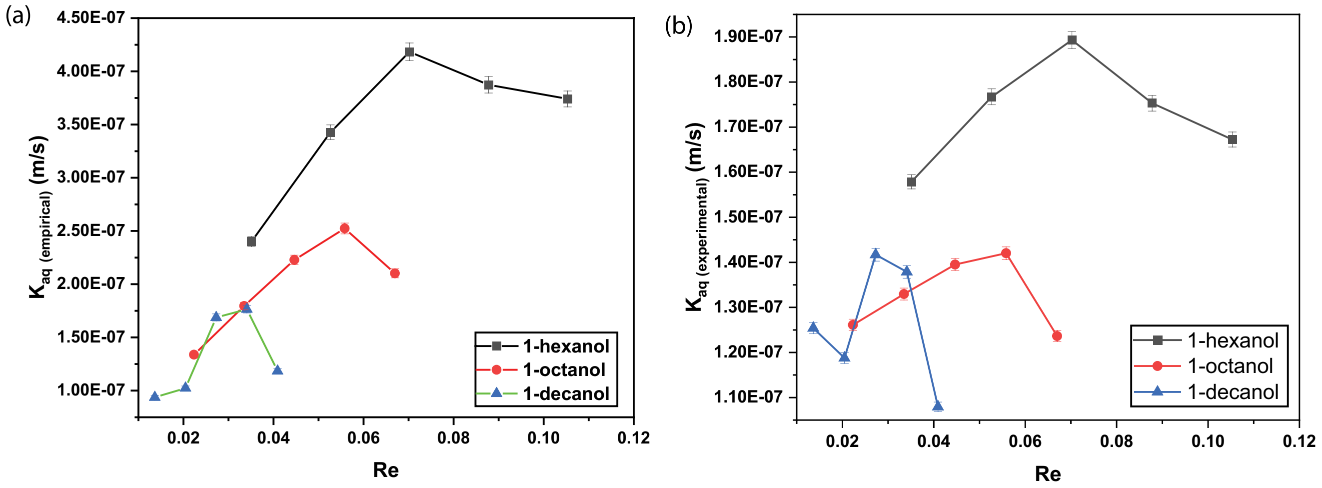

Fig. 14. Overall mass transfer coefficient as a function of Reynolds number with organic phase flowing through the shell side (a) empirical and (b) experimental.

3.3.1. Mass transfer coefficient for stripping

Based on the experimental observations indicated, the mass transfer coefficient for the stripping of phenol using NaOH is 4.25 × 10^{-7} m/s experimentally and 1.37 × 10^{-7} m/s based on empirical correlation. The mass transfer coefficient is slightly higher for stripping compared to extraction and can be attributed to the higher affinity of phenol to sodium hydroxide bordering reactive extraction.

4. Advantages of MASE over other treatment technologies for phenol

Most of the treatment methods including bio-degradation, a popular method of treatment for phenol and technologically superior advanced oxidation processes are energy-intensive and transfer the pollution burden from water to the gaseous phase as carbon dioxide aggravating the concerns of climate change. In this context, it is imperative that one should look for recovering value from the waste rather than simply complying with the environmental requirements. MASE, in this context, offers an economically beneficial process, as the cost involved for solvent inventories is much less, particularly when the system could operate in a closed-loop with recycled solvent. The process does not require energy for intimate mixing for effective mass transfer. Energy is required only for pumping the solvent and the feed through the membrane element to compensate for the pressure drop, which is quite less. In contrast adsorption, ion exchange, and chemical precipitation processes isolate the

Table 4
Kinematic viscosity of the solvents

S. No.	Solvent	Density (kg/m^3)	Viscosity (kg/m s)	Kinematic viscosity (m^2/s)
1	1-hexanol	814	4.59 × 10^{-3}	5.639 × 10^{-6}
2	1-octanol	824	7.36 × 10^{-3}	8.932 × 10^{-6}
3	1-decanol	830	12.05 × 10^{-3}	1.452 × 10^{-5}

