



Hybrid coagulation/membrane process treatment applied to the treatment of industrial dyeing effluent

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Received 11 August 2014; Accepted 18 January 2015

ABSTRACT

A combined system of coagulation and membrane processes was investigated in this study for reactive dyeing wastewater treatment. Microfiltration (MF) and ultrafiltration (UF) membranes were tested in order to study the effect of the membrane type on the hybrid system performances. Additionally, membrane resistance analyses were conducted in order to understand the membrane fouling mechanism. Two different coagulants were used: $\text{Al}_2(\text{SO}_4)_3$ (Alum) and Amerfloc445. The influence of the coagulation conditions including coagulant nature and shear rate and duration on the UF behavior was studied. Indeed, a procedure of flocs breakage–reformation under different shear intensities was followed in the coagulation step, during these tests, flocs size and sensitivity to breakage as well as their regrowth ability were examined. The filtration results indicated that the coagulation step did not enhance the MF performances. The coagulation/ultrafiltration system was found to be better not only in term of permeate quality but also in fouling minimization. Although, Amerfloc445 generated the largest flocs with the best regrowth ability, but these flocs were more sensitive in increasing shear rate. As a result, the flocs breakage dropped the UF normalized flux by at least 22% with Amerfloc445 against a maximum of almost 12% with Alum. The extension of the shear duration from 5 min to 10 min affected the UF behavior especially in the presence of Amerfloc445; indeed the normalized flux decrease reached 14% against just 3% for pre-coagulated effluent with Alum.

Keywords: Coagulation; Membrane filtration; Dyeing effluents; Shear

1. Introduction

The treatment of textile effluents is an urgent need due to their potential effects on the environment if directly discharged. Textile industries are conducted towards the treatment of their effluents using modern technologies in an attempt to meet the requirements of

the increasingly stringent regulations. However, in Tunisia, the manufacturers still prefer the use of conventional technologies, such as biological treatment and coagulation/flocculation, despite their sensitivity to concentration fluctuations and their failure to produce reusable water.

The current trends recently followed in the treatment of dyeing wastewater can be based either on the management of a cleaner sustainable production

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plants [1,2] or on innovative treatment approaches, in which combinations between two or more processes can be considered.

Membrane processes, which are considered among the cleanest water treatment technologies, are increasingly used in the treatment of textile wastewaters regarding their ability to remove a wide variety of pollutants. Different membrane processes are available for this aim; the choice depends on the nature of the compound to be removed. Microfiltration (MF) and ultrafiltration (UF) processes are generally used for the elimination of organic pollution, such as suspended solids and colloids, and can be applied as pretreatment [3] or main treatment [4], nanofiltration (NF) and reverse osmosis (RO) can remove dissolved compounds, ions and dyes, and are generally involved for a reuse aim [5]. Despite their efficiency in pollutants removal, fouling still the major limitation of the membranes used in the textile effluents treatment, which can cause severe permeate flux decline [6].

To minimize the fouling intensity on the membrane surface, pretreatment seems to be a good alternative. Many possible combinations of membrane processes were carried out in different studies. Generally, MF and UF are assumed to be the pretreatment function for NF and RO. Tahri et al. [7] studied the efficiency of a combined system of MF and NF in the treatment of heavily polluted dye bath, they found that almost 100% of color and suspended solids were rejected and high removal of chemical oxygen demand (COD) and salt was achieved by 73–85% and 47–52%, respectively, they also demonstrated that the treated water can be reused in the dyeing process. Marcucci et al. [8] compared UF/ NF and UF/ RO systems in the treatment of a mixture of textile effluents and found that the NF did not reach the retention performances achieved by RO, especially in term of salt removal.

2. Literature review

Due to the high operational cost of the membrane processes especially NF and RO, another approach based on the pretreatment of textile effluents prior to membrane process can be envisaged, it consists of a hybrid treatment. In this approach, membranes are generally applied after biological treatment [9,10] or coagulation/flocculation (CF) [11,12]. The coupling of CF or simple coagulation (C) prior to membrane processes is widely applied due to the ability of C and CF to form voluminous complex with pollutants, which can be easily retained by the membrane. Indeed, in the coagulation of dye solutions, colloid

particles contained in the effluent have to be destabilized due to the action of coagulant, which contributes to weaken the repulsion forces present between particles with same charges. Due to this fact, particles can aggregate to each other and form bigger particles that can be able to precipitate. Zahrim et al. [13] stated that about 20% of NF flux improvement was achieved when a CF pretreatment was introduced. Lee et al. [14] compared MF and UF performances for pre-coagulated textile effluent, they found that the addition of the coagulant led to the decrease of MF permeate flux and severe pore clogging, whereas, the UF performances were improved when coupled with coagulation. Rozzi et al. [15] tested the hybrid system of C/MF for textile wastewater treatment and claimed that the coagulant use was necessary to obtain a satisfactory performance regarding quality while rapid membrane fouling occurred.

