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Hollow fiber liquid membrane: A promising approach for elimination of pharmaceutical compounds from wastewater

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ABSTRACT

Pharmaceutical compounds present in water pose significant challenges, particularly due to their low concentrations in water streams. Hollow fiber liquid membranes provide a flexible and easily manageable solution, enabling the concentration of specific contaminants. This concentration step significantly improves their effective removal from water systems. The study focused on using hollow fiber liquid membrane technology to effectively remove diclofenac (DCF) and ibuprofen (IBU), two pharmaceutical compounds. A concentration of 40% Cyanex 923 (Cy923) dissolved in kerosene was selected as the preferred extractant due to its stability and quick extraction properties. The stability of the system was tested with a pseudo-emulsion, enabling repeated use of the system. Additionally, an analytical model was developed to calculate the membrane's permeability. In order to enhance the degradation and mineralization of the pharmaceutical compounds and their byproducts, ozonation was integrated with the hollow fiber liquid membrane system in a single system. Measurement of total organic carbon (TOC) revealed a significant reduction of 72% for diclofenac and 57% for ibuprofen with an initial ozone concentration of 10 mg/L and operating under the optimal conditions of hollow fiber liquid membrane.

1. Introduction

Membrane-based separation techniques have gained significant attention over conventional methods like solvent extraction, precipitation, and ion exchange [1]. Particularly, liquid membrane (LM) processes are well known for their minimal extractant requirement, sustained operational effectiveness, and remarkable selectivity. Their concept involves the use of an organic extractant to selectively transport certain components or substances from one solution to another and the ability to combine extraction and stripping within a single unit. In this context, liquid membranes are widely employed in various applications, including extraction processes, chemical separations, and environmental remediation. They offer advantages such as high selectivity and efficiency, making them a valuable tool in industries ranging from pharmaceuticals to wastewater treatment. The composition of the liquid membrane can vary depending on the specific application and the substances being separated or transported [2] [3]. Supported liquid membranes (SLMs) consist of an organic solvent held within the pores of hydrophobic solid support. They are available in two configurations including flat sheets and hollow fiber. However, at a larger scale, the most common configuration adapted is the hollow fiber. Hollow fiber-supported liquid membranes (HFSLMs) are commonly studied for industrial application and implementation as they offer a large interfacial area per volume unit and easy regeneration of the degraded membranes [3]. HFSLM has been used in various applications to remove phenol, carboxylic acids, arsenic, and several metals. Also, they are adapted for analytical detection and environmental analysis. Patil el al. (2017) discussed the selective separation of different carboxylic acids such as acetic acid, phenylacetic acid, and formic acid from diluted streams with aliphatic amines using hollow fiber liquid membrane techniques [4]. In recent studies, the combination of HFSLM extraction and HPLC-UV analysis has showcased its capabilities in quantifying five bisphenols present in environmental water samples. This approach not only ensures precise quantification and reproducibility but also combines the extraction, clean-up, and enrichment processes into a single step [5]. They are also applied for extracting various drugs and pharmaceutical compounds from water for chromatographic analysis using green solvent [6].

However, it is essential to conduct a comprehensive study to enhance the performance of hollow fiber membranes when it comes to efficiently

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removing trace pharmaceutical concentrations from water. This is especially crucial for their potential large-scale applications in wastewater treatment and industrial water treatment [7,8]. One of the key elements to consider is the stability of these membranes during the process which can limit their performance. The problem of instability associated with LM is caused by the loss of the organic extractant out of the pores of the support due to different operational and physiochemical factors [9]. To overcome these issues in HFSLM, a pseudo-emulsion-based hollow fiber supported liquid membrane (PEHFSLM) has been developed to enhance stability and long-term performance. This technique combines the properties associated with emulsion liquid membrane by offering a greater surface area and maintaining continuous transfer of organic solution to the porous support. PEHFSLM is used over a wide range of organic extractants. To remove different contaminants from water [10]. Shirasangi et al. (2021) conducted a comparison between hollow fiber-supported liquid membrane (HFSLM) and pseudo-emulsion hollow fiber membrane strip dispersion (PEHFSD) for the separation of methylparaben from water. Their findings proved that PEHFSD exhibited better performance over extended periods of time [11]. In another study, the complete removal of propylparaben from water by PEHFSLM system was achieved using 1.4% w/v of Aliquat 336 [12]. Diclofenac (DCF) and ibuprofen (IBU) are two pharmaceuticals belonging to the non-steroidal anti-inflammatory group. They both contain a carboxylic group connected to the aromatic ring in their structure [13]. Although these pharmaceuticals are known to be completely metabolized, they can be administered in a gel leading to the possibility of the unmetabolized form being washed away. Within this frame, ibuprofen and diclofenac and their transformation products have been detected in various water bodies [14]. Ibuprofen, one of the most commonly used anti-inflammatories, shows adverse model organisms at low concentrations (250 ng/L) [15]. On the other hand, diclofenac has been included in the first watch list of the European Union for consecutive years, demonstrating its negative impact on the environment [15]. In the pharmaceutical industry, hollow fiber membranes are highly integrated for analytical measurements. The ability of HFSLM to pre-concentrate the stream and remove a variety of metals with low and less toxic solvents has been usually investigated, but few are applied to pharmaceutical contaminants [15]. Therefore, in this study, the feasibility of hollow fiber liquid membrane to remove diclofenac and ibuprofen with Cyanex 923 (Cy923) is investigated.

Regarding the improvement in performance, recent efforts to optimize HFSLM include incorporating strengthened carbon nanotubes (CNTs) into organic extractants [16]. Padabni et al. (2015) investigated molecular imprinted hollow fiber solid-phase as solid sorbents. In this case, the molecularly imprinted polymers (MIP) are prepared and coated on the surface of the hollow fiber for the extraction and determination of diclofenac. Introducing solid adsorbents has shown promising results in removing and pre-concentrating the targeted analytes [17]. Nonetheless, drawbacks associated with the use of these membranes should be considered, such as membrane fouling, high equipment cost, and low or moderate permeation fluxes. In addition, most works reported on polymer inclusion membranes are mainly conducted with flat sheet modules [16].

