Removal of dye from aqueous solution using a combination of advanced oxidation process and nanofiltration

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Abstract

In order to have energy and cost effective separation of dyes, a combination of advanced oxidation process (AOP) using Fenton's reagent and nanofiltration (NF) is proposed. Three combinations of AOP and NF are studied using a synthetic solution of eosin dye. Scheme-1 is AOP followed by NF. Scheme-2 is NF followed by AOP. And Scheme-3 is two-step NF. The concentration of eosin dye studied in the first step of each of the schemes is in the range of 70–200 mg/l. The operating transmembrane pressures for NF steps are 552, 689 and 828 kPa. The crossflow velocities are 0.46, 0.69 and 0.91 m/s. The schemes are compared for permeate flux, permeate concentration and duration of operation. In Scheme-1, AOP is conducted for 30 min, and then subjected to NF, whereas in Scheme-2, the time needed for AOP is more than 3 h to achieve the concentration level of the dye below 1 mg/l. Thus, it is found that Scheme-1 is superior to Scheme-2 due to lesser time requirement. However, Scheme-3 involving no AOP, is also suitable for dye separation as the final eosin concentration in the permeate falls below 1 mg/l. Scheme-1 is found suitable for dye concentration of 70 mg/l and the most appropriate composition of Fenton's reagent is 1665 mg/l of H_2O_2 and 347.5 mg/l of $FeSO_4·7H_2O$. Suitable NF operating conditions in step 2 of Scheme-1 is transmembrane pressure of 689 kPa and crossflow velocity of 0.91 m/s. In Scheme-3, the suitable operating conditions for NF in both the steps are 828 kPa transmembrane pressure and 0.91 m/s crossflow velocity. Scheme-2 is found to be unsuitable.

1. Introduction

Synthetic dyes are extensively used in many technologically important processes, e.g., in textile [1], leather tanning [2], paper production [3], food technology [4], agricultural research [5], light-harvesting arrays [6], photo-electrochemical cells [7], hair coloring [8], etc. It is estimated that over 10,000 tonnes of dyes are produced all over the world per year. About 1–2% dyes are lost during production and 1–10% is lost during the use [9]. Due to the large-scale production and extensive application, synthetic dyes can cause considerable environmental pollution and serious health hazards [10]. Traditional wastewater treatment technologies like activated sludge processes have proven to be markedly ineffective for handling wastewater containing synthetic textile dyes because of the chemical stability of these pollutants. A wide range of methods has been developed for removal of synthetic

dyes from water and wastewater [11]. The technologies involve adsorption on inorganic or organic matrices, decolorization by pholocatalysis and/or by oxidation processes and microbiological decomposition [12]. Chemical oxidation is reported to be very effective but the efficiency strongly depends on the type of oxidant and the nature of dye [4].

Advanced oxidation process (AOP) is defined as the oxidation process, which generates hydroxyl radicals in sufficient quantity to effect water treatment. AOP uses Fenton's reagent to achieve high performance [13]. Presence of ozone and UV radiation enhances the performance of Fenton's reagent and is sometimes used for AOP [14]. Hydroxyl radicals have very high oxidizing power, next only to fluorine, and degrade the organic hazardous dyes to CO_2 and H_2O [15].

In literature, Fenton and Fenton-like reactions are found to be efficient for decolorizing and detoxifying of textile effluents [16–23]. Fenton reactions and O_3 oxidation are still the most basic and yet practical advanced oxidation processes for the treatment of industrial effluents including textile effluents [24,25].

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AOPs have common principles in terms of the participation of hydroxyl radicals that are assumed to be operative during the reaction. Due to the instability of OH^* radical, it must be generated continuously in situ through chemical or photochemical reactions [26]. Hydroxyl radicals are generated by the reaction between H_2O_2 and ferrous ions. The slow regeneration of Fe^{3+} to Fe^{2+} is the rate-determining step of the overall reaction. Thus, in AOP, rate of dye degradation is fast in the beginning due to high initial concentration of Fe^{2+}. However, subsequently the rate drastically reduces due to the drop in the concentration of Fe^{2+} and poor rate of its regeneration [27].

In literature, it is reported that AOP using Fenton's reagent can reduce the eosin concentration of 678 mg/l by 20% in 1 h when treated with 278 mg/l $FeSO_4 \cdot 7H_2O$ and 3400 mg/l hydrogen peroxide. The reduction after 24 h is reported to be 53%. Certain dyes like poly B-411 and evans blue can be degraded to a larger extent, whereas for dyes like phenol red, the degradation is much lower [28].

Membrane separation is becoming more attractive because of its purely physical nature of separation principle as well as the modular design of membrane processes [29]. Performance of separation without phase change, less energy consumption, operability at ambient temperature, etc., have given an edge to membrane processes over the conventional processes [30]. The permeate flux and the composition of the unwanted dye in the permeate primarily depends on molecular weight cut-off (MWCO) of the membrane, transmembrane pressure and dye concentration in the feed stream. In the case of Nanofiltration (NF), the membranes can retain solutes whose molecular weight is in the range 300–1000 g/mol. NF is a membrane process that meets the necessary standard for dye removal from wastewater streams as NF can retain ions as well as relatively small organic molecules [31–34]. It is reported that dye retention for dyes like reactive blue 2 and reactive orange 16 at a pH of 9.3 are up to 86.4% and 92%, respectively [35].

