Effective separation of toxic phenol from aquatic system using membrane assisted solvent extraction system

E. Poonguzhali[a], Ashish Kapoor[a,*], P. Senthil Kumar[b], S. Prabhakar[a]

[a]*Department of Chemical Engineering, College of Engineering and Technology, SRM Institute of Science and Technology, Potheri, Kattankulathur – 603203, Chengalpattu District, Tamil Nadu, India, emails: ashishko@srmist.edu.in (A. Kapoor), kuzhali21@gmail.com (E. Poonguzhali), sivaprabha50@gmail.com (S. Prabhakar)*
[b]*Department of Chemical Engineering, Sri Sivasubramaniya Nadar College of Engineering, Chennai – 603110, India, email: senthilchem8582@gmail.com*

ABSTRACT

Membrane contactor, an evolving device has the potential to simplify mass transfer between two contacting phases because of the inherent features including non-dispersion of the phases, operational safety, simplicity of operation and easy adaptability. Solvent extraction, a proven and useful separation operation conventionally, has many practical challenges. Membrane assisted solvent extraction could not progress due to the compatibility of shell material of the hollow fiber membrane element with aggressive solvents. Considering that the membrane polymers are resistant to many solvents, experiments were carried out by allowing the passage of solvent through the tube side and aqueous phase through the shell side. Hence, experimental investigations were undertaken to establish the potential of membrane assisted solvent extraction using polyvinylidene fluoride-based hollow fiber membrane with phenol as a model contaminant in the aqueous phase and 1-hexanol as a solvent for the organic phase. A comparative assessment of the conventional vs. membrane assisted solvent extraction indicated that the percent removal of phenol is relatively higher for the latter. No deterioration of shell material or the membrane is observed with the solvent flowing through the tube side. Additional features such as the possibility of seamless recycling of solvent, safe operation, and easy scale-up, indicate the potential of membrane-assisted solvent extraction for the recovery of contaminants from waste streams. With an estimated mass transfer coefficient of around $1.2–1.3 \times 10^{-7}$ m/s both for extraction and stripping indicated that pore diffusion of phenol to be the rate-controlling step.

Keywords: Membrane system; Extraction; Toxic phenol; Mass transfer coefficient; Stripping; Separation

1. Introduction

With increasing environmental concerns, the concept of waste management is undergoing a paradigm shift towards zero discharge of waste. The major pollution load emanates from many small-scale industries as the economics and space constraints do not permit the adoption of conventional wastewater treatment technologies. The waste is normally sent to the common effluent treatment plants for generalized secondary and tertiary treatment before discharge to the environment [1–3]. The conventional technologies trans-locate the contaminants from liquid to solid phase shifting the environmental burden without any remediation in the real sense [4]. This calls for a strategy, by which the offending contaminant is treated as a value lost, which is more often true. The recovery of contaminants from spent streams can be achieved using conventional separation

---

* Corresponding author.

operations if only one can isolate the contaminant streams at the source. It is difficult to separate the components when mixed, a common practice followed by the industries at present. Isolation of spent streams at source is highly challenging considering the economics, safety, logistics and footprint requirements of conventional unit operations like chemical precipitation, adsorption, solvent extraction, and distillation [5,6], particularly for small and medium industries.

In the last two decades, the increasing demand for freshwater has made it imperative to recover water from spent streams for reuse, which is made possible by the development of membrane-based reverse osmosis technology [7,8]. However, it is not an ideal solution as the process leaves a concentrated stream containing all the contaminants for disposal after incorporating them in a solid matrix [9]. Considering that the recovery and reuse of the contaminants from the spent streams is the safest option to save the environment, processes need to be developed, which are useful for smaller capacities, safe, compact and above all cost-effective.

Membranes are physical barriers that physically separate the contacting phases and at the same time facilitate mass transfer under an appropriate motive force. The physical, physicochemical, or chemical nature of the membrane facilitates the preferential transport of the species. Pressure-driven membrane processes like, reverse osmosis, nanofiltration and ultrafiltration are extensively used in desalination, water purification, water recovery and recycle [10,11]. Membrane contactors enable the contact of two phases without dispersion facilitating mass transfer because of the large interfacial contact area between the phases [12]. The potential of membrane contactors facilitating conventional unit operations such as liquid–liquid extraction [13], membrane distillation [14], membrane crystallization [15], and membrane chemical and biochemical reactors [16] are being explored and a few of them are being used commercially as well, like membrane bioreactors [17] and for gaseous separations [18].

Studies with size enhanced ultrafiltration [19,20] have shown that contaminants particularly the trace heavy metals could be removed and recovered from waste streams [21,22]. Besides, being modular in nature, the process can be adopted at any scale of operation, without the need to tweak the operating conditions. A membrane bioreactor, which immobilizes the micro-organisms in confined space, offers a large interfacial contact area for the biodegradation of the organic contaminants, making the secondary treatment of industrial wastewater fast and efficient. Solvent extraction is one of the important techniques used for the separation and recovery of the organics and heavy metal species from a mixture of components [23]. Conventional methods have several constraints in terms of solvent selection, mixing and separation. The use of membrane contactors has the potential to reduce the operational constraints besides becoming viable for small scale operations. Supported liquid membranes operate on the principle of liquid–liquid extraction with the solvent immobilized in the pores of the membrane [24,25]. The process enables uphill transport, besides being highly selective. The solvents D2EPHA, TOPS-99, LIX-841and Cyanex 272 extract either by chelation or solvation [26]. However, the large-scale application of this technique is constrained by the stability of the membranes and the high cost of macro-molecular solvents.

Membrane-assisted solvent extraction has been used as a pre-concentration step for the environmental contaminants before analytical estimation through techniques such as gas chromatography, mass spectrometer, etc. using porous polypropylene membrane in bag form [27]. A few studies have reported the application of membrane assisted solvent extraction for the removal of contaminants using Celgard and polypropylene membranes [28,29]. The studies visualize a continuous loop for solvent extraction but are mostly confined to the study of mass transfer aspects of the process. Even among the few experiments conducted, the solvent is passed through the shell side of the hollow fiber membrane element, which has many significant process limitations [30], with reference to the compatibility of shell material.

Even though solvent extraction is very effective in the separation of trace contaminants, it is seldom used except in the nuclear industry due to considerations related to safety, operational aspects and energy requirements. A few studies were carried out, allowing the passage of organic solvent through the shell side which resulted in the damage of the shell. It is believed that membrane assisted solvent extraction which involves dispersion – less mass transfer with a potential for recycling the solvent is quite conducive to adopt the process for field applications, overcoming the challenges of conventional solvent extraction.

In this context, with the objective of demonstrating the potential of membrane assisted solvent extraction, experimental investigations are carried out with the objective of demonstrating the potential of membrane assisted solvent extraction by circulating the solvent through the tube side and also indicating the recovering the contaminant as value. Conventional solvent extraction under similar conditions are also carried out to assess the relative performance.

2. Materials and methods

2.1. Materials

Phenol, 1-hexanol and sodium hydroxide used in the process were of analytical reagent grade and obtained from M/sSISCON, India Ltd. All chemicals have been used without further purification. The solutions were prepared with reverse osmosis treated water containing less than 10 ppm of total dissolved solids. A solution of 1,000 mg/L of phenol was prepared by dissolving 1 g of phenol in a 1,000 mL capacity volumetric flask. This has been treated as a stock solution of phenol. The aqueous feed solutions were prepared by diluting the stock solution. 1-hexanol is used as the organic solvent for extraction. 0.5 N sodium hydroxide was used for stripping.