The development of efficient technologies that combine removal yield, cost, practicality, environmental effect, and reliability are attractive subjects for researchers. However, existing technologies have distinct advantages and disadvantages. Therefore, the combination of two treatment methods offers the potential to achieve optimal pharmaceutical removal while mitigating individual drawbacks [18]. Several studies have proposed the integration of advanced membrane processes with well-established technologies.[19,20]. For instance, nanofiltration is recently employed following reverse osmosis to mitigate the fouling effect and improve the pre-treatment procedure. [21, 22]. In another study, Baumgarten et al. (2007) compared the efficiency of combining MBR with each of powdered activated carbon (PAC), ozone, and membrane processes to remove different types of antibiotics from water effluent [18]. Also, Zhang et al. (2006) studied the removal of tetracycline with PAC and reverse osmosis systems to overcome the problem of fouling affecting these systems [23]. Numerous approaches have combined powdered activated carbon with traditional treatment methods yet an additional step is required to activate or regenerate the selected adsorbent. One of the attractive subjects of research about water and wastewater treatment is the coupling membrane filtration and advanced oxidation processes (ozonation, H_2O_2, Fenton, photolysis) mainly to decrease fouling and enhance the degradation of generated concentrated pollutants [21,22]. Lu et al. (2020) investigated the effect of pre-ozonation to sustain the flux in ceramic membranes for raw secondary effluent, they have found that pre-ozonation can extend the filtration cycle time by approximately 5 times for ceramic membranes [24]. Nonetheless, the application of ozonation as a pre-treatment stage can form oxidized foulants capable of blocking the pores of the membrane. In recent years, the application of ozonation has been a growing interest for wastewater treatment, especially to remove persistent pollutants and emerging contaminants such as synthetic dyes, carboxylic acids, phenolics, amoxicillin, and other pharmaceuticals [25–27]. Yet to date, achieving a complete mineralization on an industrial scale with ozone is challenging due to the high ozone dosages needed, its inability to effectively remove low concentrations, and the associated high costs [27]. For these reasons, the integration of ozonation with membrane processes emerges as a viable alternative to address these issues [28].

In fact, ozone can be joined with membrane processes in three ways either as a pre-treatment step to primarily degrade contaminants. The second option is a post-treatment step to eliminate the non-rejected organic in the output of the membrane or in the highly concentrated stream of the retentate. Finally, ozonation and membranes can be integrated with a single hybrid process where they are operated simultaneously as a batch or recirculation flow process. Coupling AOPs, such as ozonation, with membrane technologies offers a promising solution to address the challenges associated with energy demand and mass transfer [28]. The hybrid process not only improves the efficiency of the treatment but also provides flexibility in operation and scalability for various water treatment applications [28]. Recently, many studies have focused on using hollow fiber membrane contactors as an alternative option for bubble systems to diffuse ozone in water and increase its mass transfer [28,29]. To this date, the ability to scale up ozone membrane contactors is rarely put into practice because of the potential instability of polymeric membranes when exposed to ozone molecules [30].

The main objective of this study is firstly to investigate the removal of diclofenac and ibuprofen in a hollow fiber liquid membrane. The focus was on developing a simplified and effective analytical model to calculate the permeability in these systems. Several experiments were conducted to increase the stability and improve the extraction efficiency. Furthermore, the integration of HFSLM and ozonation was explored to tackle the limitation associated with ozonation treatment and enhance the degradation and removal of pharmaceutical compounds.

2. Model development

A simplified model to calculate the permeability in hollow fiber module is developed assuming pseudo-steady state and plug flow behaviour. The co-current flow was adopted in the hollow fiber setup to ensure a consistent pressure difference between the fibers' outer shell and inner lumen side. This arrangement ensures efficient separation or exchange processes to take place within the fibers. Additionally, it is assumed that the concentration of solute of interest (pharmaceutical compounds) in the stripping phase, which is the fluid flowing through the lumen, is negligible or close to zero.

Assuming, no accumulation in the membrane, the mass balance in the cross-section of one fiber is defined by Eq.(1):

$$\text{Input} = \text{Output}$$

$$q_f \cdot C_z - q_f \cdot C_{z+\Delta z} - J \cdot A_C = q_f \cdot C_Z - q_f \cdot C_{z+\Delta z} - J \cdot \pi \cdot d \cdot \Delta z \quad (1)$$

Where q_f is the volumetric flow rate in the cross-sectional area (m^3/s), C_z and $C_{z+\Delta z}$ are the concentration of solute entering and exiting the fiber at in axial position z and z + Δz,respectively (mol/L), J is the amount of the solute transferred by diffusion through the fiber wall(per time unit and area unit, equal to the overall mass transport flux, (mol/·m^2·s) and d is the fiber inner diameter (m).

Rearranging Eq. (1), the mass balance in the cross-sectional area of a fiber is shown in the following Eq. (2):

$$-q_f \frac{dC}{dz} = J \cdot \pi \cdot d \quad (2)$$

The permeability coefficient (P) is the speed with which pharmaceuticals are transported in the membrane. This parameter is related to the flux (J) by Eq.(3):

$$J = P \cdot C \quad (3)$$

Where P is the permeability coefficient (m/s) and C is the concentration of the solute present in the feed at time t (mol/L).

The variation of concentration is calculated along the total fiber's length as shown in Eq.(4), by applying the boundary conditions at $z_0 = 0$ and z = L, and combing (Eqs.(2), and Eq, (3))

$$-q_f \cdot \ln \frac{C_{out}}{C_{in}} = P \cdot d \cdot \pi \cdot L \quad (4)$$

Given L is the total length of the fiber (m).

Subsequently, the concentration exiting the membrane module is determined in Eq.(5) whereas the total flow rate and the total area are expressed by the following equation respectively:

$Q_f = q_f * N$; $A = d \cdot \pi \cdot L \cdot N$ (with N = number of fibers)

$$C_{m.out} = C_{m.in} \cdot e^{-\frac{P*A}{Q_f}} \quad (5)$$

Given $C_{m.out}$ and $C_{m.in}$ are the concentration in the outlet and the inlet of the HFSLM, P the permeability coefficient (m/s), A total area (m^2), and Q_f is the total flow rate entering the membrane module.

Afterward, the pharmaceutical mass balance is established in the feed as described in Eq.(6).

Input − Output = accumulation

$$Q_f \cdot (C_{fin} - C_{fout}) = V \frac{dC}{dt} \quad (6)$$

With the V volume of the feed tank (m^3), $C_{f\,in}$ and $C_{f\,out}$ are the inlet and outlet concentrations.

of the feed tanks (mol/L).

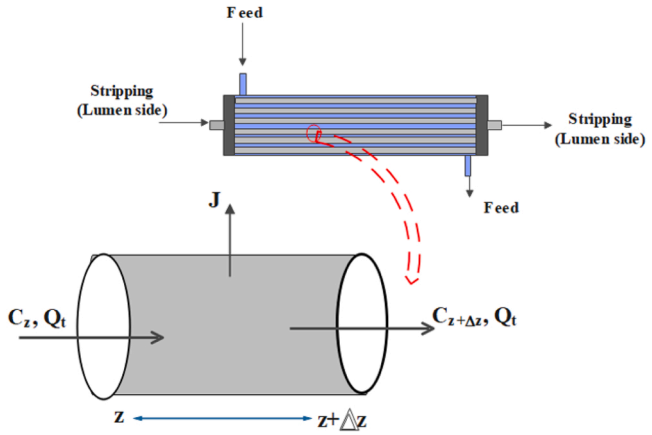

Fig. 1. Mass balance of the cross-sectional area for a lumen side of the membrane.