The major problem in membrane separation is flux decline due to membrane fouling. Solute particles accumulate over the membrane surface, under transmembrane pressure drop, known as concentration polarization, which offers resistance against the solvent flux. Majority of flux decline due to concentration polarization can be recovered after membrane cleaning. Therefore, concentration polarization is mostly reversible in nature. However, sometimes one may not be able to remove the adsorbed solute from membrane and this type of fouling is known as irreversible fouling.

The overall objective of the present work is degradation of dye and its removal by the combination of AOP and nanofiltration. In AOP, dye degradation is faster if the concentration of dye is high. But the process becomes extremely slow after some time. AOP introduces other chemicals into the system. On the other hand, NF yields higher permeate flux when the concentration of dye is low. Thus, the present study aims at combining these two operations, thereby taking the advantages of both. Three schemes are explored in this study. Scheme-1 is combination of AOP as the first operation followed by NF. Scheme-2 is combi-
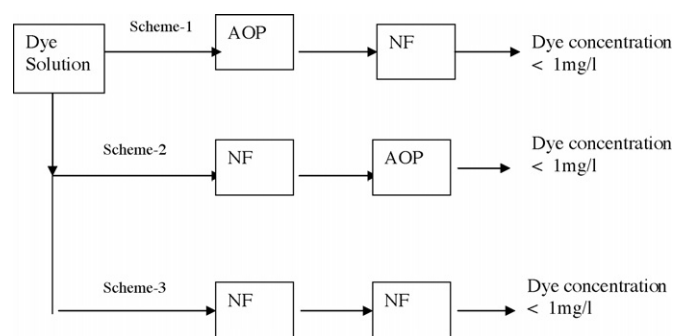

Fig. 1. Schematic of the investigated schemes for dye removal.

nation of NF as the first operation followed by AOP. Scheme-3 is a two-step application of NF. Fig. 1 schematically shows the three schemes.

2. Experimental

2.1. Materials

2.1.1. Chemicals

The experiments are performed using various concentrations of eosin Y dye. The characteristics of this dye are presented in Table 1. The chemicals used for AOP study are ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and hydrogen peroxide (30 vol.% solution). All chemicals are AR grade supplied by Merck, India and are used without further purification.

2.1.2. Membranes

The experiments are carried out in a crossflow membrane cell. The channel dimensions are 25 cm × 4.8 cm. Before each experimental run, the membrane unit is cleaned thoroughly. The membrane is compacted for 3 h before use. After every experimental run, the membrane is cleaned by 1% sodium dodecyl sulfate solution to remove any dye. Before every run, the membrane permeability is measured. The molecular weight of eosin dye is 692. Therefore, a nanofiltration membrane with a molecular weight cut-off of 400, procured from Genesis Membrane Sepratech Pvt. Ltd., Mumbai, India is used. A rectangular membrane is placed over a metallic support inside the crossflow cell. The height of the channel is 0.00076 m. Permeate is collected from the bottom of the cell.
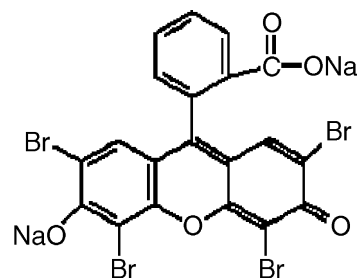
2.2. Operating conditions

The operating conditions are varied according to the requirement of the scheme. In the first step of each of the scheme, the eosin concentration studied are in the range of 70–200 mg/l. Depending on the concentration of the dye achieved after the application of first step in each of the scheme, eosin concentrations are selected for the next step. Composition of Fenton's reagent is selected based upon the requirement in the study. Thus, higher doses of hydrogen peroxide and ferrous sulfate have been used in Scheme-1 compared to Scheme-2. AOP and NF operations are carried out separately. AOP is carried out in batch reactor of 500 ml in the absence of direct sunlight at
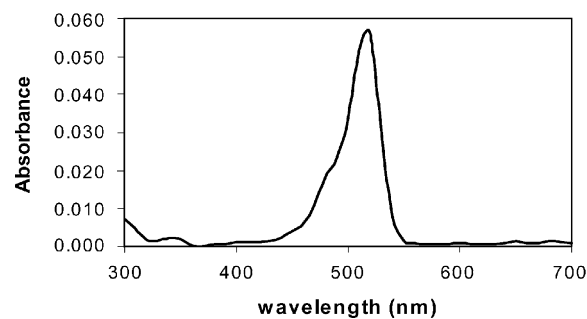
Table 1
Characteristics of eosin Y

Color index no.	CI 45380
Color index name	Acid red 87, pigment red 90
Molecular weight	691.8
Melting point	>300 °C
Absorption max (water)	515–518 nm
Chemical formula	$C_{20}H_6Br_4Na_2O_5$
Molecular structure	
UV spectra	

UV Spectra Eosin Y

2.2.1. AOP study

2.2.1.1. Scheme-1. Experiments are conducted by preparing synthetic solutions of eosin dye of 70, 100, 150 and 200 mg/l initial concentrations in the reaction mixture. The reactions are carried out in the absence of direct sunlight at a temperature of 30 °C. They are reacted with 1665, 3300 and 4995 mg/l of H_2O_2 in a batch of 500 ml of total reaction mixture. The concentrations of ferrous sulfate heptahydrate are 278.0, 347.5 and 417.0 mg/l. All possible combination of hydrogen peroxide and ferrous sulfate are used in the experiments.