2.2. Methods

2.2.1. Conventional solvent extraction and stripping studies

The feed solution phenol concentration was measured using Cary 60 UV-Vis spectrophotometer at 270 nm [15]. The absorbance of the samples was checked after ascertaining the calibration. Batch studies were carried out by mixing both the organic solvent and aqueous feed sample in a

screw-capped Erlenmeyer flask and stirred at 180 rpm for 1 h to ensure completion of extraction. The contents of the flask were transferred carefully to a separating funnel to facilitate the separation of phases. After allowing 45 min for the separation of phases to occur, the aqueous and organic phases were carefully collected. Samples were drawn from the aqueous phase for the estimation of phenol concentration using a UV spectrophotometer. The concentration of phenol in the organic phase was estimated based on mass balance. The stripping was carried out, in the same manner, using the total volume of the extract phase with an equal volume of stripping solution (0.5 N NaOH). The concentration of phenol in the stripping solution was measured at 288 nm [31].

Percent extraction, stripping, overall recovery of phenol and distribution coefficients were estimated using Eqs. (1)–(4) [32].

$$\text{Extraction percentage } \left(E\%\right) = \frac{\left(C_{\text{initial}} - C_{\text{final}}\right)}{C_{\text{initial}}} \times 100 \tag{1}$$

$$\text{Stripping percentage } \left(S\%\right) = \frac{C_{\text{stripping}}}{C_{\text{organic}}} \times 100 \tag{2}$$

$$\text{Overall recovery percentage } \left(R\%\right) = \frac{C_{\text{stripping}}}{C_{\text{initial}}} \times 100 \tag{3}$$

$$\text{Distribution coefficient } \left(D\right) = \frac{C_{\text{organic}}}{C_{\text{final}}} \tag{4}$$

where C_{initial} is the initial concentration of phenol in the aqueous phase (mg/L), C_{final} is the phenol concentration in the aqueous phase after extraction (mg/L), C_{organic} is the concentration of phenol in the organic phase (mg/L), and $C_{\text{stripping}}$ is the concentration of phenol in the stripping phase (mg/L).

2.2.2. Liquid–liquid extraction through hollow fiber membrane contactors

2.2.2.1. Characteristics of membrane used

Polyvinylidene fluoride (PVDF) hollow fiber membrane contactors used in this experimental study was procured from TECH Inc., Chennai and the basic specifications are indicated in Table 1.

The cross-section of the tube sheet is shown in Figs. 1 and 2 and are used for the estimation of number of fibers and diameter of a fiber using Image-J analysis.

It is evident that shell side clearances for the fluid flow is not uniform. Since the fibers are flexible and potted as a bunch it is difficult to maintain uniform clearances.

The membrane parameters were obtained using Image-J analysis, as given below.

The number of fibers was estimated to be around 500 and the average inner diameter of the fiber was 0.5 +/– 0.01 mm.

The packing fraction Ψ (cross-section occupied by fibers) and the void fraction or porosity ε are calculated using the formulae:

Table 1
Specifications of the hollow fiber membrane contactor

Membrane material	Polyvinylidene fluoride (PVDF)
Shell I.D. (D_s)(m)	0.036 (36 mm)
Shell O.D. (D_o)(m)	0.04 (40 mm)
Lumen (fiber) I.D. (d_i)(m)	0.0005 (0.5 mm)
Lumen (fiber) O.D. (d_o)(m)	0.001 (1 mm)
Effective fiber length (L)(m)	0.25 (250 mm)
Number of hollow fibers (N_t)	500
Porosity (ε)	0.6
Tortuosity (τ)	2
Packing fraction (Ψ)	0.4
Molecular weight cut off	100 kDa

$$\Psi = N_t \left[\frac{d_0}{D_s}\right]^2 \tag{5}$$

$$\varepsilon = 1 - \Psi \tag{6}$$

2.2.2.2. Experimental method

Figs. 3 and 4 show the schematic diagram of the experimental set-up alongside the photograph of the unit in which the experiments were carried out. With a change of inlet and outlet connections, the experiments can be done in co-current or counter-current mode.

Excepting initial trials with different membrane elements, the aqueous phase solution was circulated through the shell side of the membrane contactor continuously from the reservoir while the organic phase was circulated through the tube side (lumen) likewise.

Only inlet and outlets of the aqueous phase to the element were interchanged for maintaining counter-current arrangement. Both the phases were pumped using a peristaltic pump with a provision to vary the flow rates from 12.5 to 75 mL/min for the organic phase maintaining a constant flow rate of 25 mL/min for the aqueous phase.

The phenol concentrations were estimated using a UV-visible spectrophotometer by drawing samples (1 mL) at the interval of 15 min from the aqueous phase reservoir. Volume corrections were applied to the observed values as the total volume of the samples drawn at various intervals amount to 25 mL over the entire duration of the experiments. Besides initial and final samples which accounts for about 1.5% error. In all the experiments 250 mL each of aqueous solution and organic solvent or the extract is used. Only the flow rates were varied depending on the experimental program. The effect of flow rate was investigated in the stripping experiments for a single through co-current operation mode.

2.3. Estimation of mass transfer coefficient in membrane contactors

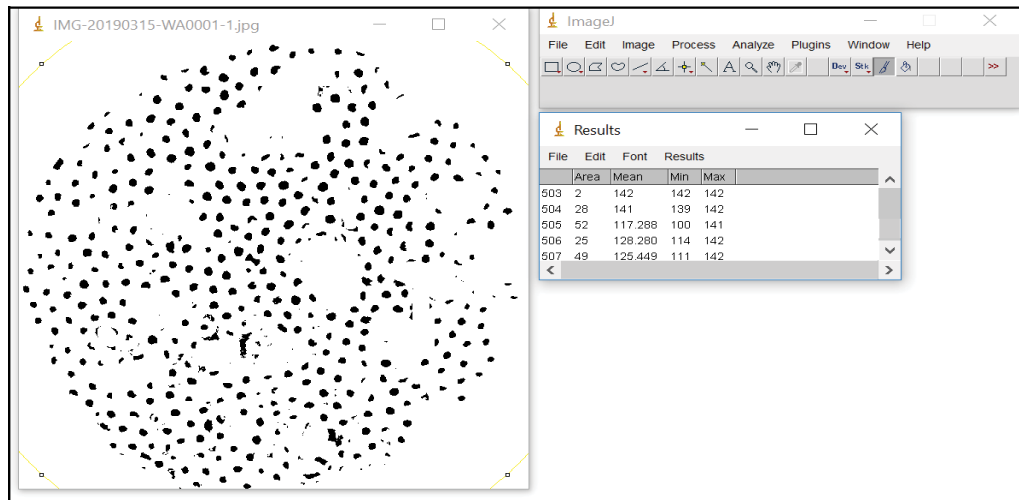Mass transfer coefficients were calculated based on the procedure indicated below.