As seen in Fig. 1 2, at specific time t,$C_{fout} = C_{mi}$ and $C_{fin} = C_{mout}$, consequently the variation of solute in the feed is obtained in Eq.(7) and the permeability coefficient in HFSLM is calculated:

$$\ln \frac{C_f}{C_{0_f}} = -\frac{Q_f}{V} \cdot \left[1 - e^{-\frac{P*A}{Q_f}}\right] \cdot t \quad (7)$$

Where $C_{0\,f}$ is the initial concentration of the solute in the feed phase.

3. Material and methods

3.1. Chemicals

All pharmaceuticals and their metabolites diclofenac (CAS No. 15307–79–2, 99%), ibuprofen (CAS No.15307–79–2, ≥98%), 4-Ethylbenzaldehyde (CAS No. 233633, ≥97.5%), 5-hydroxy diclofenac (CAS No.62248, ≥97%) were supplied by Sigma-Aldrich. Fresh test samples were prepared in adequate concentrations (1, 10, and 30 mg/L) in deionized water at ambient temperature (22 ± 2 °C). The selected concentrations were higher compared to the ones normally found in real water matrices to allow better monitoring and measurement of the removal efficiency with the available analytical techniques.

HPLC acetonitrile, reagent grade, NaOH, KI, and NaCl, were all obtained from Merck. Potassium indigo tri-sulfonate and potassium iodide were used for analysing residual ozone in the samples and were obtained from Sigma Aldrich. Cyanex 923 (91%) dissolved in kerosene at room temperature was purchased from Solvay and was selected as the organic extractant to remove ibuprofen and diclofenac [31].

3.2. Hollow fiber membrane transport

The experiments with HFSLM consisted of a hollow fiber module from Liqui-Cel™ (G-502) and its characteristics are summarized in Table 1. Firstly, the liquid membrane phase was prepared by pumping 40% (v/v) Cy923 dissolved in kerosene, through the lumen side of the module in recirculation mode for 10 min. The circulation of the organic extractant in the lumen side prior to any experimental runs ensures the proper soaking of membrane pores. Afterward, the module was washed with distilled water to remove any excess organic liquid. During the experimental runs, feed (shell side) and stripping (lumen side) streams flowed at 50 L/h in a co-current flow and a slightly positive pressure between the shell and the lumen side was maintained (P_f-P_s =0.3 bar) to prevent any Cy923 leakage to the shell side. The lab-scale plant worked with 9 L of the feed solution containing 10 mg/L of pharmaceutical contaminants and the stripping solution of 3 L consisted of distilled water at pH= 11.

According to the literature, the concentration range of pharmaceutical residues in aquatic sources is between 0.12 − 1600 ng/L [28] but with the aim to test the feasibility of this method DCF and IBU concentrations were kept at (3.5 −10 mg/L) and the pH at 5.5.

In an effort to increase the stability of liquid membranes, the organic extractant is mixed and dispersed in the stripping phase. The experimental setup is shown in Fig. 3. Pseudo emulsion is highly adapted and

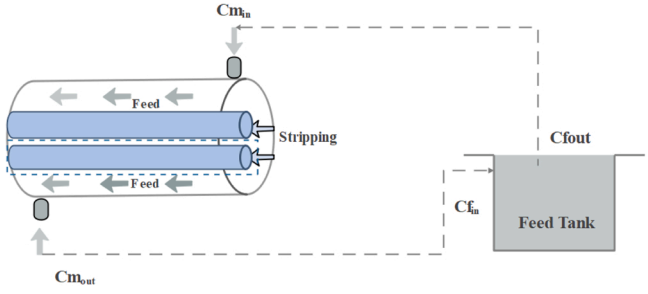

Fig. 2. Mass balance in the feed tank of a HFSLM.

Table 1
Details of Liquid gel liquid membrane G-502 from Liqui-Cel™).

Module diameter (cm)	7.7
Module length (cm)	27.7
Membrane Area (m^2)	1.4
Fibers OD/ID (μm)	300/200
Porosity (%)	40
Tortuosity	1.23
Membrane plotting material	Polypropylene /polyethylene
Hold-up volume shell side (cm^3)	400
Hold-up volume lumen side (cm^3)	150
Number of fibers	10000

strongly favoured when operating with hollow fiber membranes. Feed phase (DCF, 9 L) in one stirred tank and, pseudo-emulsion phase (V_{org}/V_{aq}=1/38) was prepared in the other stirred tank. It involves the addition of a stripping phase (distilled water at pH=11.) with a requisite amount of extractant (preferably three 3times the volume of the membrane pores). The operation mode is similar to HFSLM where the feed and pseudo-emulsion phases were passed at the same flow rate of 47 L/h in the shell and lumen sides, respectively. The organic solution containing the extractant is immobilized in the pores of the hollow fibers due to its hydrophobic nature. The transmembrane pressure was kept at 0.3 bar. DCF molecules form a complex with Cy923 and diffuses through the membrane phase, followed by stripping within the internal phase of the pseudo-emulsion. Consequently, the stripping phase becomes enriched with DCF, achieving a threefold concentration.

At different time intervals, samples are taken from the feed and the stripping phase to measure the evolution of the concentration of pharmaceuticals. DCF from pseudo-emulsion was obtained by breaking and separating the organic and stripping solutions. The stripping phase will be abundant with DCF as it concentrates the pharmaceutical by 3 times.

3.3. Integration of HFSLM and ozonation in a single process

The ozone in the concentrated stream was generated from oxygen by the Anseros ozone generator (COM-AD-04) and introduced at the reactor's bottom through a porous diffuser. The initial concentration of ozone in feed gas was adjusted with a valve mounted on the reactor and the flow was kept constant at 25 NL/h. The solution was continuously mixed with a mechanical stirrer and the diffuser was kept in the middle of the reactor to ensure a uniform distribution of ozone bubbles in the stripping tank. The dissolved ozone was determined with indigo method. The excess gas and gas outflows are forced into an ozone destruction unit containing 2% (w/v) KI solution before releasing it into the atmosphere. During the ozonation experiment, the solution in the reactor is kept at a constant temperature. The solution pH is measured with a pH meter Crison GLP21. The stripping phase containing the pharmaceutical flows through the tubes of the membrane into the ozonation tank, where the dissolved ozone present in the bulk phase reacts with the pharmaceutical contaminants.

Samples were withdrawn from the feed and stripping cells at specific time intervals to evaluate the decay of concentration of the main compound and its by-products formed during the reaction. Total organic carbon (TOC) was measured using a Shimadzu TOC-L model analyzer at the beginning and end of the experiment. The experimental setup is shown in Fig. 4.