2.2.1.2. Scheme-2. Experiments are conducted by preparing synthetic solutions of eosin dye of 2, 4, 6, 8, 10 and 12 mg/l initial concentrations in the reaction mixture. The reactions are carried out in the absence of direct sunlight at temperature of 30 °C. They are reacted with 666, 1998 and 3330 mg/l of H_2O_2 in a batch of 500 ml of total reaction mixture. The concentrations of ferrous sulfate heptahydrate are 6.9, 13.9 and 21.0 mg/l. All possible combination of hydrogen peroxide and ferrous sulfate are used in the experiments.

about 30 °C at the natural pH of the dye solution (about 6.7). NF is carried out in a crossflow cell, separately. Fresh solutions of eosin dye of appropriate concentration are prepared for every step.

2.2.2. Nanofiltration study

2.2.2.1. Scheme-1. NF study is conducted by preparing synthetic solutions of eosin dye of 40, 25 and 15 mg/l. The crossflow runs are conducted at 30 °C. The operating pressure are 552, 689, 828 kPa. The cell is operated at three crossflow velocities of 0.46, 0.69 and 0.91 m/s. The concentration of eosin dye in the permeate and permeate flux is recorded.

2.2.2.2. Scheme-2. NF study is conducted by preparing synthetic solutions of eosin dye of 200, 150 and 70 mg/l. The crossflow runs are conducted at 30 °C. The operating pressure and crossflow velocities are same as Scheme-1.

2.2.2.3. Scheme-3. NF study is conducted by preparing synthetic solutions of eosin dye of 200, 150, 70, 25, 15 and 10 mg/l. The crossflow runs are conducted at 30 °C. The operating pressure and crossflow velocities are same as Scheme-1.

The three schemes mentioned above have different experimental conditions depending upon the need of the step. For example in Scheme-1, step 1 AOPs are conducted on eosin dye at concentration ranges of 70–200 mg/l. Whereas in Scheme-2, AOPs are conducted in step 2, at eosin concentrations in the range of 2–12 mg/l as it is inferred from step 1 (NF) of Scheme-2, where eosin concentration is obtained

at 12 mg/l or less at suitable conditions of transmembrane pressure and velocities. This is discussed in detail in Section 3.2.

2.3. Experimental procedure

2.3.1. AOP

The AOP study is carried out in batches of 500 ml in absence of direct sunlight at 30 °C with stirring speed of 50 rpm. The duration of the experiments is 3 h. The concentration of the dye is measured every 30 min. The reactions are carried out at atmospheric pressure. The dye solutions are prepared by using distilled water.

2.3.2. Nanofiltration

For NF study, the membrane is compacted at 965 kPa. For determination of membrane permeability, volumetric flux of distilled water is plotted against applied pressure. The membrane permeability is determined from the slope of the resulting straight line. Permeate samples are collected every minute and the weight of the sample collected is measured. After every experimental run, the cell is dismantled and cleaned thoroughly. Furthermore, a 1% SDS solution is used for 3 h to remove any dye adhered on the membrane surface. Finally the membrane is cleaned using distilled water and its permeability is measured again. It is found that the permeability remains almost constant at around 2.42×10^{-11} m^3/N s during the course of the entire set of experiments. The schematic of the experimental setup is shown in Fig. 2.

2.4. Analysis

A UV spectrophotometer (make: Genesis 2, Thermospectronic, USA) is used to measure the absorbance of dye. The absorbance value is calibrated with known concentrations of the dye. Use of UV spectrophotometers for measuring the concentration of colored organic dyes is found extensively in the literature [15,28,36] during AOP. In this study, 10 ml of reaction mixture is taken out from the reactor every 30 min and is filtered by Whatman filter paper (Grade 1) to remove the precipitates before measuring absorbance.
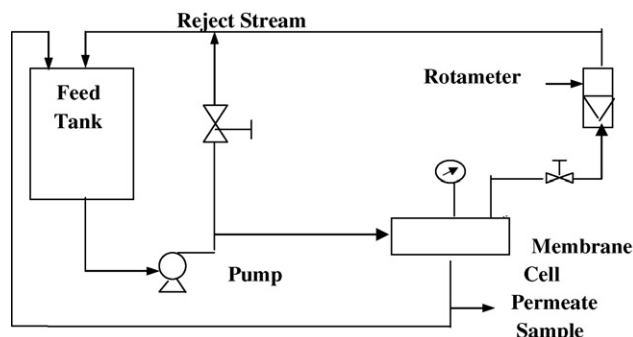
Fig. 2. Schematic diagram of crossflow NF membrane cell.

