

Treatment of silica effluents: ultrafiltration or coagulation–decantation

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Abstract

In the electronics industry, the preparation of silicon plates generates effluents that contain a great amount of colloidal silica. Two processes—decantation and ultrafiltration—are studied with in view the treatment of the effluents released by the firm Rockwood Electronic Materials. The feasibility of each of the two processes is studied separately and their operating parameters optimized. Both processes allow the recovery of a great proportion of the initial effluent (over 89%) as transparent and colorless water that can be reused at the start of a line. In view of the results and of the compared advantages and disadvantages of the two processes, ultrafiltration will be selected for the industrial unit.

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1. Introduction

The firm Rockwood specializes in the recycling of wafers (silicon plates used in the fabrication of electronic components). The effluents considered in this study come from the polishing step. Silica is one of the most difficult-to-handle inorganics for water purification processes. It can be found in three different forms: soluble, colloidal, or as suspended particles. It can be either a polymer or a crystal and its chemistry is highly complex. The literature contains many papers that deal with the treatment of aqueous solutions contaminated by silica. The presence of residues of silica can be detrimental to production efficiency. Sheikholeslami and Tan [1] have observed a significant fouling of the reverse osmosis polyamide membranes by silica during the desalination of synthetic solutions. This phenomenon has been largely stud-

ied but remains a major problem in the case of desalination by reverse osmosis [2,3] as well as in the case of ultrafiltration [4] and microfiltration [5]. For this reason, silica is used as model solution in order to better understand and enhance mass transfer in membrane processes [6–8].

During a study for the electrical industry, Konieczny et al. [9,10] came up against a specific difficulty: colloidal silica can form deposits on turbine blades, which results in less electrical energy produced. In order to reduce the amount of silica, proportional to the amount present in the feed water, they ultra-filtrated the water (2.5 at 50 mg m⁻³) going to the turbines and determined the operating parameters (TMP, SiO₂ concentration, velocity) to achieve complete retention of the colloidal silica while maintaining high permeate flux.

The present study compares two processes, ultrafiltration and coagulation–decantation that can be applied to the treatment of this type of effluents. The volume of water recovered must be as large as possible and the purity of the water must be high enough for it to be re-used at the start of the pol-

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ishing line. We have demonstrated the feasibility of each of the two processes and optimized their operating parameters. Then we have compared their advantages and disadvantages to determine which process should be chosen in view of an industrial application.

2. Analyses and effluent

2.1. Effluent

The colloidal silica contained in the effluents studied here comes essentially from the polishing step, itself composed of a preliminary step and a finishing step. The plates are polished by a chemical–mechanical process. The effluent is made up of two fractions:

- (1) The solution from the preliminary step has a content of SiO_2 of $48\text{--}50\text{ g L}^{-1}$ and a content in Na_2O lower than 35 g L^{-1} . The specific area of the silica particles—parameter justifying their use—is $40\text{--}60\text{ m}^2\text{ g}^{-1}$. The pH of the solution ranges between 10.5 and 11.5. The mean size of the particles is 50 nm. The solution density ranges between 1.37 and 1.39.
- (2) The solution from the finishing step is an opalescent liquid with a content in SiO_2 of $29\text{--}31\text{ g L}^{-1}$. The Na_2O concentration is lower than 20 g L^{-1} and the specific area of the grains ranges between 105 and $135\text{ m}^2\text{ g}^{-1}$ for a mean size of 25 nm.

All in all, $20\text{--}25\text{ m}^3\text{ h}^{-1}$ of effluents with a colloidal silica concentration of 7 g L^{-1} were eventually obtained by Rockwood. The pH of the effluent ranges between 8.5 and 9.5 for a density of about 1.20 at 20°C . This same effluent was used during the coagulation–decantation and the ultrafiltration experiments.

2.2. Analyses

In order to determine the performances of both processes in terms of mass balance and retention, a quantitative determination of the colloidal silica was done using the measure of the turbidity. Indeed, a measure of the dry weight cannot be used since the presence of stabilizing ions and mineral salts forbids assimilating the dry weight only to the amount of silica, whether in the purified liquid phase (i.e., permeate in the case of membrane processes) or in the concentrate (i.e., retentate in the case of membrane processes). Therefore, we plotted a curve giving the turbidity as a function of the concentration (Fig. 1) after several successive dilutions with distilled water of the initial solution of known concentration (49 g L^{-1}) used by the firm Rockwood at the start of the polishing step. This series of successive dilutions with distilled water was also performed on site before the solution was used for the abrasive cleaning step, which gave the silica an identical environment during the analysis (low concentration of ionic species).