Table 5
Mass transfer coefficient (shell side solvent flow)

S/F	Re (1-hexanol)	K_{aq} × 10^7 (m/s)		Re (1-octanol)	K_{aq} × 10^7 (m/s)		Re (1-decanol)	K_{aq} × 10^7 (m/s)	
		Empirical	Experimental		Empirical	Experimental		Empirical	Experimental
1	0.03511	2.4020	1.5787	0.02232	1.3382	1.2612	0.01364	0.9364	1.2541
1.5	0.05266	3.4282	1.7672	0.03349	1.7950	1.3296	0.02046	1.0237	1.1878
2	0.07021	4.1831	1.8932	0.04465	2.2289	1.3952	0.02727	1.6877	1.4169
2.5	0.08776	3.8741	1.7532	0.05581	2.5236	1.4202	0.03409	1.7646	1.3787
3	0.10532	3.7410	1.6725	0.06697	2.1023	1.2365	0.04091	1.1841	1.0793

phenolic species from the effluent stream but recovering back the value is a challenge techno-economically due to poor selectivity and logistical constraints of handling of the resultant agglomerates; adsorbents, resins, or chemical sludge.

5. Conclusions

The studies were conducted for the removal and recovery of phenol from aqueous streams both using conventional solvent extraction, and membrane-assisted solvent extraction, using three commercially available solvents such as 1-hexanol, 1-octanol, and 1-decanol.

Conventional solvent extraction indicated 96.24% extraction of phenol for 1-hexanol, 94.7% for 1-octanol and 92. 87% for 1-decanol. Similarly, the values observed for membrane-assisted solvent extraction are 95.97% for 1-hexanol, 91.01% for 1-octanol, and 89.35% for 1-decanol. Membrane-assisted solvent extraction indicated better phenol percentage extraction, compared to conventional solvent extraction, for all the solvents investigated. However, the relative performance of all the solvents was similar in both cases with 1-hexanol indicating better performance compared to 1-octanol and 1-decanol. It has also been found that the solvent passage through the lumen side of the membrane contactor not only allows the use of cheaper shell material but also provides a better mass transfer coefficient compared to when the solvent flows through the shell side. Further research is required to establish the 'Proof of the concept' with real-time effluents and demonstrate the simultaneous recovery and reuse of the solvent.

Suggestions for further research

With the encouraging performance of MASE over CSE, the next step is to extend the investigations on a pilot scale with actual effluents from the industries establishing the proof of the concept.

Symbols

C_i, C_f — Initial, final concentration of phenol in the aqueous phase, mg/L
C_o, C_s — Concentration of phenol in the organic phase and in the stripping phase, mg/L
$E\%$, $S\%$ — Extraction, stripping percentage
D — Distribution coefficient
D_s, D_o, D_H — Inner, outer and hydraulic diameter of shell, m
d_i, d_o and d_{lm} — inside, outside and log mean diameters of the hollow fiber respectively, m
L — Effective fibre length, m
N — Number of hollow fibres
ε — Porosity
τ — Tortuosity
Ψ — Packing fraction
Sh, Re, Sc, Gz — Sherwood, Reynolds, Schmidt and Graetz number, respectively
v — Average linear velocity, m/s
ρ — Density, kg/m^3
μ — Viscosity, kg/m s
A_s — Cross sectional area of flow in the shell side, m^2
D_{aq}, D_{org} — Diffusivity of the solute in the aqueous and organic phase respectively, m^2/s
k_s, k_m, k_t — Local mass transfer coefficients on the aqueous shell side, through the membrane pores and on the organic tube side respectively, m/s
K_{aq} — Overall mass transfer coefficient based on the aqueous phase, m/s

Compliance with ethical standards

Conflict of interest: On behalf of all authors, corresponding author states that there are no conflicts of interest.

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