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Extraction of Nitrophenols Using Pseudo-emulsion Based Hollow Fiber Strip Dispersion

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Abstract. The extraction of nitrophenols from aqueous solutions through a pseudo-emulsion hollow fiber strip dispersion (PEHFSD) system were conducted in a microporous hydrophobic polypropylene hollow fiber membrane contactor. The study had focused on the effects of various parameters, viz., feed and pseudo emulsion phase flow rates, types of carrier and concentration etc. Effect of multiple cycles using the same pseudo-emulsion on nitrophenols extraction was also analyzed. Almost 99% extraction of all three nitrophenols (individually) was achieved at optimum conditions.

Keywords: Nitrophenol Extraction, Pehfsd System, Feed and Pseudo Emulsion Phase Flow Rates, Carrier Concentration.

1. Introduction

Para-nitrophenol (PNP) is an important intermediate in dye and pesticide synthesis. In this role PNP contaminates large amounts of water; water that eventually must be treated or disposed off [1]. It is a typical biorefractory organic compound and considered to be one of the 114 priority toxic pollutants by US Environmental Protection Agency. Nitrophenol is highly toxic and resistant to biological treatment, so it is very important to treat nitrophenol before discharging with waste stream. In degradation methods, nitrophenols are converted into substances that are nontoxic and satisfactory for release to the environment. The main disadvantage of these degradation methods is the high cost because of the large consumption of chemicals (as in chemical degradation) or major investment in land requirement (as in biological treatment).

The liquid membrane process was used for the removal of phenol from wastewater and also for the treatment of formulated and real wastewater containing *o*-nitrophenol (ONP), m-nitrophenol (MNP) and *p*-nitrophenol (PNP) [2,3]. Supported liquid membranes (SLMs) are also very effective for the removal and recovery of nitrophenol from waste waters as they are also associated with simultaneous extraction and stripping [1-4]. In last 5 years, hollow fiber supported liquid membranes (HFSLMs) were used effectively for the separation of various metal ions, phenols, nitrophenols and its derivatives [5-8]. Despite these advantages, three major limitations in applying HFSLM are fouling of suspended or dissolved substances on the surface of the hollow fibers, instability and long-term performance of SLM and HFSLM are the important issue for industrial applications [9]. In view of this, recently, a more stable technique, that is Pseudo-emulsion hollow fiber strip dispersion (PEHFSD) technique, has been developed which utilized the merits of LM techniques and suitable for industrial use.

Till date, no investigations is reported for the removal of nitrophenols through the PEHFSD, so an effort has been made to investigate the behavior of the PEHFSD system for the extraction of p-nitrophenol from aqueous solution using NaOH as stripping solution and Trioctylmethyl ammonium chloride, Tri butyl phosphate and Tri Octyl amine as carriers. The influence of the various process variables, such as feed and pseudo emulsion phase flow rates, types of carrier and concentrations on the transportation of nitrophenol

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molecule in the PEHFSD system have been studied. Extraction of o-nitrophenol and m-nitrophenol are also carried out using same optimum conditions.

2. Experimental

2.1. Materials and method

The chemicals used in the study for the transport of Nitrophenols through PEHFSD were p-Nitrophenol, m-Nitrophenol and o-Nitrophenol (Loba Chemie, Mumbai, India). For the preparation of pseudo-emulsion, n-hexane (Finar chemicals, Ahmedabad, India) of specific gravity 0.6548 g mL^{-1} and viscosity of 0.294 cP, containing carrier like Tri butyl phosphate (TBP) (Otto Kemi, Mumbai, India), Trioctylmethyl ammonium chloride (TOMAC) (Merck, Mumbai, India) and Tri Octyl amine (TOA) (Merck, Mumbai, India) in membrane phase and NaOH (Finar, Ahmedabad, India) in stripping phase were used. 1-Decanol (Otto Kemi, Mumbai, India) to dissolve TOMAC in the n-hexane and sulfuric acid (Merck, India) are used to maintain the pH of the feed phase.

2.2. HFSLM experiments

In order to prepare HFSLM, the preferred organic solvent has been circulated in the tube side of the module for at least 45 min. During this period of time the outlet pressure of the tube side is maintained at 5-10 psi so that the solvent has been passed through the micro pores of the fibers and come out through the shell side of the module. This phenomenon is performed to ensure that the solvent is embedded in the micro pores of the fibers. The excess organic solvent has been removed by circulating distilled water at zero pressure on both sides (i.e. Tube side and shell side) of the membrane. The feed solution and the stripping solution are then pumped counter currently into the tube side and shell side of the HFSLM, respectively, in recycle mode at zero pressure.

