

Removal of Safranin T from wastewater using micellar enhanced ultrafiltration

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Abstract

Micellar enhanced ultrafiltration (MEUF) was used to remove cationic dye from aqueous solution. Sodium dodecylsulfate (SDS) and Safranin T (ST) (molecular weight 350.85) have taken as anionic surfactant and cationic dye, respectively. Regenerated cellulose membrane of molecular weight cut-off 10 kDa was used in a cross-flow ultrafiltration unit. The effects of operating conditions, i.e., feed dye concentration, feed surfactant concentration, pH and ionic strength on the permeate flux and observed retention of dye are investigated. The ultrafiltration experiments showed that anionic surfactant SDS allowed retention of Safranin T in the order of 99% in the whole range of dye and surfactant concentrations considered. High retention was also obtained at pH range from 2 to 11. Permeate flux decreases when surfactant concentration or ionic strength increases.

Keywords: Safranin T; Micellar enhanced ultrafiltration; Sodium dodecylsulfate; Permeate flux

1. Introduction

The effluent water from dyeing, textile, pulp and paper industries contains various types of dyes which should be removed before discharging the effluent to the environment. Many of these dyes are toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms.

The investigation on the removal of dyes from effluent wastewater has been going on for several years. There are four major technologies available to remove dyes from water, i.e., oxidation [1], adsorption [2], biodegradation [3] and membrane separation process [4]. Oxidation methods are only effective in wastewater with very low concentrations of organic compounds. Thus, significant dilution is necessary as a facility requirement. Adsorption is a widely used process

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but it is a slow process and its performance is limited by the equilibrium. Due to low biodegradability of dyes, a conventional biological wastewater treatment process is not very efficient. Membrane-based separation process may be an attractive alternative and it is gradually emerging as a technically significant and commercially viable process in the treatment of wastewater. Reverse osmosis (RO) and nanofiltration are the most membrane processes used for the treatment of dyes waters. However, NF/RO membranes have quite low permeability and thus require high operating pressure. Furthermore, the decline in permeate flux due to concentration polarisation and membrane fouling is the major limitation of these membrane processes. Micellar enhanced ultrafiltration (MEUF), one of the possible membrane methods to remove traces of organic pollutants from aqueous streams [5], has been recently investigated to remove dyes from water [6,7]. This method combines the high selectivity of reverse osmosis and the high flux of ultrafiltration. In this process, surfactant at a concentration greater than its critical micelle concentration (CMC) is added to a polluted aqueous solution. The surfactant molecules form micelles which can solubilise the organic solute. Micelles containing solubilised solutes were then separated by UF using membrane of suitable molecular weight cut-off (MWCO) size, capable of retaining micelles. In the present study Safranin T is selected as a model compound in order to evaluate the efficiency of MEUF for the removal of dye from its aqueous solutions. Safranin T is a water soluble phenazine dye reddish brown powder, which is mainly used as food dye in flavoring and coloring candies and cookies. It also used for dyeing tannin, cotton, bast fibers, wool, silk, leather and paper. The object of the present investigations has been to evaluate the efficiency of removal of Safranin T using MEUF. The effects of dye and surfactant concentrations, ionic strength and solution pH have been studied and obtained results are discussed.

2. Experimental

2.1. Chemicals

Safranin T $C_{20}H_{19}ClN_4$ (molecular weight: 350.85, $\lambda_{max} = 520$ nm), a cationic dye, was provided by Fluka. The structure of Safranin T is given in Fig. 1. Sodium dodecylsulfate SDS (98% purity), was used without further purification. Distilled water was used for solution preparation.

2.2. Ultrafiltration

Cross-flow membrane filtration was carried out in Minitan-S unit, from Millipore, equipped with a flat sheet polymeric membrane made of regenerated cellulose. This membrane had effective membrane area of 30 cm^2 and molecular weight cut-off (MWCO) of 10 kD. A schematic diagram of the ultrafiltration system is shown in Fig. 2.

Ultrafiltration experiments were conducted at room temperature and at fixed transmembrane pressure of 1.4 bar. An initial feed volume equal to 200 mL was introduced to the feed tank and was circulated through the module by a volumetric pump. The retentate as well as the permeate were recycled to the feed tank. After nearly thirty minutes a steady state was reached and a permeate of 10 mL was collected and analysed.

Between the runs the membrane was thoroughly washed with distilled water for at least 15 min and at a pressure of 1.4 bar. The membrane permeability was checked to ensure that the permeability remains almost constant between successive runs.