Under dosage of coagulant can be inefficient to destabilize the majority of present particles and can affect the performance of the treatment. On the other hand, over dosage can cause severe membrane fouling [16] as well as the rise of operating costs. Thus, the optimization of coagulant dosages seems to be an essential factor to advance the treatment performance. Many studies focused on the relation between the nature and dose of the coagulant on one hand, and the filtration performances on the other hand. In this context, Bes-Pia et al. [17] and Ahmad and Puasa [18] investigated the coupling of CF and membrane processes to treat textile wastewater and demonstrated that the color rejection by the membrane was strongly related to the coagulant nature and dose. Lee et al. [14] demonstrated that the optimal coagulant dose minimized the fouling as well as the cake layer resistance on UF membrane and that the permeate flux dropped when larger dose of coagulant was used. Choo et al. [16] studied the effect of the coagulant type on textile wastewater reclamation using C/UF system; they claimed that polymeric coagulant can cause fouling at a larger dosage than optimum and that membrane fouling became worse with a small dose. Also, they found that inorganic coagulants exhibited lower membrane fouling.

Another coagulation parameter which may affect the filtration behavior and that has been recently studied concerns the flocs characteristics. Wang et al. [19] investigated the flocs size, strength, and structure in the coagulation process with aluminum coagulants for the treatment of humic acid solution; they followed a floc formation, breakage, and reformation procedure to study the stability and the regrowth ability of the formed flocs as a coagulant characteristic, which can influence the coagulant selection. Xu et al. [20] studied

the influence of flocs size and structure on membrane fouling using C/UF process. They found that the optimum dose of coagulant did not correspond to the largest floc size despite the high filtration performances.

The effect of shear conditions on floc properties and fouling on C/UF system using humic acid solutions was investigated by Xu and Gao [21]. They concluded that the increase in shear rate decreased the flocs size resulting in severe flux decline. The extension of breaking time resulted in obvious increase in the cake layer resistance, which caused the decrease of the UF fluxes.

3. Objective of the study

In this work, C/MF and C/UF systems were investigated for the treatment of highly concentrated industrial reactive dyeing wastewater in pilot scale. Two types of coagulants were used in this study (organic and inorganic). First of all, the optimum dose of each coagulant was determined by following the color and COD removals. Then, a comparison between MF and UF performances was achieved. The effect of shear conditions (intensity and time) on the flocs size and on the UF behavior was then investigated.

4. Materials and methods

4.1. Experimental setup

The experimental setup was composed of a cylindrical feed tank of 40 L volume equipped with a numeric stirrer apparatus (Witeg, WiseStir HS-100D). MF or UF module can be installed subsequently to the coagulation tank (Fig. 1). MEMBRALOX module

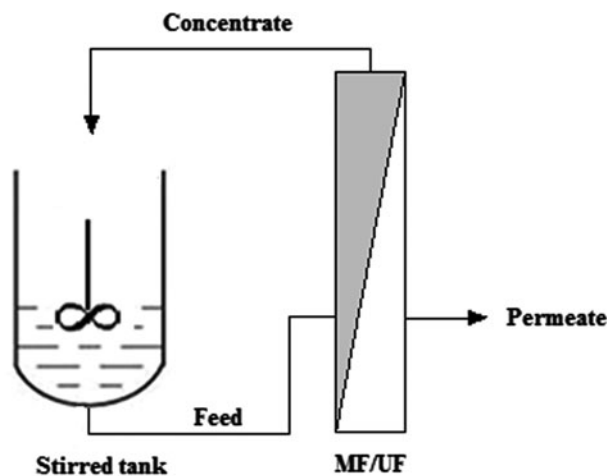


Fig. 1. Schematic representation of the experimental setup.

(1P19–40/1R19–40) of 1,020 mm length was used in the MF experiments. The membrane is multi-channel (19 channels) of 0.2 μm pore size made of ceramic based on Al_2O_3 with a surface exchange of 0.24 m^2 . The temperature was the room temperature and the operating pressure was fixed at 2 bar.

The UF runs were performed using KLEANSEP multichannel membrane (7 channels) of 1,178 mm length. The membrane was made of ceramic based on $\text{TiO}_2\text{-Al}_2\text{O}_3$ with an area of 0.15 m^2 and a molecular cut-off of 15 kDa. Runs were conducted at the room temperature and the pressure was fixed at 3 bar.

The membranes performances were evaluated by the rejection rate of color and COD determined as follows:

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

where C_p and C_f are the concentrations in the permeate and in the feed, respectively.

The variation of the filtration flux was followed with the volume reduction factor (VRF) which was calculated as follows:

$$VRF = \frac{V_f}{V_c} \quad (2)$$

where V_f and V_c are the feed and the concentrate volumes, respectively.

4.2. Industrial wastewater and coagulants

The studied effluent was collected from a dyeing machine in a textile company in Kasr Helal, Tunisia, where the experiments were conducted. The effluent is released from reactive dyeing operation and it represents a mixture of different baths used in the dyeing cycle. The dyeing procedure is represented in Table 1. The treated water is a mixture of all the baths at the same proportions, and the effluent temperature was equilibrated at room temperature before beginning the run. The averaged characteristics of the mixed wastewater are represented in Table 2. It is obvious that the effluent was heavily polluted and especially, charged with color and salt.

Two different coagulants were used; $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (Alum) and an organic cationic coagulant commercialized as Amerfloc445 by Ashland and identified by Rierra-Torres et al. [11] using IR spectrum as melamine-urea-formaldehyde (Fig. 2). Both coagulants were used in pure form and were diluted with distilled water.