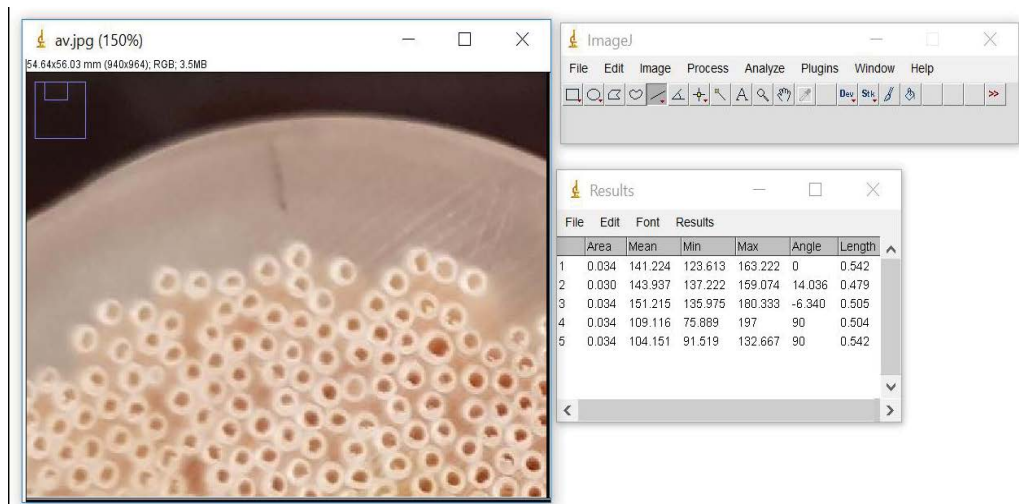Fig. 1. Estimation of number of fibers through ImageJ analysis.

Fig. 2. Estimation of fiber (lumen) diameter.

Shell side:

$$\mathrm{Re} = \frac{D_H v \rho}{\mu} \tag{7}$$

$$D_H = \frac{4X\left(\text{cross sectional area of flow}\right)}{\text{wetted perimeter}} \tag{8}$$

$$D_H = \frac{D_s^2 - N_t d_o^2}{D_s + N_t d_o} \tag{9}$$

$$v = \frac{Q_{\mathrm{aq}}}{A_s} \tag{10}$$

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

where Re is the Reynolds number for the shell side flow; D_H is the hydraulic diameter of the shell (m); v is the average linear velocity (m/s); ρ, μ is the density (kg/m^3) and viscosity (kg/m s) of the aqueous phase, respectively; D_s is the inner diameter of the shell (m); d_o is the outer diameter of the fiber (m); N_t is the number of fibers contained in the HFMC module; Q_{aq} is the flow fed into the shell side (m^3/s); A_s is the cross-sectional area of the flow in the shell side (m^2).

2.4. Estimation of mass transfer coefficient

2.4.1. Shell side

The shell side mass transfer coefficient can be predicted using the correlation expressed in terms of Sherwood number.

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

Eq. (12) is applicable for Re below 500 and Ψ between 0.04 to 0.4 [33,34].

where Sh_s is the Sherwood number for shell side; k_s is the shell side mass transfer coefficient (m/s); D_{aq} is the diffusivity of phenol in the aqueous phase (m²/s); β is the membrane constant depending on its nature (5.85-hydrophobic, 6.1-hydrophilic); Ψ is the packing fraction; L is the length of the fibers (m); Sc is the Schmidt number.

2.4.2. Tube side

Under laminar flow conditions, the Lévêque correlation is used to evaluate the tube side mass transfer coefficient using the Graetz number.

$$Gz = Re \cdot Sc \cdot \left(\frac{d_i}{L}\right) \tag{13}$$

when Gz is less than 6, Eq. (14) is recommended [34].

$$Sh_t = \frac{k_t d_i}{D_{org}} = 0.5 Re \cdot Sc \left(\frac{d_i}{L}\right) = 0.5 Gz \quad Gz < 6 \tag{14}$$

where Gz, Re, Sc is the Graetz, Reynolds and Schmidt number for tube side flow; d_i, L is the inner diameter and length of the fiber, respectively (m); Sh_t is the Sherwood number for tube side; k_t is the tube side mass transfer coefficient (m/s); D_{org} is the diffusivity of phenol in the organic phase (m²/s).

In the present study, Gz varies from 0.8 to 5.

2.4.3. Membrane

The mass transfer coefficient within the membrane is estimated using Eq. (15) [34].

$$k_m = \frac{2\varepsilon D_{org}}{\tau(d_o - d_i)} \tag{15}$$

where k_m is the tube side mass transfer coefficient (m/s); ε is the porosity; τ is the tortuosity; D_{org} is the diffusivity of phenol in the organic phase (m²/s).

2.5. Overall mass transfer coefficient

The resistance in the series model is considered suitable to estimate the overall mass transfer coefficient in a membrane contactor. The resistances include diffusion through shell side boundary layer, equilibrium governed distribution at the aqueous-organic interphase, pore-diffusion through the organic phase and finally the tube side diffusion through the boundary layer [35].

If the interface equilibrium distribution is very strong and the aqueous phase passes through the shell side, then the overall mass transfer coefficient can be estimated using the following equation [34].

$$\frac{1}{K_{aq}} = \frac{1}{k_s} + \frac{d_o}{Dk_m d_{lm}} + \frac{d_o}{Dk_t d_i} \tag{16}$$

where K_{aq} is the overall mass transfer coefficients based on the aqueous phase.

where k_s, k_m and k_t is the local mass transfer coefficients of shell side, membrane and tube side, respectively; D is the distribution coefficient; d_i, d_o and d_{lm} is the inside, outside and mean diameters of hollow fibers, respectively.

2.6. Modeling of mass transfer in hollow-fiber membrane contactors

The flux for phenol transfer through the membrane from the shell side to the tube side in the extraction process is calculated using the following equation [33].

$$J_{sol} = K_{aq} A_m \left(C_{aq} - C_{aq}^*\right) \tag{17}$$

The solute flux is related to the reducing concentration in the aqueous phase based on unsteady-state mass balance. If the feed mixing in the reservoir is uniform then the solute concentration in the aqueous phase can be estimated based on the constant distribution coefficient, D [35].

The equations for recirculating aqueous and organic phases for co-current and counter-current flows are:

For co-current flow [35]:

$$C_{aq} = \frac{V C_{aq}^o}{1+V} + \frac{C_{aq}^o}{1+V} \exp(-C_t) \tag{18}$$

where $C = \frac{Q_{aq}}{V_{aq}} \frac{(1+V)}{(1+Q)} \left(1 - \exp\left[-\frac{A_m K_{aq}}{Q_{aq}}(1+Q)\right]\right) \tag{19}$

$$K_{aq} = \frac{-Q_{aq}}{(1+Q)A_m} \ln\left(1 - C\left(\frac{V_{aq}}{Q_{aq}}\right)\left(\frac{1+Q}{1+V}\right)\right) \tag{20}$$

$$V = \frac{V_{aq}}{V_{org} X D} \tag{21}$$

$$Q = \frac{Q_{aq}}{Q_{org} X D} \tag{22}$$

For counter-current flow [35]:

$$C_{aq} = \frac{V C_{aq}^o}{1+V} + \frac{C_{aq}^o}{1+V} \exp(-C't) \tag{23}$$

where $C' = \frac{Q_{aq}}{V_{aq}}(1+V)\left(\frac{1 - \exp[\phi(Q-1)]}{1 - Q\exp[\phi(Q-1)]}\right) \tag{24}$