2.3. PEHFSD experiments

The PEHFSD process comprises a single membrane contactor for extraction and stripping. One stirred tank is used for preparing and as a reservoir of the pseudo-emulsion containing carrier + n-hexane and NaOH and another stirred tank as a feed phase reservoir. The experimental conditions are shown in Table 1. The hollow fiber device used for the investigation was obtained from membrane: Celgard ® X50-215 [9]

Table 1: Experimental conditions for PEHFSD system.

Pseudo-emulsion phase	Membrane phase + Stripping phase
Membrane phase	n-Hexane
Carrier	Tri butyl phosphate (TBP) (varied from 0.5 to 1.5% w/v)
Stripping phase	NaOH (varied from 0.01 to 1.0 M)
Flow rate of pseudo emulsion through PEHFSD	200 mL/min
Stirring speed in pseudo emulsion tank	700 rpm
Volume of pseudo-emulsion	600 mL
Feed phase Aqueous solution	p-nitrophenol (varied from 25 to 75 mg L^{-1})
Flow rate of feed through PEHFSD	300 mL/min
Stirring speed in feed tank	Maintained at 300-350 rpm
Feed: strip ratio	5:1 (22)
pH (Feed phase)	2.5

The experimental set-up also contained two gear pumps of variable flows for both phases and flowmeters. The organic solution wets the porous wall of the fiber because of its hydrophobic nature. The interface is maintained at the mouth of the pores by applying a higher pressure to the feed side (tube side) than to the pseudo-emulsion side (shell side). The differential pressure should always be kept below the breakthrough pressure. In the present case, the pressure of the feed side is 2.5 psi higher than in the pseudo-emulsion phase. The operation is carried out by passing an acidic aqueous feed containing PNP through the tube side and pseudo-emulsion through the shell side in countercurrent recirculation mode. The feed reservoir tank and the

pseudo-emulsion reservoir tank are stirred to homogenize the solution and to maintain the homogeneity of the pseudo-emulsion respectively. The recovery of PNP from pseudo-emulsion can be accomplished by breaking down the pseudo-emulsion and separating organic and stripping solutions. The recycle mode of a single-module HFSLM operation is shown in Fig. 1.

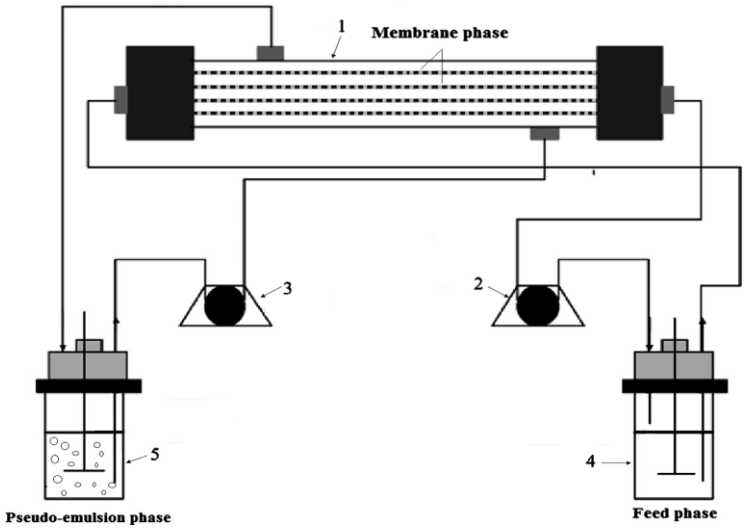

Fig. 1: Schematic view of pseudo-emulsion hollow fiber strip dispersion system operated in recycling mode for p-nitrophenol extraction from aqueous solution: (1) hollow fiber contactor; (2) feed pump; (3) pseudo-emulsion pump; (4) feed reservoir with stirrer; and (5) pseudo-emulsion reservoir with mixing arrangement; volume of feed: 1500 mL, organic phase: 300 mL and stripping phase: 300 mL.

A small volume of the aqueous streams was taken at different time intervals and analyzed for PNP concentration by UV-vis spectrophotometry (HACH make, Germany) at 317 nm wavelength. The percentage extraction of p-nitrophenol through PEHFSD can be evaluated by:

$$\%Extraction\,(Y) = \frac{[PNP]_{f,t=0} - [PNP]_f}{[PNP]_{f,t=0}} \times 100 \tag{1}$$

Reproducibility of the results was checked and found to be satisfactory using three sets of data.