Table 1
Operating conditions of the dyeing process steps

Operation	pH	T (°C)	t (min)	additives	Role
Preparation	6–7	30	5	Sequestering agent corrosion protector agent acetic acid	Attach hardening substances prevent corrosion of metallic buttons, fasteners, and zipper
Dyeing	9–11	60	110	Reactive dyes Salt (sodium chloride) sodium carbonate sodium hydroxide	Operation of attaching the dye molecule to the textile
Neutralizing	6–7	50	5	Acetic acid	Add of acid to adjust the basic pH of the tissue
Washing	6–7	80	5	Dispersing and degreasing detergent	Eliminate the excess of dyes and auxiliaries not fixed on the fiber
Softening	5–6	40	20	Acetic acid softening agent	Enhance the feel of textile

Table 2
The dyeing effluent characterization

pH	TDS (g/l)	S (g/l)	TH (°F)	Cl ⁻ (g/l)	COD (g/l)	Color ^a	Turbidity (NTU)	Zp (mV)
9.7	22.3	21.6	120	17.8	1.9	4.6	7.9	-62.3

^aIntegral of the absorbance curve in the whole visible range (400–800 nm).

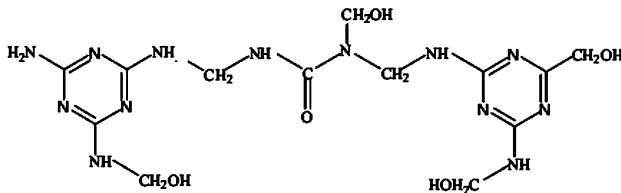


Fig. 2. Amerfloc445 structure.

4.3. The coagulation procedure

For normal coagulation test (without breakage) only 1 min of rapid mixing was considered. When a breakage-reformation procedure was followed, the coagulation runs were conducted following the protocol represented in Table 2. The optimum dose of coagulant was added to the effluent at the same time when the rapid mixing started.

4.4. Flocs characterization

The flocs size and zeta potential values were measured using dynamic light scattering device Zetasizer Nano ZSP; Particles in the sample solution move with a velocity related to their zeta potential, this velocity is measured using a laser interferometric technique. This enables the calculation of electrophoretic mobility, and from this the zeta potential is calculated. Particles size distribution was obtained with the

diffusion of laser light through the sample solution. The flocs properties could be evaluated using breakage and recovery factors, B_f and R_f , respectively [20]:

$$B_f(\%) = \left(1 - \frac{d_2}{d_1}\right) \times 100 \quad (3)$$

$$R_f(\%) = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \quad (4)$$

where, d_1 , d_2 and d_3 are the flocs sizes, respectively, before breakage, after breakage, and after regrowth.

Flocs with lower B_f value are considered stronger and those with higher R_f value are considered with better regrowth capacity.

4.5. Membrane resistance determination

In order to understand the fouling phenomenon occurring on the membrane surface and responsible for the permeate flux decline, the following resistance series model was used:

$$R_T = R_m + R_{rev} + R_{irrev} \quad (5)$$

R_T is the total membrane resistance, R_m is the inherent hydraulic resistance of clean membrane and it was

given by the manufacturer. R_{rev} is generally due to cake layer formation on the membrane surface and can be simply removed with water rinse. R_{irrev} is due to adsorption and pore-blocking, and needs a chemical cleaning to be removed.

The stabilized flux of each test was used to calculate the total resistance following Eq. (6).

$$R_T = \frac{\Delta P}{\mu J} \quad (6)$$

where ΔP is the transmembrane pressure ($\Delta P = (P_i + P_o)/2$ where, P_i and P_o represents the inlet and the outlet pressures of the membrane, respectively), μ is the dynamic viscosity of the permeate and J is the stabilized permeate flux.

After each run the membrane was rinsed with water and the permeate flux was measured giving R_{irrev} . R_{rev} was then calculated by following Eq. (5).

4.6. Analytical methods

In order to follow the evolution of the flocs size and the zeta potential with time during the coagulation step, samples were taken every 2 min during the runs. In the filtration step, only one sample was taken at the end of the essay from the collected permeate. The measurements were done with Zetasizer Nano ZSP device (Section 4.4).

Dye amounts were followed by absorbance measurements with standard dilution multiple method using a UV-visible spectrophotometer (Perkin Elmer Lambda 20 UV/VIS). Measurements were realized at the visible maximum dye absorption wavelength, determined after drawing the absorbance curve in the whole visible range (400–800 nm).

COD was estimated by open reflux method. In this method, a sample is refluxed for two hours in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_2O_7$ consumed, and the oxidizable matter is calculated. The protocol present a method derived from the standard AFNOR T90–101 [22]. Fisher Bioblock Scientific reactor COD 10,119 was used in the experiments.