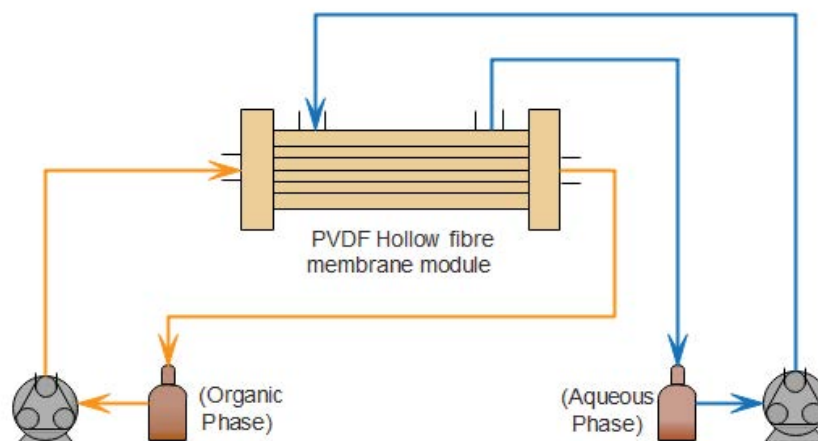$$\phi = \frac{A_m K_{aq}}{Q_{aq}} \tag{25}$$
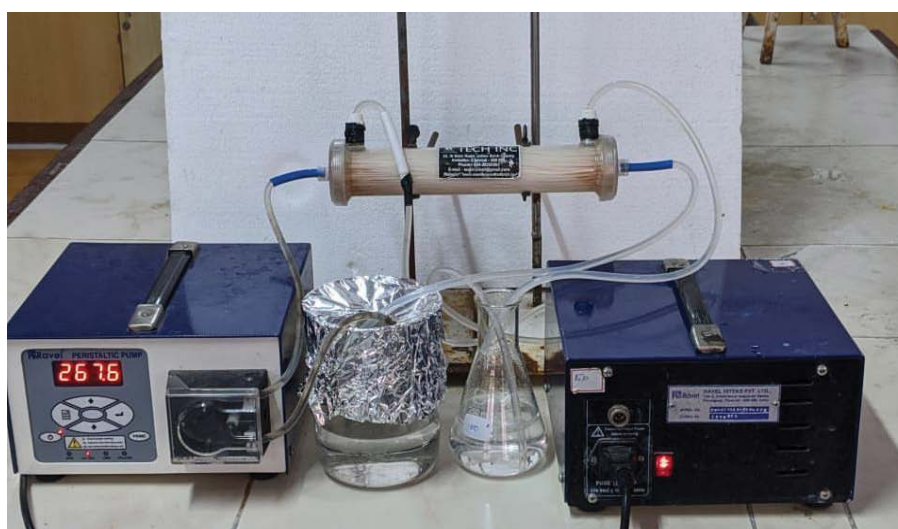
Fig. 3. Block diagram of the experimental setup.

Fig. 4. Photograph of the experimental setup.

where C_{aq} is the concentration of phenol in aqueous phase at time t (mg/L); C_{aq}^0 is the concentration of phenol in aqueous phase at time $t = 0$ (mg/L); C_{aq}^* is the concentration of phenol in aqueous phase in equilibrium with organic phase (mg/L); K_{aq} is the overall mass transfer coefficient based on aqueous phase (m/s); J_{sol} is the solute flux (kg/m² s); V_{aq} is the initial volume of aqueous phase (mL).

where V_{org} is the initial volume of organic phase (mL); Q_{aq} is the flow rate of aqueous phase (mL/min); Q_{org} is the flow rate of organic phase (mL/min); D is the distribution coefficient; A_m is the effective interfacial area of the membrane (m²); C, V, Q, C' and ϕ are constants defined by Eqs. (19), (21), (22), (24) and (25), respectively.

3. Results and discussions

3.1. Batch studies

Initially, studies were conducted for the removal of phenol from aqueous systems to generate the base data for comparison and to select an appropriate concentration of phenol for use in the experimental studies with membrane contactors. 1-hexanol has been chosen as the organic solvent which has less mutual solubility with water.

3.1.1. Effect of solvent to feed ratio in batch studies

3.1.1.1. Effect of change in initial concentration of phenol

Fig. 5 shows the observed percentage extraction of phenol as a function of initial concentration in the aqueous feed. Percentage extraction has been found to rapidly increase with initial concentration up to around 100 mg/L and then the rate of increase slows down towards near-constant values for about 400 mg/L and beyond. Comparatively less percentage extraction in the initial concentrations can be attributed to the dissociation of phenol into phenoxide ions. It is evident that phenol as a species, alone is getting extracted and a phenoxide ion, a dissociation product is not extracted. With increasing concentration, the proportion of phenoxide ions is less, resulting in higher
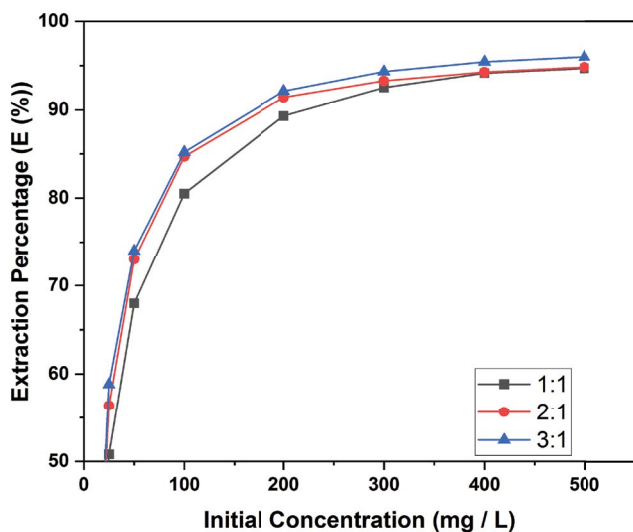
Fig. 5. Effect of the initial concentration of phenol on percentage extraction with increasing solvent to feed ratios (1:1 to 3:1).

Fig. 6. Effect of the initial concentration of phenol on distribution coefficient with increasing solvent to feed ratios (1:1 to 3:1).

percentage extraction. Because of this phenomenon, it is difficult to get beyond the maximum recovery of about 96%.

From the observations, we conclude that a maximum of 94.7% phenol could be recovered for a solvent to feed ratio of 1:1 and goes up to 96% for the solvent to feed ratio of 3:1. It is also observed that the percentage extraction of phenol increases with higher solvent ratios for the same initial concentration of phenol. The percentage increase slows down with more use of solvent as evident from the incremental improvements observed for the 2:1 and 3:1 ratio, ultimately reaching above 95%. It is also observed that the ultimate phenol removal is greater for the higher solvent to feed ratio, albeit marginally.

3.1.1.2. Observations on distribution coefficient

Distribution coefficients are derived from the basic experimental observation of percentage phenol removal with initial concentration. The variation of distribution coefficient with an initial concentration of phenol is shown in Fig. 6 and is similar, as expected. However, with increasing solvent ratios, the observed values of distribution coefficients are less because of the phenol dissociation in the aqueous phase and are affected by the relative volumes. Variation in the distribution coefficient with a concentration of phenol and its derivatives with respect to some organic solvents including hydrocarbons and alcohols have been reported and the behavior was attributed to the changes in solvent-phenol interactions [36]. It is believed that the dissociation of phenol in the aqueous phase at low concentrations is the basic reason. The variations observed with different solvent to feed ratios can be attributed to changes in the concentration of phenol with different volumes, influencing the dissociation equilibrium.