3. Results and discussion

3.1. Scheme-1

3.1.1. Effect of varying eosin concentration

In Scheme-1, AOP is used as the first step followed by NF. Fig. 3 shows the concentration profile of the dye with time for various feed concentrations of eosin in the solution. On decreasing the concentration of eosin, the rate of degradation of eosin decreases. For eosin dye concentrations of 200, 150, 100 and 70 mg/l in a solution containing 278 mg/l FeSO$_4$·7H$_2$O and 1665 mg/l of H$_2$O$_2$, the reductions in eosin concentration after 30 min are 44%, 34%, 30% and 27%, respectively. The concentration reductions after 3 h are 69%, 67%, 66% and 58%. However, in all cases the rate of degradation is very high in the first 30 min and the rate falls down drastically thereafter. This is due to the mechanism of AOP using Fenton's reagent. Initially, a large number of Fe^{2+} is present, due to which the dye degradation is fast. But during the process Fe^{2+} is converted to Fe^{3+}. The regeneration to Fe^{2+} is a slow process and hence becomes the rate-determining step after the fast initial phase of dye degradation. The amount of dye degradation also depends on the initial dye concentration [15]. Higher the initial dye concentration, the larger the dye degradation. Thus, initial eosin dye concentration at 200 mg/l falls to about 86 mg/l in 3 h and eosin dye at 70 mg/l falls to 22 mg/l. The rate of degradation of dyes has been explained by the pseudo first order kinetics in literature [15].

Variation of dye concentration with time for different H$_2$O$_2$ dosage is presented in Fig. 4. By increasing the H$_2$O$_2$ concentration, increase in the rate of dye degradation is observed. For example, by increasing the H$_2$O$_2$ concentration from 1665 to 4995 mg/l, an increase in concentration drop (after 30 min) from 29% to 49% is observed for a solution containing 200 mg/l eosin and 278 mg/l FeSO$_4$·7H$_2$O. After 3 h, the corresponding values are 57–87%, respectively.

Effect of ferrous sulfate heptahydrate concentration on dye degradation is shown in Fig. 5. By increasing the FeSO$_4$·7H$_2$O
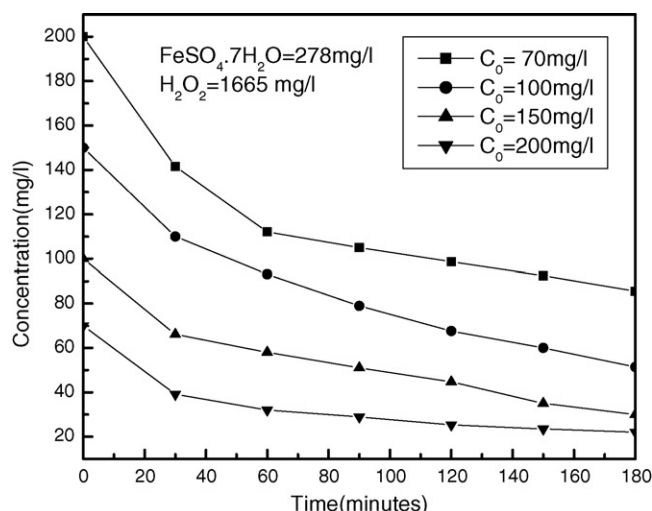
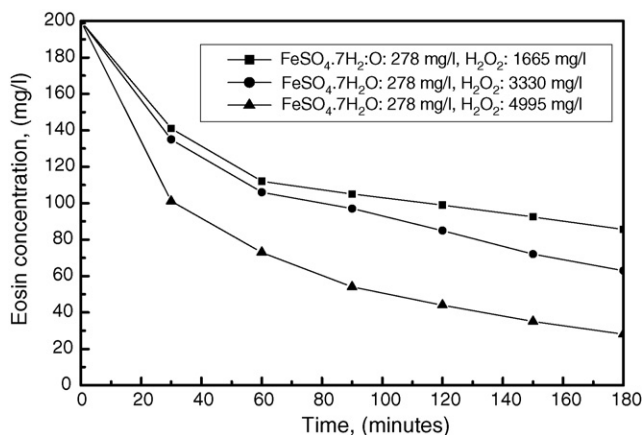Fig. 3. Effect of eosin concentration on AOP with time during reaction.

Fig. 4. Effect of H_2O_2 on degradation of eosin ($C_0 = 200$ mg/l).

concentration, from 278 to 417 mg/l in a solution containing 1665 mg/l H_2O_2 and an initial eosin concentration 200 mg/l, the drop in eosin concentration after 30 min increases from 44% to 84%. At the end of 3 h, the corresponding values are 69% and 95%, respectively. Similarly in a solution having 70 mg/l initial eosin concentration, the drop in eosin concentration after 30 min increased from 26% to 83% and after 3 h from 67% to 92%. The rate of degradation is significantly increased when the $FeSO_4·7H_2O$ concentration is increased in this range (278–417 mg/l). Therefore, increase in concentration of $FeSO_4·7H_2O$ has stronger effect on dye degradation than increase in concentration of H_2O_2. It may be mentioned here that the pH value of the solution is about 6.7 before addition of any chemicals and at the end of AOP the value of pH is in the range of 5.4–5.7 for various operating conditions.

