5th International Conference on Water Resources and Arid Environments (ICWRAE 5): 602-608
7-9 January 2013, Riyadh, Saudi Arabia

Surfactants Role in the Enhancement of the Treatment Efficiency of Dyeing Effluents with Combination of Membrane Processes

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Abstract: The industrial process of reactive dyeing of cotton is a sequence of several operations. Different types of surfactants were used several times during the dyeing process i.e., anionic, nonionic and cationic. The dyeing effluent is heavily charged with pollution especially color and salt. In a treatment at source approach, the dyeing effluent was isolated and then mixed with the other baths containing surfactants. A combined treatment involving microfiltration (MF) as pretreatment followed by nanofiltration (NF) as mean treatment, was used. The mixing of the dyeing bath with another effluent showed 100% of MF flux improvement but the color retention still higher for the single dyeing bath. The NF treatment produces a completely discolored effluent with 100% of suspended solids retention, while the chlorides removal did not exceed 50%.

Key words: Reactive dyeing · Surfactants · Microfiltration · Nanofiltration · Color removal · Chlorides retention

INTRODUCTION

Textile industry is not only a big consumer of fresh water but also it uses huge amounts of complex chemical substances. Reactive dyes, due to its fixation characteristics and chemical degradation resistance, are widely used for cellulose as well as for cotton dyeing. It was cited that 1kg of cotton requires 70 to 150l of fresh water, 0.6 kg of NaCl and 40g of reactive dye [1]. As a consequence, huge volumes of extremely polluted wastewaters are generated during various processing stages. Direct discharge of these effluents into the environment causes irreversible ecological problems; also increasing restrictive legislations referred to final disposal into the main sewage network, make industrial wastewater treatment a necessity. The current trends in the treatment of textile wastewater include conventional activated sludge (CAS) and coagulation/ Flocculation (CF). However, those systems require the input of wide range of chemicals, need an important installation space and poorly remove the widely used reactive dye [2]. So, there is an urgent need to develop more efficient and inexpensive methods which require fewer chemicals and energy consumptions and less installation spaces. Membrane technology is relatively a recent approach, but it gained a wider acceptance and became a promising technology that responds to economical and space requirements.

Membrane processes that can meet the legislative requirements are nanofiltration (NF) and reverse osmosis (RO) since they are able to retain small organic compounds as well as dye molecules [3]. However, a comparison between NF and RO shows that permeate flux of NF is greater while the energy consumption is less[4]. Because of the pore size of NF membrane (almost 10^{-9}m) as well as substances properties in the dyeing effluents including important amounts of hydrolyzed dye, salt, suspended solids and auxiliaries, membrane fouling represents the major limitation for the use of single NF treatment. Fouling is susceptible to damage the membrane as well as to reduce its lifetime and leads to high operational costs [5]. To prevent membrane fouling and to enhance NF performances, feed pretreatment was necessary. Microfiltration (MF) is a membrane separation technique that can assume the pre-filtration role with taking into account high pollution removal and space constrain. Ellouze et al. [6]observed that the use of MF as pretreatment for NF when compared with C/F gives the

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best performances regarding to the retention of color (96.2% for MF and 92.8% for C/F) and salt (26% for MF and 15.7% For C/F). Rozzi *et al*. [7] found that in most cases, COD retention was near 70% and color removal was more than 95% when MF is coupled with NF.

The dyeing effluent compared to other operations of the dyeing cycle using reactive dye is the most charged with pollution. Besides, it contains hydrolyzed reactive dyes and important amounts of salts and auxiliaries. In order to prevent this heavily colored effluent from contaminating the overall wastewater, treatment at source seems to be a good alternative. In this treatment scheme the dyeing effluent is isolated and then it can be mixed with other effluents in order to be diluted and in an attempt to have favorable reactions between different baths components [8]. In this context, the relation between the use of surfactant and the enhancement of dye removal from textile wastewater was the goal of many studies. C. Kartal et al. [9] investigated the possible interactions between anionic or nonionic surfactant with anionic reactive dye and found that while nonionic surfactant formed a complex with the dye molecule, the anionic one did not; also, it was concluded that the use of two surfactants simultaneously increased the absorbance value due to charged hydrophobic-hydrophilic balance. In the same context, H. Akbas et al. [10] studied the interactions between cationic or nonionic surfactant and anionic reactive dye; they found that the stability of the complex cationic surfactant-anionic dye was reduced when a nonionic surfactant was added. Zaghbani et al. [11] found that the use of anionic surfactants with cationic dyes enhanced color rejection by an UF membrane, which exceeds 97%.

