

Micellar enhanced ultrafiltration of eosin dye using hexadecyl pyridinium chloride

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Abstract

Surfactant-based separation of toxic eosin dye is studied to estimate the potential of micellar enhanced ultrafiltration (MEUF) using cetyl(hexadecyl) pyridinium chloride (CPC) as the cationic surfactant. The optimum feed CPC concentration is found from the experimental results of pure CPC solution in a batch cell. It is in the range of 10–20 kg/m³ to have a reasonable permeate flux and lower surfactant concentration in the permeate. Selecting 10 kg/m³ as the feed surfactant concentration, MEUF experiments are conducted to study the retention characteristics of eosin dye in the continuous cross flow system. The effects of operating conditions, i.e., feed dye concentration, operating pressure and cross flow rate on the permeate flux and observed retention of dye are investigated.

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1. Introduction

Various types of dyes are manufactured for printing and dyeing industries from coal tar based hydrocarbons such as benzene, naphthalene, toluene, etc. During the past 35 years, India has become a major producer of dyes. Most of these dyes are harmful, when brought in contact with living tissues for a long time. The discharge of these to the river stream without proper treatment causes damage to the crops and living beings, both aquatic and terrestrial. Most red inks are dilute solutions of eosin dye. It is also used in wool and silk to give red colour with a yellow fluorescence [1]. Removal of the unused dye from the effluent is a difficult requirement faced by the textile finishing, dye manufacturing, pulp and paper industries.

Many investigators have studied various techniques for removal of colored dye from wastewater, e.g., chemical coagulation/flocculation [2], different advance oxidation processes [3], ozonation [4], nanofiltration [5–10] and adsorption on (i) sludge of wastewater treatment plant [11]; (ii) different bentonites [12,13]; (iii) different types of activated carbon [14]; (iv)

fly ash [15], etc. Due to low biodegradability of dyes, a conventional biological wastewater treatment process is not very efficient in treating dye wastewater [16]. Traditional methods for the separations and/or concentration of the dye to a satisfactory level are generally energy intensive. Therefore, it is desirable to develop a low energy separation process.

Rate governed separation processes, like reverse osmosis (RO) and nanofiltration (NF) are already recognized as better technique for the separation of several inorganic and organic compounds. Permeability of RO membranes is quite low and thus to get desired throughput (permeate flux), high operating pressure is required. Therefore, a modified membrane separation process can be a competitive alternative where operating pressure requirement is low. Micellar enhanced ultrafiltration (MEUF) is one such promising technology that employs surfactant micelles to solubilize inorganic and organic contaminants from the aqueous stream [17–25]. One can also think of applying MEUF as a polishing step after NF. Apart from the experiments on MEUF of organics, MEUF can successfully be used to separate toxic dye [26,27]. The factors that determine the extent of solubilization of organic and inorganic compounds in the micelles are the structure and ionic character of both the solute and surfactant molecules and the medium of the solute–surfactant system [28]. In MEUF, the solute–

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containing stream needs to be treated with a surfactant stream with a concentration well above the critical micellar concentration (CMC). Most of the organic solute molecules are solubilized in the micelles. Micelles being larger in size can be removed along with the solubilized organic contaminants using a relatively porous membrane at lower operating pressure. The permeate stream contains unsolubilized solutes and free surfactants. In order to make the MEUF system more economical, our present research also includes a two step chemical treatment process for the recycling of the surfactant molecules present both in the retentate and permeate stream before its final disposal [18,19].

In the present work, separation of toxic eosin dye from aqueous stream based on MEUF using continuous cross flow cell is studied. From the batch cell experiments involving only CPC solution, the range of the optimum surfactant dose is determined so that minimum surfactant concentration is obtained in the permeate stream. To improve the permeate flux, continuous cross flow MEUF experiments are conducted. The effects of various operating parameters, like, feed dye concentration, transmembrane pressure drop and cross flow rate on the permeate flux and observed retention (of dye) have also been studied.

2. Experimental

2.1. Materials

The surfactant cetyl pyridinium chloride (CPC, MW: 358.01) is procured from SISCO Research Laboratories, Mumbai, India and eosin (MW 691.86) is obtained from BDH Laboratories, England. The structure of eosin is shown in Fig. 1.

