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Experimental study and modeling using Super Pro Designer of the elimination of a dispersed azo dye by coagulation-microfiltration

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ABSTRACT

The main objective in this study was to optimize the removal of a dispersed azo dye (Red Terasil) widely used in the textile industry, combining coagulation and microfiltration processes. The purpose of coagulation was to destabilize and aggregate the suspended matter mainly responsible for the coloration of the solution. The study was completed by a simulation of the process using the SuperPro Designer software (SD) (Version 9) followed by a comparison of the obtained results with the corresponding experimental values. A priori the experimental part consisted of determining the optimal coagulation conditions on a Jar-test, namely the coagulant dose and pH of the solution. The resulting solution from the coagulation process was used as a feed to the microfiltration pilot where the variation with time of several parameters such as the dye concentration, the turbidity of the permeate and the concentrate solutions, the permeate flux and the transmembrane pressure (TMP) were followed, determining also the membrane rejection coefficient. SuperPro Designer software (SD) was used to simulate the combination coagulation-microfiltration process, the monitored parameters with filtration time, in this part, were the dye concentration in the permeate and the concentrate and the permeate flux. The obtained results showed that the coagulation-microfiltration process was very effective in eliminating the dye with a considerable concentration decrease, an important reduction of the turbidity of the solution in the permeate, a reduction of its flux and the membrane rejection coefficient exceeding 98%. The results calculated by SD were in quite good agreement with the experimental results.

Keywords: Coagulation; Microfiltration; Red Terasil; Simulation; Super Pro Designer

1. Introduction

Natural or synthetic dyes have found applications in various industries such as leather, textile, paper, rubber, cosmetics, plastic, pharmaceuticals and food industries [1]. However the discharge of dye effluents from these industries into the environment may cause severe problems and damages to many forms of life [2]. For instance for the textile industry which is the main interest of this work, it is recognized that its pollutants emissions consist of recalcitrant organic molecules that cannot be treated by traditional decontamination methods [3]. These discharges are among the most poorly treated sewage and are characterized by severe colorations, strong variations in pH, high chemical oxygen demand (COD) and increased bio-toxicity to bacteria [4].

Nowadays the methods used to treat polluted discharges from textile effluents are generally designed to remove organic pollutants and turbidity. Among the most adequate techniques used to eliminate the soluble pollution, one can cite coagulation-flocculation, adsorption and

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membrane processes (osmosis, ultrafiltration, microfiltration and nanofiltration) [5].

Although the membrane processes can effectively be used to remove the dyes in wastewater, in the present work the 'red Terasil' dye was removed by coupling coagulation and microfiltration. The simulation of microfiltration was performed using SuperPro Designer (V. 9) in order to validate the experimental results. It should be noted that the coagulation tests were carried out on the jar test and those of microfiltration on a pilot of the Laboratory of Engineering of Environmental Processes (LIPE) of Process Engineering Faculty of the University Constantine 3.

2. Theory of microfiltration

The permeate flux is governed by the so-called general filtration equation (Darcy's law) given as [6]:

$$J = \frac{\Delta P}{\mu R_m} \quad (1)$$

where J (L·m^{-2}·h^{-1}) is the permeate flux, ΔP (Pa) the applied pressure, μ (Pa s) the solvent viscosity and R_m (m^{-1}) the hydraulic resistance.

In the case of filtration of polluted water and with time, Darcy's law could be given as (resistance in-series model):

$$J = \frac{\Delta P}{\mu\left(R_m + R_C + R_P\right)} = \frac{\Delta P}{\mu R_T} \quad (2)$$

with:

$$R_T = R_m + R_c + R_P \quad (3)$$

R_T, R_c and R_p are the total, clogging and polarization resistances, respectively, expressed in (m^{-1}).

3. Material and methods

This section presents the experimental modes used in this study, namely coagulation and microfiltration. After the determination of the optimal operating conditions of coagulation; microfiltration was used to reduce the maximum dye in effluents.

3.1. Coagulation

Coagulation known as a process of destabilization of suspended matter by charge neutralization was used as a pretreatment, allowing a further decrease in turbidity of the effluent as well as removing the organic pollutant [7].

The used coagulant was aluminum sulfate ($Al_2(SO_4)_3$,$18H_2O$) supplied by Sigma Aldrich. According to a Jar-test, the first part consisted of the coagulant injection at variable doses in a series of samples of colored water contained in beakers subjected to moderate agitation at speeds of 150 rpm for 3 min and then at 25 rpm for 15 min. After some time, a settling of suspended matter was observed in all the beakers, hence determining the turbidity to identify the optimal dose of coagulant. As a second step and in order to determine the optimum pH, the optimum concentration of the coagulant was used in all the beakers containing samples at different pH values [8].

Mainly the various steps involved in the coagulation process were the following [9]:

- A quick agitation during which the coagulant is introduced and dispersed; the rotational speed of the stirrer blades is 150 rpm and the adopted stirring time is 3 min.
- A slow stirring for 15 min at a rotational speed of 25 rpm.
- A settling for 30 min; this sedimentation time appeared as important and reflected the nature of the obtained floc.