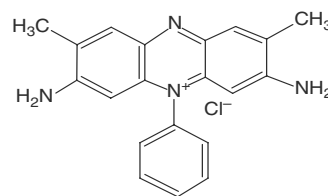


Fig. 1. The structure of Safranin T.

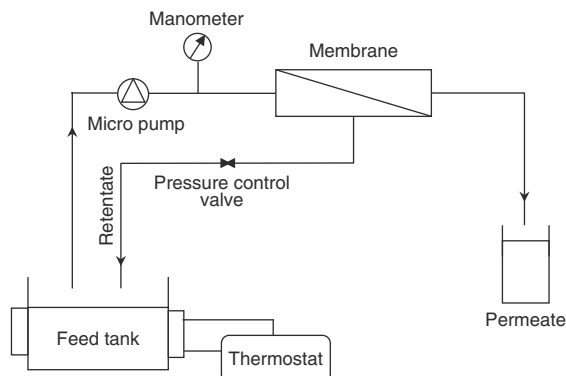


Fig. 2. Schematic of the experimental set up.

The filtration efficiency in removing the dye was evaluated through the dye rejection which was calculated using the rejection coefficient:

$$R(\%) = \left[1 - \frac{C_p}{C_0} \right] \times 100 \quad (1)$$

where C_0 is the initial concentration of the dye in the feed solution and C_p is the dye concentration in the permeate.

Permeate volume was calculated as follows:

$$J = \frac{V}{t \cdot A} \quad (2)$$

where J is the permeate flux ($\text{L h}^{-1} \text{m}^{-2}$), V denotes volume of the permeate sample collected within time t (h) and A is the effective membrane surface (m^2).

2.3. Analysis of Safranin T

Permeate concentrations of the dye are measured by a Perkin-Elmer Lambda 20 spectrophotometer using a matched pair of glass cuvettes with 1 cm optical lengths.

Fig. 3, as example, shows the visible spectra of aqueous Safranin T solution at $2 \times 10^{-6} \text{ M}$ for several SDS concentrations ranging from 0 to 20 mM. In absence of surfactant ($[\text{SDS}] = 0 \text{ mM}$) Safranin T presents a maximum absorption at 520 nm. In the presence of SDS the intensity of the band at 520 nm gradually diminished and a new band at 504 nm appeared as the concentration of SDS increased. A sharp isobestic at

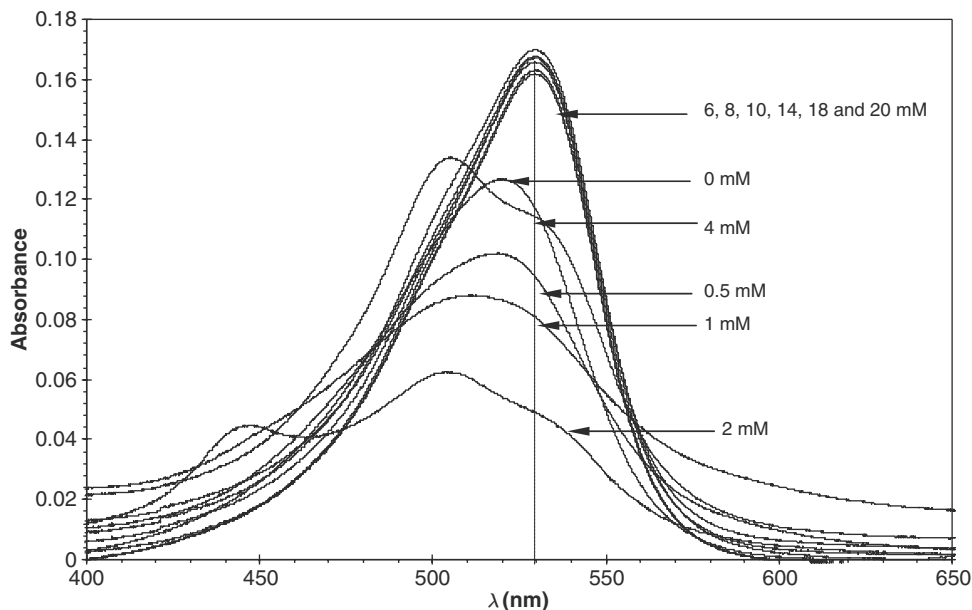


Fig. 3. The visible absorption spectra of ST dissolved in aqueous solutions containing 0 to 20 mM SDS. Concentration of ST is $2 \times 10^{-6} \text{ M}$.

