Chemical Engineering Journal 166 (2011) 483–489

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Performance of a coagulation–ultrafiltration hybrid process for water supply treatment

Rosângela Bergamasco[a], Leila Cristina Konradt-Moraes[a], Marcelo Fernandes Vieira[a], Márcia Regina Fagundes-Klen[b], Angélica Marquetotti Salcedo Vieira[a,*]

[a] Department of Chemical Engineering, State University of Maringá, Av. Colombo 5790, 87020-900 Maringá, Paraná, Brazil
[b] Department of Chemical Engineering, West Paraná State University-Toledo, Rua da Faculdade, 645 – Jd. Santa Maria, 85903-000 Toledo, Paraná, Brazil

ARTICLE INFO

Article history:
Received 30 July 2010
Received in revised form 28 October 2010
Accepted 28 October 2010

Keywords:
Chitosan
Surface water
Coagulation
Ultrafiltration
Membrane fouling

ABSTRACT

The combination of coagulation/flocculation and ultrafiltration in the process of drinking water treatment was investigated using natural (chitosan) and chemical (aluminum sulfate) coagulants. A 0.1 μm single-channel membrane was applied at pressures of 1 bar and 2 bar, using the principle of crossflow filtration. The final produced water quality was assessed considering the efficiency of removal of color, turbidity, COD, and compounds that absorb UV at 254 nm, among other physico-chemical and microbiological parameters. The coagulation/flocculation with chitosan as coagulant (CFQ) was efficient in removing compounds that add color and turbidity and that absorb UV at 254 nm, with levels that were very similar to those obtained with the coagulation/flocculation process with aluminum sulfate as coagulant (CFS). Performance evaluation of the hybrid systems (CFS-UF and CFQ-UF) showed that the permeate quality was increased when compared with individually operated systems (UF, CFS, and CFQ). The CFQ-UF process caused higher membrane fouling (79% at 2 bar), but yielded a higher stabilized permeate flux, which was approximately twice that achieved with CFS-UF. Based on the results, one can say that chitosan has a potential application as natural coagulant in CF-UF hybrid processes for treating drinking water with relatively high turbidity.

1. Introduction

Water becomes a potential risk to public health when it contains harmful agents. Thus, the treatment applied to the collected water must ensure that it is free of pathogens and chemicals that pose health risks, when distributed by the water supply system. Furthermore, physico-chemical parameters must meet the drinking water standards required by the laws of each country.

Among the new techniques for drinking water treatment is the use of natural coagulants, aiming at a better quality of treated water by reducing the use of chemicals. Thus, considering the coagulation step, the use of a natural polyelectrolyte such as chitosan could be an option with many advantages over chemical agents, particularly the biodegradability, low toxicity, low residual sludge production, and the large number of surface charges that increase the efficiency of the coagulation process [1].

Biopolymers may be of great interest since they are natural low-cost products, characterized by their environmentally friendly behavior. Among these biopolymers, chitosan may be considered as one of the most promising coagulation/flocculation materials. Chitosan is a linear copolymer of D-glucosamine and N-acetyl-D-glucosamine produced by the deacetylation of chitin, a natural polymer of major importance [2] and the second most abundant natural polymer in the world, after cellulose [3]. Chitosan is also widely applied in water and wastewater treatment because it can be conditioned and used for pollutant complexation in different forms, from water-soluble forms to solid forms [2].

The use of coagulants for drinking water treatment, in spite of being efficient in the removal of most contaminants, is not able to generate water of high potability standards, which leads to the necessity of the simultaneous use of other techniques. Membrane filtration technique is already widely recognized and can be implemented in combination with coagulation processes.

Today, ultrafiltration (UF) technology is recognized by the water industry as a very attractive process for producing drinking water. UF membranes are physical barriers that are able to efficiently remove suspended particles and colloids [4,5], turbidity, bacteria, algae, parasites, and viruses for clarification and disinfection purposes [5], as well as to control trihalomethane precursors [6]. In comparison with conventional processes such as coagulation, floc-

---

* Corresponding author. Tel.: +55 44 3011 4745; fax: +55 44 3011 3863.
E-mail addresses: rosangela@deq.uem.br (R. Bergamasco), leilackm@yahoo.com.br (L.C. Konradt-Moraes), marcelofvieira@hotmail.com (M.F. Vieira), fklen@bol.com.br (M.R. Fagundes-Klen), amsvieira@uem.br (A.M.S. Vieira).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.10.076

culation, sedimentation and/or flotation, and rapid or slow sand filtration, UF technology has many advantages such as superior quality of treated water, much greater compactness, easier control of operation and maintenance, use of fewer chemicals, and lower production of sludge. Communities are increasingly looking to UF as a safer treatment alternative [5].

To overcome the problems caused by natural organic matter (NOM) in UF applications, conjunctive use of coagulation and membranes is becoming more attractive for water treatment because the coagulation is an opportunity to join NOM with other particles present in water before NOM reaches the membrane surface [7]. The NOM found in the liquid leads to membrane fouling, flux reduction and inferior effluent quality. Therefore, the application of coagulants for the raw water pretreatment may bring about an improvement in permeates quality. This is very important, especially in the case of drinking water production [4].

Membrane processes are now economically attractive for large facilities using good quality surface water. Currently, the objectives are to extend membrane technology processes to poorer quality water for the removal of color, taste, dissolved organic matter, and disinfection by-products [8].

At present, full-scale UF applications are evenly spread over Europe and the US. As for developing countries, potable water production is potentially a very large market for UF membranes. Because one of the most critical problems in developing countries is the lack of drinking water, people in these regions are supplied with surface water that contains a significant amount of microorganisms that can cause several diseases. It should be emphasized that due to the rapid development of this fairly new technology, capital and operational costs of UF membrane technology are still expected to decrease [5].