3.2. Microfiltration

Microfiltration is a process for separating liquid-solid mixtures through a microporous medium. In the present experimental study, cross flow microfiltration was applied, circulating the liquid to be filtered tangentially to a porous membrane, creating turbulence which reduced buildup of particles on the surface of the membrane, and therefore delayed its clogging [10].

The assembly consisted mainly of a microfiltration membrane, a recirculation pump, a pressure gauge and a feed tank (Fig. 2). The solution to be filtered was stored in the reservoir and ejected through the pump in the tangential microfilter and the flow rate of the pump was controlled by

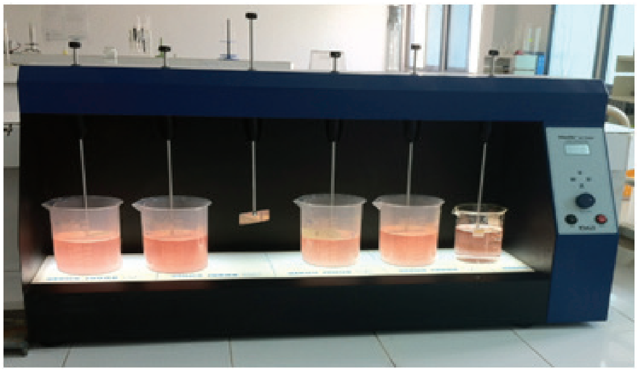


Fig. 1. The jar-test.

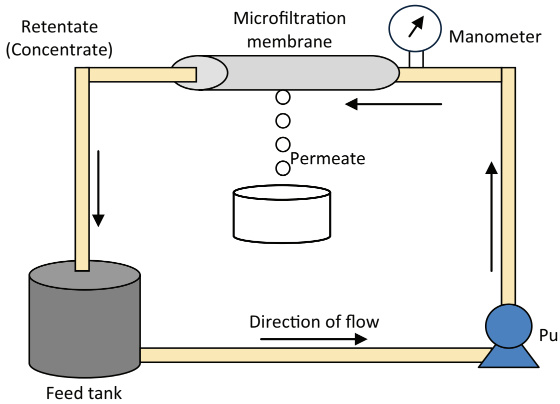


Fig. 2. Assembly of microfiltration.

a regulator with a pressure gauge displaying the pressure at the inlet of the microfilter. The retentate was automatically returned to the feed tank and the permeate (filtered water) was collected in a flask for analysis.

3.3. Characteristics of the membrane

An inorganic membrane made from zirconia (ZrO_2) was used throughout all the experiments (Fig. 3).

4. Modeling via SuperPro Designer

SuperPro Designer is an important tool for engineers and scientific researchers and may be very useful for various applications such as in pharmaceutical industries, biotechnology, water purification, wastewater treatment, air pollution control, etc. It is a good support for the modeling, assessment and optimization of processes. One of its main features is the grouping of manufacturing and environmental aspects models in a unique package making it easier for users to design and assess manufacturing and final processing processes, hence minimizing waste by preventing and controlling pollution [11].

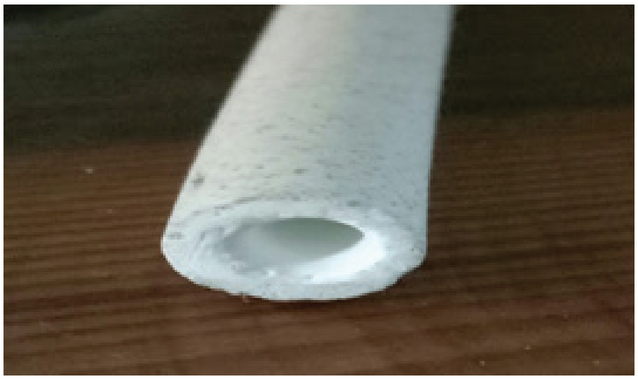


Fig. 3. Microfiltration membrane used in our work.

Table 1
Characteristics of the membrane

Membrane	
Type	ZrO_2 (inorganic)
External diameter: D_{ext} (mm)	9
Internaldiameter: D_{int} (mm)	6
Thickness: e (mm)	1.5
Length: L (mm)	235

SuperPro Designer has also proven its abilities in the development of manufacturing processes along with the induced environmental issues such as wastewater treatment and waste reduction. It also provides an economical project assessment as well as the possible impact on the environment [12].

The steps for creating a comprehensive study of a unit or any process can be summarized as follows:

- Specify the mode of operation: batch or continuous;
- Save the compounds and mixtures to treat;
- Add unit operations ;
- Add the input and output streams to connect the chosen operations;
- Initiate the currents and operations;
- Perform mass and energy balance sheets;
- Plan the process;

Following these steps leads to the final process as shown in the following diagram:

The obtained experimental data were used to assess the results obtained by the SuperPro Designer modeling.

5. Results

The results of coagulation, microfiltration as well as the comparison of experimental results with those obtained by means of SuperPro Designer, are presented in this section. Coagulation is used as a pretreatment to increase the retention efficiency of the dye by the microfiltration membrane, it serves to destabilize and agglomerate the colored suspended matter [13].

