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Treatment of synthetic textile wastewater by combined chemical coagulation/membrane processes

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ABSTRACT

Industrial textile generates large volumes of effluents which are heavily loaded with pollutants, turbidity and are highly concentrated in salts and color. A significant improvement in effluent quality is required before it is discharged into the environment. In the present work, performances of a combined process using chemical coagulation, ultrafiltration and nanofiltration were investigated in treating synthetic textile wastewater containing reactive dyes (Blue S-GLD 150 dyes) and different salt concentration. The efficiency of the combined process was evaluated in terms of effluent decolourization and turbidity removal. Experimental results showed that the optimal dose of coagulant using aluminium sulphate was 1 g/L obtained at pH = 7. The decrease of the effluent salinity improved the treated water quality by increasing the removal of color and turbidity. To explain the effect of the salinity on the optimal coagulant dose, the zeta potential was used as a control parameter. When ultrafiltration (UF) or nanofiltration (NF) were used in post treatment to coagulation-flocculation, the stabilized permeate flux was higher for UF. It remained constant until a volumetric reduction factor (VRF) reaching 4 for NF and 6 for UF at 25 L/h.m^2 and 122 L/h.m^2 respectively. The retention of color and salt were higher for NF than for UF. These results were similar for real and model effluent.

Keywords: Textile wastewater; Chemical coagulation; Ultrafiltration; Nanofiltration; Color removal; Pre-treated effluent

1. Introduction

Coagulation–flocculation using metal salts is widely used in the industrial wastewater treatment. Generally, the chemical coagulation process can be applied alone to remove suspended colloidal particles [1,2] or as pretreatment prior to ultrafiltration, nanofiltration or reverse osmosis respectively for dissolved organic substances removal and desalination [3,4]. Besides, the use of the chemical coagulation in pre-treatment allows to reduce fouling in membrane processes [5,6] and also avoids the aeration problems in the biological treatment stages by removing a great amount of colloidal particles.

The textile processing industries generate large volumes of wastewater. In the case of the manufactories that produce cotton clothes using reactive dyes, it needs up to 150 L of water to dye 1 kg of cotton. The wastewater produced contains suspended solids and dissolved

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substances such as dyes and salts and other auxiliary chemicals which lead to an organic as well as an inorganic pollution of the effluent [7].

Because of the poor biodegradability and sometimes even the toxicity of the textile wastewater components, the chemical coagulation treatment is generally applied. Physico-chemical treatment reduces colloidal matter and dissolves suspended matter but eliminates neither the color nor the salt.

Besides, the presence of specific cations and anions in the textile industry effluent may affect the coagulation behaviour. In the case of the aluminium sulphate which is traditionally used as coagulant, the presence of salt in the effluent may affect the metal ions hydrolysis reaction and precipitation as mentioned in the literature [8].

In many works, membrane technologies like UF and NF have been applied to recover colloidal matter, dissolved suspended matter and salts from textile wastewater. These processes are usually used as a post-treatment to biologically or physicochemically treated effluent.

Bes-Pia and al. [9] proposed a combination of a biological process and nanofiltration to reuse textile effluent in the washing process. They observed that the fouling was not important and that the membrane performances regarding COD and salt retention under a concentration mode (VRF = 3) provided a high quality of the treated water. Fersi and al. [10] showed that the combination of ultrafiltration and nanofiltration used for treating textile effluents previously treated biologically allowed a stable permeate flux until a VRF of 2.77. At these conditions more than 90% of dye and salt removal was observed.

PhThe combination of membrane technology and coagulation–flocculation had been considered by many authors [11–14]. More than 90% of salt rejection and color removal was observed when nanofiltration had been applied. An enhancement of COD removal was also obtained.

The objectives of the present work are: 1) to determine the performance of aluminium sulphate treatment in terms of clarification and decolourisation of model dyeing effluents differing with the concentration of salt, 2) to analyze the effects of the aluminium sulphate dose on the turbidity and colour removal, 3) to determine the influence of the various factors such as ionic strength, pH and zeta potential on the coagulation behaviour, 4) to enhance the quality of the treated effluent by adding ultrafiltration or nanofiltration in post-treatment after chemical coagulation, in order to reduce environmental impact.