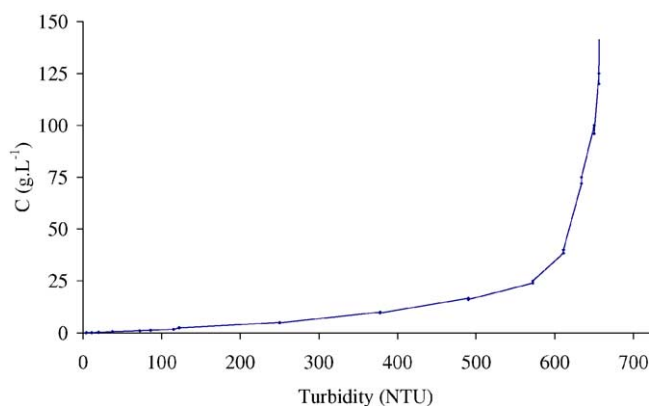


Fig. 1. Variation of the silica concentration as a function of turbidity.

The equipment and protocol of each of the two processes will be detailed later.

3. Coagulation–flocculation–decantation

The decantation process used to separate suspended matter in a liquid of low density seemed perfectly suited to the treatment of our effluents which contained a concentration in silica in the order of 7 g L^{-1} . However, as our colloidal silica had a granular distribution lower than 50 nm, it took a long time to settle (more than 24 h) and so we tested a process of coagulation–flocculation–decantation, which could accelerate the sedimentation.

3.1. Protocol

Coagulation–flocculation–decantation tests were carried out on the effluents in 1 L graduated tubes. After homogenization of each starting effluent (1 L), the coagulant—here either a solution of 13% FeCl_3 or solid CaCl_2 —was added. The use of FeCl_3 requires that the pH be adjusted between 10.5 and 11. Since the cationic flocculants used—Cartaretin 10CE (India) (very low toxicity) and Eurochem Basic (low toxicity)—are active within the pH range 5.5–7, it was necessary to set the pH within this range before adding the flocculant. The particles were then uniformly dispersed to encourage the formation of flocs. Stirring was applied at 200 rpm for 5 min and then at 40 rpm for 30 min until the flocs formed. The solution was then poured into a graduated tube and the interface height measured versus time. The turbidity of the supernatant and the quantity of dry matter in the sludge were measured.

3.2. Results

The effect of the flocculants is not significant in terms of settling speed and supernatant quality and will therefore not be discussed further in this paper. When CaCl_2 was used as coagulant (Table 1 and Fig. 2) and whatever its concentra-

Table 1
Variation of the quality of the supernatant as a function of coagulant (nature and concentration)

Quantity of coagulant	Dried matter (g kg ⁻¹)	Turbidity of the supernatant (NTU)	Volume of the concentrate (ml)
Initial effluent	3.3	200	
Effluent + CaCl ₂			
1 g	22.2	5.4	165
2 g	23.7	1.7	165
3 g	23.4	1.6	175
5 g	22.7	1.7	165
Effluent + FeCl ₃			
0.1 mL at pH 5.5	No decantation		
0.25 mL at pH 5.5	No decantation		
0.5 mL at pH 5.5	34.0	2.3	110
2 mL at pH 5.5	34.2	1.9	158
7 mL at pH 5.5	–	–	195
1 mL at pH 4.66	No decantation		
1 mL at pH 7.07	0	8.8	145