In our studies using 1-hexanol, the distribution coefficient has been found to increase with initial phenol concentration similar to the trend observed with percentage removal. Distribution coefficients are much less for higher solvent
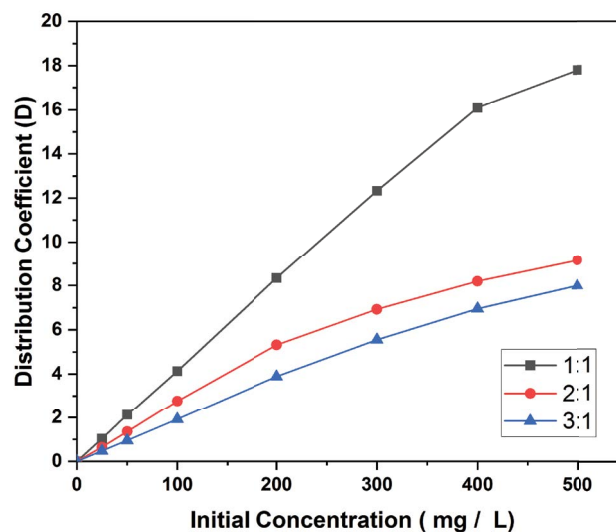
to feed ratios even though all of them stabilize beyond a particular feed concentration of phenol.

3.1.1.3. Implication of batch studies for membrane assisted solvent extraction

The following conclusions emerge from our experiments:

- Maximum recovery of about 94%–96% is achievable from aqueous solutions of phenol.
- The assumption of constant distribution coefficient for the extraction of phenol is valid beyond an initial concentration of 400 mg/L.
- For a higher solvent to feed ratios the distribution coefficient decreases.

3.2. Membrane assisted solvent extraction

Membrane solvent extraction is a continuous process. As the process is continued phenol concentration decrease in the aqueous phase while in the organic phase phenol concentration increases. The solvent to feed ratio in MASE can be changed by changing the relative flow rates of feed and solvent.

3.2.1. Need for a hollow fiber membrane contactor

The interfacial contact area is the basic requirement for solvent extraction to enable the mass transfer of desired species. The hollow fiber membrane element is compact and provides maximum interfacial area through a large number of small pores. Since the fiber diameters are small many fibers are packed in an element. The cross-sectional area for the fluid flow in the tube side is less and invariably, flow corresponds to the laminar regime. Consequently, lateral mixing would be negligible.

In commercial membrane elements, the net cross-sectional area for the shell side would be less as most of

the area is occupied by the fibers, sometimes intertwined among themselves. The effective cross-sectional area for the shell side flow would also be less with some dead volume hence it would be difficult to maintain a turbulent flow regime.

Solvent extraction which deals with the mass transfer of desired species is driven by chemical affinity and is achieved by bringing both phases close to each other. Unlike conventional extraction equipment where forced mixing is achieved by micro-dispersion, in MASE, the diffusion through the membrane pores is the critical step for mass transfer which is at least one order slower than unhindered diffusion. This shortcoming is however compensated by having a large number of pores. It is also clear that the flow pattern of the fluids on either side of the membranes may not have a significant effect beyond a particular limit where constant availability of species to be extracted is available.

Normally for membrane assisted solvent extraction, hydrophobic membranes are used in which the organic phase gets filled in the pores of the membrane. The effective mass transfer is hence controlled by the diffusion of the species through the organic phase. Of course, the diffusion cannot be a free diffusion but has to be considered as hindered diffusion.

Above all the hollow fiber unit is compact and fully contained. Any failure of the hollow fibers will lead to the mixing of the two fluids but may not spill out thus ensuring the safety of the system while in operation.

3.2.2. Selection of solvent flow through the tube side

Commercially available hollow fiber membrane contactors used in water treatment applications are made of polymers like polyethersulfone (PES), polyvinylidene fluoride (PVDF) or polypropylene (PP). The membrane fibers made of the polymers PP, PVDF and PES were soaked in 1-hexanol. PES membranes became softer while the other two membranes did not show any observable deterioration after a week. In view of this PVDF membrane has been chosen for detailed studies initially. However, the shells of these membrane elements are made of commercially available polymeric materials such as polyvinyl chloride, Perspex (acrylic polymer) and high-density polyethylene which are compatible with aqueous systems. When bought out membrane elements were directly contacted with the organic phase in the shell, shell fluid was found leaking after a few days of operation and a few cracks on the module surface were noticed. Since the flow is laminar without much of lateral mixing, the heat of reaction between the extracted species and the organic solvent does not get dispersed leading to differential expansion resulting in the development of cracks followed by leaking of the organic phase. Earlier investigators [33,35,37] have carried out the experiments using an organic solvent on the shell side. Since it was an experimental setup purchased directly from the membrane vendor, the unit must have been designed accordingly. To overcome these difficulties there are two options: either to have a metallic shell that can disperse the thermal energy easily or have the organic phase flow through the tube side.

The decision to use the organic solvent through the tube side is governed by the following reasons:
- Membrane material is compatible with the organic solvent.
- Interfacial contact of the solvent with the feed stream will be more efficient as the flow of the solvent phase would be uniform.
- The tube diameter is small and the fact that the contact occurs along the periphery, the number of solvent molecules simultaneously taking part in the extraction would be high.
- Even in a twisted tube, the solvent flow is akin to plug flow and has no chance of dead volumes. In case the tube gets blocked the net area may become less.
- On the shell side, the fluid would be in contact with the external side of the membrane. When more hollow fiber membranes, which are flexible are squeezed, the clearances between the different membranes are not uniform, leading to distorted flow patterns as well creating some dead zones as free movement is hindered.
- Due to poor thermal conductivity the heat solvation may create a crack due to differential thermal expansion.
- Efficiency of solvent contact with tube side aqueous fluid will be less as there is a possibility viscous solvent adhering to the wall of the shell.
- Metallic shell would be heavy. Being better thermal conductor crack resistance due to differential expansion would be higher. However, the cost may be higher.

As a general practice, valuable fluid is always taken on the tube side to prevent inadvertent losses in both heat and mass transfer applications. In view of these factors, the organic phase is allowed to pass through the tube side.

3.2.3. Performance of membrane contactor

3.2.3.1. Extraction

The initial feed concentration of phenol was maintained at 500 mg/L for all the experiments and the flow rates of the organic phase were varied from 12.5 to 75 mL/min relative to a constant aqueous phase feed rate of 25 mL/min. It is presumed that higher flow rates of organic phase correspond to the higher solvent to feed ratio as more solvent would be in contact with a fixed volume aqueous phase. The experiments were conducted both in co-current and counter-current mode.

Figs. 7 and 8 provide the percentage extraction of phenol with reference to time in the co-current and counter-current mode respectively leading to the following observations.