NF membranes are generally charged negatively [12]. In this case, electrostatic interactions drive the membrane behavior with charged particles. J.M.M. Peeters et al. [13] found that salts rejection with negatively charged NF membrane is controlled by Donnan effect; it is a potential difference created at the interface membrane-solution to counteract the transport of anions through the membrane negatively charged.

The purpose of this study was to investigate the behavior of combined MF/NF processes in the treatment of real reactive dyeing wastewater in the presence of surfactants coming from the different effluents of the dyeing cycle. The possible interactions between the different species such as anionic reactive dye molecules and anionic, cationic and nonionic surfactants and the impact of the different baths combinations on the filtration behavior were studied. The capacity of NF in salts removal especially chlorides was studied taking into account interactions between membrane and pollutants.

MATERIALS AND METHODS

Dyeing Cycle and Baths Mixing: The effluents, which constitute the object of this study, were collected from a dyeing machine of cotton using reactive dyes. Data regarding the different operations forming the dyeing cycle, the operating conditions and auxiliaries added in each step were collected in Table 1. It is noticed that after each operation the effluent was drained out and fresh water was used in the next step.

Surfactants were used three times in the dyeing cycle, anionic surfactant in the preparation bath, nonionic in washing and cationic in softening. In order to study the impact of surfactants on the treatment of the dyeing bath using membrane processes, different mixtures were realized: The first 3 configurations were obtained by mixing the dyeing bath with one other bath (D+P, D+W, D+S), then, to study the effect of more than one surfactant on the treatment behavior, configurations 'D+P+W', 'D+P+S' and 'D+W+S' were realized. In order to highlight the surfactants contribution on the treatment, the dyeing bath was treated separately.

Table 1: Operating conditions of the dyeing process steps

Operation	pH	T (°C)	T (min)	Additives
Preparation (P)	6-7	30	5	anionic surfactant Acetic acid
Dyeing (D)	9-11	60	110	Reactive dyes (anionic) Sodium chloride Sodium carbonate Sodium hydroxide
Neutralizing (N)	6-7	50	5	Acetic acid
Washing (W)	6-7	80	5	nonionic surfactant
Softening (S)	5-6	40	20	Acetic acid cationic surfactant

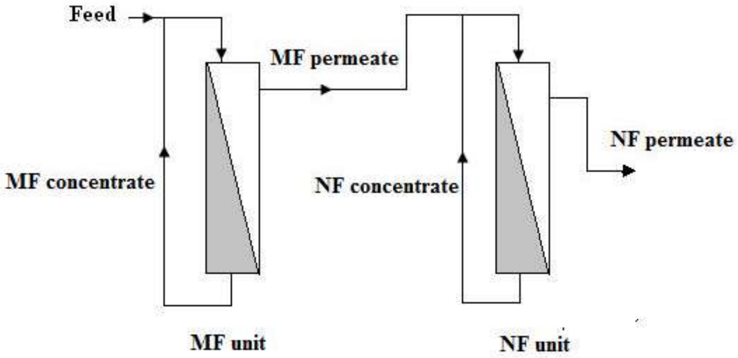

Fig. 1: Schematic presentation of the experimental set-up of MF/NF combination

Combined MF/ NF Treatment: In the coupled treatment, MF and NF membranes are connected. The MF permeate was fed to the NF membrane. The concentrates obtained from MF and NF are gathered and fed back into the MF feed tank. NF permeate was recovered for reuse in dyeing tests (Fig. 1).

For the MF experiments, membralox module (1P19-40/1R19-40) of 1020 mm length was used. The membrane is a multi-channel type (19 channels) made of porous ceramic based on alumina with an area of 0.24 m^2 and pore size of 0.2 µm. The NF membrane is DESAL membrane product (DK2540F1073) having spiral configuration with a length of 1016 mm, an active area of 2.5 m^2 and a weight cut off (MWCO) of 200 Da. After each test, membranes were chemically cleaned following: base cleaning with NaOH solution (T= 80°C, ΔP=2 bar for MF and T= 40°C, ΔP=6 for NF), rinsing then acid cleaning with HNO_3 solution (T=60°C, ΔP=2 bar for MF and T= 30°C, ΔP=6 for NF).