Despite all the advantages presented regarding the use of membrane filtration, some aspects should be considered, which can compromise the efficiency of the process. Among the most critical factors responsible for the decline in permeate flux, are concentration polarization, cake formation, solute adsorption, as well as plugging of the pores [9]. All these introduce additional resistances on the feed side to the transport across the membrane. Resistance-in-series models that consider membrane resistance, adsorption resistance, concentration polarization resistance, and cake resistance have been applied to describe such processes [10].

The phenomenon of concentration polarization always occurs; it is reversible and inherent to the processes of membrane separation, that is, once the operation is finished and the cleaning operation is performed, the membrane permeability to pure solvent must be recovered. Due to this polarization phenomenon, the flux at the end of operation is always smaller than the original value. However, when the steady-state conditions are reached no further decrease in flux is observed and the flux becomes constant with time. The continuous decrease in flux is the result of membrane fouling, which can be defined as an (ir)reversible deposition of retained particles, colloids, emulsions, suspensions, macromolecules, salts, etc. on or in the membrane [9].

Several researchers, such as Zularisam et al. [11], Konieczny et al. [12], Barbot et al. [13], Mo and Huang [14], Sakol et al. [7], and Xia et al. [4] have used the hybrid process of coagulation/flocculation followed by UF (CF-UF) or microfiltration for water treatment. However, the vast majority of authors studied the treatment of water with low turbidity and used inorganic salts as coagulants, mainly iron salts and aluminum sulfate. Application of the CF-UF hybrid process using the natural polymer chitosan as coagulant has been poorly investigated. Bergamasco et al. [15] evaluated the combined coagulation/flocculation/microfiltration process using chitosan and achieved a significant increase in the quality of treated water.

Table 1
Quality of the surface water from Pirapó River.

Water quality parameter	Values
Apparent color (Hu)[a]	1695
True color (Hu)[a]	1045
Turbidity (NTU)	240
Chemical oxigen demand (COD) (mgO_2/L)	19.3
Total organic carbon (TOC) (mgC/L)	6.4
UV_{254} (cm^{-1})	0.923
pH	8.17
Total suspended solids (TSS) (mg/L)	1332
Total dissolved solids (TDS) (mg/L)	228
Total coliforms (CFU/100 mL)[b]	3955
Escherichia coli (CFU/100 mL)[b]	800

[a] Hu = mg_{Pt-Co}/L.
[b] CFU/100 mL = Colony forming units per 100 mL of water sample.

Thus, the present study aimed to evaluate the hybrid process CF-UF in ceramic membrane using chitosan as a natural coagulant and aluminum sulfate as a commercial coagulant to obtain drinking water. Process efficiency was evaluated in terms of reduction of physical and chemical parameters of treated water compared to surface water, as well as in terms of decrease in permeate flux during the CF-UF process.

2. Materials and methods

2.1. Surface water source and characterization

Surface water samples (SW) were collected from the Pirapó River at Maringá – PR, Brazil. Chemical, physical, and microbiological parameters were analyzed before and after the proposed treatment, in order to verify the efficiency of removal of color, turbidity, COD, coliforms, etc. and the quality of treated water.

All the analytical methods followed APHA's Standard Methods [16]. Turbidity measurements were conducted using a turbidimeter (HACH, 2100P). A digital pH meter (Digimed DM-2) was used for pH measurements. Color measurements were conducted using HACH DR/2010 spectrophotometer – Method 8025. COD values were determined using HACH DR/2010 – Method 10129. TOC was determined using an Aurora 1030C TOC Analyzer with 1088 Rotary TOC Autosampler.

Absorbance measurements at 254 nm were performed using a Logen Scientific UV-Vis spectrophotometer. UV absorbance at 254 nm was also used in this study as an indication of the removal of organics from water. UV absorbance is commonly used as an index of the aromatic level [17].

Pathogen indicators, such as total coliforms and *Escherichia coli*, were quantified using 3 M Petrifilm plates, according to APHA [16].

Commercial aluminum sulfate ($Al_2(SO_4)_3$) and chitosan with medium molecular weight from Aldrich were used as coagulants.

The amount of sludge formed was determined in Imhoff cone (20 min), with the water–solids mixture, after the coagulation/flocculation process. The volume was measured and the water–solids mixture was subsequently subjected to a rapid filtration system for the determination of the mass produced.

All experiments were performed at least in triplicate. The surface water quality is presented in Table 1.

2.2. Coagulation/flocculation tests

Coagulation/flocculation tests were carried out in a six-jar tester (Nova Ética – Model 218 LDB) with digital rotation control of the mixing rods, simultaneous addition of reagents and sample collection. The pH was adjusted to 5.0 and concentration of natural chitosan coagulant was 1.0 mg/L. When using aluminum sulfate as coagulant (15 mg/L) pH was maintained at 7.0. In the rapid mixing

Fig. 1. Experimental ultrafiltration unit.

step the speed was kept at 120 rpm for 2.5 min, whereas the speed used in the slow mixing step was 20 rpm for 20 min [18]. Temperature was maintained at 25.0 ± 2 °C during coagulation/flocculation.