5. Results and discussion

5.1. Optimization of coagulants doses

To identify the optimum doses of coagulants to be used in the runs, jar tests were conducted with a

range of Alum and Amerfloc445 (from 0.1 to 1.2 g/L). Fig. 3 shows the variation of COD and color retentions in the supernatant with coagulant dosage. The removal efficiency increased with higher coagulant dose for both coagulants until the optimum value. It should be noted that for Alum, the dose of 0.9 g/L contributed to the best COD and color eliminations, by 63 and 44%, respectively. While for Amerfloc445, the optimum dosage was 0.5 g/L, and it achieved 69 and 67% of COD and color removals, respectively. It was obvious that optimal coagulant dose was smaller for Amerfloc445 than for Alum, however, it contributed to better pollution removal efficiency, this could be attributed to better charge neutralization ability, which can led to more voluminous aggregates.

5.2. Flocs study

In this section, the breakage-regrowth procedure (Table 3) was followed in the coagulation step; optimum doses of coagulants were used. The variation of the flocs size during the tests was presented in Fig. 4.

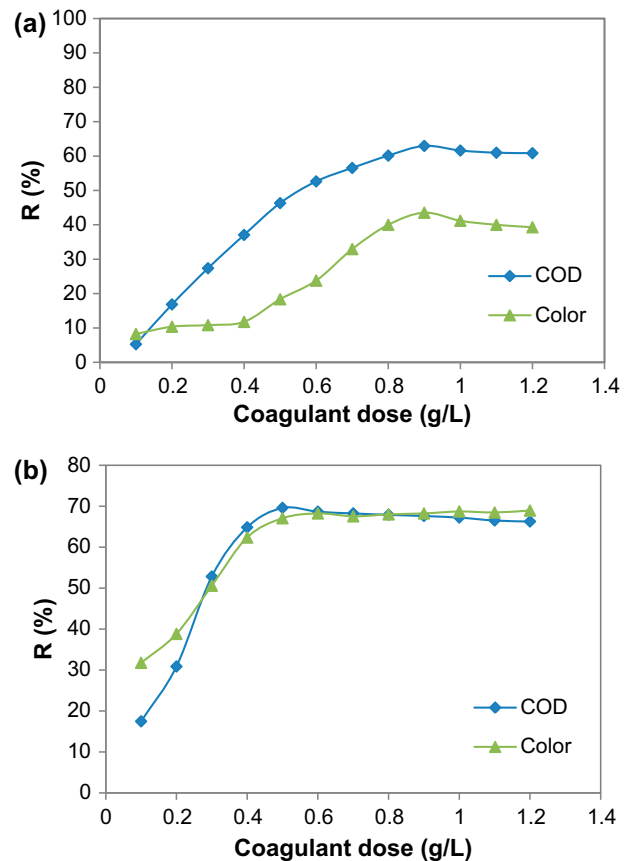


Fig. 3. Retentions of COD and color as a function of (a) Alum and (b) Amerfloc445 dosages.

Table 3
Breakage-reformation procedure

	Rapid mixing	Flocculation	Settling	Breakage	Regrowth
t (min)	1	15	30	5 or 10	15
N (rpm)	400	200	0	300 500 700	200
G (s^{-1})	243.4	153.9	0	188.5 243.4 288.0	153.9

When coagulant was added, the flocs diameter increased rapidly then remained constant. The flocs formed with Alum (488 μm) were distinctly smaller than those formed with Amerfloc445 (845 μm). Once the breaking shear was introduced, the flocs size dropped dramatically, the reduction of the shear rate in the reformation step induced the regrowth of the flocs; this behavior was in agreement with the results obtained by Xu et al. [23].

B_f and R_f factors were calculated according to Eqs. (3) and (4) and the results were represented in Table 4. The B_f decreased when higher breaking shear rate was applied, this behavior was expected since a

severer floc breakage resulting from more vigorous stirring gives smaller flocs size. This result was in accordance with the study of Serra et al. [24] who observed that, for latex flocs breakage, the flocs size decreased with increasing shear rates. R_f decreased with increasing shear regardless the coagulant.

The flocs formed with Amerfloc445 showed a higher sensitivity to breakage than those formed with Alum; these flocs loose between 62.7 and 75.3% of their initial size against a breakage factor below 45.4% for Alum when increasing stirring rate was applied. In addition, the flocs formed with Amerfloc445 seems to be also more recoverable; they can recuperate at least 30% of their initial size, contrary to the flocs formed with Alum which were unable to recover more than 26.5% of their size before breakage.

Zeta potential measurements showed that it dramatically increased after the coagulation as it was -62.4 mV for the dyeing effluent (Table 2), moreover, it remained negative. This is due to the coagulant action which contributed to weaken the repulsion forces between the negatively charged particles. Also, this suggests that particles coagulation was caused by positively charged ions [25].