2.2. Membranes

Organic polyamide membrane of molecular weight cut-off (MWCO) 1000, obtained from Permionics, Borada, Mumbai, India, is used for all the MEUF experiments in both the batch and cross flow cell. The membrane material is hydrophilic in nature and is used without any further treatment. Pure water flux at various operating pressures is measured and the membrane permeability is determined from the slope of the flux versus pressure plot. The value of the membrane permeability is found to be 3.57×10^{-11} m/Pa s. A rectangular cell is used for the cross flow experiments.

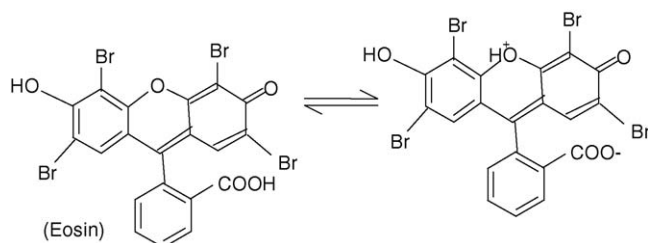


Fig. 1. Structure of eosin dye.

2.3. Experimental set up

2.3.1. Batch cell

The unstirred batch experiments are conducted in a 50 ml capacity filtration cell (MILLIPORE, model 8050, USA). Inside the cell, a circular membrane is placed over a base support. The effective membrane area is 13.4×10^{-4} m². The maximum allowable pressure is 518 kPa. The permeate is collected from the outlet of the cell at the bottom. The cell is pressurized by nitrogen. The schematic of the experimental set up is shown elsewhere [27].

2.3.2. Cross flow cell

A rectangular cross flow cell, made of stainless steel, is designed and fabricated. The cell consists of two matching flanges. The inner surface of the top flange is mirror polished. The bottom flange is grooved forming the channel for the permeate flow. A porous stainless steel plate is placed on the lower plate to provide mechanical support to the membrane. A teflon gasket is placed over the membrane. The effective length of the membrane is 37.3×10^{-2} m and width is 5.2×10^{-2} m. The channel height after the tightening of the flanges is found to be 3.44×10^{-3} m. The micellar solution with solutes is placed in a stainless steel feed tank of 10 l capacity. A reciprocating pump is used to feed the solution in the cell. The retentate stream is recycled to the feed tank. The permeate stream is also recycled to maintain a constant concentration in the feed tank. A bypass from the pump delivery to the feed tank is provided. The two valves in the bypass and the retentate lines are used to vary the pressure and the flow rate through the cell, independently. The schematic of the experimental set up is available elsewhere [18].

2.4. Operating conditions

Filtration experiments are carried out with (i) only surfactant solution in the batch and cross flow cell and (ii) the mixture of surfactant and eosin with different concentrations and pressure in aqueous solution in the rectangular cross flow cell. The experiments are conducted for about 60 min for the solution of only surfactant. Experiments are designed to observe the effects of the variation in the concentration of surfactant and eosin, transmembrane pressure drop and cross flow rate (for cross flow experiments) on the permeate flux and retention of both eosin and surfactant. Various operating conditions used during the batch and cross flow experiments are given in Table 1.

2.5. Procedure

The fresh membrane is compacted at a pressure of 500 kPa for 3 h using distilled water. The feed solution of each batch is prepared by weighing measured amounts of solute and surfactant and using distilled water. The batch cell is pressurized by nitrogen. Permeate from the bottom of the cell is collected and its cumulative weight is measured with the help of an electronic balance. The density of the permeate stream is measured and the cumulative weights are converted to cumulative volumes. From the slope of the cumulative volume versus time curve, the