5.1. Coagulation

5.1.1. optimal coagulant dose

The determination of the optimal concentration of coagulant is an essential parameter for the destabilization of a large amount of suspended matter. A coagulant overdose

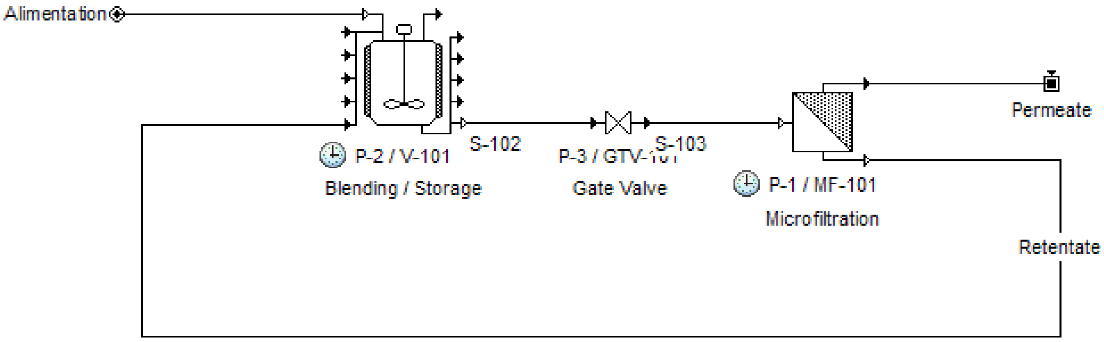


Fig. 4. Microfiltration process with recycling by SuperPro Designer.

may cause a destabilization of the suspended solids along with a free amount of coagulant dissolved in the solution. The optimal dose of the coagulant can be determined through a monitoring of the turbidity, varying these doses, using the jar-test. All these experiments were carried out for free pH of the dye equal to 8.5.

A steady decline in turbidity in different solutions can be observed from the results shown in Fig. 5, as the coagulant dose increased from 15 to 34 mg/L. This turbidity reduction resulted in the destabilization of colloidal colored matter which promoted better sedimentation [9]. However for coagulant doses greater than 34 mg/L, a turbidity rise was noted again this may be due to the presence of an excess of coagulant. Therefore it could be concluded that the optimal dose of coagulant obtained during these experiments was 34 mg/L.

5.1.2. Determination of optimal pH

The pH is an important factor in coagulation since its variation may allow a significant change of the species contained in the solution. It is well known that the suspended solids are negatively charged, requiring then for their neutralization a choice of a positively charged coagulant, Al^{3+} ions in the present case, facilitating their aggregations. A pH change can alter the charge of the coagulant and according to the literature the optimum coagulation pH is between 5 and 7 [9]. It is important to note that the amount of coagulant used in different beakers was the same and equal to 34 mg/L (optimal dose).

From Fig. 6 it is observed that turbidity decreased as the solution pH increased in the range between 5 and 7 with the solutions becoming discolored in a remarkable manner. For pH values between 3 and 5 the turbidity rather increased. All these experiments were performed three times while achieving the same results. This could be explained by the fact that the aluminum ions were normally in the form of Al^{3+}. An increase of the pH above 7 led to an increase of the turbidity of the solution again, discoloring completely these solutions. Therefore at neutral pH (equal to 7), an effective coagulation of the colored water can increase the efficiency of removal of color and turbidity.

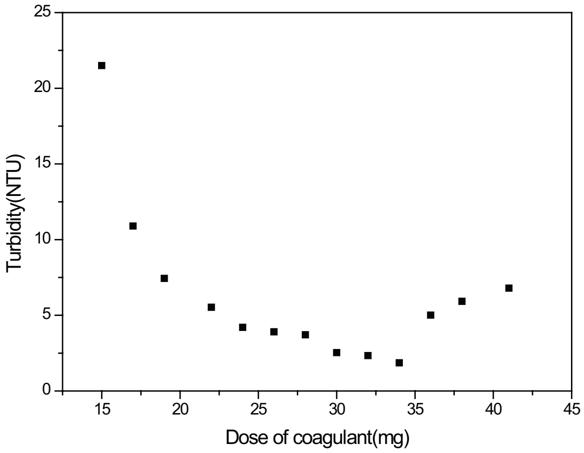


Fig. 5. Variation of turbidity as a function of the coagulant dose at free pH (pH = 8.5, C_0 = 10 mg/L, initial turbidity = 50.5 NTU, volume of solution = 800 mL).

5.2.Microfiltration

After the destabilization of suspended solids and after decantation, the solution was introduced into the supply vessel of the microfiltration pilot. Several parameters such as the change in permeate flux over time and with the transmembrane pressure (TMP), the variation of the concentration and turbidity of the concentrate and the permeate as a function of time and TMP, were studied in this part, determining the rejection rate (retention) of the membrane as a function of TMP and time.

5.2.1. Justification of choice of the hybrid process coagulation-microfiltration

The obtained results from the experimental measurements concerning both microfiltration and coagulation-microfiltration hybrid processes are shown in Figs. 7 and 8, presenting the variation of concentration of dye and flux with time, respectively, at the same operating conditions, particularly a TMP of 0.8 bar and initial dye concentration of 10 mg/L, for a reliable performance comparison.