Analytical Measurements: The removal of dye was followed by absorbance measurements at the visible maximum dye absorption wavelength (560 nm) using a UV-visible spectrophotometer (Perkin Elmer Lambda 20 UV/VIS). Chlorides amounts were calculated after a simple dosage by $AgNO_3$. For the evaluation of MF rejection, the percent reduction of color was determined from the absorbance value in the feed and in the MF permeate (A_f and $Ap._{MF}$ respectively) as follows:

$$R(\%) = \left(1 - \frac{A_{p,MF}}{A_f}\right).100 \quad (1)$$

The mass percentages present in the dye mass balance are calculated from the concentration values using the Beer Lambert law connecting linearly the absorbance value to the concentration. The chlorides removal after the NF treatment was calculated from the chloride amounts in the MF and NF permeates ($C_{p,MF}$ and $C_{p,NF}$ respectively) using the rejection parameter as follows:

$$R(\%) = \left(1 - \frac{C_{p,NF}}{C_{p,MF}}\right).100 \quad (2)$$

RESULTS AND DISCUSSION

Effluents Characterization: Before studying the treatment perforamances, it was necessary to identify the pollution level of the different effluents. Table 2 represents the characterization of all realized configurations. It can be seen that the dyeing effluent was heavily loaded with salts and color compared with the other effluents. On the other hand, all these effluents represented a pH above the isoelectric point (IEP) of the MF membrane, which is between 6 and 7.5 for ceramic membrane [14]. This will lead to a negative charge of the membrane surface.

MF Filtration Flux: Figure 2 illustrates the filtration flux versus time for all baths mixtures. During the filtration tests, permeate fluxes decrease dramatically in the first 20 minutes then remains relatively constant, this behavior is attributed to the establishment of the membrane fouling. This phenomenon can be explained by the increased concentration close to the membrane surface due to the pollutant retention.

When one surfactant was used, the filtration flux was enhanced at least by 90% since the stabilized permeate flux varies from 60 l/h.m^2 for the dyeing effluent to a value between 100 and 120 l/h.m^2 for the effluent coming from baths mixture. Also, when two baths containing different surfactants were mixed with the dyeing effluent,

Table 2: Characterization of the different baths combinations

configuration	pH	TDS (g/l)	S(g/l)	SS (mg/l)	TH (°F)	Cl-(g/l)	COD (g/l)	color[a]	Turb (NTU)
D	11.49	102.8	107.2	140	220	44.37	3.2	11.4	16.2
D+P	10.37	23.4	21.3	142	120	14.2	1.7	4.5	9.7
D+W	11.25	35.1	36.4	120	260	19.88	1.5	4.6	11.9
D+S	10.58	33.2	34.4	64	172	18.85	2.3	5.1	9.5
D+P+W	9.71	19.93	20.1	42	208	9.23	1.2	3.4	9.79
D+P+S	10.03	24.13	23.7	70	251	13.65	1.7	3.1	9.7
D+W+S	9.93	23.1	22.9	115	180	12.78	2.6	4.4	8.4

[a] Integral of the absorbance curve in the hole visible range (400-800 nm).

MF Performances

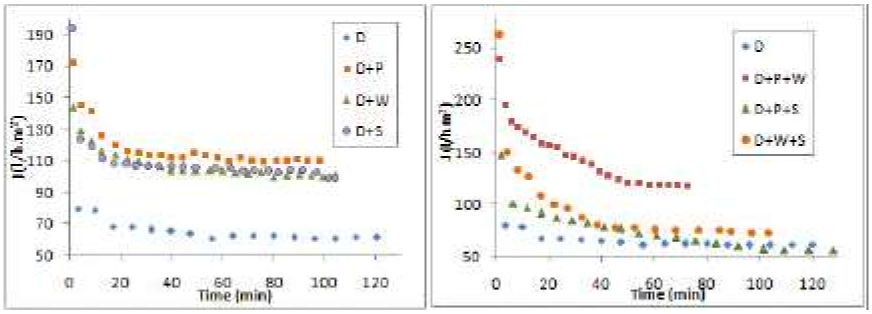

Fig. 2: Variation of the MF filtration flux versus time.