Table 1
Experimental conditions for the batch and cross flow cell

Mode of operation	Solute used	Concentration (kg/m)		Pressure (kPa)	pH	Cross flow rate (l/h)
		Surfactant	Eosin ($\times 10^3$)			
Batch	CPC	2, 5, 20, 30, 40, 50	–	345	6.7–6.8	–
		10	–	345, 414, 483	6.75	–
Cross flow	CPC	10, 20, 30	–	345, 414, 483	6.75–6.8	60 ($Re = 630$)
		10	–	345	6.75	30 ($Re = 315$) and 90 ($Re = 950$)
	CPC + eosin	10	4, 5, 20, 30, 40	276	6.8–7.05	30 ($Re = 315$)
		10	10	345, 414	6.92	30 ($Re = 315$)
		10	10	276	6.92	45 ($Re = 475$) and 75 ($Re = 790$)

Table 2
Molar extinction coefficients of different CPC and eosin

Wave length (nm)	Extinction coefficients ($m^3/kg\ cm$)	
	CPC	Eosin
259	3880	10.5
517	28920	75462

permeate flux is obtained as a function of operating time. The permeate concentrations of the collected samples are determined spectrophotometrically. In the cross flow experiments, duration of experiments is 1 h.

After each experiment, the membrane is thoroughly washed, in situ, by distilled water for 15 min. The cross flow channel is dismantled thereafter, and the membrane is dipped in distilled water for about 30 min and washed carefully with distilled water to remove the traces of the surfactant. The cross flow cell is reassembled and the membrane permeability is measured again. It is observed that the membrane permeability remains almost constant between successive runs. All the experiments have been conducted at a room temperature of $32 \pm 2^\circ\text{C}$.

2.6. Analysis

Feed and permeate concentrations of surfactant and eosin are measured by a UV spectrophotometer (make: Thermo Spectronic, USA; model: GENESYS 2). The wavelengths at which maximum absorption occurs are 259 and 517 nm, for CPC and eosin, respectively. The extinction coefficients of CPC and eosin are obtained from the measurements of the pure components and are shown in Table 2. A standard method is used to calculate the concentrations of CPC and eosin from the solution [29]. The observed retention is defined as $R_0 = 1 - C_p/C_0$, where C_p and C_0 are the concentrations in the permeate and feed, respectively.

3. Results and discussions

This section is divided into two parts. Variations of permeate concentration of surfactant and flux during ultrafiltration of only surfactant solution in the batch and cross flow cell at different experimental conditions are discussed in the first part. The second part explains the effects of the operating variables on

the permeate flux and retention characteristic of the dye during cross flow MEUF experiments.

3.1. Ultrafiltration of surfactant solution

3.1.1. Unstirred batch experiments

3.1.1.1. Variation of permeate flux and permeate concentration with time and different pressure at a feed CPC concentration of 10 kg/m^3 . Fig. 2a and b show the variation of permeate flux and