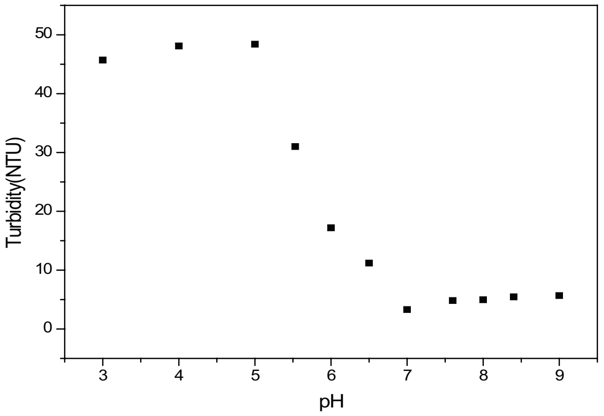


Fig. 6. Variation of turbidity according to pH (C_0 = 10 mg/L, initial turbidity = 50.5 NTU).

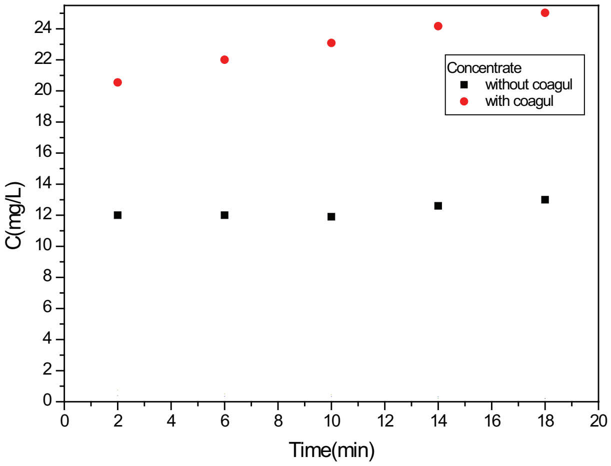


Fig. 7. Variation of the dye concentration in the concentrate as a function of time (microfiltration and coagulation-microfiltration) (TMP = 0.8 bar and C_0 = 10 mg/L).

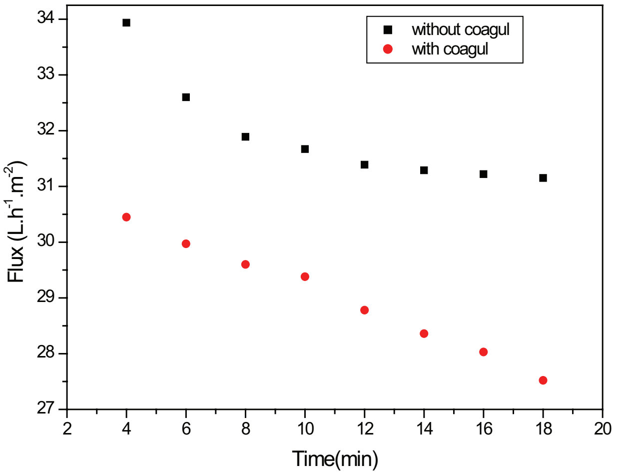


Fig. 8. Variation of permeate flux as a function of time for processes (microfiltration and coagulation-microfiltration) (TMP = 0.8 bar and C_0 = 10 mg/L).

According to Fig. 7, it is shown that the concentrations of the dye in the concentrate at all times are very significant in the case of the coagulation-microfiltration method compared to the that from just microfiltration, this can be explained by the large amount of dye retained by the membrane when the hybrid process coagulation-microfiltration is used.

Fig. 8 also shows the permeate fluxes for both processes and the values corresponding to the microfiltration process are much higher than for the coagulation-microfiltration hybrid one, this may be due to the retention of a considerable quantity of dye by the microfiltration membrane, thus the hybrid coagulation-microfiltration process can recover a significant amount of dye, it is also observed that the flux decreases as a function of the filtration time and this for both cases without and with coagulation.

Therefore the use of the coagulation-microfiltration hybrid process is more than justified, according to the enhanced membrane performance.

5.2.2. Variation of permeate flux with time

Fig. 9 shows the permeate flux variation of the colored solution in terms of time for a TMP = 0.8 bar. Its decline shows that the membrane retains the solute and is also an indicator of the polarization of the membrane.

Fig. 9 shows that the permeate flux decreases with time, indicating that a significant amount of dye was retained by the microfiltration membrane.

5.2.3. Variation of flux with TMP

The permeate flux of pure water can be an indicator of either the deterioration of the membrane or its blockage. It should be noted that the membrane was cleaned by pure water after each daily manipulations. If the same amount of flow was obtained at the same operating conditions, then the membrane was clean and was ready for further experiments, otherwise if the flow becomes more important the membrane may be deteriorated and clogged, requiring cleaning with an acid solution (0.1 N HCl) and then with a basic solution (0.1 N NaOH). Fig. 10 shows the variation of the pure water flow and that of the dye solution according to the transmembrane pressure.