It is important to notice that zeta potential decreased with the increase of the breakage rate; indeed, severer shear contributed effectively to split more intensively the flocs and led to wider variety of

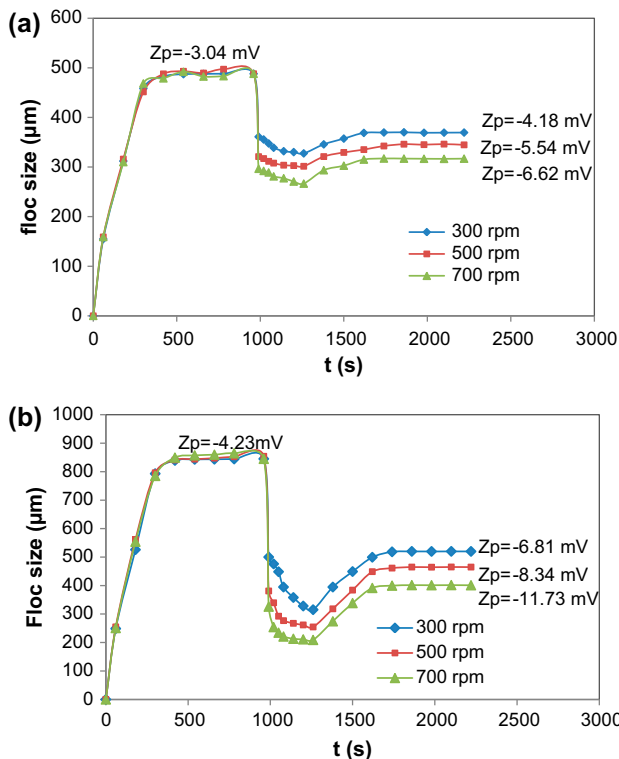


Fig. 4. Evolution of the flocs size during the breakage–reformation procedure under different stirring rates for short breakage period (5 mn) for (a) Alum and (b) Amerfloc445.

Table 4
Breakage and recovery factors of flocs formed with Alum and Amerfloc445 under different shear rates

Coagulant	Alum			Amerfloc445		
Short breakage period (5 mn)						
N (rpm)	300	500	700	300	500	700
B_f (%)	33.9	38.2	45.4	62.7	70.2	75.3
R_f (%)	26.5	23.9	22.8	38.7	35.1	30.3
Long breakage period (10 mn)						
N (rpm)	300					
B_f (%)	35.2			66.7		
R_f (%)	19.6			28.2		

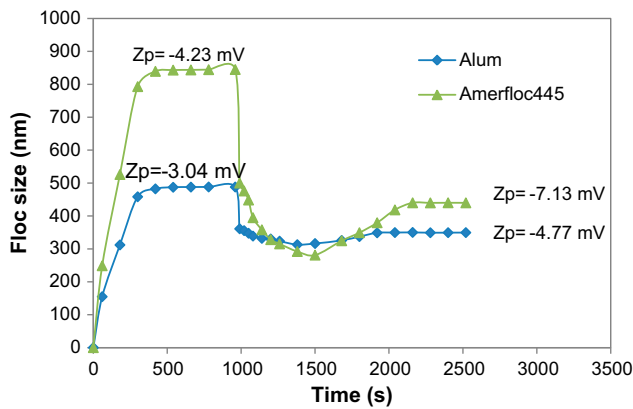


Fig. 5. Variation of flocs size for Alum and Amerfloc445 under breaking shear at 300 rpm for long breakage period (10 mn).

new complexes. Under 700 rpm, Z_p varied before and after breakage from -3.04 mV to -6.62 mV and from -4.23 mV to -11.73 mV for Alum and Amerfloc445, respectively. Certainly, as a polymer with long chain, under the shear effect, Amerfloc445 flocs can be split into wider variety of stable complexes than Alum aggregates.

The extension of the breaking period from 5 to 10 min at the same shear (300 rpm) affected the flocs size in the breakage step as well as in the regrowth step regardless the coagulant (Fig. 5). It could be observed according to Table 3 that B_f increased by 1.3 and 3.7%, while R_f decreased by 6.9 and 10.5%, respectively for Alum and Amerfloc445. This behavior was expected since the flocs exposed to a longer shear lost more of their size before breakage. This result confirmed that the flocs formed with Amerfloc445 were more sensitive to breakage but still more recoverable than particles formed with Alum.

5.3. Comparison between MF and UF performances

5.3.1. Filtration performances

MF and UF runs, using the pre-coagulated effluents with Alum and Amerfloc445 coagulants at their optimum dosages without breakage, were conducted in order to compare the performances of MF and UF. The variations of the normalized permeate flux with time for both coagulants were given by Fig. 6. The quality of MF and UF permeates was also evaluated regarding color and COD removals (Fig. 7). The MF results showed that the addition of Alum coagulant improved the normalized flux by almost 30%. The addition of alum coagulant led to color and COD

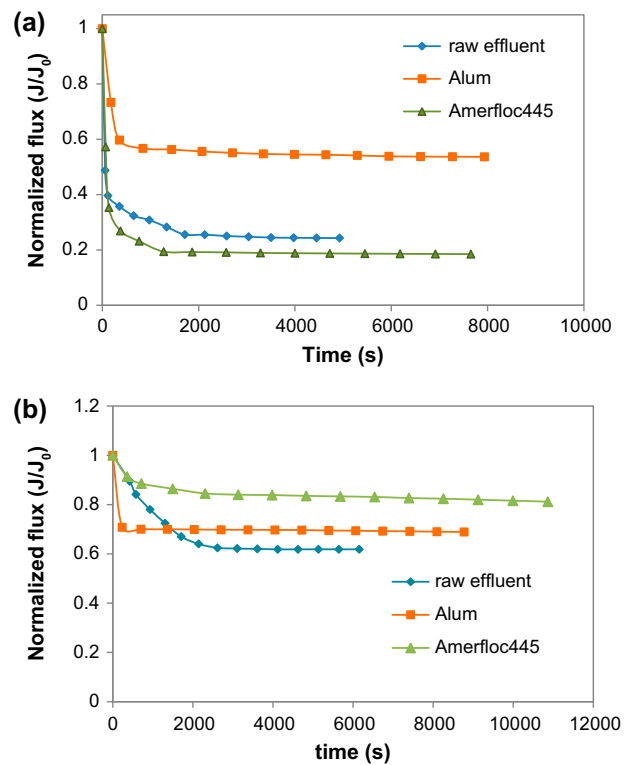


Fig. 6. Variation of the normalized flux with time under different conditions: for raw effluent and pre-coagulated with Alum and Amerfloc445 using (a) MF and (b) UF processes.