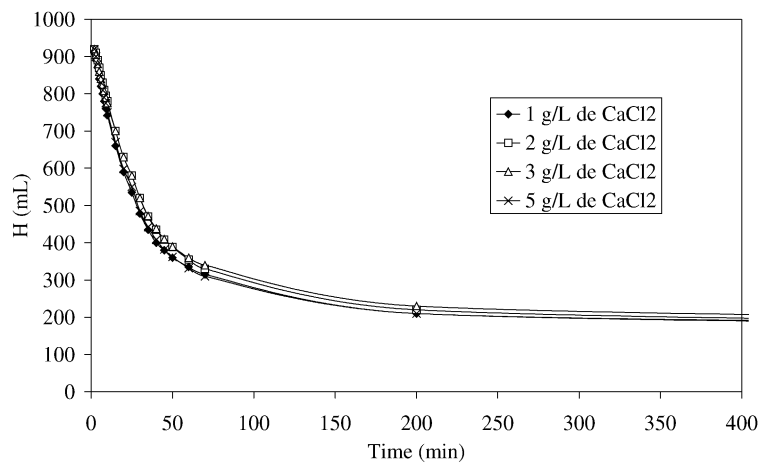


Fig. 2. Variation of the supernatant as a function of the quantity of CaCl₂.

tion, the decantation took place, the decanted volume was small and the supernatant was clear. Taking into account the supernatant turbidity, we chose a concentration of 2 g L⁻¹ in CaCl₂. When FeCl₃ was used as coagulant, the results showed (Table 1 and Fig. 3) that an optimum quantity was 0.5 or 2 mL L⁻¹ depending on the selection criterion, respec-

tively the settling velocity or the supernatant turbidity. These two FeCl₃ concentrations did not lead to a significant difference in supernatant turbidity, we chose the concentration of 500 ppm of FeCl₃ for the dimensioning of the decanter. At lower concentrations, the decantation did not take place, and higher concentrations did not yield significant improve-

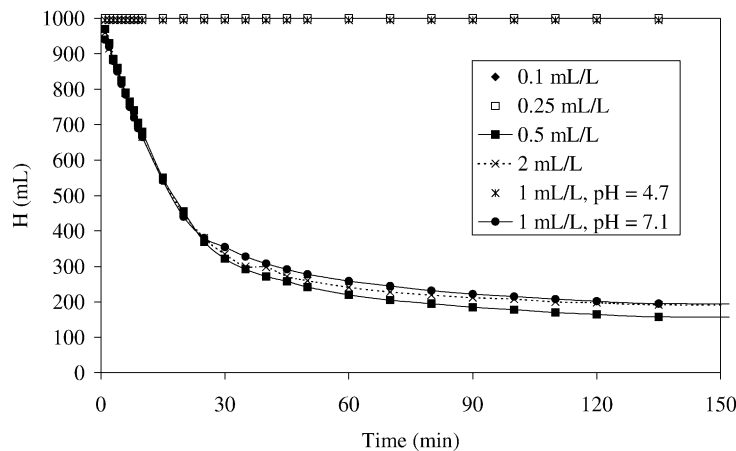


Fig. 3. Variation of the supernatant as a function of the quantity of FeCl₃.

ments: it is better to use a coagulant concentration as little as possible. The supernatant turbidity was 2.3 NTU. For a starting effluent volume of 1 L, we were able to recover 89% of the water at the end of the decantation process. At a pH of 4.7 the decantation did not take place whereas it did at a pH of 7, which shows the importance of the pH.

A comparison of the Kynch curves relative to the use of Ca^{2+} (Fig. 2) or Fe^{3+} (Fig. 3) showed that the height of the sludge obtained with Fe^{3+} was three times as little as that obtained when Ca^{2+} was used (for 20 min). The slowing down started after 20 and 70 min with Fe^{3+} and Ca^{2+} , respectively. This difference is mostly due to the ability of the trivalent ion Fe^{3+} to agglomerate more particles than the divalent ion Ca^{2+} .

We dimensioned the decanter by means of the Kynch theory which applies to a plug flow sedimentation and exploits the part of the curve before the compression point while distinguishing two parts: there is a part of linear variation which shows a constant displacement velocity of the interface called w_0 and another (w_i) of progressive slowing down of the displacement velocity. The Kynch theory assumes that the speed of fall of a particle, whatever its size and density, depends only on the local particle concentration of the zone it goes through. It is well known that Kynch theory is not directly valid for practical application due to compression. Basically, Kynch assumes that the settled solid at the bottom of the vessel is incompressible. To simplify and to approximate the size of the decanter, the compression velocity is not taken into account and no compression model are used. The determination of (C_i , w_i) is necessary to calculate the decanter area (C_i is the interface sludge concentration). If w_i is small, this value can be calculated by

$$w_i = \frac{h_i - H_i}{t_i}$$

with h_i , virtual height [if the concentration of sludge was uniform and equal to C_i] (m); H_i , interface height (m), t_i , time (s); w_i , decantation velocity (m s^{-1}).