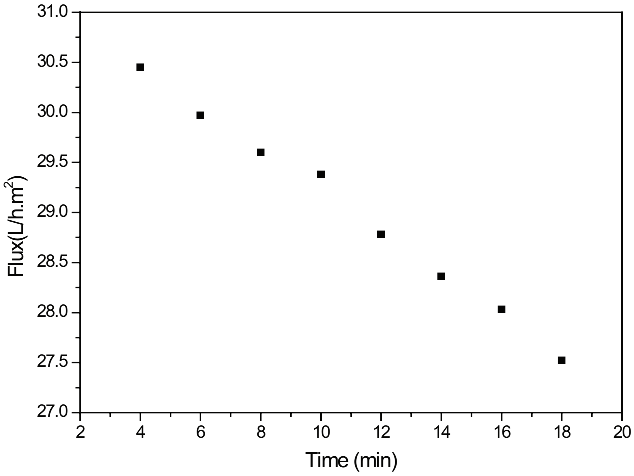


Fig. 9. Variation of permeate flux with time (TMP = 0.8 bar, C_0 = 10 mg/L). (Coagulation-microfiltration).

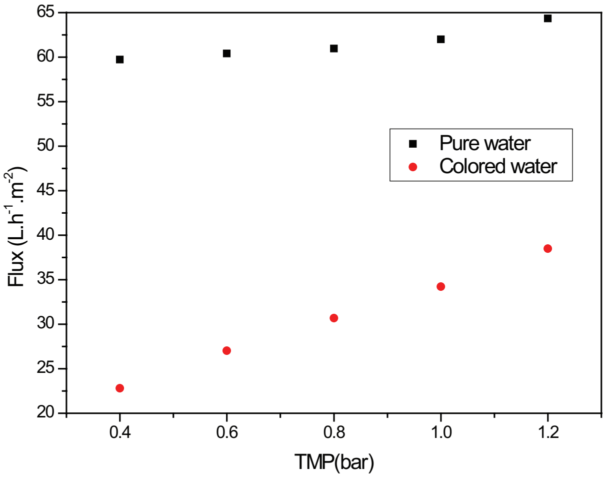


Fig. 10. Variation of the pure water flux and that of the dye solution with TMP (coagulation-microfiltration).

Fig. 10 shows the evolution of pure water permeate flow and colored water as a function of the transmembrane pressure (TMP) ranging from 0.4 to 1.2 bar, the filtration time is fixed at 5 min. Note that these flows are not of the same order of magnitude, they are more important in the first case (pure water), which is logical because the suspended matter contained in the colored water can form some resistance to that transfer is added to the resistance of the membrane, and prevents the water to pass through the microfiltration membrane. It is also shown that the permeate flux increases with the transmembrane pressure for different solutions according to Darcy's law [6].

A transmembrane pressure of 0.8 bar is chosen for the majority of the experimental work since it represents an average between 0.4 and 1.2 bar, and based on our experimental work of the removal of the red terasil by microfiltration alone (already realized), where several transmembrane pressures are used obtaining qualitatively similar variations.

5.2.4. Variation of the concentration of permeate and concentrate according to time

The monitoring of the dye concentration in the permeate and the concentrate can confirm that the microfiltration membrane retains or not the studied dye. Fig. 11 shows the variations of permeate and concentrate concentrations with time.

For an initial quantity of dye (red terasil) of 10 mg/L, it is clearly shown from Fig.11, the dye concentration in the permeate is very low compared to that of the concentrate, the latter increases with time because the solution is recycled to the feed tank; all such variations explain that this dye was well removed from the solution.

Under these conditions the TOC (total organic carbon) is measured to know the total amount of organic carbon, present in the permeate and retentate, since the dye is composed of carbon, the total organic carbon results are presented in Table 2.

According to the results of Table 2, it is found that the total organic carbon in the retentate is significantly lower than in the permeate; this confirms the retention of the organic matter by microfiltration membrane, and therefore of the dye.

5.2.5. Variation of the turbidity of permeate and concentrate according to time

Turbidity is an optical characteristic of the water. It is due to the presence in the water of inorganic or organic particles in suspension; Figs. 12 and 13 show monitoring the turbidity as a function of time, of the permeate and concentrate, when the dye solution passes through the microfiltration membrane after coagulation.

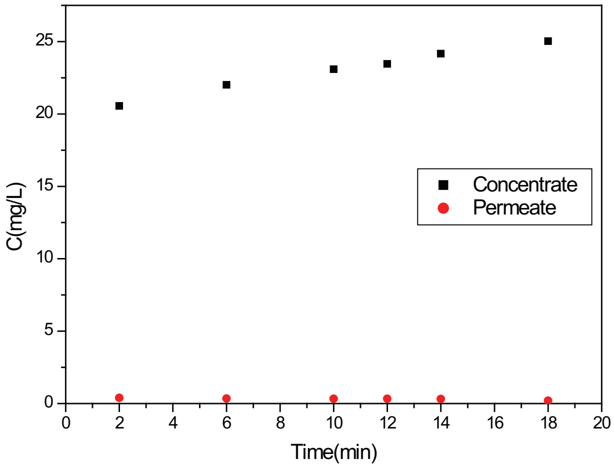


Fig. 11. Variation of the concentration of permeate and concentrate according to time (TMP = 0.8 bar, C_0 =10 mg/L) (coagulation-microfiltration).