removals by 45 and 62%, respectively, which are almost the same percentages found after the single coagulation step (Fig. 3). This indicated that MF assumed simply a sieving role and it retained flocs only. The use of Amerfloc445 dramatically decreased the normalized flux to reach only 18% of the initial flux value, although, the color and COD retentions were 97 and 92%, respectively. Wang et al. [26] stated that the MF permeability in C/MF system was driven by the cake layer porosity. Thus, the high removal rates given by Amerfloc445 in C/MF process was probably due the flocs capacity to develop a porous cake layer assuming the role of dynamic UF membrane superposed on the MF surface which made it more selective and able to give such high color and COD rejections. This phenomenon also explained the severe flux decline with Amerfloc445 coagulation (82%).

UF results showed that the addition of coagulants reduced the flux decline of the raw effluent by 7 and 20%, respectively, for Alum and Amerfloc445. It was obvious that coagulation improved significantly the UF performances especially with Amerfloc445. This

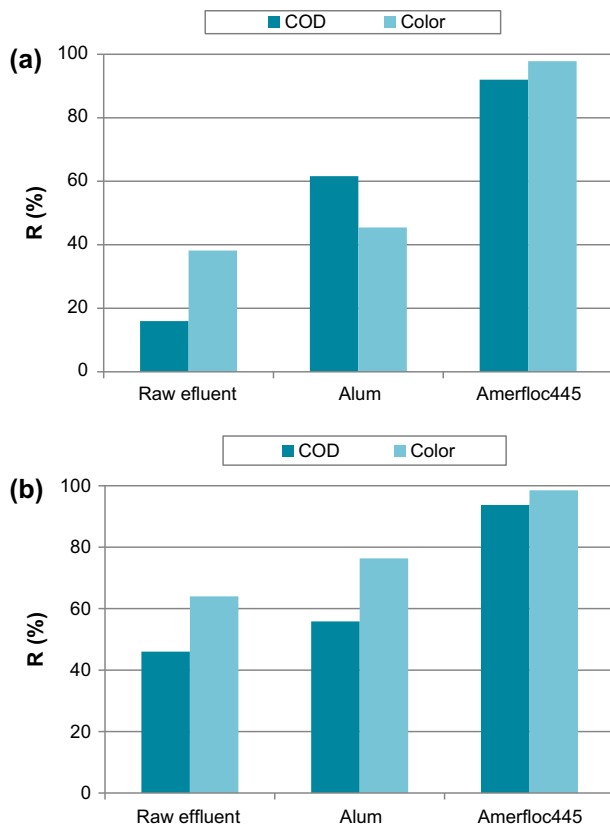


Fig. 7. COD and color rejection with (a) MF and (b) UF membranes.

result confirmed the finding of Barbot et al. [27] who stated that, the pretreatment by coagulation contributed to decrease the cake resistance, limit pore blockage, and mitigate fouling intensity of UF which can reduce the flux decline especially with larger flocs. The COD and color removals by the UF membrane were 46 and 64% for raw effluent, 56% and 76% with Alum and 94 and 98% with Amerfloc445. The high COD and color retentions given by C/UF were distinctly higher than those obtained by C/MF, similar results were found by Harrelkas et al. [12].

5.3.2. Fouling study

Resistance analysis was conducted in order to study the fouling mechanism occurring on the MF and UF membrane surfaces following the procedure described in Section 4.5. Fig. 8 represents the different resistance distributions (R_m , R_{rev} , and R_{irrev}).

The MF resistance analysis showed that R_{irrev} was larger when a coagulant was added (53% for the raw effluent against 61 and 80% for Alum and Amerfloc445, respectively). This can be explained by the