2. Materials and methods

2.1. Materials

The SARTEX textile factory utilizes different reactive dyes and chemical substances such as detergents, salts and auxiliaries (e.g. surfactants, emulsifiers). In order to be quite near the characteristics of the real effluent produced by the washing baths in the dyeing step (salinity between 3 and 10 g/L), model effluents with the same composition than the real ones were prepared (Table 1). Solution with concentration of 1 g/L of Beavin BPA was first prepared under stirring during 15 min, then Reactive Blue S-GLD 150 dye at a concentration of 1 g/L and NaCl solution were added under stirring during 3 h at a temperature of 95°C. The salinity is adjusted to have four model solutions.

2.2. Chemical coagulation

Chemical coagulation was performed using aluminum sulphate '$Al_2(SO_4)_3 16H_2O$' (AS) which is the coagulant used by SARTEX manufactory at a dose of 1 g/L. A Jar test apparatus (Stuart Scientific Flocculator, UK) was used to determine the optimal dose of coagulant. The coagulation procedure involved rapid mixing at 250 rpm for 5 min followed by slow stirring at 50 rpm for 60 min. Then, a settling period of 120 min followed the slow stirring. This ends to the evaluation of the turbidity removal.

In each test, the predetermined concentration of coagulant and NaOH solution volume leads to achieve the required dose of salt and pH respectively.

2.3. Filtration rigs

Membrane experiments were performed in a pilot plant. The ultrafiltration (UF) and nanofiltration (NF) experimental units were classical filtration set-ups. The membranes characteristics used in this study are given in Table 2.

Table 1
Physicochemical characteristics of both real and model effluents

Parameters	Real effluent: AS (1 g/L) Salinity (3 g/L)	Model effluent: salinity (0.15 g/L)	Model effluent: salinity (3 g/L)	Model effluent: salinity (9 g/L)	Model effluent: salinity (18 g/L)
Turbidity (NTU)	245	4	8	10	12
pH	6.8	7.2	7	7.6	7.8
Conductivity (mS/cm)	4	0.176	3.52	10.58	21.17
Color (620 nm)	0.156	0.25	0.82	0.83	0.82

Table 2
Main characteristics of the membranes used

Membrane type	Area (m^2)	Length (cm)	Molecular weight cut-off (MWCO)	Material	Geometry
NF membrane	2.5	120	500 Da	Polyamide	Spiral
UF membrane	0.155	120	15 KDa	Al_2O_3/TiO_2	Multitubular

2.4. Conduction of experiments

The operating parameters were the feed solution, transmembrane pressure (ΔP) and temperature (T). During each experiment, cumulative permeate volumes were collected and analyzed. The volume reduction factor (VRF) are then determined: VRF = V_i/V_r where V_i represents the initial volume and V_r the volume of the retentate.

During each filtration experiment, the retention rate (TR) were determined; for example: for color retention rate (%): TR = (1 – color (permeate) / color (feed)).

In all experiments, each run had been carried out three times.

2.5. Analysis

Physico-chemical parameters of raw effluents and of permeates were determined using the following methods: turbidity (turbidimeter, HACH RATIO 2100A), conductivity (conductimeter, Tacussel model 123), pH (pH-meter, Metrohm 744), and the colour intensity (UV absorbance at 620 nm: Perkin Elmer Lamba 20 UV/VIS Spectrophotometer). The zeta potential (Malvern Zetasizer 3000, UK).

3. Results and discussion

3.1. Effect of the dose of coagulant on wastewater clarification and decolourisation

The effect of the aluminium sulphate dose on turbidity for the different model effluents was illustrated in Fig. 1. It can be seen that the coagulation occurs at an optimal aluminum sulphate dose of 1 g/L for the four model solutions. The turbidity decreases when the salinity drops. Turbidity below 1NTU was obtained for the effluent having a salinity of 0.15 g/L. The percentage of turbidity removal was the best at the optimal dose of the coagulant of 1 g/L for all model effluents.

The maximum turbidity removal (80.5%) was obtained for the model effluent with the lowest salt concentration. Thus, by increasing the effluent salinity, the removal of turbidity decreased and then remained almost stable around 60% for a salinity of 9 and 15 g/L.