In order to determine the minimum decantation surface, the mass flow was plotted as a function of the concentration C_i (C_u = concentration of the extracted sludges (g L^{-1})) (Fig. 4).

$$J = \frac{w_i}{1/C_i - 1/C_u}$$

with J , mass flow ($\text{g m}^{-2} \text{s}^{-1}$).

It was thereby possible to determine the minimum flow limiting the decanter capacity as well as the minimum decanter surface in order to separate the effluent containing the silica (flow rate Q_0 , concentration in solid C_0):

$$\Omega = \frac{Q_0 C_0}{J_{\min}}$$

The minimum mass flow thereby obtained was $0.38 \text{ g m}^{-2} \text{ s}^{-1}$. The minimum surface necessary for our decantation was about 6 m^2 . Even if the settling speed was weak, the decanter surface was sufficient to treat the $25 \text{ m}^3 \text{ J}^{-1}$.

4. Ultrafiltration

4.1. Protocol

Ultrafiltration retains molecules whose sizes range between 0.1 and $0.001 \mu\text{m}$. Prior to extrapolating a membrane process to the industrial scale, the configuration of the membrane and the optimum operating conditions must be determined. When a mineral membrane reportedly resistant to this type of effluents is used, its active layer is abraded and this can limit the industrial development of this type of membrane. However, polysulfone organic membranes have already been successfully used on an industrial scale [11] for similar effluents. We thus used a Microza module from the firm Pall-Exekia containing 900 hollow polysulfone fibers ($d_i = 0.8 \text{ mm}$, $L = 0.8 \text{ m}$, $S = 1 \text{ m}^2$, Cutoff = 100 kDa, $Lp_0 = 160 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$). We first studied the influence of the operating parameters and then, for various circulation

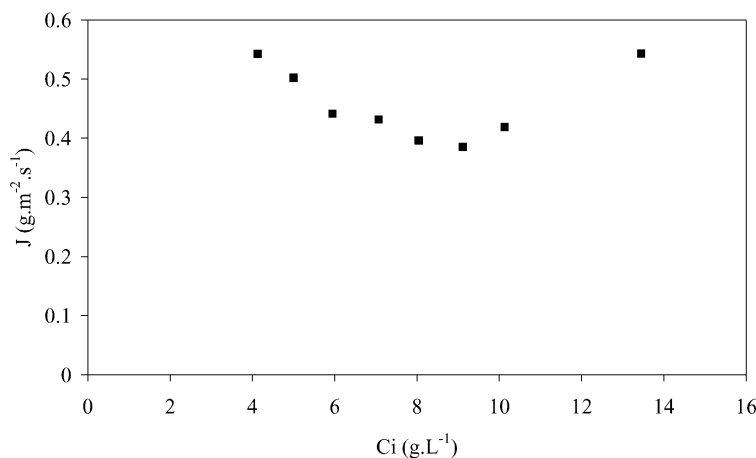


Fig. 4. Variation of the flux as a function of the concentration: determination of the area decanter by the Kynch theory.

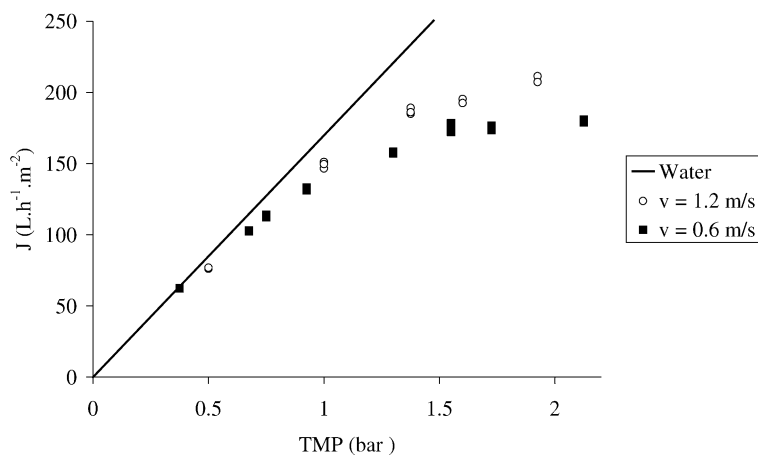


Fig. 5. Variation of the permeate flux as a function of the transmembrane pressure for different flow rates (i.e., velocities) (high 1.2 m s^{-1} , low 0.6 m s^{-1}) ($T = 20^\circ \text{C}$, constant concentration).