The effects of concentrations of ferrous sulfate and hydrogen peroxide on the degradation of dye require some discussion. Ferrous sulfate reacts with hydrogen peroxide to generate hydroxyl radicals which in turn degrades the dye according to the following reactions [27]:
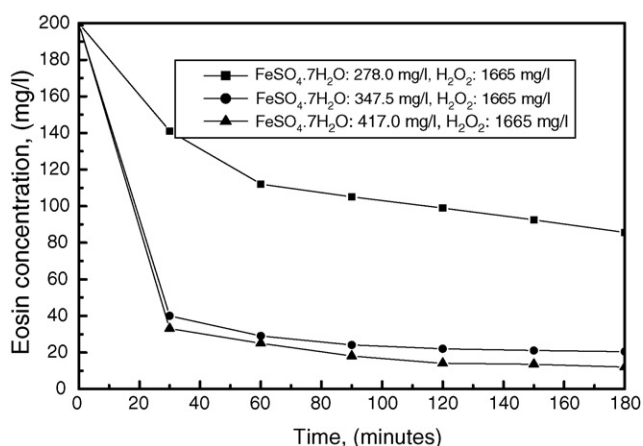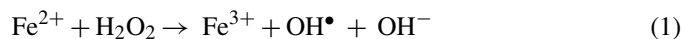
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^• + OH^- \tag{1}$$

$$RH + OH^• \rightarrow H_2O + R^• \tag{2}$$

Fig. 5. Effect of $FeSO_4·7H_2O$ on degradation of eosin ($C_0 = 200$ mg/l).

From Eq. (1), it can be observed that the amount of the generation of hydroxyl radicals depends upon the concentration of both ferrous sulfate and hydrogen peroxide. In this study, the molar ratio of ferrous ions to hydrogen peroxide is much smaller than 1.0. Therefore, increase in the concentration of ferrous ions has more pronounced effect in generation of hydroxyl radicals compared to the increase in the concentration of hydrogen peroxide. This is reflected in Figs. 4 and 5. It can be observed from these figures that dye degradation is more in case of increase in concentration of $FeSO_4·7H_2O$ (Fig. 5).

During AOP, it is observed that dye concentrations drops below 40 mg/l within first 30 min for a solution having an initial eosin concentration of 200 mg/l for $FeSO_4·7H_2O$ concentration of 347.5 mg/l (or more) for all concentrations of hydrogen peroxide considered in this study. For 70 mg/l initial eosin concentration, the corresponding dye concentration after 30 min is 14 mg/l. Thereafter it is seen that the concentration reduction is a slow process spanning over 3 h. Therefore, the composition of Fenton's reagent selected for the rest of the experiments is 347.5 mg/l $FeSO_4·7H_2O$, and 1665 mg/l H_2O_2 and duration of AOP is selected as 30 min. Since, AOP reduces the dye concentration to the range of 15–40 mg/l after 0.5 h, for a feed range of 70–200 mg/l, the feed concentration for the subsequent NF study are selected as 40, 25 and 15 mg/l. Durations of NF experiments are about 0.5 h. However, the permeate flux becomes steady after 2–3 min from the start of the operation. The steady state permeate flux values for all the operating crossflow velocities and feed concentrations are shown in Table 2. The water flux using distilled water is also shown in Table 2. It may be observed from Table 2 that the flux values vary in a narrow range for various crossflow rates and feed concentrations at a fixed transmembrane pressure. This range is from about 43 to 47 l/m² h at 552 and 828 kPa, it is from 64 to 68 l/m² h. The decrease in permeate flux with respect to pure water flux is more at higher operating pressure. For example, at 552 kPa, water flux is about 48 l/m² h which is 2% higher than the highest flux at 552 kPa corresponding to $u_0 = 0.91$ m/s and $C_0 = 15$ mg/l. At 828 kPa, the water flux is 72.5 l/m² h and it is about 7% higher than the highest flux at this pressure. This decline in flux at higher pressure is due to concentration polarization. As the transmembrane pressure increases, more solutes accumulate on the membrane surface resulting in an increase in the osmotic pressure at the membrane-solution

Table 2
Permeate flux data for NF under Scheme-1

Sl. no.	C_0 (mg/l)	Crossflow velocity, u_0 (m/s)	Permeate flux (l/m² h)		
			552 kPa	689 kPa	828 kPa
1	15	0.46	46.2	58	66.6
2	15	0.69	46.6	58.2	67.6
3	15	0.91	47	58.6	68.5
4	25	0.46	45.1	57.6	65.7
5	25	0.69	45.7	58.1	66.9
6	25	0.91	46.0	58.3	67.5
7	40	0.46	44.4	56.1	64.6
8	40	0.69	44.7	56.5	65.1
9	40	0.91	46.1	57.6	66.8
10	0 (distilled water)	–	48.0	59.8	72.5

interface, causing increasing flux decline by reduction of driving force. Therefore, the permeate flux does not show a linear increase with pressure (like pure water flux). A close look at Table 2 reveals that at the same pressure and feed concentration, the flux is more at the higher crossflow velocity. This is due to the reduction in concentration polarization by the sweeping action of the crossflow on the membrane surface. At the same crossflow velocity and operating pressure, flux is more for lower feed concentration due to lesser buildup of the solute molecules on the membrane surface leading to lower osmotic pressure.