- Irrespective of the solvent to feed ratio ranging from 0.5: 1, to 3:1 it is possible to recover more than 90% of phenol.
- With higher solvent to feed ratios the percentage removal of phenol is marginally higher.
- Counter current solvent extraction appears to be marginally faster in the removal of phenol in this study. By extrapolation, it may be more efficient in the phenol
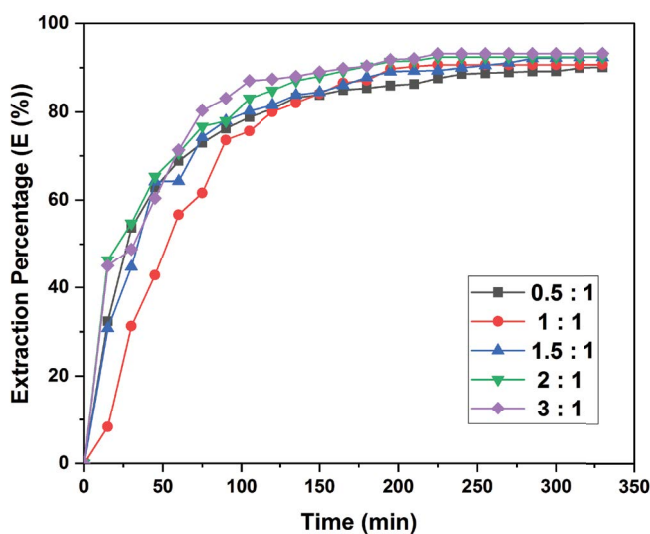
Fig. 7. Effect of time on extraction percentage with increasing solvent to feed ratios (1:1 to 3:1) for a co-current mode of operation.
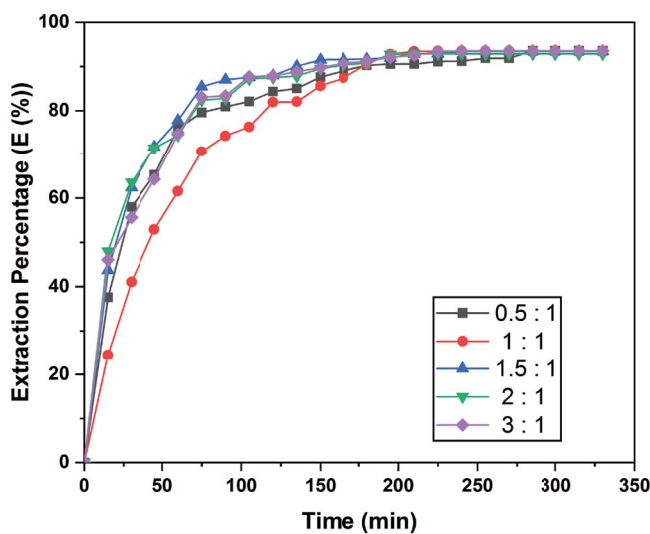

Fig. 8. Effect of time on extraction percentage with increasing solvent to feed ratios (1:1 to 3:1) for the counter-current mode of operation.

removal from the aqueous phase when longer membrane elements are used.

If the organic phase flow rate was to be the controlling step, then the percentage extraction should have increased substantially and the time for attaining maximum percent removal should be significantly less, with higher flow rates.

Being hydrophobic membrane, the pores are filled with the solvent establishing faster mass transfer at the interphase. The mass transport from the aqueous phase to the organic phase is controlled by affinity while transport through the membrane is governed by diffusion in the pores of the membrane which may be recognized as hindered
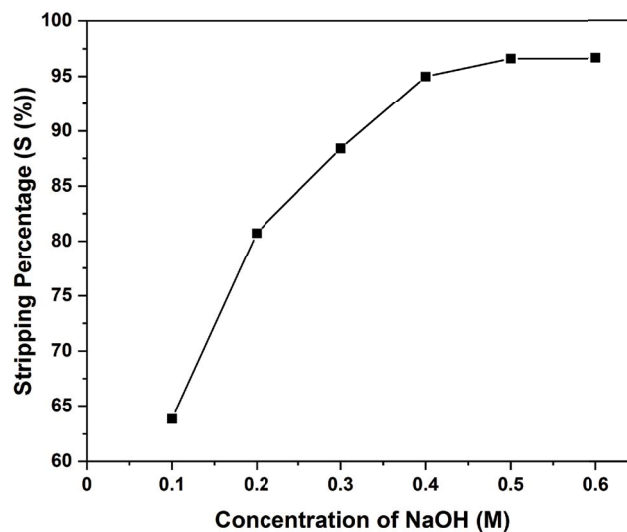

Fig. 9. Effect of concentration of NaOH on stripping percentage.

diffusion and that is the rate-controlling step. Higher organic phase flow rates help in improving the removal of diffused species more governed by extraction equilibrium. At higher concentrations where speciation is marginal, the difference in the removal rate is marginal.

Accordingly, it is evident that membrane assisted solvent extraction can have performance on par with conventional extraction and the behavior with changing solvent to feed ratio is akin to conventional extraction.

3.2.3.2. Recovery of phenol from the organic phase (stripping)

The concentration of sodium hydroxide at which stripping of the organic phase for recovery of phenol, was decided based on the batch experiment. The observations as shown in Fig. 9 indicates that 0.5 M NaOH [38,39] solution can be used to recover the maximum amount of phenol.

Stripping of the extracted phenol in the organic phase was carried out, in a similar manner to extraction experiments with the phenol loaded organic phase on the tube side and 0.5 N NaOH solution on the shell side. The volumes of both organic and stripping phases were 250 mL.

The experimental studies as indicated in Fig. 10 show that stripping efficiency is higher with increasing organic phase flow rates. During the stripping step phenol gets converted to phenoxide in contact with sodium hydroxide solution, resulting in faster movement of phenol species. It further indicates that organic phase flow rate only marginally alters the rate of stripping and takes almost equal time to reach the maximum value.

It can be concluded that the time required for stripping is nearly equal to extraction, opening the possibility of coupling both the extraction and stripping in a single loop. However, before embarking on the loop it is necessary to assess the effect of increasing the surface area of the membrane either by increasing the length of the lumen or increasing the number of lumens per element.
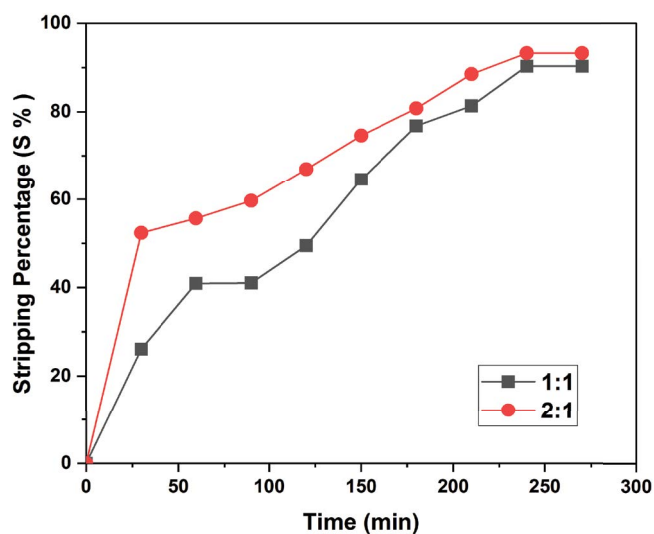
Fig. 10. Effect of time on stripping percentage with increasing organic phase to aqueous phase ratio (1:1 and 2:1) for a co-current mode of operation.

3.2.4. Estimation of mass transfer coefficient

Mass transfer coefficients were calculated based on the correlations published in the literature as a function of the Reynolds number of the organic phase. Figs. 11a and b provide the mass transfer coefficient calculated based on experimental values in comparison with those obtained from the model [33,35] for both co-current and counter-current mode of operation.

The overall mass transfer coefficients (K_{aq}) calculated from the experimental studies and model prediction are presented in Figs. 11a and b for both co-current and counter-current studies. Mass transfer coefficients are nearly constant (1.33–1.37 × 10^{-7} ms^{-1}) both for co-current and counter-current extraction at least with reference to our

experimental system where the contact time between the two phases are hardly a few seconds. The values experimentally obtained are also in agreement with those reported in most of the literature [25]. The corresponding model predicted overall mass transfer coefficients are also shown. Indeed, the predicted values are of the same order of magnitude as that of the experimental data [40]. The experimental mass transfer coefficient was found to be nearly constant independent of the organic phase Reynolds number indicating that the tube side flow is not offering much resistance to mass transfer. For the stripping step, the mass transfer coefficient has been estimated to be 1.23 × 10^{-7} m/s which is almost similar to that of the extraction step. This would be advantageous when extraction and stripping are to be carried in series so as to recycle the solvent, almost under the same fluid dynamic conditions.