510 nm indicated a complex formation between ST and SDS molecules. On further increase in SDS concentration, the absorbance reaches its limiting value and a shift of λ_{\max} to longer wavelength 530 nm was observed. The spectral shifts of λ_{\max} are generally interpreted as polarity changes of the immediate microenvironment of the chromophore [8], the polarity of the microenvironment felt by ST ions at micellar region is different from water. Fig. 4 shows clearly the variation of the absorbance of ST at $\lambda_{\max} = 530$ nm as a function of SDS concentration for three ST concentrations. Since the absorbance remains almost constant above CMC we have adjusted the concentration of surfactant in the samples and in the standard solutions to a value higher than CMC in order to analyse ST in presence of SDS. The ST absorbance versus concentration plot follows Lambert-Beer law from 0 to 8 μM .

3. Results and discussion

3.1. Ultrafiltration of dye solution with and without surfactant

The variation of ST retention with and without surfactant is presented in Fig. 5 for different

dye concentration and at transmembrane pressure 1.4 bar using $2 \cdot 10^{-2}$ M of SDS surfactant. It is observed from the figure that in absence of surfactant the dye retention is less than 5% whereas in presence of SDS solutions the retention has been significantly increased to 99%. This clearly indicates that dye molecules are solubilised within the surfactant micelles, which are subsequently retained by ultrafiltration membrane.

The variation of the permeate flux with and without surfactant is shown in Fig. 6. In both cases the permeate flux decreases when the dye concentration increases. However, the flux decline in presence of surfactant is higher than that of without surfactant. This is due to the fact that the major contribution of resistance against the solvent comes from the deposited layer of SDS micelles which are larger than dye molecules. On the other hand, it is observed that in presence of dye only the flux decreases slightly with time while in presence of surfactant a decrease of flux is observed during initial stage of filtration, and thereafter, the flux remains almost constant. Indeed, the retained dye-micelle species accumulate at the membrane surface where their

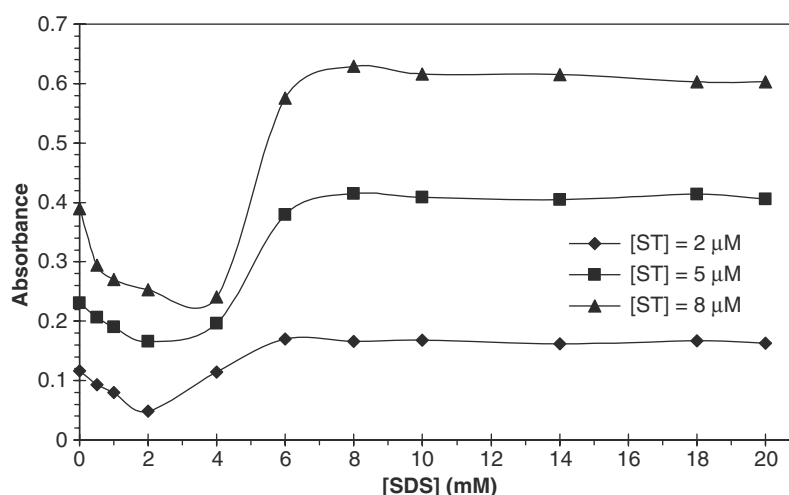


Fig. 4. Absorbance of Safranin T as a function of SDS concentration for different ST concentrations (2×10^{-6} M; 5×10^{-6} M and 8×10^{-6} M) at $\lambda = 530$ nm.

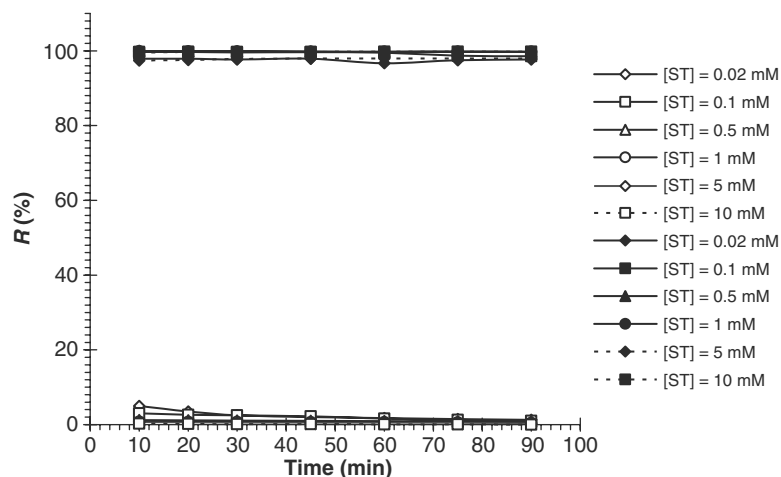


Fig. 5. Variation of retention of ST with time at different feed ST concentrations in the absence and in the presence of SDS.

concentration will gradually increase. Such a concentration build-up will generate a diffusive flow back to the bulk of the feed, but after a given period of time steady-state conditions will be established [9].