velocities, and then we recorded the variations of the permeate flux and of the retention factor as a function of the volumic concentration factor (VCF) for large volumes of effluents.

The effluents were likely to contain several solid or aggregated elements coming from the silicon plates or generated by friction against the brushing mat. A usual pretreatment, a pre-filtration at $100 \mu\text{m}$ was thus required to prevent the membrane module from quickly deteriorating. The industrial pre-filter had to be cleaned regularly (every 20–30 min). Not only did this pre-filtration protect the membrane but it also trapped some colloidal silica in the aggregates. Consequently the effluent reaching the ultrafiltration membrane had a turbidity lower than 100 NTU, which is lower than that of the effluent treated by coagulation–decantation (200 NTU).

4.2. Results

In order to study the operating parameters, the upstream concentration was kept constant by recycling the permeate and the retentate. When studying the influence of the transmembrane pressure, it can be noted that the permeate flux reaches a limiting value decreases whatever the circulation velocity (Fig. 5). The transmembrane pressure usually used, ranges between 70 and 80% of the limiting pressure [11]. We decided to work with a transmembrane pressure close to 1 bar, which limits the fouling of the membrane. For this transmembrane pressure, the permeate flux is close to the water flux. We studied the influence of the circulation velocity and of the retention by performing concentration experiments on large volumes (larger than 100 L): in this case only the retentate was recycled. The results (Fig. 6) show that the permeate flux increases with the circulation velocity. This is the result of a significant shear stress, which reduces the fouling of the membrane and the concentration polarization. Moreover, if the circulating velocity is high enough— 1.8 m s^{-1} —the permeate flux is not only very great but also quasi-constant regardless of the volume concentration factor. Its numerical

value is very close to the value of the permeability of the membrane to water: $150 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$. The values of the transmembrane pressure and of the circulation velocity are in agreement with the existing industrial references for another silicon-containing effluent released by an electronics plant, respectively 1 bar and 1.6 m s^{-1} for a temperature of 25°C [11]. Considering the selectivity of this ultrafiltration process, we can state that the turbidity of the permeate was constante, about 1 NTU, irrespective of the turbidity in the retentate in the interval 100–600 NTU. The quality of the water at the end of the ultrafiltration process is similar to that obtained by the coagulation–decantation process. Taking into consideration the error of measurement, the turbidity of the water recovered by the two processes is comparable to that of distilled water: the permeate can be re-used.

The retention rate of silica remains constant as a function of time, regardless of the upstream concentration (Fig. 7). The retention factor is calculated from their concentration in the retentate and the permeate according to the following

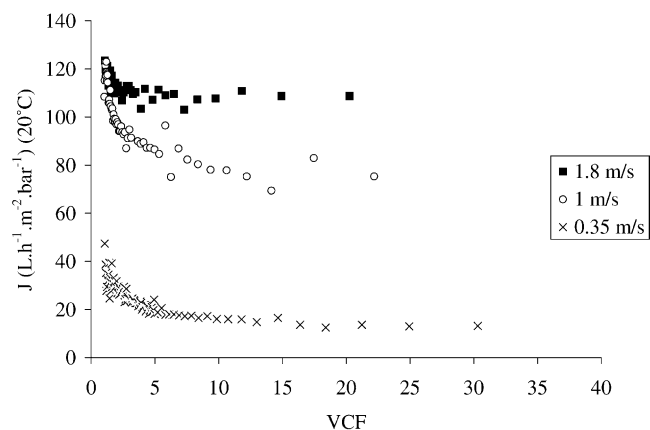


Fig. 6. Variation of the permeate flux as a function of the volumetric concentration factor for different flow rates (i.e., velocities).