The equations describing the material balance for PEHFSD system would result in the following equation, which shows first-order kinetics:

$$V_f \left(\ln \frac{[PNP]_{f,t=0}}{[PNP]_f} \right) = St \tag{2}$$

where S is the coefficient dependent on the linear velocity of the fluids, the geometry of the fibers and module the overall permeability of the system and V_f Volume of the feed (cm^3). This overall permeability can be obtained for the system running in the recycling mode, from the experimental values of the slope S, as :

$$P_{PNP} = \frac{-Q_f}{2\pi r_i LN} \left[\ln \left(1 - \frac{S}{Q_f} \right) \right] \tag{3}$$

where L, Length of fibre (cm), N number of fiber in module, P permeability coefficient (cm s^{-1}), Q_f total flow rate of feed solution flowing through tube side ($cm^3 s^{-1}$), r_i internal radius of hollow fiber membrane(cm).

3. Results

3.1. Effects of feed and pseudo emulsion phase flow rates of PNP transport

In order to attain effective permeation of PNP in a PEHFSD system, it is necessary to examine the effect of the feed flow and strippant flow on permeability coefficients. For that a series of experiments were

conducted, keeping PNP concentration at 25 ppm in feed phase, the NaOH concentration of 1 M in stripping phase and n-hexane with 0.5% (w/v) TBP as membrane phase to acquire satisfactory hydrodynamic conditions.

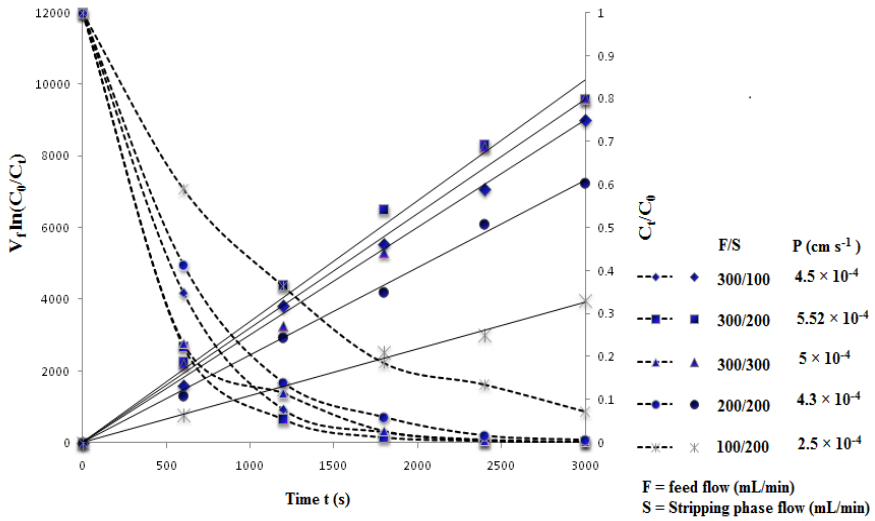

Fig. 2: Effect of feed and pseudo emulsion phase flow rates on the extraction of p-nitrophenol through PEHFSD.

The permeability coefficient was studied as a function of the flow in the feed and strippant solutions. The obtained results are shown in Fig. 2 in terms of permeability coefficient and extraction efficiency, respectively. The increase of the permeability coefficient with the increase of feed flow was due to decrease in the thickness of the aqueous feed boundary layer and aqueous strippant boundary layer, whereas the decrease of P_{PNP} value might be because of lower residence time at higher flow rates, which provided insufficient time for solute to react with the strippant. Agarwal et al. [10] noticed similar result in the recovery of Cu(II) from sulphate solutions using PEHFSD. From Fig. 2, it is observed that permeability coefficient is more dependent on the feed flow as compared to the strippant flow. Thus, 300 cm^3 min^{-1} of feed flow and 200 cm^3 min^{-1} of strippant flow were taken as optimum hydrodynamic conditions for further experiments.

3.2. PEHFSD system versus HFSLM system

To determine the advantages and uses of the pseudo emulsion hollow fiber strip dispersion (PEHFSD) system over the hollow fiber supported liquid membrane (HFSLM) system, the experiments were conducted by keeping PNP concentration at 25 ppm in feed phase, the NaOH concentration of 1 M in stripping phase and n-hexane with 0.5% (w/v) TBP as membrane phase in both of the systems. It was observed that PEHFSD system extracted more p-nitrophenol over the HFSLM system during the 40 min of time span due to stability of the pseudo emulsion membrane. Thus, on the basis of operational stability, PEHFSD is more preferable as compared to HFSLM. Sheng et al. [11] also observed the same result in the recovery of fumaric acid by hollow-fiber supported liquid membrane with strip dispersion using trialkylamine carrier.