In Fig. 2, the percentage of color removal in the different model effluents was also plotted as a function of aluminum dose. One can notice that for high salinities 9 and 18 g/L, the color removal increased at the low doses of coagulant then stabilizes at 75% and 70% respectively when the coagulant dose reach the optimal value of 1 g/L. However, for salinities of 3 and 0.15 g/L, the percentage of color removal was important (80–90%) and occurred at a lower aluminum sulphate dose (0.5–1 g/L). These results proved that the performances of coagulation depended

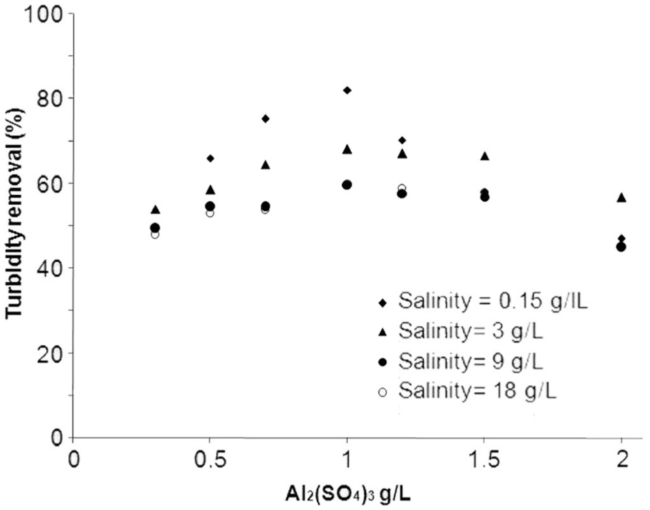

Fig. 1. Turbidity removal as a function of aluminum sulphate dose for model effluents used.

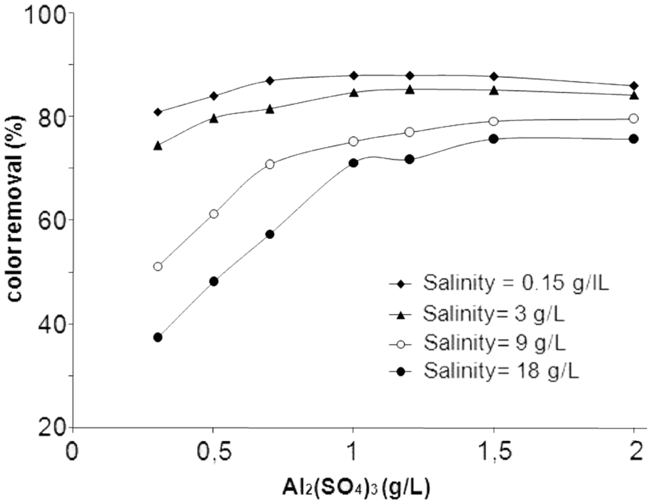

Fig. 2. Variation of color removal with aluminum sulphate dose for model effluents used.

highly on effluent salinity. For coagulation-flocculation using aluminum sulphate, the solubility of the aluminum hydrolysis products have been affected by the salt concentration. The variation of the salt concentration causes profound effect on aluminum precipitation and modifies the charge properties of colloids [15].

3.2. Variation of zeta potential of aluminium precipitates in the various model effluents

The presence of salt with different concentrations in the model dyeing effluents may affect the coagulation behavior by modifying the surface properties and the surface charge of the colloidal suspensions. The measurements of zeta potential showed that the net charge for the colloid before and after coagulation fall down when the salt concentration rises (Fig. 3). The results indicate also the progressive charge neutralisation of the coagulated colloids with increasing aluminium dose. 0.6 g/L of coagulant corresponds to a complete neutralisation charge for all four types of model effluents. Consequently, the necessary dose of aluminium sulphate to reach zero colloidal charge increases from 0.2 g/L for the effluent with the salinity of 0.15 g/L, to around 0.3 g/L, 0.5 g/L and 0.6 g/L for the effluent with salinity of 3, 9 and 18 g/L, respectively. However, with 1 g/L dose witch corresponds to the lowest turbidity value for the four model effluents, the net charge of the coagulated colloid was positive for all types of model effluents.

As a conclusion, significant differences have been found between the doses needed to reach zero colloidal charge and those necessary to have a minimum turbidity. This result suggests that optimal coagulation performance does not occur at a coagulant dose corresponding to complete charge neutralisation.