3.4. Analytical measurement

The concentration of pharmaceutical compounds and their transformation product were analysed by high-performance liquid chromatography (HPLC, Agilent 1220 infinity series) with a diode array detector at 280 nm or 230 nm for diclofenac, and ibuprofen, respectively. The column used was Zorbax Eclipse Plus C18 (2.1×50mm) and the mobile phase consisted of a mixture of formic acid (25 mM) in water and Acetonitrile at 60:40 (v/v) with a flow rate of 0.2 mL/min and an injection volume of 50 μL. The identification of by-products for IBU and DCF was accomplished with a combination of UHPLC Liquid Chromatograph and a Thermo Scientific™ Orbitrap IDXTribrid mass spectrometer equipped with an ESI interface. The column used was C18 column (4 ×25 mm) supplied by Agilent. Isocratic elution was conducted using a mixture of 25 mM formic acid (A) and acetonitrile (B) at a ratio of 60/40 (A/B), and the total runtime was 15 min. Mass spectrometry detection was performed using heated electrospray ionization settings in both negative and positive ionization modes.

4. Results and discussion

4.1. Removal of pharmaceuticals with HFSLM and PEHFLM

Hollow fiber supported liquid membrane (HFSLM) has been one of the most frequently used for extraction and preconcentration of several types of target analytes. Typical kinetic plots showing the removal of IBU and DCF from water are presented in Fig. 5.

The process is rather fast for DCF since more than 90% removal was transported in less than 1 h and 89% for IBU in two hours with 40% Cy923. The effectiveness of the selected organic solvent is assessed

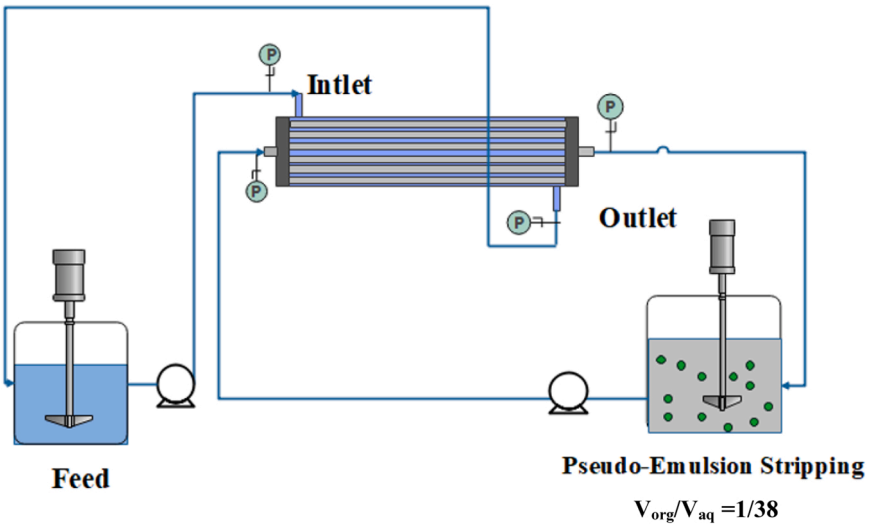

Fig. 3. Experimental setup with pseudo-emulsion in the stripping phase.

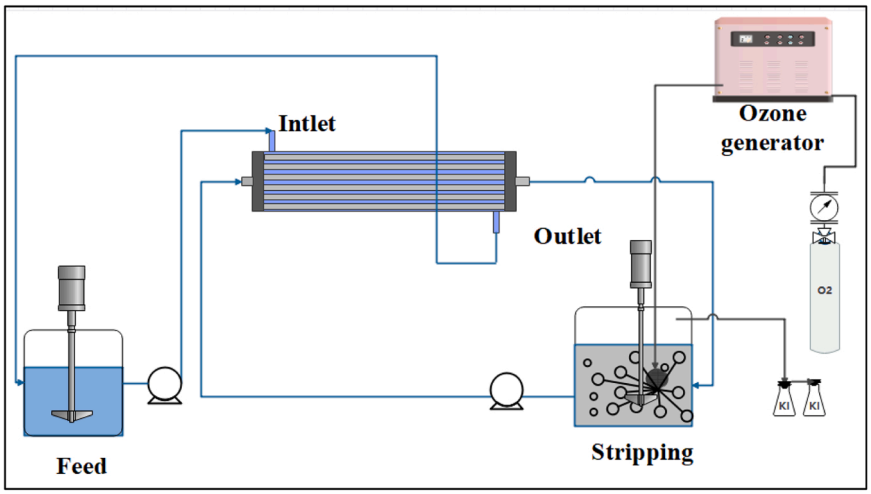

Fig. 4. Experimental setup of HFSLM and ozonation.

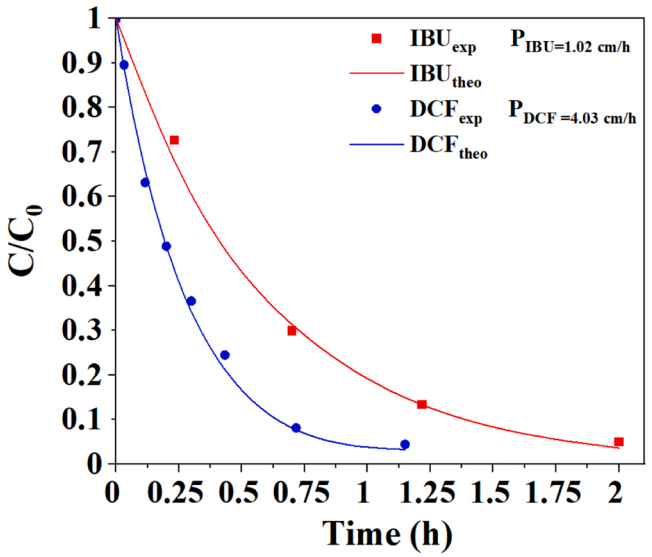

Fig. 5. Pharmaceuticals concentration vs time in HFSLM. (Feed: C_0 =10 mg/L, pH = 5.5; Q= 47 L/h; Organic extractant: 40% (v/v) Cy923/kerosene; Stripping phase: Q= 47 L/h; pH= 11).

based on its ability to efficiently extract the desired solutes. It should also be compatible with the fiber, immiscible with the feed and the stripping phase, and have low volatility (high boiling point) to prevent losses [32]. Madikizela et.al. (2020) have reported the use of hydrophobic organic solvents such as 1-octanol for the enrichment of pharmaceuticals from the aqueous phase [33]. The optimal conditions to transport DCF and IBU were obtained previously with flat sheet module (FSSLM) and thereafter, selected to be applied in the following study to achieve the highest permeability coefficient for both compounds [31]. In flat sheet configuration, the permeability coefficient obtained with 40% (v/v) Cy923 was higher than the permeability coefficients obtained with HFSLM, measuring 11.2 cm/h and 7.2 cm/h for diclofenac and ibuprofen, respectively [31]. This can be attributed to different factors. Initially, the type of polymer and membrane specifications are diverse and it is well understood that the membrane characteristics play a major role in the variation of the permeability coefficients of two different membranes. The permeability coefficient can be related using the diffusion coefficient, the extraction equilibrium constant (k_{ext}), the carrier concentration, the thickness (δ), and the tortuosity(τ), and the porosity (ε) given the following expression [34]:

$$P = D * K_{ext} * \frac{\varepsilon}{\tau * \delta} \quad (8)$$

Similar observations were presented when the permeability coefficient for rare earths was calculated in both flat sheet and hollow fiber-supported liquid membranes [31]. In addition, the effect of Cy923 concentrations ranging from 0.33 to 0.99 mol/L (equivalent to 10–60% v/v) was studied in HFSLM to remove DCF from water. The results obtained in Fig. 6 show a nonlinear increase in the permeability coefficient with extractant concentration. The highest permeability was obtained at 40% Cy923 in kerosene. Using a higher concentration of the organic extractant did not lead to increased permeability, thus confirming that 40% Cy923 is sufficient. Similar findings have been observed in various studies examining the relationship between organic extractant concentration and permeability [34] [35]. These studies indicate that beyond a certain concentration of organic extractant, the permeability does not improve. This occurs because of the increase of the viscosity in the membrane pores.