Table 2
Determination of TOC in the permeate and retentate (TMP = 0.8 bar, C_0 = 10 mg/L) (coagulation-microfiltration)

Solution	TOC (mg/L)
Permeate	2.93
Retentate	4.17

Figs.1 2 and 13 show a significant reduction of the turbidity in the permeate, by against increases in the concentrate as a function of time; these results confirm that the microfiltration membrane can retain this type of dye.

5.2.6. Rejection coefficient of the membrane

The rejection coefficient (TR) is one way to assess a membrane performance. It is defined by the following relationship [6]:

$$TR = \frac{C_0 - C_P}{C_0} = 1 - \frac{C_P}{C_0} \tag{4}$$

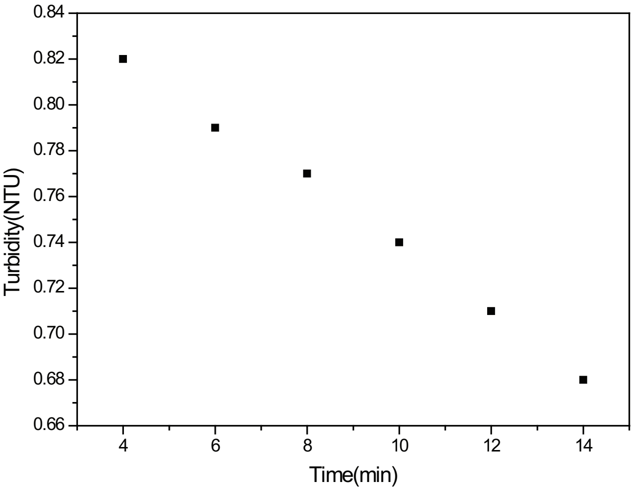


Fig. 12. Variation of the permeate.

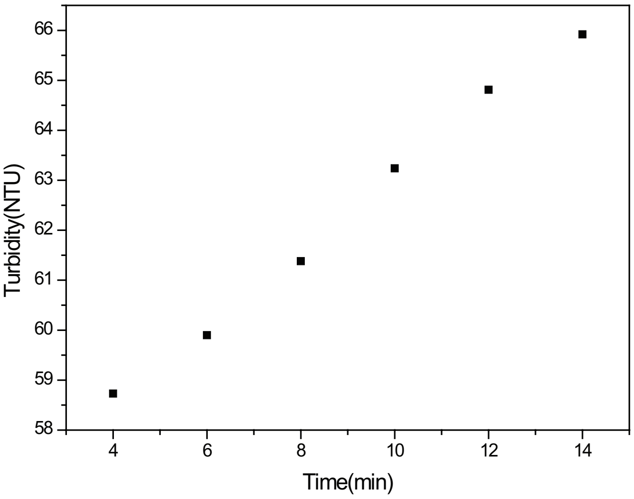


Fig. 13. Variation of the concentrate turbidity with time (TMP = 0.8 bar). Turbidity with time (TMP = 0.8 bar).

where C_0 is the concentration of the species in the solution and C_p is the concentration of the same species in the permeate.

Fig. 14 presents the variation of membrane retention rate depending on the time.

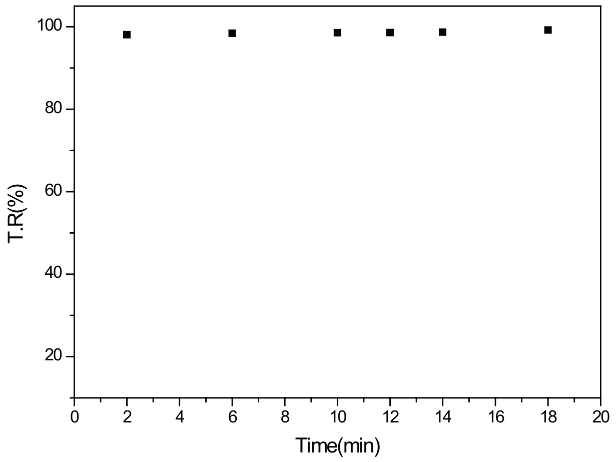


Fig. 14. Variation of rejection coefficient with time.