Variation of steady state permeate concentration with operating pressure at various operating conditions is presented in Fig. 6. It may be observed from this figure that the permeate concentration increases marginally for 15 and 25 mg/l feed dye concentration. For 40 mg/l feed concentration, permeate concentration increases with pressure for 0.69 and 0.91 m/s of crossflow velocities up to a pressure of 690 kPa and the increase is marginal thereafter. For 0.46 m/s, crossflow velocity and 40 mg/l feed concentration, the eosin concentration in permeate increases steadily with pressure. With increase in pressure, membrane surface concentration increases due to concentration polarization as described earlier. This enhances the diffusive flux of the dye through the membrane leading to marginal increase in the permeate concentration with pressure. For 40 mg/l (highest initial concentration) and 0.46 m/s crossflow velocity (lowest crossflow velocity), concentration polarization is most severe (among all the operating conditions in this study). The enhanced solute diffusion through the membrane, results in increase in permeate concentration with pressure. The effect of crossflow velocity on the permeate flux is also evident from the figure. With increase in crossflow velocity, the membrane surface concentration decreases due to the sweeping action of crossflow. As a result, the permeate concentration decreases. For example, at 828 kPa pressure and 25 mg/l feed concentration, the permeate concentration is about 2 mg/l at 0.46 m/s crossflow velocity but it is reduced to 1 mg/l for 0.91 m/s of crossflow velocity. It is also clear from Fig. 6 that increase in feed concentration increases permeate

concentration for the same values of the other operating variables. As discussed earlier, increase in feed concentration results in increase in concentration polarization leading to enhanced osmotic pressure buildup on the membrane surface. This leads to more permeation of solute through the membrane. For example, at 828 kPa pressure and 0.91 m/s crossflow velocity, the permeate concentration is about 1 mg/l when feed concentration is 25 mg/l, whereas the permeate concentration is about 2.4 mg/l when feed concentration is 40 mg/l. It is observed from Fig. 6 that for maximum crossflow velocity (0.91 m/s) and lower feed concentration (15, 25 mg/l), the permeate concentration is about 1 mg/l. For all other conditions, permeate concentration varies in the range from 1 to 6 mg/l. Therefore, for Scheme-1, if the starting feed concentration is between 100 and 200 mg/l, AOP for 0.5 h followed by NF, may not lead to a desirable quality of the permeate (with dye concentration < 1 mg/l). For lesser feed dye concentrations (up to 70 mg/l), AOP followed by NF may be viable.

3.2. Scheme-2

In Scheme-2, NF is adopted first and AOP is employed thereafter. The variations of steady state flux with operating pressure under various feed concentrations and crossflow velocities are presented in Fig. 7. The figure shows the usual trends, i.e., the permeate flux increases with pressure and crossflow velocity but decreases with feed concentration. Interestingly, it may be noted that the range of permeate flux at 552 kPa for different crossflow velocity and feed concentration is in between 36 and 46 l/m^2 h and at 828 kPa, it is between 57 and 63 l/m^2 h. At higher pressure (828 kPa), the flux is less compared to that of NF in Scheme-1 (range of flux 62.5–68 l/m^2 h in Scheme-1). This is quite expected as the feed concentration of dye is much higher in this case (70–200 mg/l) compared to that of NF in Scheme-1 (15–40 mg/l). As discussed earlier, higher feed concentration favours concentration polarization and resulting in more flux decline. The drop in permeate flux with respect to pure water
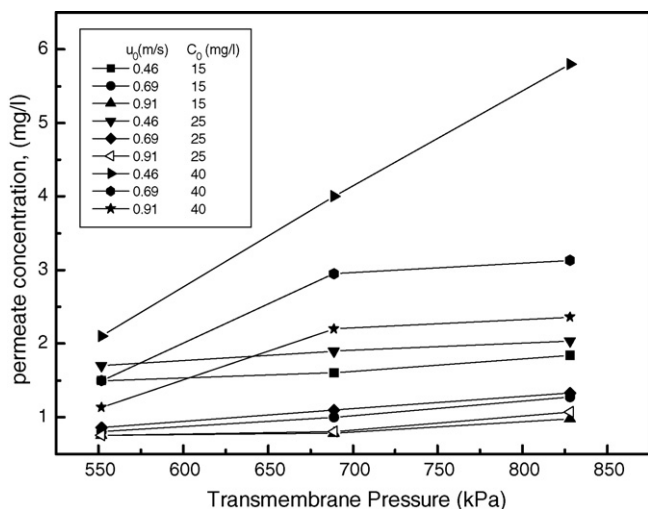