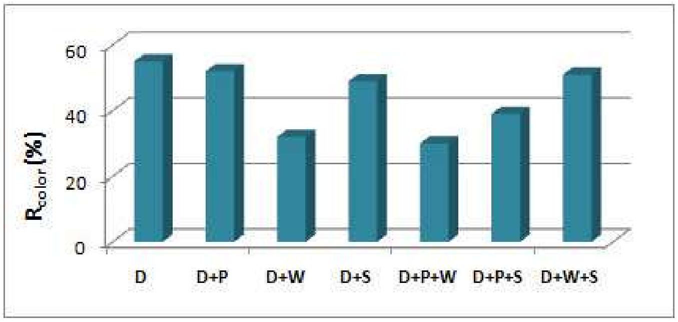

Fig. 3: Color removal by MF for different configurations.

an improvement in the stabilized flux value occurred for the combination D+P+W containing anionic and nonionic surfactants, from 60 l/h.m^2 to 130 l/h.m^2. The other configurations showed lower fouling intensity than the dyeing effluent filtration, but the stabilized flux didn't show an important enhancement.

Color Removal by MF: Figure 3 represents the percentage of color removal for all configurations after MF. It was not possible to translate these results without understanding the membrane behavior towards dyes particles. In order to study the fouling phenomena taking place on the membrane surface, a color mass balance was realized (Table 2).

The best color retention value was given by the dyeing bath (55%). However, more than 48% of the initial dyes were found in the concentrate and only about 18% were fixed by the membrane (Table 3). Due to the alkaline nature of the effluent, probably an electrostatic repulsion occurred between the membranes charged negatively and anionic dyes which prevented the passage of dye

Table 3: Dye mass balance for MF process

Configuration	m_p (%)	m_c(%)	□(%)
D	33,60	48,68	17,72
D+P	36,08	50,56	13,37
D+W	50,93	45,11	3,97
D+S	41,93	44,61	13,47
D+P +W	52,58	45,14	2,29
D+P+S	45,64	43,29	11,07
D+W+S	36,79	43,75	19,46

m_p: mass percentage of dye load in the permeate; m_c: mass proportion of dye load in the concentrate and □: mass proportion of dye fixed on the membrane.

particles through the membrane. Also the relatively important amount of adsorbed dye is often due to the great dye concentration in the feed causing a pore size reduction, which contributed to the significant color removal.

About 53% of color was removed when the dyeing effluent was mixed with the preparation bath containing anionic surfactant (D+P); from the mass balance estimation, about 50% of dye was present in the concentrate, this can be explained by the increase of repulsion forces applied on the dye molecule resulting from the membrane surface and the anionic surfactant. D+S configuration also led to a color removal above 50% due to the ability of the cationic surfactant to form voluminous complex with anionic dye, which can be retained by the membrane [10]. From the mass balance, it can be seen that adsorption of dye on the membrane surface took place for this last configuration since the amount of adsorbed dye is more than 13%.

However, the addition of the washing effluent reduced the color removal of D+P configuration and improved it for D+S. This is attributed to the ability of nonionic surfactant present in the washing bath (W) to interact strongly with anionic surfactant (P) and weakly with cationic one (S). Thus, the mixture of anionic and nonionic surfactants changed the hydrophobic-hydrophilic balance [9].

It was expected that the presence of the softening bath would improve the adsorption behavior of the membrane due to the ability of the cationic surfactant to interact strongly with the reactive dye molecules or with the anionic surfactant. This is approved by the dye mass balance results showing that the amount of dye adsorbed by the MF membrane was among the most important values, almost 13, 11 and 19% respectively for D+S, D+P+S and D+W+S mixed baths.

NF Performances

NF Filtration Flux: Figure 4 represent the variation of the NF filtration flux with time for different configurations. The curves show a typical behavior of a NF membrane, the fluxes drop slightly in the first 15 minutes then remain relatively constant. This is a typical behavior of NF membrane and can be explained by the membrane fouling due to the increasing concentration of the feed and the matter accumulation on the vicinity of the membrane. With a stabilized flux of 25 l/h.m^2 for the single dyeing effluent treatment, it is clearly observed that the baths mixing enhanced the filtration performances especially for the configurations D+P (stabilized flux of 42 l/h.m^2) and D+P+W (stabilized flux of about 39 l/h.m^2). The configuration D+P+W exhibits low fouling intensity; the initial filtration flux is about 46 l/h.m^2 and it stabilizes at 42 l/h.m^2.

Chlorides Removal by the NF Membrane: After the NF treatment, color and suspended solids were completely removed but salts amounts still relatively high in the NF permeate. The important amounts of sodium chloride used to fix dyes on the substrate are responsible on the high salts concentration in the dyeing effluent. Therefore, the chlorides retention by the NF membrane was calculated for each configuration (Fig. 5).