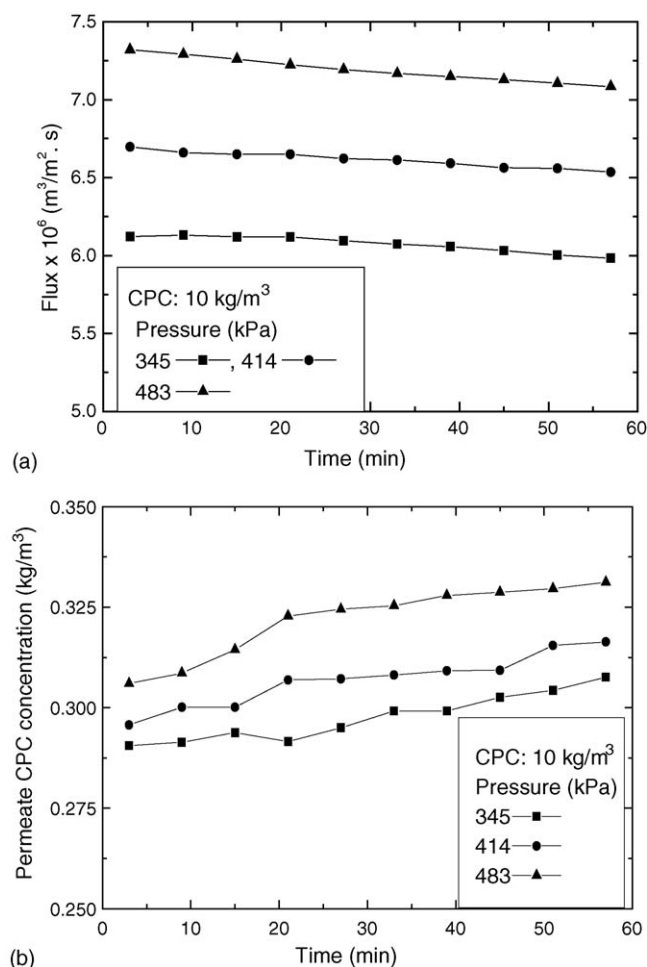


Fig. 2. (a) Variation of permeate flux with time and different pressure at a feed CPC concentration of 10 kg/m^3 . (b) Variation of permeate CPC concentration with time and different pressure at a feed CPC concentration of 10 kg/m^3 .

permeate concentration with time at different pressures and at a typical feed CPC concentration of 10 kg/m^3 . From Fig. 2a, it is observed that permeate flux increases with pressure. It may also be observed in Fig. 2a that the permeate flux decreases marginally with the time of filtration. This is due to the deposition of a layer of aggregated micelles on the membrane surface. Furthermore, the reduction in the feed volume over the time of operation is approximately 60% for various operating pressures. This would also give rise to an increase in feed concentration that may also contribute to the slight decrease in permeate flux over the time of operation. The overall decrease in permeate flux relative to the pure water flux varies with operating pressure. For example, for an operating pressure of 414 kPa, the pure water flux is $14.8 \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s}$ whereas the flux at the end of 1 h is about $6.5 \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s}$, that is about a decrease of 56% from the pure water flux. The reductions at 345 and 483 kPa are 51 and 58%, respectively. From Fig. 2b, it is evident that all the micelles are rejected by the membrane as the permeate CPC concentration is below CMC (0.322 kg/m^3 [30]) for the operating pressure 345 and 414 kPa. For 483 kPa pressure, after about 22 min of operation, the permeate concentration of CPC exceeds the CMC concentration due to permeation of smaller sized micelles. However, the increase in permeate surfactant concentration is not much beyond the CMC value at this operating pressure. Since both the flux decline and variation of permeate concentration of CPC is not significant with the time of filtration, the batch experimental data are reported at the end of the experiment in the subsequent section. The values of CPC concentration at the end of the run are 0.31 and 0.33 kg/m^3 for the pressure of 345 and 483 kPa, respectively.

3.1.1.2. Variation of permeate flux and permeate concentration of CPC with feed CPC concentration to get the optimum surfactant concentration. The effects of feed CPC concentration (above CMC) on the permeate flux and permeate concentration are shown in Fig. 3 at the end of batch experiment and at 345 kPa pressure. It is evident from the figure that the permeate flux decreases sharply with feed CPC concentration. This is due

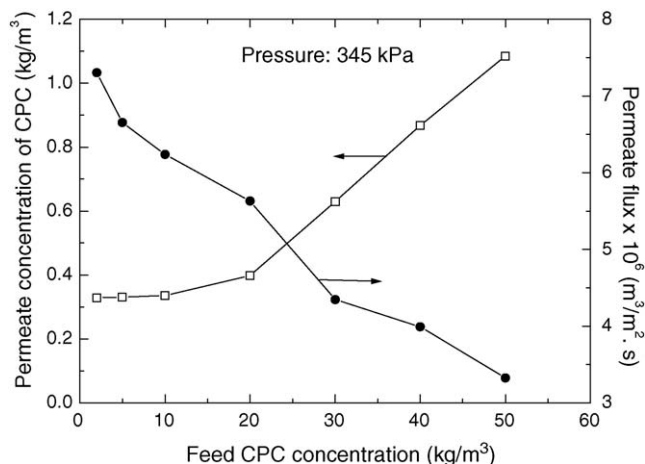


Fig. 3. Variation of permeate flux and permeate concentration of CPC with feed CPC concentration at the end of experiment and at 345 kPa pressure.