Fig. 6. Variation of eosin concentration in permeate with transmembrane pressure under different operating conditions in Scheme-1.
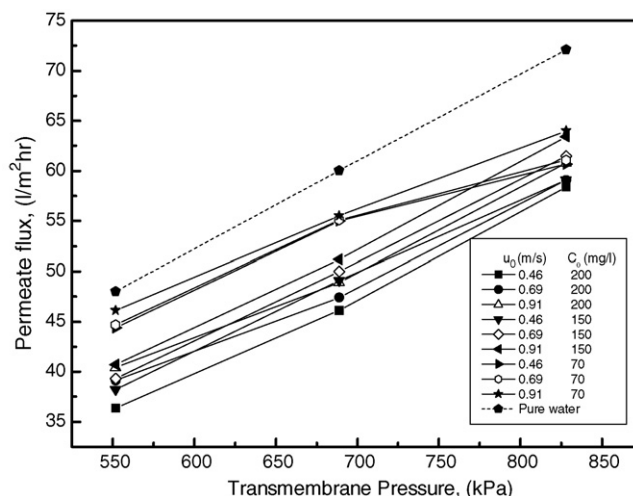

Fig. 7. Permeate flux vs. transmembrane pressure under different operating conditions in Scheme-2.
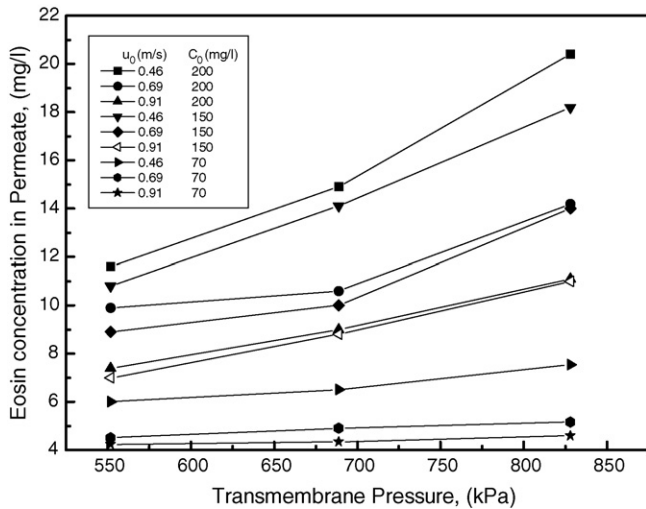
Fig. 8. Variation of eosin concentration in permeate with transmembrane pressure under different operating conditions in Scheme-2.

Table 3
Permeate flux data for NF under Scheme-3

Sl. no.	C_0 (mg/l)	Crossflow velocity, u_0 (m/s)	Permeate flux (l/m² h)		
			552 kPa	689 kPa	828 kPa
1	10	0.46	46.3	58.3	67.1
2	10	0.69	46.7	58.6	68.1
3	10	0.91	47.1	58.9	68.9
4	15	0.46	46.2	58	66.6
5	15	0.69	46.6	58.2	67.6
6	15	0.91	47	58.6	68.5
7	25	0.46	45.1	57.6	65.7
8	25	0.69	45.7	58.1	66.9
9	25	0.91	46.0	58.3	67.5
10	0 (distilled water)		48.0	59.8	72.5

flux is also more in this case (Scheme-2), about 12–20% compared to 6–13% drop in Scheme-1.

The variation of steady state permeate concentration with pressure is shown in Fig. 7. The permeate dye concentration is in the range of 4–12 mg/l at 552 kPa pressure and about 5–21 mg/l at 828 kPa. Therefore, although higher transmembrane pressure leads to increase in flux, the permeate concentration deteriorates significantly. Since, the permeate dye concentration after NF is in the range of 4–12 mg/l at lower pressure, AOP is employed to treat this range of concentration with various dosage of ferrous sulfate and H_2O_2 (as given in Section 2.2.1.2). A typical dye degradation plot with a typical composition of Fenton's reagent is shown in Fig. 9 for various initial dye concentrations. It is observed from Fig. 9 that even after 3 h, dye concentration does not fall below 1 mg/l for most of the feed concentrations, apart from 2 mg/l. For feed concentrations of 4–12 mg/l, the dye concentrations are in the range of 1.5–4.7 mg/l after 3 h. Therefore, Scheme-2 results into lower permeate flux during NF, higher
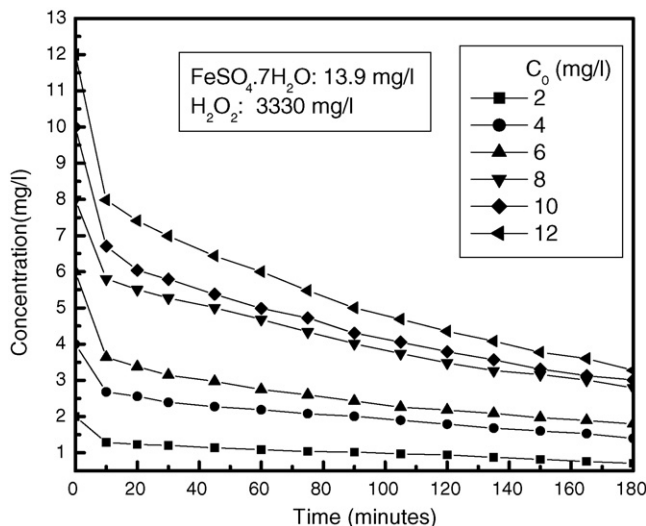
operating time for AOP and hence should not be employed to treat the textile effluent.