2.3. Ultrafiltration experiments

After the coagulation/flocculation tests, the coagulated water (CF), without prior sedimentation, was transferred to the feed tank of the UF module using a peristaltic pump at low speed to avoid breaking coagulated flocs. The whole process including coagulation/flocculation and UF steps was named as CF-UF. Surface water coagulated with chitosan and aluminum sulfate was named as CFQ and CFS, respectively. As initial feed volume (V_o), 20 L of solution were used, and the final volume of the concentrated current (V_f) was 2 L. For all the tests with the combined process the value of the concentration factor (CF) was 10, independently of the filtration time. CF was determined using Eq. (1), where V_p is the permeate volume:

$$\mathrm{CF} = \frac{V_o}{V_f} = \frac{V_o}{V_o - V_p} \tag{1}$$

UF tests with membranes were carried out in a micro-ultrafiltration unit (NETZSCH), presented in Fig. 1, using the principle of crossflow filtration. The filtration module was made of stainless steel with Al_2O_3/ZrO_2 (0.1 μm) ceramic membranes (TAMI, France). The system was equipped with pressure gauges at the inlet and outlet to control the transmembrane pressure (1 bar and 2 bar), and connected to a thermostatic bath for temperature control of the solution contained in the feed tank at 25 ± 2 °C. The output of permeate was collected by opening the valve and the concentrate was returned to the feed tank by the hose.

Initial UF tests were performed with deionized water (DW) to characterize the flux of the membranes. Permeate samples were collected at predetermined times, during a given time interval, and the fluxes were calculated from Eq. (2), where J is the permeate flux, m is the mass of water collected, $\rho_{25\,^\circ\mathrm{C}}$ is the water density at 25 °C, Δt is the time interval in which the sample was collected, and Am is the membrane filtering area:

$$J = \left(\frac{m}{\rho_{25\,^\circ\mathrm{C}}}\right).\Delta t.\mathrm{Am} \tag{2}$$

UF tests were then performed using surface water without any pretreatment (SW), after coagulation/flocculation with chitosan (CFQ), and after coagulation/flocculation with aluminum sulfate (CFS).

The removal efficiency of each analyzed parameter of the different processes was calculated by Eq. (3), where C_i and C_f are the initial and final concentrations, respectively, for each parameter:

$$\%\,\text{Removal efficiency} = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \tag{3}$$

Deionized water fluxes before each experiment (J_{initial}) and after UF of the solutions SW, CFQ, and CFS (J_{final}), considering predetermined time intervals for the stabilization of the permeate flux, were used to determine membrane fouling through Eq. (4):

$$\%\,\text{Fouling} = \left(\frac{J_{\mathrm{initial}} - J_{\mathrm{final}}}{J_{\mathrm{initial}}}\right) \times 100 \tag{4}$$

Surface rinsing of the tested membrane with deionized water continued for 10 min with no pressure applied and the rinsing water was discarded. Deionized water flux was determined with deionized water immediately after surface rinsing (J_{fw}).

The resistance-in-series model was applied to evaluate the filtration characteristics. In general, the intrinsic resistance (R_m) can be obtained when only the pure solvent is filtered. That is, deionized water flux (J_w) is given by Eq. (5), where J_w is the permeation flux, ΔP_T is the trans-membrane pressure, and η is the permeate viscosity:

$$J_w = \frac{\Delta P_T}{\eta \cdot R_m} \tag{5}$$

Considering fouling and concentration polarization as both responsible for clogging of the membrane, total resistance (R_t) may be obtained by the sum of the intrinsic membrane resistance (R_m), the concentration polarization resistance formed by the layer deposited over the membrane surface (R_{cp}), and the fouling resistance (R_f), which is the resistance caused by solute adsorption into the membrane pores and walls (Eq. (6)). Each resistance value can be obtained through Eqs. (7)–(9):

$$R_t = R_m + R_{cp} + R_f \tag{6}$$

$$R_m = \frac{\Delta P_T}{\eta \cdot J_{iw}} \tag{7}$$

$$R_f = \frac{\Delta P_T}{\eta \cdot J_{fw}} - R_m \tag{8}$$

$$R_{cp} = \frac{\Delta P_T}{\eta \cdot J} - (R_m + R_f) \tag{9}$$

In these equations, J_{iw}, J_{fw}, and J are flux values determined experimentally. J_{iw} is the initial deionized water flux before ultrafiltration, J_{fw} is the final water flux after removing cake layer, and J is the stabilized flux with SW, CFQ, or CFS [19].

The stabilized average flux for each solution was determined by the arithmetic mean of the values of permeate flux during the period for which all flows were stabilized. This period extended from 50 to 150 min of filtration.

3. Results and discussion

3.1. Performance of the combined coagulation/ultrafiltration system

Table 2 presents removal efficiencies of CF and combined CF-UF processes, using chitosan and aluminum sulfate, at the pressures of 1 bar and 2 bar.

Removal of UV_{254} absorbing compounds showed a significant increase when the hybrid process was used, changing from 85.8% with CFQ to 99.4% with CFQ-UF at 2 bar.

The UV absorbance of organic matter, in the range of 254–280 nm, reflects the presence of unsaturated double bonds and π–π electron interactions such as in aromatic compounds. However, it is known that natural organic matter (NOM) is a mixture of

Table 2
Removal efficiency (%) of CF and CF-UF processes at 1 bar and 2 bar, using chitosan (CFQ) or aluminum sulfate (CFS) for the coagulation of surface water.