3.2. Effect of transmembrane pressure and feed SDS concentration

The variation of ST retention with pressure is shown in Fig. 7a. It can be observed that the retention of dye remains independent of pressure.

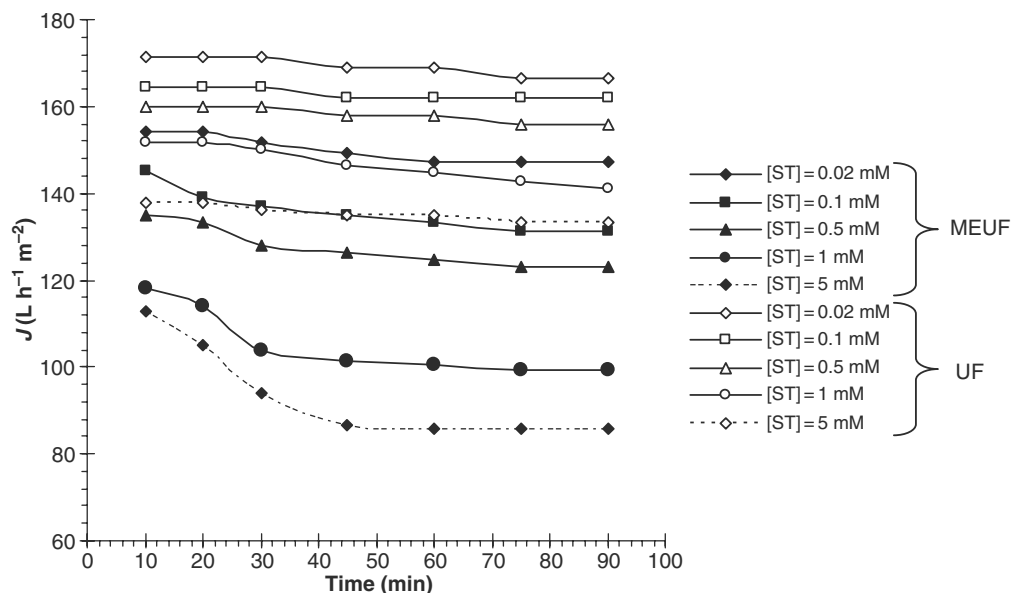


Fig. 6. Variation of permeate flux of ST with time at different feed ST concentrations in the absence (a) and in the presence (b) of SDS (2×10^{-2} M). Feed ST concentration is: 0.02; 0.1; 0.5; 1; 5 and 10 mM. SDS concentration is 2×10^{-2} M.