3.3. Scheme-3

In Scheme-3, a two-step NF process is employed. The results of first stage NF for permeate flux and concentration are already presented in Figs. 8 and 9, respectively. The first stage NF results in permeate concentration in the range of 4–21 mg/l. Hence, a range of feed concentrations from 10 to 25 mg/l is considered for the second stage NF. It may be observed from Table 3, that for all the operating conditions, at 552 kPa, the permeate flux is in the range of 45–47 l/m² h and that at 828 kPa pressure, is from 65 to 67 l/m² h. The flux values at higher crossflow velocity and lower feed concentrations are quite closer to pure water flux values. Permeate flux profiles follow the usual trends with the operating conditions.

In Fig. 10, the variations of the permeate concentration with pressure under various operating conditions are presented. The range of variation of permeate dye concentration is from 0.6 to 2.0 mg/l. It may be observed that at 552 kPa pressure, the

Fig. 9. Variation of concentration with time during AOP of Scheme-2.
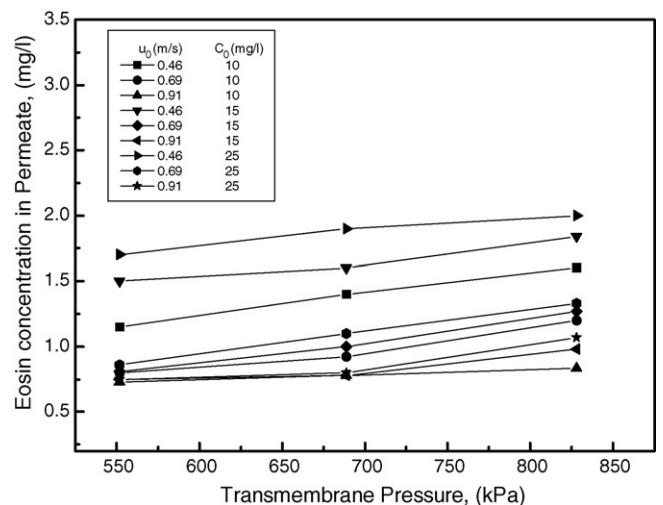

Fig. 10. Variation of eosin concentration in permeate with transmembrane pressure under different operating conditions in Scheme-3.

permeate dye concentration is in the range 0.6–0.8 mg/l for all feed concentrations and crossflow velocities except the lowest crossflow velocity, i.e., 0.46 m/s. Even at the highest operating pressure of 828 kPa, the permeate concentration is below 1 mg/l for the highest crossflow velocity, 0.91 m/s. Another advantage of two-step NF is, unlike AOP, no additional chemicals are added to the system. Therefore, Scheme-3 is comparable to Scheme-1 for the treatment of textile effluent.

4. Conclusions

- Scheme-1 is found suitable for eosin dye removal for dye concentration up to 70 mg/l. For higher concentration (100–200 mg/l), it is difficult to reduce dye concentration below 1 mg/l. The appropriate composition of Fenton's reagent is 1665 mg/l of H_2O_2 and 347.5 mg/l of $FeSO_4 \cdot 7H_2O$. Suitable NF operating condition in step 2 of Scheme-1 is 689 kPa transmembrane pressure and 0.91 m/s of crossflow velocity. The permeate flux increases and the permeate concentration decreases with the crossflow velocity.
- Scheme-2 is not found suitable for dye removal as the eosin concentration is not reduced to less than 1 mg/l even in 3 h in the AOP step.
- Scheme-3, i.e., two step NF is the most suitable among all the three schemes, as it reduces eosin concentration to less than 1 mg/l at all the feed concentrations (70–200 mg/l) of eosin studied herein. It may be noted here that this scheme-is attractive as there is no need of additional chemicals, like Fenton's reagents. The suitable NF operating conditions in both steps of this scheme-are 828 kPa transmembrane pressure 0.91 m/s as the crossflow velocity.
- As indicated in the study, the time required to reduce the concentration of dye to the level of 1 mg/l by AOP is large, even though the initial rate of dye degradation is fast. Similarly, a one step NF cannot reduce the dye concentration below 1 mg/l. Thus, a combined process like Scheme-1 or -3 is a viable alternative to dye removal from the aqueous stream. Therefore, a combined process makes the removal of dye more feasible.

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