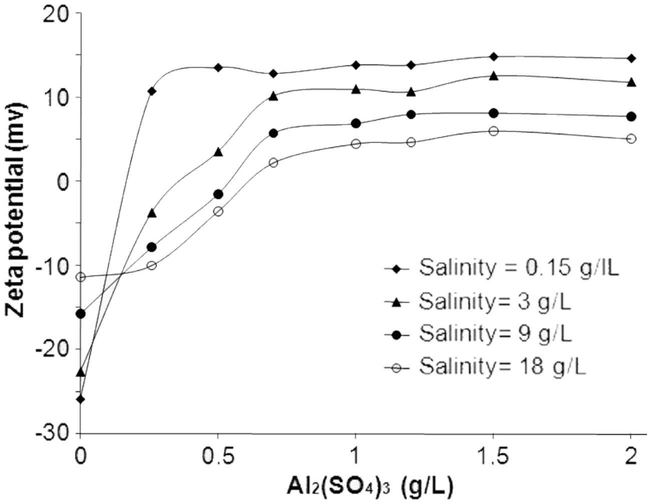

Fig. 3. Variation of zeta potential with aluminum sulphate dose for model effluents used.

3.3. Effect of pH

To analyze the effect of pH on zeta potential, the model effluent having a salinity of 3 g/L has been considered since the real effluent have a close salinity value.

Fig. 4 shows the effect of pH on color removal and zeta potential using a dose of aluminium sulphate of 1 g/L which corresponds to the optimum dose previously determined to obtain minimum turbidity. pH was brought to values between 4 and 10 with adding NaOH or HCl, with regards to the selected aluminium dose. The pH of the original model effluent was 7. The greatest color removal was obtained at pH of around 7 that corresponded to the minimum solubility of Al^{3+}. At higher pH values, color removal decreased.

It can also be seen that the zeta potential increased with pH until 7 < pH < 8, presumably as a result of deprotonation, and then remained almost stable.

At pH of 7, the zeta potential of the aluminium sulphate hydroxide precipitate was strongly positive (+13 mV) and almost did not change for values above 7. These results may be explained taking in account the following equilibrium that shifts to the right side with increasing pH:

$$Al^{3+} \rightarrow Al(OH)^{2+} \rightarrow Al(OH)_2^{+} \rightarrow Al(OH)_3 \rightarrow Al(OH)_4$$

At low pH, only Al^{3+} exists in a significant amount. At pH range 6–7, hydrolysis occurs and aluminium sulphate hydroxide precipitate appears. For alkaline values of pH, a dissolution of the precipitate occurs to form $Al(OH)_4^-$ anion. As a result, the destabilization of the colloidal system was not observed witch conduct to the decrease of the color removal.

Fig. 5 shows the influence of pH on the zeta potential at different dose of coagulant. The surface charge of the coagulated colloids varies with coagulant dose: at the lowest doses of 0.3 g/L and 0.5 g/L, a negative zeta potential

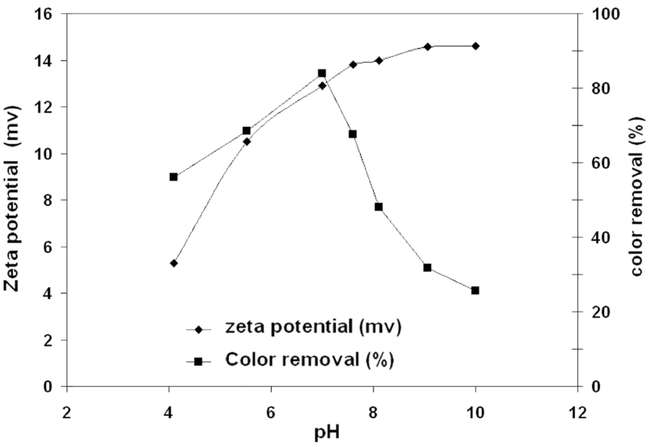

Fig. 4. Effect of pH on color removal and zeta potential (mV).

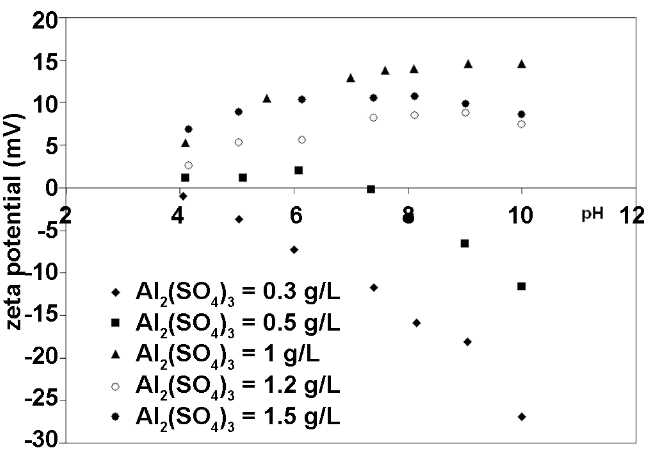

Fig. 5. Influence of pH on the coagulation process at different doses of coagulant.