Parameter	CFQ (%)	CFQ-UF (%)		CFS (%)	CFS-UF (%)	
		$P = 1$ bar	$P = 2$ bar		$P = 1$ bar	$P = 2$ bar
Apparent color	98.1	99.4	99.1	99.8	99.2	100
True color	97.1	99.2	99.1	99.3	99.1	99.8
Turbidity	99.3	99.9	99.9	99.2	99.8	99.8
UV_{254}	85.8	91.8	99.4	83.4	96.3	88.5
COD	59.9	90.9	97.4	38.1	89.3	85.1
Total coliforms	62.5[a]	99.0	99.0	99.0	99.0	99.0
Escherichia coli	99.0	99.0	99.0	99.0	99.0	99.0
TSS	60.3	97.8	88.8	94.8	93.5	97.9
TDS	41.9	40.2	86.1	7.52	49.3	42.9

[a] Reduction of 62.5% in the number of UFC/100 mL initially present in the surface water.

organic compounds called humic materials, but proteins, polysaccharides and other classes of biopolymers also contribute to NOM [20]. This indicates that besides the compounds detected by UV_{254} absorption, other organic compounds may also be present in surface waters, and therefore this parameter is not a suitable indicator of NOM removal. Other parameters should be considered for a better understanding of the process.

The removal of TSS was also significantly increased, changing from 60.3% with CFQ to 97.8% with CFQ-UF at 1 bar. According to Schäfer et al. [21], a pore size of less than 6 nm is required to achieve a substantial removal of organics (>50%), and the rejection of UV-absorbing compounds is greater than that of dissolved organic carbon (DOC).

Comparing CFQ and CFS processes, the main differences in removal efficiency are observed with respect to COD removal (59.9% using CFQ and 38.1% using CFS) and TDS removal (41.9% for CFQ and 7.5% for CFS).

It is also observed in Table 2 that the process of coagulation/flocculation with the natural coagulant chitosan was very effective in removing compounds responsible for color and turbidity, as well as UV_{254} absorbing compounds. Similar results were observed by other authors such as Roussy et al. [22] and Rizzo et al. [23]. For the same conditions of pH and concentration of chitosan, Rizzo et al. [23] obtained 78% and 38% removal of turbidity and UV_{254} absorbing compounds, respectively. These values are lower than those obtained in the present study (99.3% for turbidity and 85.8% for UV_{254}). However, this should be balanced by the fact that the turbidity of the surface water used in the present study (240 NTU) was much higher than that used by those authors.

Coagulation pretreatment allows a higher rejection of organics by microfiltration and UF and the cut-off criterion due to initial membrane pore size is no longer valid [21]. The most consistent system was CFQ-UF at the pressure of 1 bar, achieving removal efficiencies above 90% for all parameters assessed, except for TDS, which had 40.2% removal. But if the use of CFS-UF is considered, TDS removal reached a maximum of 49.3%. Another relevant parameter to be analyzed is COD, whose removal was higher when using CFQ-UF at 2 bar (97.4%) than when using CFS-UF at the same pressure (85.1%).

The efficiencies of reduction of physical and chemical parameters obtained by the UF process at 1 bar and 2 bar are presented in Table 3. UF was found to be very efficient in removing bacteria, as expected, reducing the initial microbial load in nearly 100%. As for other factors such as COD and TDS, however, membrane efficiency was lower for both pressures.

Table 3
Efficiency of surface water ultrafiltration using pressures of 1 bar and 2 bar.

Parameter	Removal efficiency (%)—UF	
	$P = 1$ bar	$P = 2$ bar
Apparent color	98.2	100
True color	97.5	99.8
Turbidity	99.6	99.7
UV_{254}	92.9	96.0
COD	86.7	88.9
Total coliforms	99.0	99.0
Escherichia coli	99.0	99.0
TSS	97.0	99.5
TDS	72.0	44.2

According to Dulekgurgen et al. [24], particles in wastewaters have conveniently been grouped into operational size categories, namely dissolved (<1 nm), colloidal (1–10^3 nm), supracolloidal (10^3–10^5 nm) and settleable (>10^5 nm). The membrane used in this paper had a pore size of approximately 100 nm, justifying the removal of more than 97% of suspended solids in treated water, while the removal of dissolved solids was around 72% for the operating pressure of 1 bar. Increasing the pressure to 2 bar decreased the removal of dissolved solids to 44%. An increase in transmembrane pressure favors the passage of particles with size close to the membrane pore size, contributing to lower process efficiency in terms of removal of the analyzed parameters, as observed for TDS. As for the other parameters, the values obtained for the two different pressures were close. This fact may be due to a greater compression of the filter cake and clogging of the pores, thus retaining some particles and contributing to the increase in final removal.

According to Tables 2 and 3, the experimental results were excellent from the point of view of rejection of microorganisms when UF and CF-UF processes were used, reaching nearly 100% removal for both processes. The coagulation step alone is not sufficient to the complete disinfection of the treated water, thus justifying the use of UF. Therefore, the tested membrane can be successfully applied to water disinfection, since overall efficiency of UF for disinfection has been widely studied and demonstrated [7,8]. Unlike conventional processes, removal of microorganisms by UF is complete without the addition of other reagents, and regardless of variations in the quality of the supply.

Comparing the removal values of the parameters presented in Tables 2 and 3 one can observe that both hybrid processes CFQ-UF and CFS-UF showed higher removal efficiencies than the processes that use only CF (CFQ or CFS) or UF, thus producing water of better quality.

As a rule, the hybrid process using UF and chitosan as coagulant showed better results than the other processes studied in this work for surface water treatment, considering the removal efficiency of the examined parameters.

3.2. Permeate flux profiles

Figs. 2 and 3 show the decrease of permeate flux with time for the ultrafiltration of SW, CFQ, CFS, and DW at 1 bar and 2 bar, respectively.