It can be deduced that the transport of the pharmaceutical was

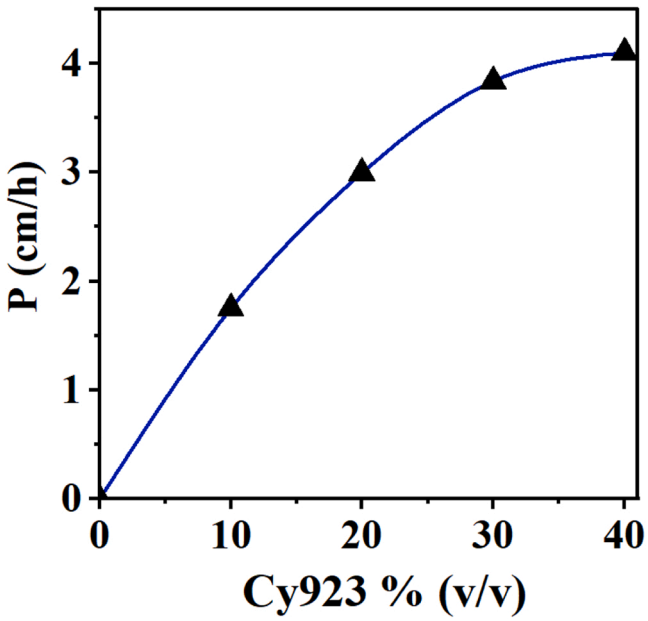

Fig. 6. Effect of Cy923 concentration on the permeability in HFSLM (Feed: C_0 =10 mg/L, pH = 5.5, Q=47 L/h;. Stripping phase: Q= 47 L/h; pH = 11).

governed by the diffusivity effect and by the viscosity [35].

4.2. Stability study

To test the efficiency of HFSLM, several experiments were conducted with diclofenac (10 mg/L), by replacing the feed and the stripping tanks by fresh solutions. Diclofenac was selected for the multiple runs as more than 95% of pharmaceuticals were transported in less than 1 h. The results of successive runs are shown in Figs. 7 and 8. The permeability reaches its minimum value of 0.7 cm/h after five runs. It was also observed a significant shift in removal efficiency after the third run which corresponds to an experimental duration of 3 h. One potential interpretation of results obtained is that when the trans-membrane pressure surpasses the capillary pressure, the organic extractant within the fiber's pores may be displaced, resulting in membrane failure [36]. The instability of SLM is the main key that hinders their industrial application. The major reason for a supported liquid membrane to become unstable is the loss the organic carrier from the pores of the support. This can be caused by several factors such like the pressure difference over the membrane wetting of support pores, and blockage of the pores [36,37]. Several researchers have investigated different methods to increase the stability of SLM, unfortunately, most of these techniques are only applicable to flat sheet membranes which are easily manipulated. To overcome the issue of stability and ensure continuous operations, HFSLM systems are usually upgraded to pseudo-emulsion hollow fiber supported liquid membranes (PEHFSLM). Their main objective is to reduce and limit any possible displacement of organic extractant out of the porous membrane. It is one of the best alternatives that can increase the stability, save time required for cleaning, and improve the performance of the system [36,37].

4.3. Pseudo-emulsion hollow fiber

In the subsequent study, the stripping phase was mixed with 80 mL of Cy923/kerosene. The amount is added accounting the volume of the

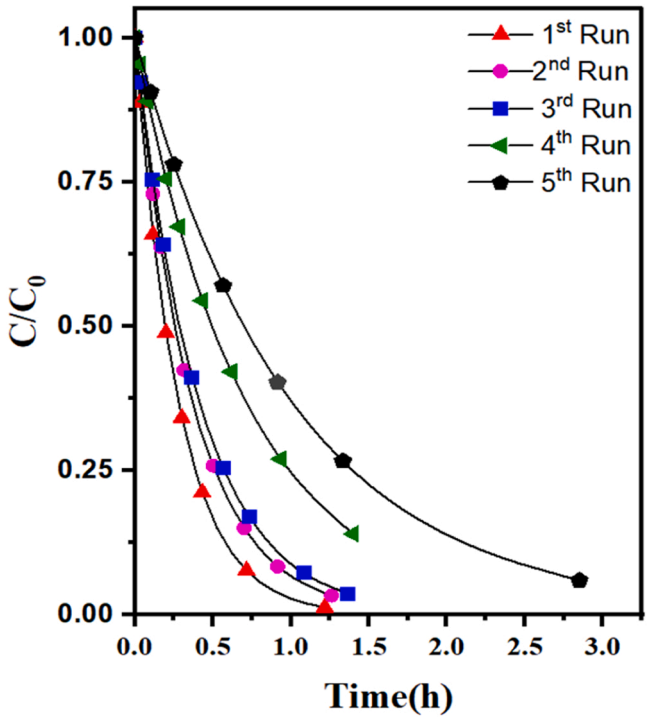

Fig. 7. Concentration change of DCF for successive runs.(Feed: $C_{0=}$10 mg/L; pH = 5.5; Q=47 L/h. Organic extractant: 40% (v/v) Cy923/kerosene. Stripping phase: Q= 47 L/h; pH = 11).