to the fact that at higher CPC concentration, the deposited layer of micellar aggregates offers more resistance against the solvent flux. It may also be observed from the figure that the permeate concentration of CPC remains below its CMC value up to a feed concentration of 10 kg/m^3 . The increase of permeate CPC concentration becomes gradual when feed CPC concentration increases from 10 to 20 kg/m^3 , but beyond that, the permeate concentration increase sharply. This increase in permeate concentration is due to the concentration polarization over the membrane surface which promotes the convective transport of CPC molecules through the membrane along with smaller size micelles to the permeate side. From this figure it is clear that the feed CPC concentration during MEUF should be in the range of $10\text{--}20 \text{ kg/m}^3$ to get the optimum value of CPC retention and permeate flux.

3.1.2. Cross flow experiment

3.1.2.1. Variation of permeate flux and permeate CPC concentration with feed CPC concentration and pressure at constant cross flow rate to estimate the flux enhancement. The continuous cross flow experiments are expected to yield better performance in terms of permeate flux and concentration due to minimization of the concentration polarization effects. The variations of the permeate flux and permeate concentration of the surfactant with feed surfactant concentration are studied at a constant flow rate (60 l/h). The results are presented in Fig. 4. It may be observed from this figure that the steady state permeate flux values in cross flow experiments are 8–15% higher at the three pressures compared to the flux values at the end of the batch experiments for 10 kg/m^3 feed surfactant concentration (Fig. 2a). The permeate flux decreases sharply with the feed surfactant concentration due to enhanced concentration polarization effects as already discussed. It may be interesting to note from this figure that at 10 kg/m^3 , the permeate concentration is around the CMC value for all the operating pressures which is confirmed by the batch cell experiments (Fig. 2b). Beyond feed CPC concentration of 10 kg/m^3 , the permeate concentration increases sharply exceeding the CMC value. Therefore, 10 kg/m^3 may be considered as the best CPC concentration to get a rea-

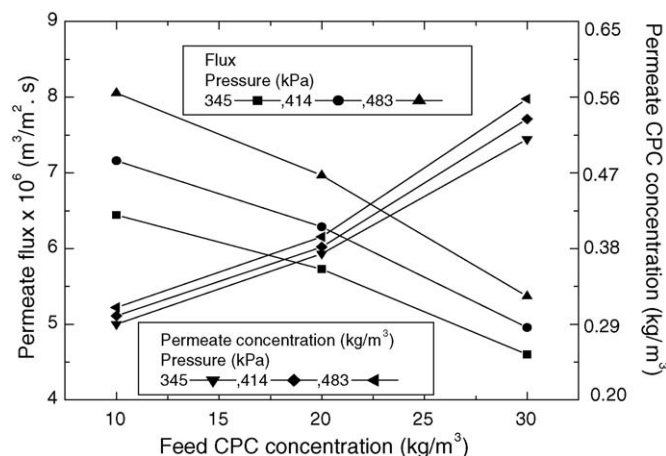


Fig. 4. Variation of permeate CPC concentration and flux with feed CPC concentration and pressure at cross flow rate 60 l/h.

sonable permeate flux and low surfactant concentration in the permeate.

3.2. Cross flow micellar enhanced ultrafiltration of eosin

Once the operating feed surfactant concentration is selected, the mixture is subjected to a steady state cross flow ultrafiltration as this should substantially improve the permeate flux and retention. A detailed parametric study is also conducted to observe the effects of the operating conditions on the permeate flux and observed retention.

3.2.1. Effect of the feed eosin concentration on the permeate flux and retention of eosin

The effect of eosin concentration in the feed on the retention of eosin and permeate flux is shown in Fig. 5. In this case, CPC concentration is kept constant at the optimum level, i.e., 10 kg/m^3 . It may be observed from the Fig. 5 that the flux remains almost unchanged. This is due to the fact that the major contribution of resistance against the solvent flux comes from the deposited layer of CPC micelles which are quite large compared to the dye molecules. Since CPC concentration remains constant and the solute concentration varies over a range between 4 and $40 \times 10^{-3} \text{ kg/m}^3$, the permeate flux remains almost unaltered. On the other hand, the retention of eosin decreases with the feed CPC concentration. Since the concentration of the micelles in the feed is constant (due to fixed CPC concentration), the concentration of unsolubilized eosin increases in the feed which permeate through the membrane, resulting in a reduction of the retention value.