As a way to assist in understanding the profile of permeate flux, the relative fluxes of the membrane were calculated according to Reddy et al. [25] by comparing the permeate fluxes (J) with the deionized water flux before ultrafiltration (J_w), using Eq. (10). As can be observed in Fig. 2, SW and CFQ had very similar profiles throughout the period of filtration. Relative flux with CFQ was 33%, while for SW this value was 25%. Permeate flux with CFS decreased up to about 60 min, when the relative flux stabilized at 30%:

$$\text{Relative flux}\,(\%) = \left(\frac{J}{J_w}\right) * 100 \qquad (10)$$

The profiles presented in Fig. 3 for the pressure of 2 bar are quite different from those shown in Fig. 2 for the pressure of 1 bar. With increasing pressure, a higher permeate flux is expected, especially

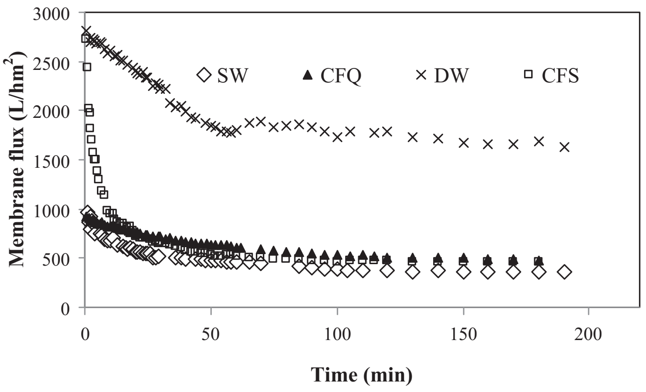

Fig. 2. Permeate flux of DW, SW, CFQ, and CFS for the UF process at 1 bar.

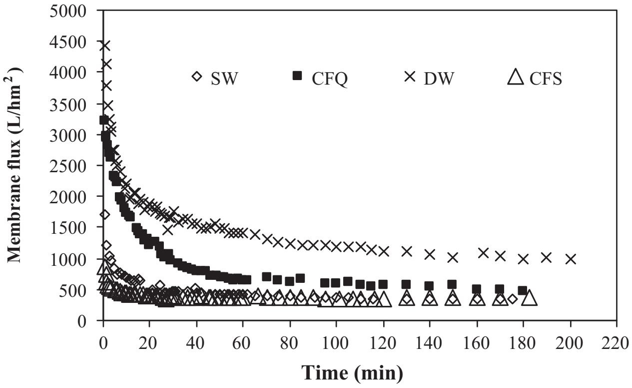

Fig. 3. Permeate flux of DW, SW, CFQ, and CFS for the UF process at 2 bar.

at the beginning of the UF process, when the gel layer was still not formed. However, what was observed in this case was a significant increase in the permeate flux with CFQ, in comparison with SW and CFS.

It was observed in Fig. 2 (pressure of 1 bar) that the permeate fluxes of CFQ and CFS came close to each other after 20 min of filtration, while in Fig. 3 (pressure of 2 bar) that happened only after 160 min of filtration.

In terms of relative flux, SW remained around 28% throughout the filtration, while for CFS there was a slight increase from 17% to 37% during the 200 min of filtration. The largest relative flux was achieved with CFQ, reaching 85% in the first 10 min of UF and stabilizing around 49% after 46 min.

Konieczny et al. [12] confirmed in their experiments of river water treatment that the hybrid process provides satisfactory results regarding the removal of organic compounds when compared with the UF process alone and that the intensity of membrane fouling depends on the type of coagulant used. The characteristics of material and pore size of membranes used are of extreme importance for the determination of final permeate fluxes and pore blockage. More open membranes tend to have higher permeate fluxes, but the retention efficiency of certain compounds can be compromised.

The flux curve can be divided into two domains. Domain 1 corresponds to the initial flux decline for time tending to zero and it involves internal fouling. Domain 2 corresponds to the remaining flux decline for time much larger than zero and it is believed to involve external membrane fouling [26].

Table 4
Average permeate flux as a function of transmembrane pressure for the studied processes.

Process	Average permeate flux (L/h m^2)	
	Pressure = 1 bar	Pressure = 2 bar
UF of SW	419	388
CFQ-UF	570	626
CFS-UF	496	368

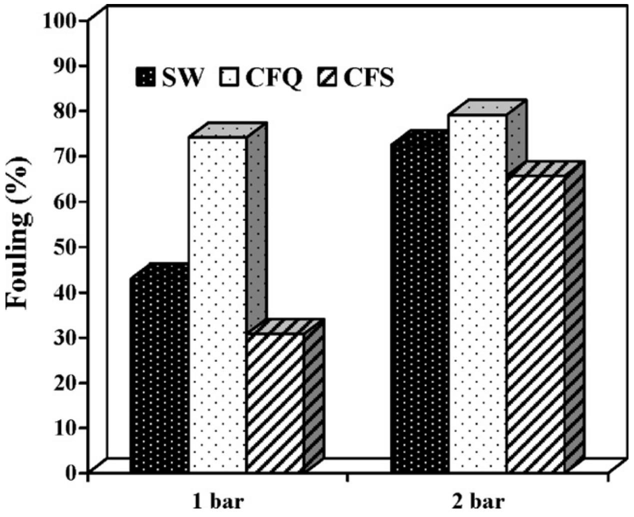

Fig. 4. Membrane fouling for the ultrafiltration of SW, CFQ, and CFS at 1 bar and 2 bar. Total operating time of 150 min.

As shown in Figs. 2 and 3 the initial flux for CFQ-UF is high and falls during the filtration process, stabilizing more quickly when the process is conducted at 2 bar than at 1 bar. However, one should take into account the average permeate flux over the filtration process, which is presented in Table 4 for all the studied processes and transmembrane pressures.