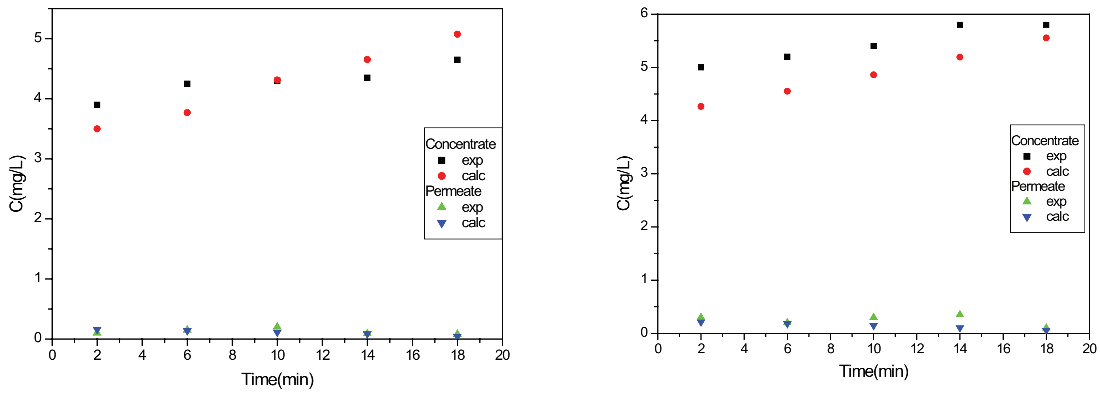
According to Fig. 14, it was found that the retention rate of the microfiltration membrane was greater than 98% throughout the filtration time. This result shows that a good retention of the dye by the microfiltration membrane was observed using the hybrid process.

5.2.7. Comparison of experimental and calculated results of coagulation-microfiltration process

A comparative study was carried out between experimental and calculated results obtained using SuperPro Designer software, concerning the hybrid process coagulation-microfiltration, in order to know the limits of use of this software and confirm the experimental results. Two parameters were studied and were permeate and retentate-concentrations and the variation of permeate flux with filtration time.

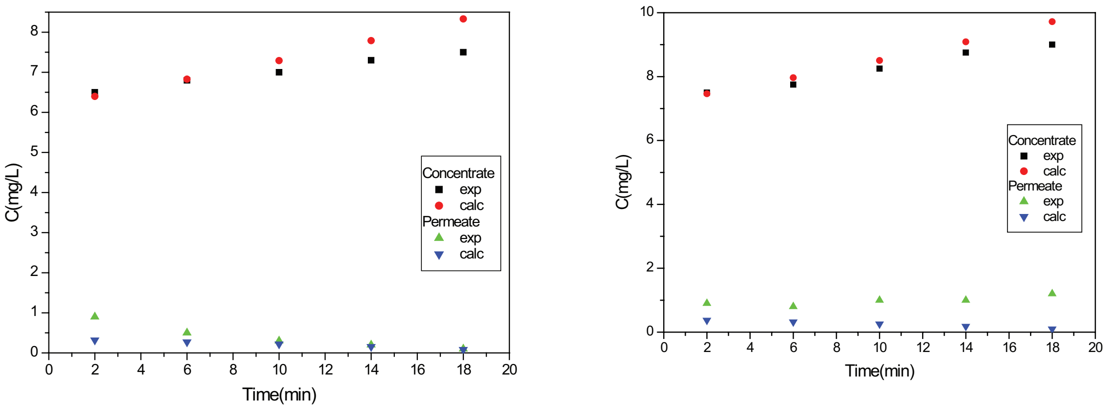
5.2.7.1. Comparison of concentrations

Fig. 15a, 15b, 15h show the comparison of the experimental and calculated concentrations vs. time for the process coagulation-microfiltration using the same initial conditions.