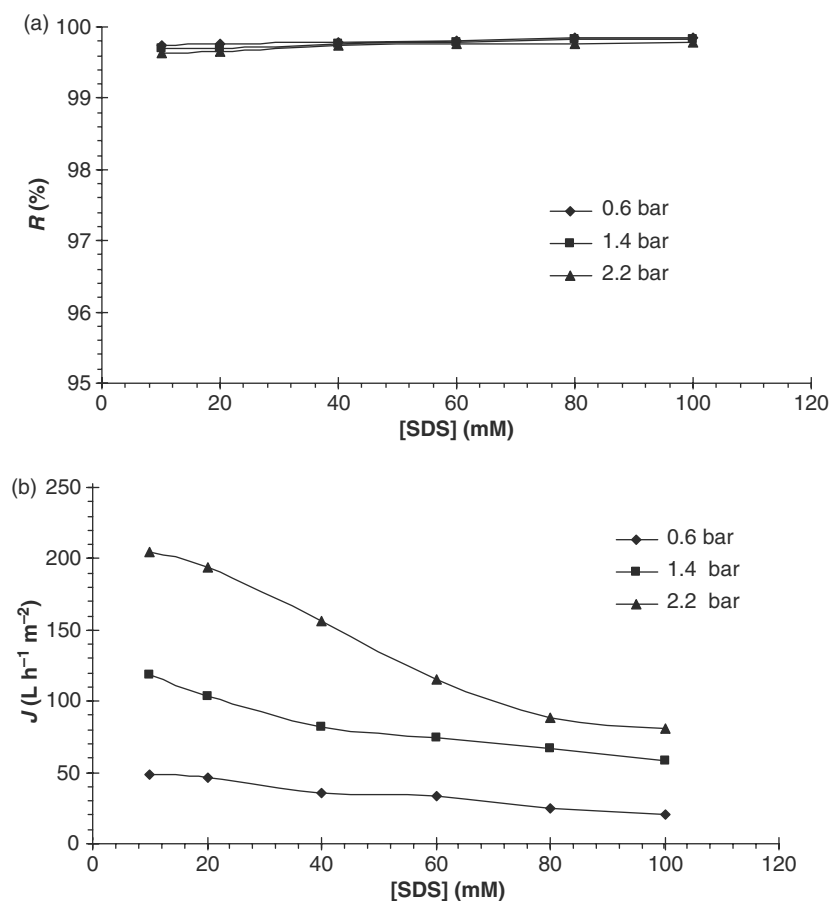


Fig. 7. (a) Effect of transmembrane pressure and feed SDS concentration on the retention of ST. $[ST] = 10^{-3}$ M. (b) Effect of transmembrane pressure and feed SDS concentration on the permeate flux. $[ST] = 10^{-3}$ M.

This observation indicates that the solubilisation of the dyes in the micelles and retention of the micelles by the membrane governs overall dye retention. The effect of applied pressure on the permeate flux is presented in Fig. 7b. The increase in the permeate flux is not surprising, since the pressure difference between retentate and permeate is the driving force for process. The figure shows that the permeate flux decreases with feed SDS concentration at a fixed transmembrane pressure. At pressure equal to 2.2 bar, as example, the flux decreases from 204.99 to 80.53 $L/h m^2$ when SDS concentration increases from 10 to 100 mM. This result may be attributed to the fact that at higher SDS concentration, the

deposited layer of micellar aggregates offers more resistance against the solvent flux. Also, the increases of the osmotic pressure difference across the membrane (related to the micelle concentrations in the retentate and permeate) reduces the effective transmembrane pressure and consequently the permeate flux.

3.3. Effect of added NaCl

The influence of the ionic strength of the solution was also studied. In reality, effluents from textile and dyeing industries would contain a high concentration of salts which may effect the removal of dye. An increase in the ionic strength

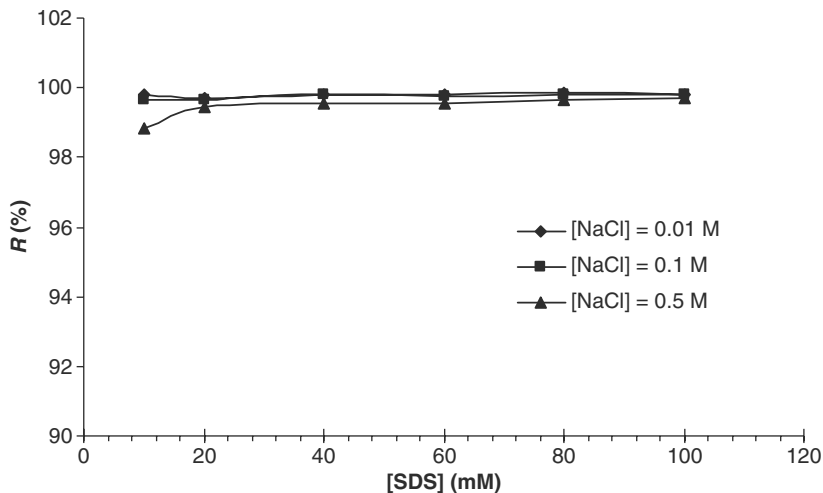


Fig. 8. Effect of added NaCl on the ST retention as a function of feed SDS. Feed ST concentration is: 10^{-3} M. NaCl concentration is: 0.01; 0.1; and 0.5 M.

increased the free counter ion concentration, thereby decreasing the energy of repulsion between charged head group of micelles. It is resulted a decrease in the CMC and an increase in the aggregation number and volume of the micelles. As a consequence, the addition of electrolyte to solutions of surfactant increases the extent of solubilisation of hydrocarbons that are solubilised in the inner core of the micelle and decreases that of polar compounds that are solubilised in the outer portion of the palisade layer

[10]. The effect of added NaCl concentration on ST retention is shown in Fig. 8 where it can be seen that ST retention decreases slightly upon increasing the sodium chloride concentrations from 0.01 to 0.5 M. The low decrease of solubilisation, and then ST retention, upon increasing the salt concentration may be due to the solubilisation of Safranin T in both inner and outer region of the micelle.