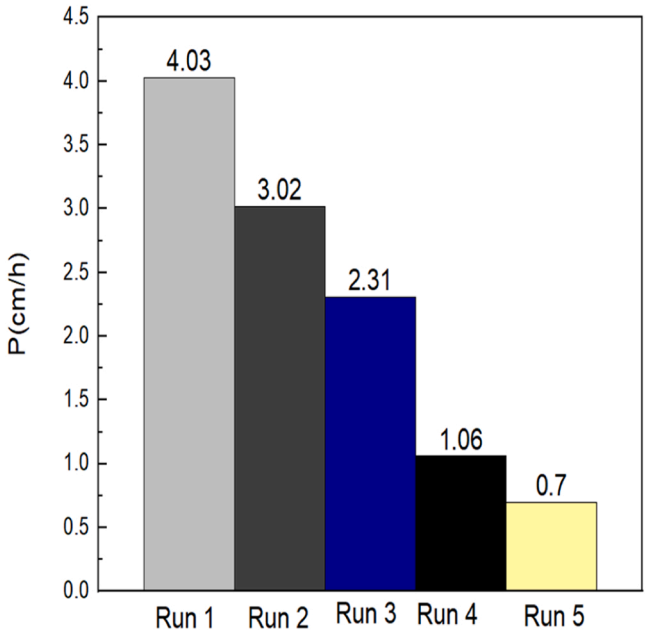

Fig. 8. Permeability obtained for each consecutive run with HFSLM.

membrane to ensure that the pores are completely filled with the organic extractant. The evolution of DCF concentration in the feed and stripping phase for PEHFSLM and HFSLM are presented in Fig. 9. 10 The regeneration of the liquid membrane layer can automatically and continuously replace the loss of organic extractant to counter the liquid membrane instability and prevent its degradation [35]. An efficient approach based on the strip dispersion method was introduced and reported by several studies [10,11,38]. Mixing the organic extractant can tackle the instability of the liquid membrane and improve the recovery efficiency of target analytes [35,38]. SLM strip dispersion system was able to improve the yield of cephalexin removal from 32% to 42% with hollow fiber membrane using Aliquat 336 as the organic extractant [39].

As shown in the Figs. 8a and 8b the initial transport rate with PEHFSLM is lower compared to the hollow fiber. The permeability obtained for DCF (10 mg/L) with 40% Cy923 was 2.04 cm/h. Diclofenac at a concentration of 10 mg/L was successfully extracted within a two-hour period with pseudo emulsion, and the diclofenac was concentrated in the stripping phase. After the two-hour extraction period, the highest concentration recuperated were 21 mg/L for HFSLM and 19.5 mg/L for PEHFSLM.

Nonetheless, after 6 consecutive runs, the transport rate was maintained and the permeability coefficient obtained was between 2.04 and 2.11 cm/h.

The overall mass transfer for the diffusion process in hollow fiber membrane depends on three mass transfer resistances [40]: the aqueous boundary layer formed on the internal side of the fiber, the diffusion of the DCF-carrier complex across the liquid membrane, and the aqueous boundary layer formed on the external side of the fiber [39,40]. Several operational parameters can affect the performance of pseudo emulsions such as the size of droplets size and their distribution. This decrease of the overall permeability is due to a lower interfacial coefficients for the internal and external aqueous boundary layers. Similar observations were reported with when comparing peudo-emulsion hollow fiber strip dispersion and aqueous stripping phase to remove diclofenac with Di-2-ethylhexyl phosphoric acid. Although the stability was maintained, the permeability was lower [41]. Moreover, when it comes to recycling battery waste, the use of Cy923 in the emulsion phase during the stripping process shows a comparable pattern of initial transport rate reduction. [34].

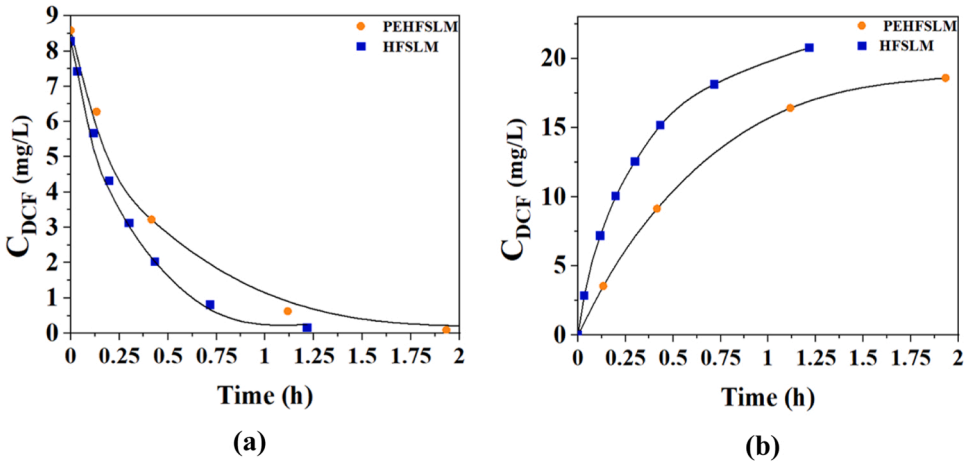

Fig. 9. Comparison between HFSLM and PEHFSLM in (a) Feed phase: $C_{0=}$10 mg/L, pH = 5.5, V= 9 L,Q= 47 L/h. Organic extractant: 40% (v/v) Cy923/kerosene and (b) stripping phase: V= 3 L; Q= 47 L/h; pH = 11).

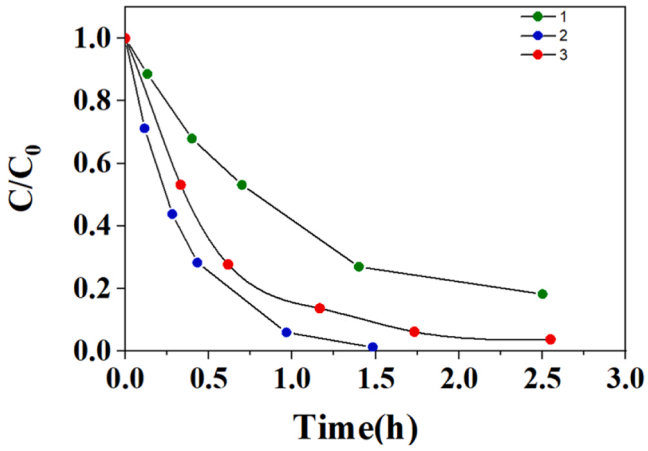

Fig. 10. Recyclability of pseudo-emulsion phase.(Feed Phase: C_0 =1 mg/L,V= 9 L, Q=47 L/h, pH=5.5; Organic extractant: 40% (v/v) Cy923/kerosene; Stripping phase: V= 3 L, Q= 47 L/h, pH= 11, Vorg/Vaq= 1/38).

4.4. Recyclability of pseudo-emulsion phase

In the aim to make the process more economical, the regeneration of stripping phase was investigated. The recycling operations were carried out with optimum conditions. The recyclability of the pseudo-emulsion stripping phase was examined by contacting the fresh feed (1 mg/L DCF, 9 L) with the same stripping solution for three consecutive runs. (3 L). DCF extraction from the feed are shown in Fig. 9. During the 3rd run, DCF removal decreased by ~79% when the fresh feed was contacted with the pseudo-emulsion phase compared to the removal efficiency obtained from 1st run. Extraction efficiency decreased due to a decrease in the concentration gradient of DCF molecules. Kohli et al. (2019) conducted a study on the recyclability of the pseudo emulsion phase to remove endocrine-disrupting compounds from water. The findings revealed that the removal efficiency decreased to 43% after the third run within a total time of 120 min [42]. Hence, several factors could contribute to this observation. One possibility is that the stripping phase becomes saturated and reaches its maximum capacity to extract further substances. Another factor could be the alteration of the solvent composition due to its solubility in the aqueous phase.