4. Conclusions

The passage of solvent through the tube side of the membrane in membrane assisted solvent extraction requires mainly the membrane to be solvent stable and not the shell, which leads to possible utilization of commercially available units, used for aqueous systems. The tube side flow of the organic phase enables the seamless passage both in the extraction and stripping section providing the possibility of real-time recirculation of solvent. The percent removal of phenol under similar chemical parameters including solvent to feed ratio, feed concentration, etc. is higher for membrane-assisted solvent extraction compared to conventional solvent extraction. The mass transfer coefficients estimated through the experiments are independent of organic phase flow rates, indicating that pore diffusion of the species to be the rate-controlling step. The experimental investigations indicate that pollutant phenol is not only removable but also recoverable as value, a win-win situation both for the environment and the industry. The process indicates sustainability due to less solvent inventory and operational
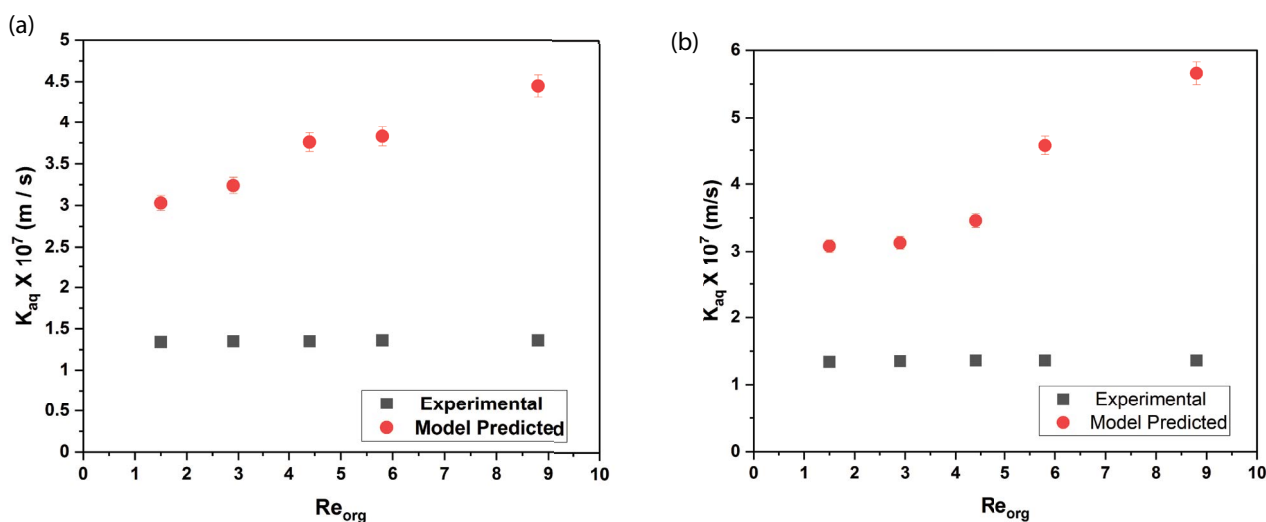

Fig. 11. Experimental and predicted overall mass transfer coefficients as a function of organic phase hydrodynamics in the extraction step for (a) co-current and (b) counter-current operation mode respectively.

safety. The modular nature makes it easy for adoption at any capacity, particularly for small scale industries.

Symbols

$C_{initial}$, C_{final}	—	Initial and final concentration of phenol in the aqueous phase, mg/L
$C_{organic}$	—	Concentration of phenol in the organic phase, mg/L
$C_{stripping}$	—	Concentration of phenol in the stripping phase, mg/L
$E\%$	—	Extraction percentage
$S\%$	—	Stripping percentage
$R\%$	—	Overall recovery percentage
D	—	Distribution coefficient
D_s, D_o	—	Inner and outer diameter of the shell, m
D_H	—	Hydraulic diameter of the shell, m
d_i, d_o and d_{lm}	—	Inside, outside and log mean diameters of the hollow fiber respectively, m
L	—	Effective fiber length, m
N	—	Number of hollow fibers
ε	—	Porosity
τ	—	Tortuosity
Ψ	—	Packing fraction
β	—	Membrane constant
Sh	—	Sherwood number
Re	—	Reynolds number
Sc	—	Schmidt number
Gz	—	Graetz number
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
Re$_{org}$	—	Reynolds number for the organic phase
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
J_{sol}	—	Solute flux, kg/m^2 s
A_m	—	Effective membrane interfacial area, m^2
C_{aq}	—	Concentration of phenol in the aqueous solution at time t, mg/L
C_{aq}^0	—	Concentration of phenol in aqueous phase at time $t = 0$, mg/L
C_{aq}^*	—	Concentration of phenol in the aqueous phase in equilibrium with the organic phase at the same time t, mg/L
Q_{aq}, Q_{org}	—	Aqueous and organic phase flow rates, respectively, m^3/s
V_{aq}, V_{org}	—	Volumes of the aqueous and organic phases respectively, m^3
C	—	Fitting coefficient

References

[1] P. Kehrein, M. van Loosdrecht, P. Osseweijer, M. Garfí, J. Dewulf, J. Posada, A critical review of resource recovery from municipal wastewater treatment plants - market supply potentials, technologies and bottlenecks, Environ. Sci. Water Res. Technol., 6 (2020) 877–910.

[2] M.N. Murty, S. Kumar, Water Pollution in India: An Economic Appraisal, University of British Columbia, 2011.

[3] S. Veenstra, G. Alaerts, M.R. Bijlsma, Chapter 3 – Technology Selection, R. Helmer, I. Hespanhol, Eds., Water Pollution Control – A Guide to the Use of Water Quality Management Principles, World Health Organization (WHO)/United Nations Environment Programme (UNEP), London (UK), 1997, pp. 1–39.

[4] S. Rasalingam, R. Peng, R.T. Koodali, Removal of hazardous pollutants from wastewaters: applications of TiO$_2$-SiO$_2$ mixed oxide materials, J. Nanomater., 2014 (2014) 617405, https://doi.org/10.1155/2014/617405.

[5] G. Crini, E. Lichtfouse, Advantages and disadvantages of techniques used for wastewater treatment, Environ. Chem. Lett., 17 (2019) 145–155.

[6] A.J. Tóth, F. Gergely, P. Mizsey, Physicochemical treatment of pharmaceutical process wastewater: distillation and membrane processes, Period. Polytech., Chem. Eng., 55 (2011) 59–67.

[7] B.L. Pangarkar, M.G. Sane, M. Guddad, Reverse osmosis and membrane distillation for desalination of groundwater: a review, ISRN Mater. Sci., 2011 (2011) 523124, https://doi.org/10.5402/2011/523124.

[8] L. Malaeb, G.M. Ayoub, Reverse osmosis technology for water treatment: state of the art review, Desalination, 267 (2011) 1–8.

[9] A. Abbas, On the performance limitation of reverse osmosis water desalination systems, Int. J. Nucl. Desal., 2 (2007) 205–218.

[10] E. Drioli, G. Di Profio, E. Curcio, Hybrid membrane operations in water desalination and industrial process rationalisation, Water Sci. Technol., 51 (2005) 293–304.