The combined process using coagulation/flocculation with chitosan and ultrafiltration showed higher permeate fluxes compared with UF of SW and CFS-UF under the same pressures. For the pressure of 2 bar the permeate flux of the CFQ-UF process was approximately twice that of the CFS-UF process, thus justifying the use of chitosan as a coagulant prior to the ultrafiltration step for surface water treatment.

3.3. *Influence of SW, CFQ, and CFS on the fouling characteristics*

Fig. 4 presents the membrane fouling results for the UF process treating SW, CFQ, and CFS at the pressures of 1 bar and 2 bar.

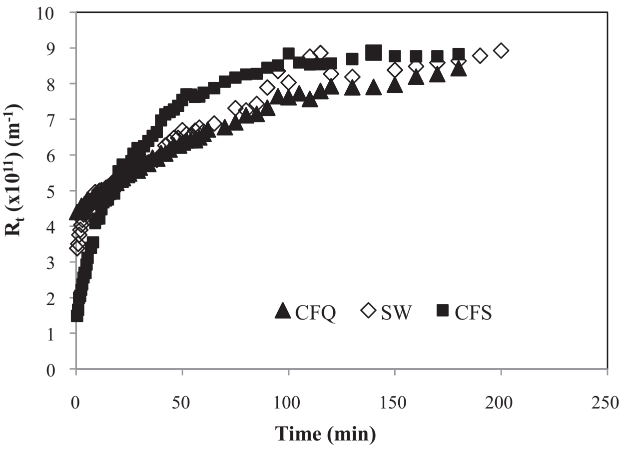

Fig. 5. Effect of total resistance versus time of UF at 1 bar.

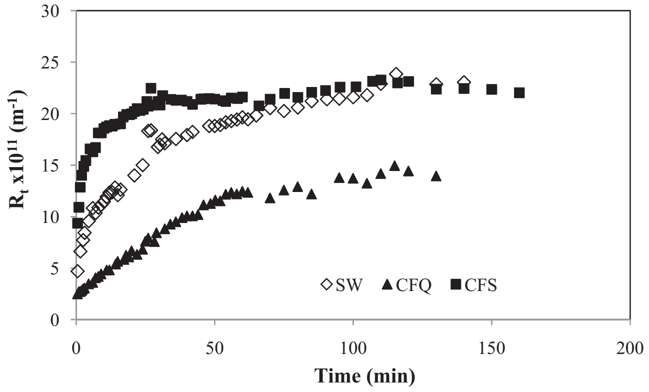

Fig. 6. Effect of total resistance versus time of UF at 2 bar.

Table 5
Resistances on the membrane during the ultrafiltration process with SW, CFQ, and CFS at 1 bar and 2 bar.

	Resistance ($\times 10^{11}$ m^{-1})		
	R_f	R_{cp}	R_t
SW			
$\Delta P = 1$ bar	1.22	6.79	9.62
$\Delta P = 2$ bar	8.11	9.58	20.76
CFQ			
$\Delta P = 1$ bar	4.63	0.82	7.06
$\Delta P = 2$ bar	9.92	0.12	13.11
CFS			
$\Delta P = 1$ bar	0.42	5.78	8.11
$\Delta P = 2$ bar	5.89	12.89	21.86

Two phenomena were observed in determining membrane fouling. The first relates to the addition of aluminum sulfate as coagulant, which should reduce the rate of fouling in UF when compared with surface water without previous coagulation. This was confirmed, as shown in Fig. 4 for the pressure of 1 bar, where the fouling with SW was 43%, while it was 31% with CFS.

These results are in agreement with those experimentally obtained by Bouchard et al. [27] and Guigui et al. [8]. When there is coagulation, colloids are destabilized and cluster forming larger flocs, thus contributing to reduce membrane fouling. Xia et al. [4] also observed that the membrane flux declines slowly with coagulant added to get a positive value in the coagulation/UF process. According to the authors, this may be due to the fact that coagulation helps to remove organic matter, thus reducing membrane fouling.

The second phenomenon, namely the use of chitosan as an organic polymer coagulant, tends to increase membrane fouling, which reached 74% and 80%, respectively at 1 bar and 2 bar. This result is consistent with the work of Bergamasco et al. [15] who used the combined process of coagulation–microfiltration for the treatment of river water, using chitosan as coagulant. The authors concluded that the combined process improved the treated water quality, but there was an increase in membrane fouling when compared with the microfiltration process alone.

The average permeate flux data presented in Table 4 is in accordance with the membrane fouling data presented in Fig. 4, that is, as the transmembrane pressure is increased, a higher permeate flux is promoted. However, the effects of cake formation, gel layer formation, and deposition on the membrane pores are also evidenced.

The tests to determine the formation of sludge under the coagulation conditions showed variation in density, which depends on the coagulant used in the coagulation/flocculation process. In the present conditions, surface water coagulated with aluminum sulfate generated sludge with SVI (sludge volume index) of 38.7 mg/mL, and the sludge formed by coagulation using chitosan showed SVI of 56.8 mg/mL. According to McLachlan [28], the biggest advantage of chitosan over aluminum sulfate as coagulant is the fact that it is biodegradable, generating an easy to handle organic sludge that can be taken to a common landfill. Furthermore, chitosan improves the sedimentation step, as the flocs are more compact.

Another fact that should be taken into consideration when applying UF for water treatment is the mechanism of clogging that occurs in the membranes, which causes a drop in permeate flux and is a result of a set of phenomena related to the solution nature and to the characteristics of the membrane. This fact can be explained by two mechanisms, commonly attributed to the removal of organic matter by UF: sieve retention and adsorption sequestration. In sieve retention the UF membrane acts as a barrier for particle penetration. The particles are retained on the membrane surface and form a cake that grows in thickness as the filtration progresses. The second mechanism involves the entry and capture of the particles into the membrane matrix [5].