4.5. Ozonation and generation of by products

Ozone was introduced in the stripping phase (pH = 11 and V = 2 L) therefore the indirect reaction of ozone is favoured through generation of hydroxyl radicals [43]. A preliminary series of experiments was done to select the initial ozone concentration, the inlet ozone concentration was set at 10 mg/L and the gas flowrate at 25 NL/h. A pharmaceutical containing feed solution with initial concentration of 10 mg/L was extracted from the shell side into the lumen side of the membrane. The concentrated stream was subsequently exposed to ozone to eliminate diclofenac and ibuprofen respectively. The reaction of diclofenac with $OH^{\bullet}$ radical is very fast; therefore, the diclofenac transported through the membrane was completely eliminated after 10 min. On the other hand, the conversion of ibuprofen was at a lower rate since the concentration of ibuprofen transported from the feed was still detected after ozonation. The degradation of pharmaceuticals with ozone was previously studied and diclofenac is proven to be highly reactive with ozone [25,43].

The reaction of ozone with diclofenac and ibuprofen can result in the formation of intermediates and by-products which further undergo transformation or mineralization. The expected attack site after identifying the by-products by LC-MS for each of diclofenac and ibuprofen are shown in Fig. 11, Tables 2 and 3.

The degradation of DCF through ozonation is quite fast as evidenced by the absence of detectable traces of the pharmaceutical in the stripping phase at the end of the experiment. The reaction of ozone with diclofenac involves the hydroxylation reaction. This reaction leads to the incorporation of one or more oxygen atoms into the diclofenac molecule, indicating the formation of hydroxylated byproducts [45,46]. 5-Hydroxydiclofenac (BP1) is a significant hydroxylated compound formed during the degradation of diclofenac. This by-product is generated when a hydroxyl group (-OH) is added to the diclofenac molecule through a hydroxylation reaction In the case of ibuprofen degradation, multiple reactions contribute to its breakdown, including hydroxylation, decarboxylation, and demethylation [48]. The hydroxylation reaction results in the addition of a hydroxyl group (OH) or an oxo group to the ibuprofen molecule. LC/MS analysis of the degradation products revealed the presence of prominent by-products, notably 4-ethyl benzaldehyde (BP3) and 2-[4-(1-hydroxy-2-methylpropyl) phenyl] propionic acid (BP1).

4.6. Degradation of by-products in the stripping phase

The effect of ozone on DCF and IBU and their transformation products was investigated individually. The concentration changes of both transformation products were monitored and the results are presented in Figs. 12 and 13. The by-products shift during the reaction as some compounds decrease while new ones are formed. Initially, BP1 (5

Fig. 11. Expected attack site of pharmaceuticals toward molecular ozone.

Table 2
Mass spectrometry-Liquid chromatography (MS-LC) data for diclofenac oxidation products.

Compound	High Resolution Ms data [M-H]⁻	Retention time (min)	Molecular Formula	Reference
DCF	295.02	10.4	$C_{14}H_{11}NO_2Cl_2$	This study
BP1	310.02	3.7	$C_{14}H_{12}NO_3Cl_2$	[44–46]
BP2	308.99	2.94	$C_{14}H_{10}NO_3Cl_2$	[45,46]
BP3	326.01	1.46	$C_{14}H_{12}NO_4Cl_2$	[44,45]
BP4	326.01	1.74	$C_{14}H_{12}NO_4Cl_2$	[44–46]
BP5	284.01	3.0	$C_{12}H_{10}NO_3Cl_2$	[45,46]
BP6	279.91	1.62	$C_{13}H_{10}NO_2Cl_2$	[44]
BP7	277.05	1.62	$C_{14}H_{10}NOCl_2$	[45,46]
BP8	296.95	3.05	$C_{13}H_{10}NO_3Cl_2$	[45,46]
BP9	258.95	1.39	$C_{10}H_8NO_3Cl_2$	[44,46]

Table 3
Mass spectrometry-Liquid chromatography (MS-LC) data for ibuprofen oxidation products.

Compound	High Resolution Ms data [M-H]⁻	Retention time (min)	Molecular Formula	Reference
IBU	205	13.2	$C_{13}H_{18}O_2$	This study
BP1	221.12	4.65	$C_{13}H_{17}O_3$	[47,48]
BP2	177.13	3.05	$C_{12}H_{17}O$	[47,48]
BP3	133.07	3.5	C_9H_9O	[47,48]

hydroxydiclofenac) was found in the greatest abundance indicating that the DCF degradation is initiated by the hydroxylation of the phenylacetic ring. After three hours of continuous ozonation in the stripping side, the concentration of BP1 reached a minimum level and the parent compound was removed completely. Regarding ibuprofen (Fig. 12), the rate of degradation when exposed to ozone at pH 11 is comparatively slower than that of DCF. Even after continuous ozonation for 4 h, a minimal amount of the transported ibuprofen can still be detected in the stripping phase (0.3 mg/L). In addition, The reaction rate of the detected by-product when exposed to ozone was initially slow which is in accordance with Huang et al. (2015) in which they studied the process of ozone disinfection of ibuprofen.[49].

Assessing the mineralization efficiency of pollutants such as ibuprofen (IBU) and diclofenac (DCF) is of paramount importance for environmental considerations. The highest TOC removal efficiency measured at the end of reaction time was 72% for DCF while for IBU the TOC decreased by 57% after 5 h. Ozone can initiate oxidation reactions that break down organic compounds into simpler inorganic forms through a process called mineralization [50]. It is important to note that the mineralization process involves the complete decomposition of organic molecules, typically through the successive oxidation of their chemical bonds which requires sufficient exposure time and ozone concentration. The specific conditions necessary for complete mineralization can vary depending on factors such as ozone concentration, temperature, pH, and the presence of other chemical species. Environmental factors and wastewater characteristics play a significant role in determining the extent of mineralization [51,52]. In another study by Hama et al. (2017), TOC removal efficiency peaked during the degradation of DCF using a photocatalytic ozonation process [53]. Additionally, Olak et al. (2021) demonstrated the effectiveness of ozonation for the degradation of ibuprofen and its derivatives with an initial ozone concentration of 11.38 mg/L, they achieved a removal of 91.52% and 98.43% for IBU and its metabolite OHIBF, respectively, and a corresponding 44% removal of TOC [54]. Another study compared the mineralization percentage of IBU using ozone alone and catalytic ozone, reporting a 55% TOC removal efficiency at an initial concentration of 10 mg/L with solely ozone. [55]. Removal efficiency and mineralization rate can be further enhanced by combining ozonation with different catalytic reactions to promote the elimination of persistent pharmaceutical contaminants.