Fig. 9 shows the variation of permeate flux as a function of feed concentration of SDS. The flux

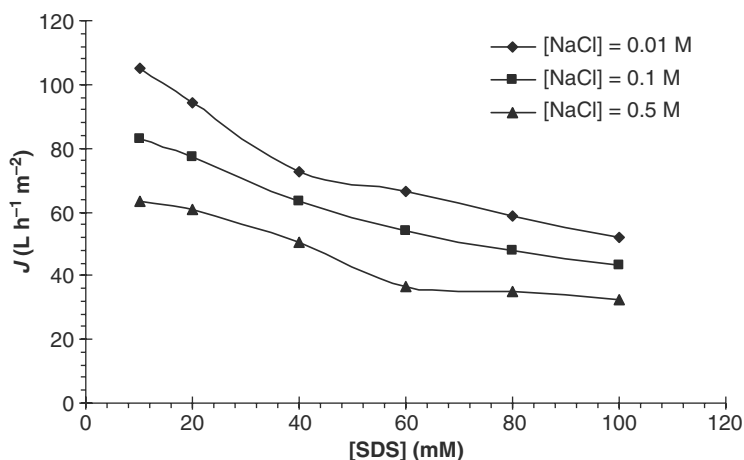


Fig. 9. Effect of added NaCl on the permeate flux as a function of feed SDS. Feed ST concentration is: 10^{-3} M. NaCl concentration is: 0.01; 0.1; and 0.5 M.

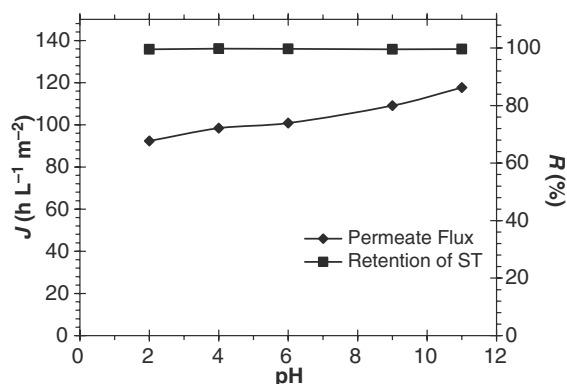


Fig. 10. Effect of pH on the retention of ST and on the permeate flux. $[\text{ST}] = 10^{-3} \text{ M}$ and $[\text{SDS}] = 2 \times 10^{-2} \text{ M}$.

of permeate decreased when the concentration of NaCl increased. Larger fraction of SDS micelles are formed which enhance the effect of polarisation concentration.

3.4. Effect of pH

The effect of pH was investigated at SDS and ST concentrations of $2 \times 10^{-2} \text{ M}$ and 10^{-3} M respectively. The pH was varied from 2 to 11 by adding chloride acid or sodium hydroxide. Fig. 10 shows that practically there was no effect of pH on the retention of the dye. It was found that retention of inorganic ions such as Cu^{2+} [11] or Cd^{2+} [12] were very sensitive to pH. The sharp decrease obtained in copper and cadmium removal efficiency below $\text{pH} = 4$ might be due to the competition between these cations and protons to bind to micelles.

The figure shows also the variation of flux of permeate. The flux increased progressively when pH increased from 3 to 11. This can be attributed to the fact that the membrane became more hydrophilic as a result of deprotonation of carboxylic group of the active layer of membrane.

4. Conclusions

The retention of Safranin T was in the order of 99% in the range of dye concentration from

$2 \cdot 10^{-5}$ to $5 \cdot 10^{-3} \text{ M}$. This retention depended slightly on the surfactant and dye concentrations, ionic strength and pH. This was due to the high interaction between SDS and ST. However the flux decreased when the surfactant and dye concentration and ionic strength increased. From the experimental results, the MEUF process can effectively be used for the separation of Safranin T from aqueous medium at a high ionic strength and wide range of pH. The dye was concentrated in feed solution and the permeate was completely discoloured. However the permeate stream contains free surfactant and it is necessary to recycle the surfactant to make the MEUF process more economical.

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