According to Guo et al. [5] the direct filtration of natural organic matter by UF is due to adsorption sequestration, which is not easy to clean and forms irreversible fouling. If coagulation is combined with UF, the fine particles can be aggregated to be sieved by the UF membrane, which form concentration polarization that is considered as reversible fouling and easy to clean by physical methods when the filtration progresses.

Table 5 presents the results obtained by the resistance-in-series model for the different types of resistance observed in the UF step using SW, CFQ, and CFS at pressures of 1 bar and 2 bar. The intrinsic resistance of the membrane (R_m), as determined from deionized water filtration, was 1.61×10^{11} m^{-1} at 1 bar and 3.08×10^{11} m^{-1} at 2 bar.

It was observed by means of Table 5, that for the same type of water (without treatment, coagulated with chitosan, or coagulated with aluminum sulfate) the fouling resistance (R_f) due to solute adsorption into membrane pores and walls [19] increased with increasing transmembrane pressure, and this can be explained by the higher compression. This type of resistance can be eliminated only by washing the membrane. It was also observed that R_f was greater for CFQ than for SW and CFS, but concentration polarization resistance (R_{cp}) and R_t were lower for CFQ than SW and CFS at 1 bar and 2 bar.

Floc cake resistance is lower than resistance due to the unsettled floc and the uncoagulated organics, as reported by Guigui et al. [8].

Different coagulants lead to the formation of different floc size and structure. Organic coagulants are more likely to form resistant flocs than mineral coagulants [13], and this may be the cause of the higher fouling resistance found for UF of CFQ.

The use of chitosan as a coagulant can lead to the formation of denser flocs. Thus, its negative impact on the filtration can be explained. The cake is formed by large aggregates, decreasing the average flux through and among these aggregates.

Table 6 presents the relative contributions of the different resistances to the permeate flux decrease in the UF process. Tables 5 and 6 show that the use of chitosan as coagulant in a

Table 6
Relative contributions of the different resistances to the flux decrease in the UF process.

ΔP (bar)	SW			CFQ			CFS		
	%R_m	%R_f	%R_{cp}	%R_m	%R_f	%R_{cp}	%R_m	%R_f	%R_{cp}
1	16.77	12.63	70.60	22.84	65.60	11.56	23.55	5.18	71.27
2	14.81	39.05	46.14	23.46	75.65	0.90	14.07	26.95	58.98

step prior to UF increases fouling resistance, and this resistance (R_f) contributes the most (with 65.60%) to the total resistance of the membrane after UF at 1 bar. When the pressure is increased to 2 bar, the contribution of R_f is even greater (75.65% for CFQ).

The highest contributions of concentration polarization resistance (R_{pc}), above 70%, were achieved for SW and CFS at 1 bar. As for CFQ the most important contribution was found to come from fouling resistance (R_f), that is, solute adsorption into membrane pores. Figs. 5 and 6 show the profiles of total resistance versus time of SW, CFQ, and CFS ultrafiltration at the pressures of 1 bar and 2 bar.

When the curve of total resistance versus time is concave up, fouling by pore blocking mechanism is suggested, whereas if the curve is concave down for most of the filtration time, a mechanism of fouling by cake filtration is indicated, according to Duclos-Orsello et al. [29]. All curves in Figs. 5 and 6 are concave down, indicating a mechanism of fouling by cake filtration. However, with increasing operating time, these curves presented a slight tendency to reverse the concavity, due to a higher compression and larger clogging of membrane pores.

4. Conclusions

Performance evaluation of the hybrid systems (CFS-UF and CFQ-UF) showed that the permeate quality was increased when compared with individually operated systems (CFS and CFQ). This is justified by the excellent ability of the UF process to remove particles and colloids.

Using the CFQ-UF process, reductions of over 90% were achieved for most of the parameters. The reduction of some parameters showed significant improvement at the end of the combined CF-UF process, such as the reduction of COD, which changed from 59.9% with the CF step to 90.9% (at 1 bar) and 97.4% (at 2 bar) at the end of the CFQ-UF process.

The results indicate that when applying CF-UF at optimal conditions, a hygienic barrier effect was achieved for the treatment scheme, in which nearly 100% removal of total coliforms and *E. coli* was obtained at the end of the process.

The efficiency of the CF-UF hybrid process is highly correlated to coagulant nature. The coagulation step does not necessarily imply an increase in permeate flux.

The CFQ-UF process caused higher membrane fouling (79% at 2 bar), but yielded a higher average permeate flux, which was twice that achieved with CFS-UF, thus justifying the use of the natural coagulant prior to the ultrafiltration step for surface water treatment.

Curves of total membrane resistance showed a mechanism of fouling by cake deposition for all cases studied. However, with increasing time of operation, a slight tendency to a mechanism of fouling by clogging of membrane pores was observed at both pressures.

Given the above considerations, one can say that chitosan has a potential application as natural coagulant in CF-UF hybrid processes for treating drinking water with relatively high turbidity. This process can be used reliably to produce drinking water of excellent quality.

Acknowledgements

The authors acknowledge the financial support provided by the research agencies Capes and CNPq.

References

[1] D. Zeng, J. Wu, J.F. Kennedy, Application of a chitosan flocculant to water treatment, Carbohydrate Polymers 71 (2008) 135–139.

[2] F. Renault, B. Sancey, P.M. Badot, G. Crini, Chitosan for coagulation/flocculation processes—an eco-friendly approach, European Polymer Journal 45 (2009) 1337–1348.

[3] M. Rinaudo, Chitin and chitosan: properties and applications, Progress in Polymer Science 31 (2006) 603–632.