(a) TMP=0.6 bar; C_0=3mg/L

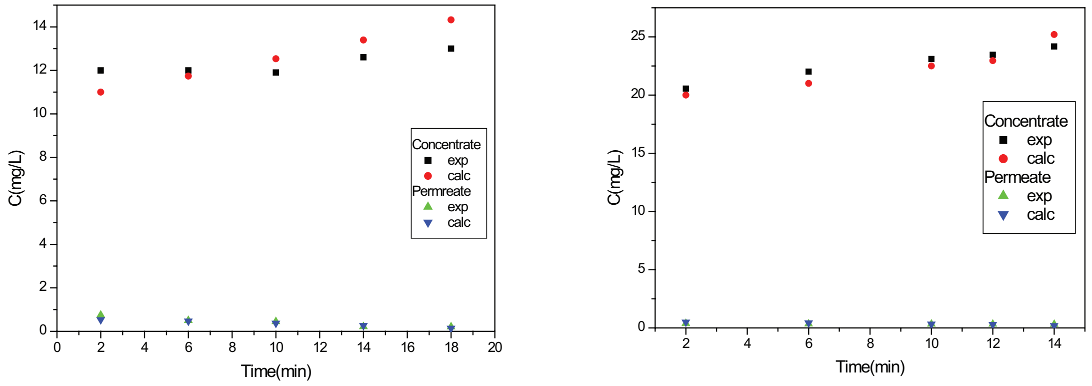
(b) TMP=0.6 bar; C_0=4 mg/L



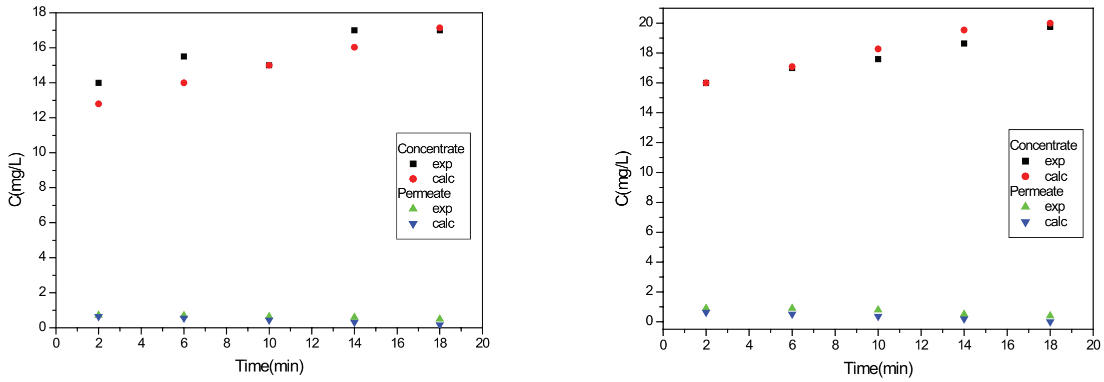
(c) TMP=0.6 bar; C_0=6 mg/L

(d) TMP=0.6 bar; C_0=7 mg/L

Fig. 15. Variation of experimental and simulated concentrations by SuperPro Designer of the permeate and concentrate versus time (Microfiltration with coagulation).



(e: TMP=0.6 bar; C_0=10 mg/L) (f) TMP=0.8 bar; C_0=10 mg/L



(g): TMP=0.6 bar; C_0=12 mg/L (h): TMP=0.6 bar; C_0=14 mg/L

Fig. 15. *(Continued)* Variation of experimental and simulated concentrations by SuperPro Designer of the permeate and concentrate versus time (Microfiltration with coagulation).

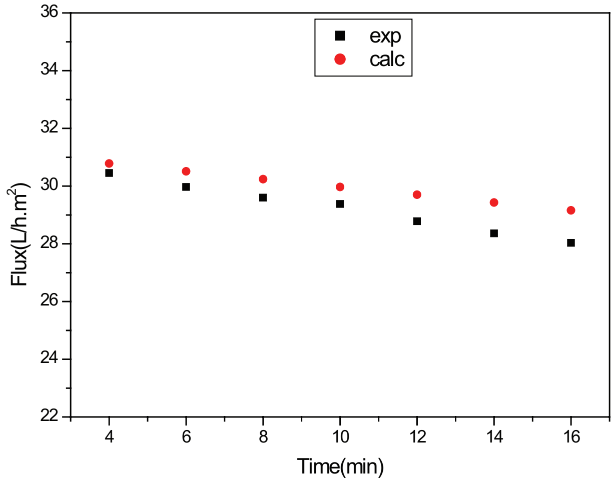


Fig. 16. Variation of experimental and calculated flux of permeate with time (TMP = 0.8 bar, C_0 = 10 mg/L).

According to Fig. 15a–h, it is noted that the variation of the concentration with time is similar for different operating conditions. It is also noted that the concentrations of the dye in the permeate are much lower than those in the retentate both for the experimental and calculated results. However a slight deviation is observed, especially for the retentate, except in the case where the TMP is 0.6 bar and the initial dye concentration equal to 7 mg/L, where a difference is rather observed between the concentrations in the permeate. By comparing Fig. 15e and 15f (where the initial concentrations of the dye are the same, and the TMP are 0.6 and 0.8 bar respectively), the deviation between the experimental and calculated concentrations is less for the case when the TMP is equal to 0.8 bar. In general, the SuperPro Designer software gave concentrations which were very close to the experimental ones while maintaining the same operating conditions. Clearly this confirms the reliability of the Superpro Design software.

5.2.7.2. Comparison of flux

Fig. 16 shows the comparison between the experimentally measured and the calculated permeate fluxes at different coagulation-microfiltration process times.

Both set of results *i.e.* calculated and experimental show linear variations with nearly the same rates (slopes). However the calculated results are slightly higher than the corresponding experimental ones and this difference may be due to errors during the measuring process. These results confirm once more the capability of the SuperProDesigner software to deal with the design of membrane filtration processes and encourage its use for this purpose.

6. Conclusion

The present study showed experimentally the performance of the coagulation and microfiltration combination process tested in the removal of color and turbidity of water containing disperse dye like red Terasil.

Aluminum sulfate was the considered coagulant and showed to be an efficient due to its cationic properties that allow a neutralization of the negative charges of suspended solids that are responsible for coloring of the solution. However its overdose may destabilize these latter by increasing the turbidity of the water. Therefore an optimization of some of the operating parameters such as the coagulant dose and the pH of the solution was also included and showed an optimum efficiency of the coagulant at a dose of 34 mg/L and a neutral pH.

The process was modeled by means of the SuperPro Designer software the reliability of which was confirmed through comparisons of the calculated results and the experimentally measured values concerning the concentrations of the permeate and the concentrate as well as the permeate fluxes, when varying with time. Both sets of results were very close, encouraging the use of the software for this type of processes.

Finally it can be concluded that the results showed that the membrane microfiltration assured good retention of suspended matter, as confirmed by the concentrations and turbidity of permeate that are significantly lower than those of the concentrate, and a rejection coefficient exceeding 98%.

Also the use of microfiltration in the treatment of textile dyes is an interesting approach and the combination with coagulation has improved the overall performance and it would be worth testing this process for the case of real textile industries effluents.

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