3.3. Effect of types of carriers and carrier concentrationon the extraction of PNP

In this series of experiments, three different carriers like TOMAC, TOA and TBP were used in order to choose the right one for the transport of the PNP. The experiments were carried out in PEHFSD by keeping PNP concentration at 25 ppm in feed phase, the NaOH concentration of 1 M in stripping phase and n-hexane with 0.5% (w/v) of the respective carrier in membrane phase. In case of TOMAC, 2.0 % (v/v) of n-decanol was also added in the membrane phase to avoid the formation of third phase. From Fig. 3, it was observed that TBP as a carrier extracted maximum amount of PNP (99% within 40 min) and showed highest permeability (P_{PNP} $\times 10^4$ cm s^{-1} = 5.52) as compared to TOMAC and TOA (0.639 and 0.223).

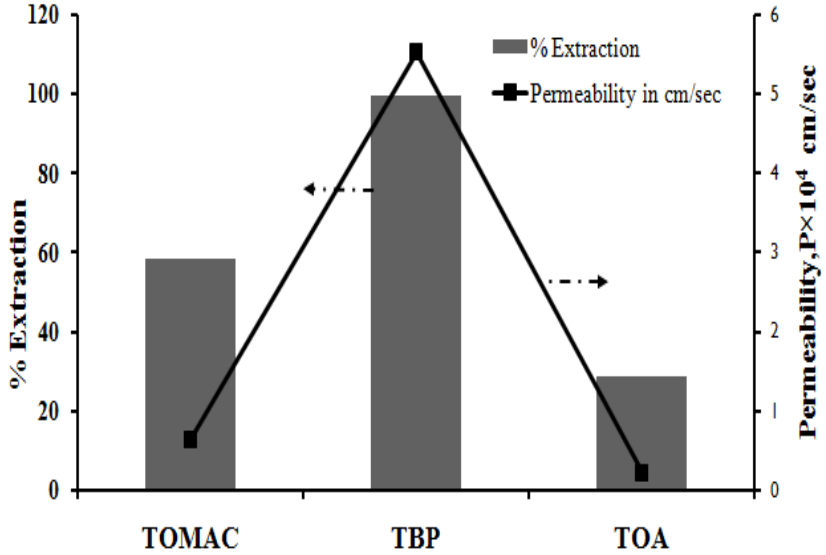

Fig. 3: Effect of carriers on the extraction of p-nitrophenol through PEHFSD.

3.4. Effect of multiple cycles

Multiple operations of the PNP extraction using the same strip solution were conducted under optimum process conditions to increase the concentration of PNP in the strip solution and to examine the availability of the extraction module for cyclic use, which minimizes time and efforts of module cleaning, drying and reassembling. In this experiment, the feed solution was replaced at each cycle of five hours of extraction operation. It was observed that up to four cycles, there was no considerable drop in the PNP transport rate through PEHFSD.

3.5. Facilitated transport of o-nitrophenol and m-nitrophenol through PEHFSD system

So far, the study of extraction of p-nitrophenol through PEHFSD was investigated using tri butyl phosphate as a carrier, n-hexane as an organic solvent and NaOH as a stripping reagent.

Table 2: Facilitated transport of nitrophenols through PEHFSD.

Type of nitrophenol	Organic solvent used	Carrier used	Ratio of feed to strippant flow	Feed concentration in mg/L	Carrier concent-ration % (w/v)	Stripping phase concentration (M)	% Removal of Nitro-phenols
p-nitrophenol	n-hexane	TBP	300/200	25	1.5	1	99.12
o-nitrophenol	n-hexane	TBP	300/200	25	1.5	1	99.41
m-nitrophenol	n-hexane	TBP	300/200	25	1.5	1	99.23

The parameters optimized were feed and pseudo emulsion flow rates, types of carrier and carrier concentration. The facilitated transport of the of the o- and m-nitrophenols through PEHFSD system have been also studied using optimum conditions of all parameters obtained from the above study. The results obtained are tabulated as shown in Table 2.

4. Conclusion

The present study demonstrates the feasibility of the PEHFSD technology for the extraction and recovery of p-nitrophenol from the aqueous solutions employing various carriers such as Tri butyl phosphate (TBP), TOMAC and Tri Octyl amine. Among these, Tri butyl phosphate was found to be the best carrier in the extraction of the p-nitrophenol from the aqueous solutions. Effects of other parameters, viz., feed and pseudo emulsion phase flow rates, carrier concentration etc were also studied. Almost 99% extraction of all three nitrophenols (individually) was achieved at optimum conditions.

6. References

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