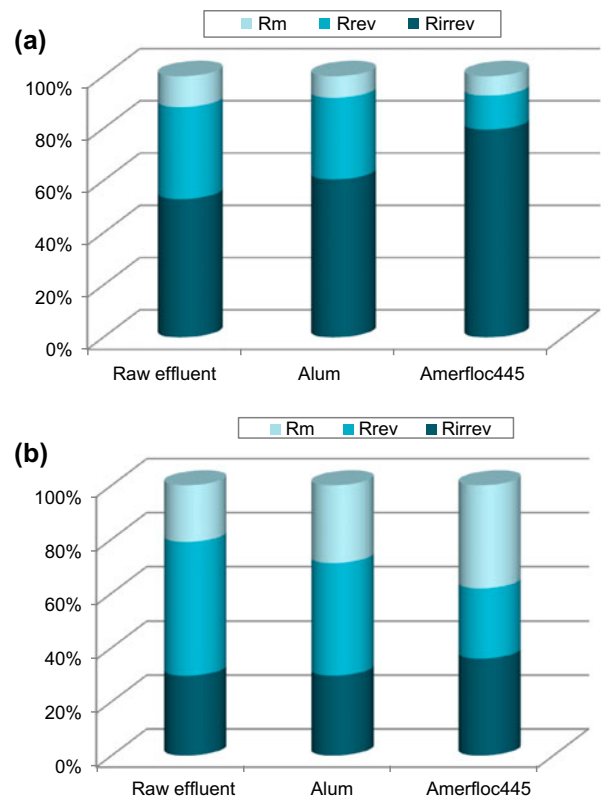


Fig. 8. Resistance analysis of (a) MF and (b) UF membranes.

ability of coagulants to reduce the repulsion forces between the membrane charged negatively due to the alkaline nature of the raw effluent [4] and the anionic particles of pollutants especially dyes.

The UF resistance analysis showed that the extrinsic filtration resistance ($R_{rev} + R_{irrev}$) represents between 50 and 75% of the total resistance while this value was more than 80% for the MF. The pre-coagulated effluent with Amerfloc445 showed the lowest reversible resistance (only 25%); this suggests that this configuration exhibited the lowest resistance to mass transfer through the cake layer. Choi et al. [28] reported that cake layer formed with large flocs is less compact than that formed with smaller ones. So, the voluminous Amerfloc445 aggregates contributed to form more porous cake layer than Alum particles which mitigated the reversible resistance.

MF consumes less energy than UF, furthermore, it can theoretically produce further permeate volume. However, the results provided that the fouling was more important for MF membrane inducing a severe flux decline with Amerfloc445 and very poor removals ability of color and COD with Alum. These results were in agreement with those of Lee et al. [14] whose,

compared MF and UF performances for pre-coagulated textile wastewater and reclaimed that UF was more suitable regarding fouling. As consequence, the UF was retained for the following study.

5.4. Effect of shear conditions on the UF performances

5.4.1. Effect of shear rate

Different breakage rates were applied in the coagulation of the dyeing effluent following the breakage-regrowth procedure represented in Table 2. After this, effluents were treated with UF in order to investigate the effect of increasing shear rate on the membrane performances. Fig. 9 shows that the increasing shear rate affected notably the membrane permeability which was closely related to the floc size.

For both coagulants, with no breakage, the normalized flux dropped rapidly to reach a constant value at

a VRF of 1.11 and 1.3 for Alum and Amerfloc445, respectively. Whereas, under different breakage shear rates varying from 300 to 700 rpm, the normalized flux decreased until a VRF of 1.5 and 2.31 for Alum and Amerfloc445, respectively, before being unchanged. These results can be explained by the effect of flocs size reduction which mitigated the mass accumulation rate.

It could also be observed that the flux reduction was slighter when the coagulation was done with Alum which showed a permeate flux decline about 32, 43, 46, and 48%, respectively, without breakage, under breakage at 300, 500, and 700 rpm, while these values were in the case of Amerfloc445, 19, 40, 45, and 49%.

According to the values presented in Table 4, the Amerfloc445 flocs recovered after a breakage shear at 700 rpm showed the highest sensitivity ($B_f = 75.3\%$), it corresponded to the severer flux reduction in comparison to the value without breakage (about 30%). So, higher

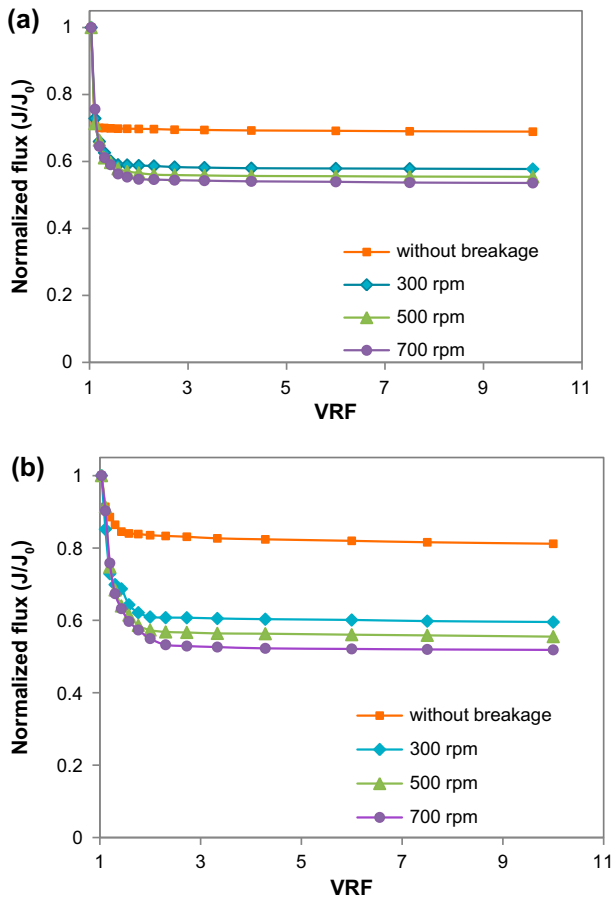


Fig. 9. Variation of the normalized UF permeate flux for a) Alum and b) Amerfloc under different breakage rates in the coagulation step with the VRF.