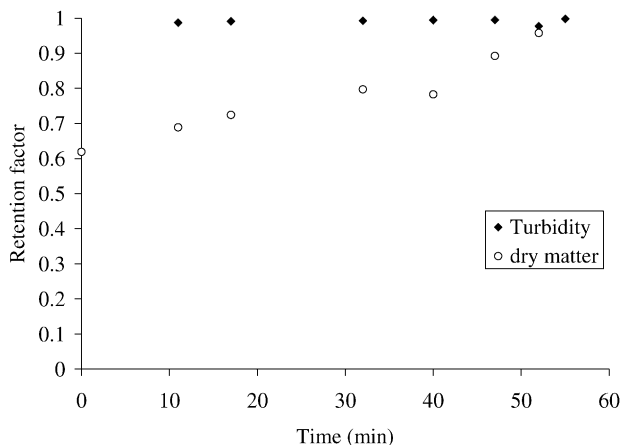


Fig. 7. Variation of the retention factor as a function of time for two analysis methods (turbidity and dried matter).

equation:

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

where $R\%$ = retention factor, C_p = ion concentration in the permeate (mg L^{-1}) and C_r = ion concentration in the retentate (mg L^{-1}).

Comparing this value to the retention rate calculated with regard to the dry matter allows us to validate our analysis method. With an ultrafiltration membrane cutoff of 100 kDa, only the colloidal silica is retained and the downstream concentration in stabilizing ions, which differs only slightly from the upstream concentration, will remain constant throughout the filtration step. For low upstream concentrations in colloidal silica, the amount of stabilizing ions being almost the same on both sides of the membranes, the silica retention rate is small: 60% (calculated with regard to the dry matter). This value is consistent with the ions/silica ratio of our effluents. As the upstream concentration increases, the quasi-constant concentration in stabilizing ions becomes negligible compared with the concentration in silica which itself increases and therefore the retention rate gets closer to the exact value calculated from the turbidities.

The relation between the permeate flux J and the VCF is generally of the form $J = J_0 - k \ln(\text{VCF})$. The VCF is the concentration factor calculated with the feed volume and the retentate volume (V_f/V_r). The membrane area determined by the dimensioning of the industrial unit is around 8 m^2 for a VCF of 20, that is a permeate flux of around $125 \text{ L h}^{-1} \text{ m}^{-2}$ at 20°C and a silica concentration in the retentate of 24 g L^{-1} .

5. Discussion and conclusion

In this study we have demonstrated the feasibility of two processes—coagulation–decantation and ultrafiltration—for the treatment of silica-containing effluents released by the

electronics industry. With both processes we recovered a large fraction of the initial effluent, 89 and 95%, respectively, as transparent and colorless water, which can be recycled at the entrance of the firm. In both cases, a relatively small floor area of 6 m^2 was necessary for the decanter while a relatively small area of 8 m^2 was necessary for the membrane.

If the decantation process is used in a plant where the industrial floor area available is limited, the decanter floor area, even small, can still be a problem. Besides, the value given here is a minimum value, which means that if the inlet conditions are modified some silica may appear in the supernatant. It will therefore be necessary to use a larger unit floor area to take into account the possible variations of the silica concentration or of the effluent flow rate (in case of an extension of the plant). On the contrary, if the ultrafiltration process is used, the unit floor area will be only slightly modified and will remain very small. Only the membrane surface will be increased to take into account the possible above-mentioned variations.

The management of the sludges or of the concentrates is still to be studied for both processes, but we already know that it will be more problematic in the case of the decantation, which gives off greater volumes of iron-rich sludges.

Ultrafiltration can be readily automated and has a great flexibility. The treatment of the effluent is faster by ultrafiltration because of the very slow settling velocity of the silica. The disadvantages of this process are inherent to membrane processes: fouling of the membrane and need for a pre-treatment. However, the fouling can be limited by increasing the circulation velocity up to 1.8 m s^{-1} , circulation velocity that has already been used in the industry. A pre-filtration treatment on a backflush pre-filter not only protects the membrane but also reduces the turbidity of the effluent to be treated by trapping the colloidal silica.

In view of the results obtained in this study, the ultrafiltration process was selected. The cost of industrial unit equipped with a pre-filter manufactured by Pall-Exekia was estimated at €100,000.

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