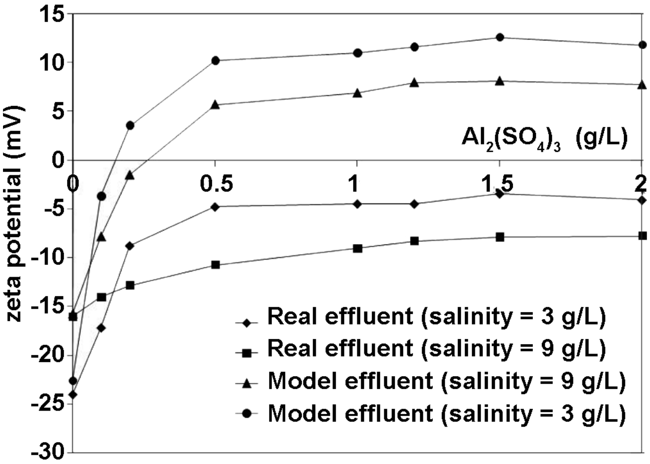

Fig. 6. Comparison between real and model effluent coagulation behaviour (pH = 7).

was observed whose absolute values increased from pH 4 to pH 10. It is noticed also a charge neutralization at pH = 7. For a higher dose of coagulant to 1 g/L, the zeta potential was positive and increased with pH until a value of 7. For pH comprised between 7 and 10, the zeta potential value remained constant indicating that the colloids charges do not vary.

Hence, the pH and the concentration of coagulant are the most important parameters on which depends the liberation of the hydrolyzed ionized and non ionized species of hydroxide aluminum.

3.4. Comparison between real and model effluent coagulation behaviour

Fig. 6 shows the effect of the aluminium dose on the zeta potential in the case of the treatment of real and model effluent having a salinity of 3 and 9 g/L.

Concerning the real effluent, the zeta potential was initially negative varies only according to the salinity and increases according to the dose of coagulant, but remains negative and stabilizes at values of –5 and –10 mV respectively for the salinity of 3 and 9 g/L.

For the model effluent, the zeta potential was initially negative and increases with the dose of coagulant to attain zero under the doses of 0.1 to 0.2 g/L for the respective salinities of 3 g/L and 9 g/L. Then, it becomes positive and stabilizes up to a dose of 0.5 g/L at zeta potential value of 10 and 7 mV respectively for salinities of 3 g/L and 9 g/L.

The difference in the behaviour between the real and model effluent is the result of the suspended matter and organic pollutant charge (COD) the real effluent contains due to the use of auxiliaries and chemical products to fix the dyes on the support.

3.5. Addition of membrane treatment

3.5.1. Nanofiltration of real and model effluent

The nanofiltration has been applied after a pre-treatment by chemical coagulation using a dose of aluminium sulphate of 1g/L on real and model effluent (Fig. 7).

We notice that the initial permeate flux is more important for model effluent: 38 L/h.m^2 against 27 L/h.m^2 for the real effluent. In both cases, the flux decreased to reach a stabilised value of 20 L/h.m^2 for real effluent and 25 L/h.m^2 for model effluent.

The characteristics of the permeate are illustrated in Table 3. A total color retention and a high turbidity removal were obtained (almost 100%). The retention of the salinity depends on the effluent quality (38% for model effluent and 24.5% for real effluent).

3.5.2. UF and NF membrane performances

To enhance treatment performances in terms of color and turbidity removal, ultrafiltration (UF) and nanofiltration (NF) were applied in post-treatment after chemical coagulation using aluminium sulphate at optimum dose (1 g/L).