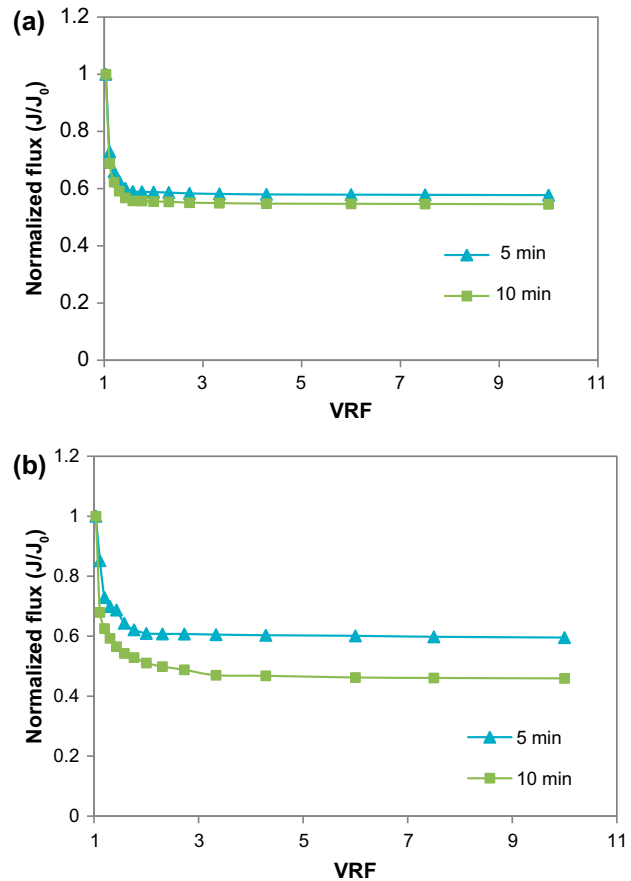


Fig. 10. Variations of the normalized UF permeate flux for (a) Alum and (b) Amerfloc under 5 and 10 min of breakage at 300 rpm breakage rate in the coagulation step with the VRF.

was the B_f , more sensitive were the flocs and sharper was the permeate flux reduction compared to the flux decline without breakage. This result was in agreement with Xu et al. [20] studies.

5.4.2. Effect of shear duration

The effect of longer breakage period (10 min) on the membrane behavior under fixed breaking shear (300 rpm) was studied. The variation of the normalized flux with the VRF was considered for pre-coagulated effluents with Alum and Amerfloc445. Fig. 10(a) shows that the extension of the breaking period gently affected the normalized flux which remained close to 0.6 beyond a VRF of 1.2 for the effluent pre-coagulated with Alum. Whereas, with Amerfloc pre-coagulation (Fig. 10(b)), the duration expansion had a notable effect on the normalized flux decline which varied from 0.6 to 0.48. Based on the data in Table 4, the B_f varied from 33.9 to 35.2% for Alum and from 62.7 to 66.7% for Amerfloc445, when the breakage duration was raised. This confirmed that higher sensitivity is consistent with severer flux decline. Indeed, in the case of Amerfloc445 coagulation, the VRF after which the normalized flux remains unchanged varied from 2 ($J/J_0 = 0.6$) to 3 ($J/J_0 = 0.46$) when the shear duration varied from 5 to 10 min. For Alum coagulation, no significant variation was shown. This was in agreement with the suggestion in the previous section that smaller flocs need more time to be accumulated on the membrane surface during the filtration.

6. Conclusion

After a comparison between MF and UF performances in the treatment of pre-coagulated dyeing effluent with Alum and Amerfloc445 coagulants, UF was found to give better results in terms of permeate quality as well as fouling.

Amerfloc445 coagulation generated voluminous flocs (845 μm) when compared to Alum aggregates (488 μm) and provided better COD and color removals. However, the Amerfloc445 particles were more sensitive to breakage but with higher recovering ability. Using the C/UF configuration, which was retained to study the effect of shear intensity and duration on the filtration behavior, Alum flocs were more resistant to shear rate and duration modification than Amerfloc445 flocs, which can be due to their small initial size. Nevertheless, Alum coagulation caused severe UF reversible fouling by the build-up of a compact cake layer with high resistance to mass transfer

contrarily to the voluminous Amerfloc445 flocs. It was also concluded that more sensitive were the flocs severer was the permeate flux reduction.

So, it seems that C/UF system efficiency can be improved with the coagulant Amerfloc445 more than Alum. But the coagulation conditions, especially shear intensity, have to be well controlled due to the sensitivity of the flocs.

Acknowledgment

Authors gratefully thank SARTEX Company for their financial and material support of this project.

List of symbols

COD	—	chemical oxygen demand
C/ F	—	coagulation/ flocculation
MF	—	microfiltration
NF	—	nanofiltration
R	—	retention
RO	—	reverse osmosis
S	—	salinity
TDS	—	total dissolved solids
TH	—	total hardness
UF	—	ultrafiltration
VRF	—	volume reduction factor
Zp	—	zeta potential

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