[4] S. Xia, X. Li, Q. Zhang, B. Xu, G. Li, Ultrafiltration of surface water with coagulation pretreatment by streaming current control, Desalination 204 (2007) 351–358.

[5] X. Guo, Z. Zhang, L. Fang, L. Su, Study on ultrafiltration for surface water by a polyvinylchloride hollow fiber membrane, Desalination 238 (2009) 183–191.

[6] A. Bottino, C. Capannelli, A. Del Borghi, M. Colombino, O. Conio, Water treatment for drinking purpose: ceramic microfiltration application, Desalination 141 (2001) 75–79.

[7] D. Sakol, K. Konieczny, Application of coagulation and conventional filtration in raw water pretreatment before microfiltration membranes, Desalination 162 (2004) 61–73.

[8] C. Guigui, J.C. Rouch, L. Durand-Bourlier, V. Bonnelye, P. Aptel, Impact of coagulation conditions on the in-line coagulation/UF process for drinking water production, Desalination 147 (2002) 95–100.

[9] M. Mulder, Polarization phenomena and membrane fouling, in: Basic Principles of Membrane Technology, Kluwer, Academic Publishers, Boston, 1991 (Chapter 7) pp. 281–311.

[10] R.S. Juang, H.L. Chen, Y.S. Chen, Membrane fouling and resistance analysis in dead-end ultrafiltration of *Bacillus subtilis* fermentation broths, Separation and Purification Technology 63 (2008) 531–538.

[11] A.W. Zularisam, A.F. Ismail, M.R. Salim, M. Sakinah, T. Matsuura, Application of coagulation–ultrafiltration hybrid process for drinking water treatment: optimization of operating conditions using experimental design, Separation and Purification Technology 65 (2009) 193–210.

[12] K. Konieczny, D. Sąkol, J. Płonka, M. Rajca, M. Bodzek, Coagulation–ultrafiltration system for river water treatment, Desalination 240 (2009) 151–159.

[13] E. Barbot, S. Moustier, J.Y. Bottero, P. Moulin, Coagulation and ultrafiltration: understanding of the key parameters of the hybrid process, Journal of Membrane Science 325 (2008) 520–527.

[14] L. Mo, X. Huang, Fouling characteristics and cleaning strategies in a coagulation–microfiltration combination process for water purification, Desalination 159 (2003) 1–9.

[15] R. Bergamasco, C. Bouchard, F.V. Silva, M.H.M. Reis, M.R. Fagundes-Klen, An application of chitosan as a coagulant/flocculant in a microfiltration process of natural water, Dealination 245 (2009) 205–213.

[16] APHA—American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 19th ed., 1995, Washington, DC.

[17] M.H. Kim, M.J. Yu, Characterization of NOM in the Han River and evaluation of treatability using UF–NF membrane, Environmental Research 97 (2005) 116–123.

[18] L.C. Konradt, R. Bergamasco, C.R.G. Tavares, M.C. Bongiovani, D. Hennig, Utilization of the coagulation diagram in the evaluated of the natural organic matter (NOM) removal for obtaining potable water, International Journal of Chemical Reactor Engineering 6 (2008) 1–6.

[19] I.S. Chang, S.-O. Bag, C.-H. Lee, Effects of membrane fouling on solute rejection during membrane filtration of activated sludge, Process Biochemistry 36 (2001) 855–860.

[20] N. Ates, M. Kitis, U. Yetis, Formation of chlorination by-products in waters with low SUVA–correlations with SUVA and differential UV spectroscopy, Water Research 41 (2007) 4139–4148.

[21] A.I. Schäfer, A.G. Fane, T.D. Waite, Cost factors and chemical pretreatment effects in the membrane filtration of waters containing natural organic matter, Water Research 35 (2001) 1509–1517.

[22] J. Roussy, M. Van Vooren, B.A. Dempsey, E. Guibal, Influence of chitosan characteristics on the coagulation and the flocculation of bentonite suspensions, Water Research 39 (2005) 3247–3258.

[23] L. Rizzo, A. Di Gennaro, M. Gallo, V. Belgiorno, Coagulation/chlorination of surface water: a comparison between chitosan and metal salts, Separation and Purification Technology 62 (2008) 79–85.

[24] E. Dulekgurgen, S. Dogruel, O. Karahan, D. Orhon, Size distribution of wastewater COD fractions as an index for biodegradability, Water Research 40 (2006) 273–282.

[25] A.V.R. Reddy, J.J. Trivedi, C.V. Devmurari, D.J. Mohan, P. Singh, A.P. Rao, S.V. Joshi, P.K. Ghosh, Fouling resistant membranes in desalination and water Recovery, Desalination 183 (2005) 301–306.

[26] G.T. Vladisavljevic, P. Vukosavljevic, B. Bukvic, Permeate flux and fouling resistance in ultrafiltration of depectinized apple juice using ceramic membranes, Journal of Food Engineering 60 (2003) 241–247.

[27] C. Bouchard, E. Laflamme, J.-B. Serodes, D. Ellis, M. Rahni, M. Rodriguez, Étude en la laboratoire de l'ultrafiltration et de la coagulation–ultrafiltration d'une eau colorée, in: 17iéme Symposium de l'Est du Canada sur la Recherche Portant sur la Pollution de l'eau 2, 2001, pp. 139–148.

[28] D.R.C. McLachlan, Aluminium and the risk for Alzheimer disease, Environmetrics 6 (1995) 233–275.

[29] C. Duclos-Orsello, W. Li, C.-C. Ho, A three mechanism model to describe fouling of microfiltration membranes, Journal of Membrane Science 280 (2006) 856–866.