Fig. 8 represents the variation of UF and NF permeates flux with VRF for model effluent of salinity of 3 g/L after

Table 3
Performances of NF for both model and real effluents (VRF = 4)

Characteristics	Model effluent	Real effluent
RR color (%)	100±2	100±2
Turbidity (NTU)	0.20 ±0.01	0.10±0.01
RR salinity (%)	38.0±0.5	24.5 ± 0.5
J (L/h.m²)	25 ± 1	20 ± 1

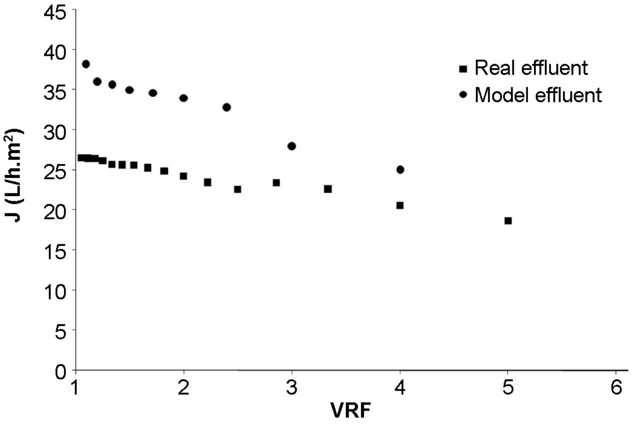

Fig. 7. Treatment by nanofiltration after a pretreatment by coagulation–flocculation (1g/L) for both model and real effluents.

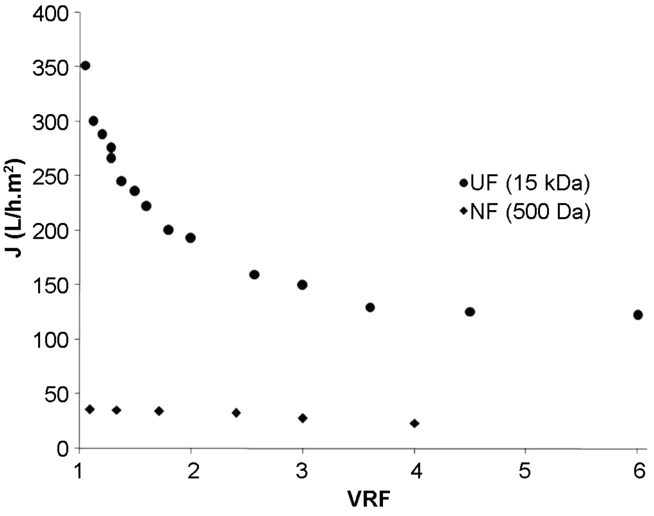

Fig. 8. Variation of permeate flux of NF and UF membranes with VRF (model effluent of salinity of 3 g/L).

pretrament by coagulation. For UF process, the permeate flux dropped rapidly with increasing concentration until VRF = 2, then, it seems to stabilize at 122 L/h.m^2 at VRF = 4. Similar tests were conducted using NF process. It is clear here that the VRF has a little effect on permeate flux which remains sensitively stable at 25 L/h.m^2. In comparison with UF performances, this value represents almost 20% of that obtained with UF membrane.

UF and NF permeates characteristics are given in Table 4. Almost a total retention of color and turbidity (around 100%) for the two permeates is noticed. This was associated with a reduction of salinity by 38% using NF process and 13% using UF process.

Table 4
Performances of NF and UF treatment

Parameters	UF (T = 30°C; ΔP = 3 bar)	NF (T = 30°C; ΔP = 12 bar)
pH	7.36	7.42
Turbidity (NTU)	0.26±0.01	0.1±0.01
Conductivity(mS/cm)	3.2	2.2
RR salinity (%)	13.0±0.5	38.0±0.5
RR color (%)	92±2	100±2
J (L/h.m^2)	122±1	25±1
VRF	6	4

4. Conclusion

The results of this study show that the performance of coagulation-flocculation depends on the quality of the textile effluent in term of salinity and pH.

The application of chemical coagulation using aluminium sulphate to four model textile effluents differing by salt concentration 0.15 g/L; 3 g/L; 9 g/L and 18 g/L, showed that the low turbidity value obtained at the optimum dose of coagulant didn't correspond to colloidal charge neutralisation which depend on the initial salt concentration and on the auxiliaries products added in the case of the real effluent.

Using membrane processes like ultrafiltration and nanofiltration in post-treatment to coagulation-flocculation for textile wastewater treatment enhance the performances of the treatment and provides a relatively good quality of the treated water. The permeate flux was four time more important in the case of UF than NF. However, similar quality in term of turbidity and color was obtained after the two processes. More than 90% of color and turbidity were removed. The salinity retention was higher for NF (38% against 13%).

Based on these results, NF and UF are suitable process which could be added to coagulation-flocculation to enhance the treated wastewater quality for reuse.

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