3.2.2. Effect of the pressure drop on the observed retention of eosin and permeate flux

Variation of the eosin retention with the applied pressure is shown in Fig. 6 using 10 kg/m^3 of CPC and $10 \times 10^{-3} \text{ kg/m}^3$ of eosin. It may be observed from the figure that the retention of eosin remains almost independent of pressure. This observation indicates that the solubilization of the dyes in the micelles

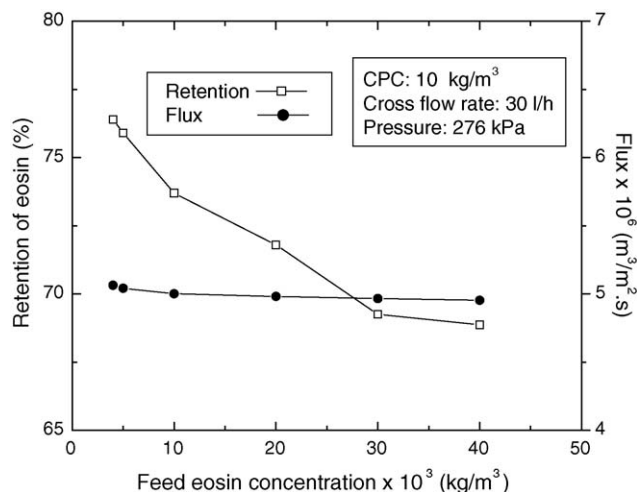


Fig. 5. Effect of feed dye concentration on observed retention of dye and permeate flux during MEUF in cross flow cell.

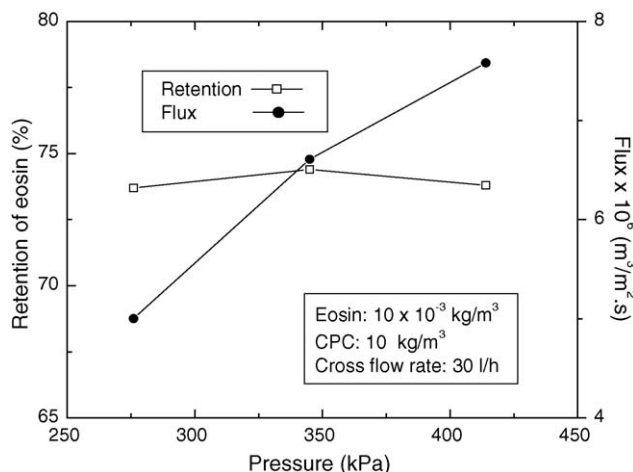


Fig. 6. Effect of pressure on observed retention of dye and permeate flux during MEUF in cross flow cell.

and retention of the micelles by the membrane governs overall dye retention. The observed retention of eosin is about 74% for the pressure range studied herein. The effect of the operating pressure on the permeate flux is also presented in Fig. 6. The figure shows that the flux increases with pressure almost linearly within the pressure range. This occurs due to an increase in the effective driving force. Hence, application of pressure in the higher range results in higher permeate flux.

The effects of cross flow rate on permeate flux and observed retention of eosin dye are observed to be marginal in the range of cross flow rate studied in this work. The permeate flux is increased by about 4.5% when cross flow rate increases from 30 to 75 l/h and the retention of the dye is about 74% for all the cross flow rates.

4. Conclusion

MEUF is employed for the separation of the eosin dye using CPC as surfactants. A wide range of feed eosin and surfactant concentrations are chosen. From the batch cell experiments of CPC only, it is observed that for a feed surfactant concentration range of $10\text{--}20 \text{ kg/m}^3$, surfactant concentration in the permeate is close to the CMC level. The cross flow experiments reveal that the observed retention of eosin (maximum about 74%) is almost independent to the operating pressure whereas, the permeate flux increases significantly with pressure. The permeate flux increases marginally (about 4.5%) for higher cross flow rates, studied herein.

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