Since the chloride molecule size is about 0.25 nm and NF membrane pore size is almost 1 nm, the removal of chlorides will not be possible by the NF membrane. However, Fig. 5 shows a chlorides removal of at least 20%. Taking into account this behavior and the negative charge of the membrane, it is to be expected that chloride elimination by NF membrane was driven by Donnan effect and an electrostatic repulsion occurred between the membrane and the anions [12, 13].

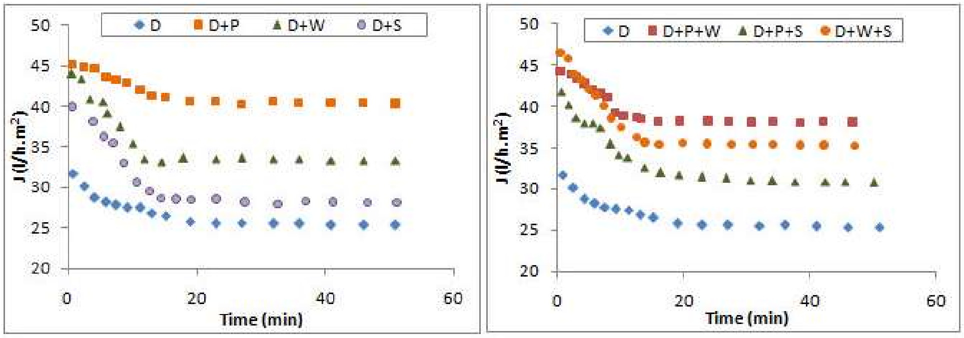

Fig. 4: The variation of the NF filtration flux versus time

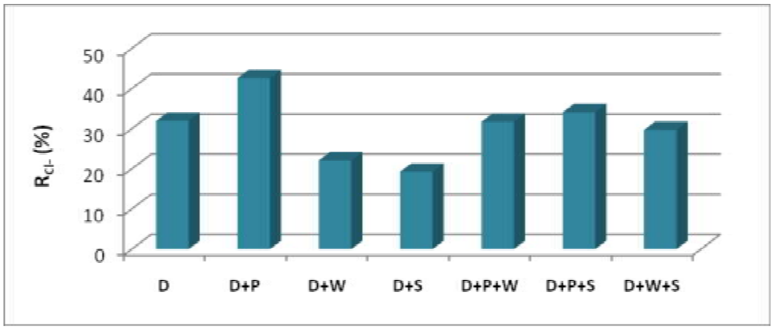

Fig. 5: Chloride retention by NF membrane.

The NF treatment of the dyeing bath shows a chlorides removal of 31%. The addition of the preparation effluent to the dyeing bath (D+P) enhanced the chloride removal to 42%; this behavior is due to the increase of repulsion forces applied between the chloride molecule, the anionic surfactant (P) and the membrane. Both configurations (D+W) and (D+S) represent chlorides removals respectively of 22% and 19%; this reduction of the chlorides elimination capacity of the NF membrane is probably due to the neutralization of some negative charges due the presence of nonionic or cationic surfactants in the washing and softening effluents.

The D+P+W, D+P+S and D+W+S configurations give respectively 31%, 34% and 29% of chlorides retention, these values are around the retention given by the dyeing effluent (31%). This can be explained either by high elimination of surfactants by MF membrane or by the possible interactions between nonionic surfactant and anionic ones [9, 10] as well as between anionic and cationic surfactants. In this case, it is to be expected that the membrane behavior was similar to its behavior in the treatment of the single dyeing bath.

CONCLUSIONS

Membrane filtration showed to be a promising technology for the treatment of dyeing wastewaters. A combined treatment of MF and NF was investigated in this study. The dilution of the heavily colored dyeing bath with other effluents containing different types of surfactants before the treatment enhanced the membranes efficiency especially in term of filtration flux. Indeed, the addition to the dyeing bath of the effluents containing one surfactant enhanced the MF filtration efficiency by 90% at least and of NF by 70% for ‘D+P’ configuration. The color removal by MF membrane is the highest when the dyeing effluent was treated separately due to the great concentration of dye in this effluent and the negative charge of the membrane, which is responsible for the electrostatic repulsion with the anionic dye. The chlorides rejection by NF membrane was driven by Donnan effect, but it was not sufficient to provide a chloride removal exceeding 50%. For the different configurations considered in this study, the combined treatment provides almost 100% of color and turbidity removal, but salt rejection was less than 50%. Surfactants assuming particularly an important role in the dyeing cycle, can be useful for color removal from wastewater with MF/ NF treatment, however, suitable mixture of the different baths is needed to obtain the best performances regarding permeate flux and quality.

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