[11] E.O. Ezugbe, S. Rathilal, Membrane technologies in wastewater treatment: a review, Membranes (Basel), 10 (2020) 89, https://doi.org/10.3390/membranes10050089.

[12] A. Gabelman, S.-T. Hwang, Hollow fiber membrane contactors, J. Membr. Sci., 159 (1999) 61–106.

[13] S.K. Gupta, N.S. Rathore, J.V. Sonawane, A.K. Pabby, R.R. Singh, A.K. Venugopalan, P.K. Dey, B. Venkatramani, Hollow fiber membrane contactor: novel extraction device for plutonium extraction, BARC Newsletter, Founder's Day Special Issue, (2003) 181–189.

[14] E. Curcio, E. Drioli, Membrane distillation and related operations—a review, Sep. Purif. Rev., 34 (2005) 35–86.

[15] K.K. Sirkar, Membranes, phase interfaces, and separations: novel techniques and membranes–an overview, Ind. Eng. Chem. Res., 47 (2008) 5250–5266.

[16] K.K. Sirkar, P.V. Shanbhag, A.S. Kovvali, Membrane in a reactor: a functional perspective, Ind. Eng. Chem. Res., 38 (1999) 3715–3737.

[17] R.M. Ben Aim, M.J. Semmens, Membrane bioreactors for wastewater treatment and reuse: a success story, Water Sci. Technol., 47 (2003) 1–5.

[18] P. Arehjani, A. Kargari, Chapter 17 – Prospects of Nanocomposite Membranes for Gas Separation by Membrane Contactors, M. Sadrzadeh, T. Mohammadi, Eds., Nanocomposite Membranes for Water and Gas Separation: Micro and Nano Technologies, Elsevier Inc., Amsterdam, 2020, pp. 439–456.

[19] E. Kavitha, M. Dalmia, A.M. Samuel, S. Prabhakar, M.P. Rajesh, Modeling and optimization of removal of strontium and cesium from aqueous streams by size enhanced ultrafiltration using chitosan derivative, Desal. Water Treat., 185 (2020) 262–276.

[20] E. Kavitha, R. Kedia, N. Babaria, S. Prabhakar, M.P. Rajesh, Optimization of process using carboxymethyl chitosan for the removal of mixed heavy metals from aqueous streams, Int. J. Biol. Macromol., 149 (2020) 404–416.

[21] E. Kavitha, M.P. Rajesh, S. Prabhakar, Removal and recovery of heavy metals from aqueous solution using β-cyclodextrin polymer and optimization of complexation conditions, Desal. Water Treat., 122 (2018) 219–230.

[22] E. Kavitha, A. Sowmya, S. Prabhakar, P. Jain, R. Surya, M.P. Rajesh, Removal and recovery of heavy metals through size enhanced ultrafiltration using chitosan derivatives and

optimization with response surface modeling, Int. J. Biol. Macromol., 132 (2019) 278–288.

[23] T. Tow Teng, Y. Yusup, L. Wei Low, Heavy metal ion extraction using organic solvents: an application of the equilibrium slope method, A. Innocenti, Ed., Stoichiometry and Research - The Importance of Quantity in Biomedicine, IntechOpen, 2012, doi: 10.5772/33199.

[24] N. Othman, N.F.M. Noah, L.Y. Shu, Z.Y. Ooi, N. Jusoh, M. Idroas, M. Goto, Easy removing of phenol from wastewater using vegetable oil-based organic solvent in emulsion liquid membrane process, Chin. J. Chem. Eng., 25 (2017) 45–52.

[25] A. Nanoti, S.K. Ganguly, A.N. Goswami, B.S. Rawat, Removal of phenols from wastewater using liquid membranes in a microporous hollow-fiber-membrane extractor, Ind. Eng. Chem. Res., 36 (1997) 4369–4373.

[26] P.K. Parhi, K. Sarangi, Separation of copper, zinc, cobalt and nickel ions by supported liquid membrane technique using LIX 84I, TOPS-99 and Cyanex 272, Sep. Purif. Technol., 59 (2008) 169–174.

[27] B. Hauser, M. Schellin, P. Popp, Membrane-assisted solvent extraction of triazines, organochlorine, and organophosphorus compounds in complex samples combined with large-volume injection-gas chromatography/mass spectrometric detection, Anal. Chem., 76 (2004) 6029–6038.

[28] E.A. Fouad, H.J. Bart, Separation of zinc by a non-dispersion solvent extraction process in a hollow fiber contactor, Solvent Extr. Ion Exch., 25 (2007) 857–877.

[29] M. Quilaqueo, G. Seriche, S. Valetto, L. Barros, S. Díaz-Quezada, R. Ruby-Figueroa, E. Troncoso, H. Estay, An experimental study of membrane contactor modules for recovering cyanide through a gas membrane process, Membranes (Basel), 10 (2020) 10050105, https://doi.org/10.3390/membranes10050105.

[30] W. Cichy, J. Szymanowski, Recovery of phenol from aqueous streams in hollow fiber modules, Environ. Sci. Technol., 36 (2002) 2088–2093.

[31] Y.S. Ng, N.S. Jayakumar, M.A. Hashim, Behavior of hydrophobic ionic liquids as liquid membranes on phenol removal: experimental study and optimization, Desalination, 278 (2011) 250–258.

[32] M.B. Rosly, N. Othman, H.A. Rahman, Liquid membrane component selection for removal of phenol from simulated aqueous waste solution, Malaysian J. Anal. Sci., 22 (2018) 702–714.

[33] S.F. Shen, K.H. Smith, S. Cook, S.E. Kentish, J.M. Perera, T. Bowser, G.W. Stevens, Phenol recovery with tributyl phosphate in a hollow fiber membrane contactor: experimental and model analysis, Sep. Purif. Technol., 69 (2009) 48–56.

[34] S. Shen, S.E. Kentish, G.W. Stevens, Shell-side mass-transfer performance in hollow-fiber membrane contactors, Solvent Extr. Ion Exch., 28 (2010) 817–844.

[35] M.J. González-Muñoz, S. Luque, J.R. Álvarez, J. Coca, Recovery of phenol from aqueous solutions using hollow fibre contactors, J. Membr. Sci., 213 (2003) 181–193.

[36] P.R. Kiezyk, D. Mackay, The screening and selection of solvents for the extraction of phenol from water, Can. J. Chem. Eng., 51 (1973) 741–745.

[37] Z. Lazarova, S. Boyadzhieva, Treatment of phenol-containing aqueous solutions by membrane-based solvent extraction in coupled ultrafiltration modules, Chem. Eng. J., 100 (2004) 129–138.

[38] S. Wang, D. Shi, R. Yang, Y. Xu, H. Guo, X. Yang, Solvent extraction of phenol from aqueous solution with benzyl 2-ethylhexyl sulfoxide as a novel extractant, Can. J. Chem. Eng., 93 (2015) 1787–1792.

[39] X. Yang, A. Zou, J. Qiu, S. Wang, H. Guo, Phenol removal from aqueous system by bis(2-ethylhexyl) sulfoxide extraction, Sep. Sci. Technol., 49 (2014) 2495–2501.

[40] M. Xiao, J. Zhou, Y. Tan, A. Zhang, Y. Xia, L. Ji, Treatment of highly-concentrated phenol wastewater with an extractive membrane reactor using silicone rubber, Desalination, 195 (2006) 281–293.