5. Conclusions

The application of a hollow fiber liquid membrane, containing 40% Cy923, has demonstrated high efficiency in extracting diclofenac and ibuprofen from aqueous solutions. The system's stability has been significantly improved through the incorporation of a pseudo emulsion, enhancing its longevity and extraction efficiency. Moreover, the solvent used in the process can be recycled indefinitely unless it degrades or its solubility increases. It is recommended to introduce fresh solutions of organic extractant after the second run. The integration of the hollow fiber membrane system with ozonation in a single step has led to a significant reduction in the concentration of diclofenac and ibuprofen, along with their abundant by-products 5-hydroxydiclofenac and 4-ethybenzaldehyde, enabling the degradation of the extracted pharmaceutical compounds and other organic pollutants in the system. The results show that high mineralization of 72% was achieved for diclofenac and around 52% for ibuprofen at the end of experiment time, thus improving overall water quality. Despite the generation of ozone- by-products, this approach, which includes hollow fiber liquid membrane extraction, improved pseudo-emulsion stability, and ozonation, provides a promising solution for detecting and selectively treating pharmaceutical contaminants found at low concentrations.

CRediT authorship contribution statement

Mary Farah: Methodology, Software, Validation, Investigation, Writing – Original Draft, Writing – Review & Editing; **Agustín Fortuny**: Conceptualization, Methodology, Formal analysis, Writing – Review & Editing Supervision, **Jaume Giralt**, Writing – Review & Editing, **Frank Stüber** Writing – Review & Editing, **Azael Fabregat:** Review & Editing –Supervision **Josep Font** Writing – Review & Editing, Project administration funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

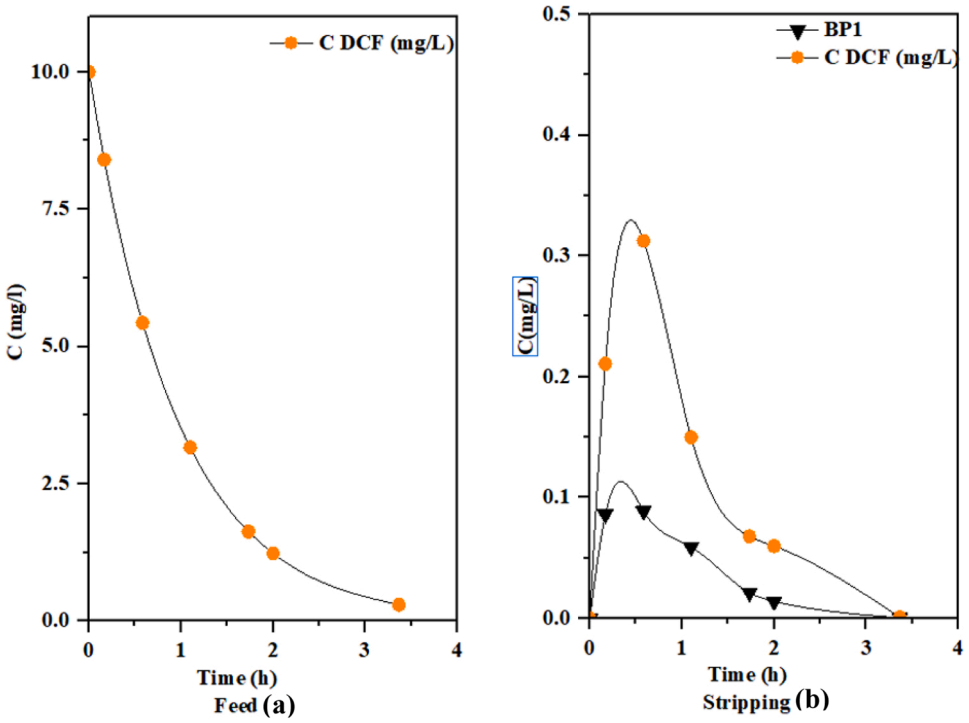

Fig. 12. Concentration of DCF and by-product BP1 in (a) Feed: C_0 = 10 mg/L, V= 9 L, Q= 47 L/h, pH= 5.5; Organic extractant: 40% (v/v) Cy923/kerosene (b). Stripping phase: V= 2 L; pH= 11; Q= 47 L/h; Inlet ozone concentration 10.2 mg O_3/L.

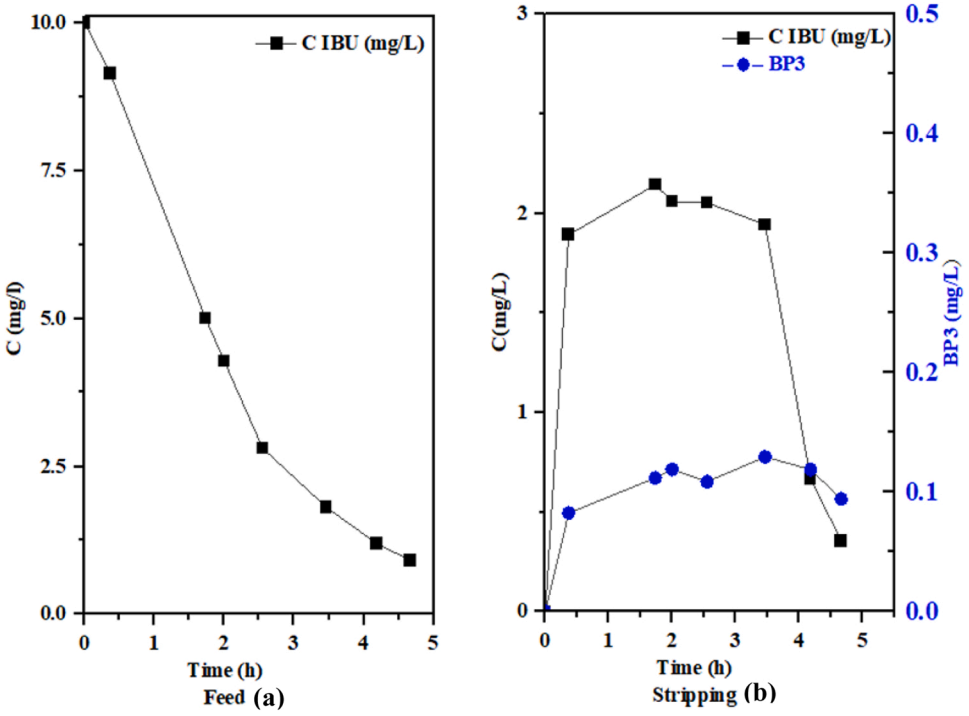

Fig. 13. Concentration of IBU and by-product BP3 in (a) Feed: C_0 = 10 mg/L, V= 9 L, Q= 47 L/h, pH= 5.5; Organic extractant: 40% (v/v) Cy923/kerosene (b). Stripping phase: V= 2 L; pH= 11; Q= 47 L/h; Inlet ozone concentration 10.2 mg O_3/L.

the work reported in this paper.

Data Availability

Data will be made available on request.

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