

1 **IE2010-298**

2 **Combining coagulation, softening and flocculation to dispose reverse osmosis**

3 **retentates**

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1 **ABSTRACT**

2 The concentrated stream of a reverse osmosis unit was treated by coagulation,  
3 softening and flocculation to reduce conductivity and refractory organic matter  
4 content. Different polyaluminium chlorides and one ferric salt were used as  
5 coagulants, lime was added as softener, and two polymers (anionic and cationic  
6 polyacrylamides) were tested as flocculants. Coagulants reduced significantly  
7 the presence of refractory compounds by themselves, although conductivity  
8 increased. Lime addition decreased conductivity forming precipitates of  $\text{CaCO}_3$   
9 and  $\text{Mg}(\text{OH})_2$ . When coagulation was combined with flocculation without  
10 adding lime, the anionic flocculant was more effective than the cationic one  
11 because the specific high hardness of water supplied enough  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to  
12 promote the formation of bigger flocs, bridging the slightly negative coagula  
13 and anionic groups of the polymer; although they also reduced the efficiency of  
14 the cationic polyacrylamide. None of the tested flocculants showed any effect  
15 on conductivity and refractory organic matter reduction when lime was added.

16

17 **Keywords:** reverse osmosis retentate; coagulation; flocculation; softening;  
18 refractory organic matter.

19

## 1 **1. Introduction**

2 Recovered paper industry is one of the most sustainable industries worldwide. Beyond  
3 re-using paper to produce recycled paper, this sector is also working hard to reduce fresh  
4 water consumption recycling its own effluent [1,2]. The closure of the water circuits  
5 depends on the type of paper product and process [3]. While water circuits are mostly  
6 closed for brown grades, which production does not require the high quality of water  
7 imposed by pulp bleaching processes; a total closure is difficult to achieve for white  
8 ones without the application of advanced treatments.

9         Pressure-driven membrane processes, i.e. microfiltration (MF), ultrafiltration  
10 (UF), nanofiltration (NF) and reverse osmosis (RO), are taking advantage as polishing  
11 stages to reclaim industrial effluent aiming to return it back into the process. Two  
12 interconnected factors are however the main drawbacks for their implementation: (i) the  
13 risk of membrane fouling [4], which may require extensive water pretreatment or  
14 intensive chemical cleaning of the membranes, shortening its lifetime and increasing the  
15 maintenance cost; and (ii) the need for further treatment of the concentrated fraction.  
16 Although forcing NF and RO membranes to work at very high recoveries to yield the  
17 minimal retentate current would be highly recommended, this would cause a lot of  
18 trouble in terms of fighting against fouling and treating concentrates.

19         There are mainly two options for a further treatment of rejected streams: (1)  
20 water removal from the concentrate; and (2) removal of specific components by a  
21 selective treatment. In both cases, water can be reused again into the process, or  
22 discharged (directly or indirectly via sewage systems) whenever water quality  
23 parameters fulfil the requirements established by the corresponding environmental  
24 authority [5-7]. Discharge into the sewer system can adversely affect subsequent  
25 biological sewage treatment, as microbial growth may be limited by the inhibitory effect

1 of high salinity, or by the refractory character and biotoxicity of typical organic  
2 constituents of membrane retentate [8,9].

3 Water removal from concentrated streams comprises zero liquid discharge (ZLD)  
4 systems [10], like thermal evaporators [11,12] or crystallizers [13]. These systems drive  
5 the recovery to approach the 100% and, if they are combined with a high recovery  
6 brackish-water RO system, they can produce permeate with only 10 mg/L of total  
7 dissolved solids (TDS). However, the cost of these thermal systems is typically much  
8 higher than the cost for implementing a desalination membrane facility, both considered  
9 in economic and energetic (operative) terms. Therefore, this option for the treatment of  
10 retentated streams is only feasible for very small flows of concentrates [14].

11 The selective treatment of specific components of rejected streams may be  
12 achieved by the application and combination of different available technologies (e.g.  
13 advanced oxidation, ionic exchange, chemical precipitation or activated carbon  
14 adsorption). Particularly, much of the research conducted on the management of  
15 concentrates has been reported within the dyeing industry sector because their effluents  
16 are highly loaded with organic compounds and mineral salts. For example, Balanoski et  
17 al. [15] reported the degradation by the Fenton reaction of dyeing NF membrane  
18 concentrates from biologically treated secondary effluent. A reduction in total organic  
19 carbon (TOC) of around 50% was achieved, and the optical absorbance was reduced  
20 between 20-50% after 3 hours of Fenton treatment. In the same line, van Hege et al. [16]  
21 applied electrochemical oxidation for the treatment of recalcitrant organic constituents  
22 and ammonia nitrogen contained in RO retentate produced in the textile industry,  
23 achieving the following removal efficiencies: >80% of the colour, 50% of the  
24 absorbance at 254 nm, 25% of the chemical oxygen demand (COD) and 10% of the total  
25 ammonia nitrogen.

1           On the other hand, Allegre et al. [17] proposed a coagulation-flocculation-  
2 decantation train to treat these concentrated streams, paying special attention to the  
3 selection of chemicals because the settling velocity and supernatant absorbances were  
4 very sensible to the added products. Finally, Dyalinas et al. [18] compared the efficiency  
5 of coagulation and activated carbon adsorption with three different advanced oxidation  
6 processes (electrochemical treatment, photocatalysis and sonolysis) as alternative  
7 treatments to the rejected stream coming from a RO system placed after a membrane  
8 biological reactor (MBR), located in a municipal wastewater treatment plant (Chania,  
9 Western Crete, Greece). The best results were achieved by activated carbon adsorption,  
10 which was able to reach a 91.3% reduction of the dissolved organic carbon (DOC). All  
11 the three advanced oxidation methods showed similar results, removing 36%, 34% and  
12 50% of the DOC, respectively. Coagulation with  $\text{FeCl}_3$  removed 52% of the DOC.  
13 Therefore, since the efficiency of the treatment depends on each specific case, nowadays  
14 there is not a universal solution to treat these retentates.

15           The main scope of the present study is the assessment of coagulation, combined  
16 with flocculation and lime softening, as an alternative for the treatment of RO  
17 concentrates characterized by a high content of refractory organic matter (>2000 mg/L  
18 of COD) and a high conductivity (>9 mS/cm). Although previous studies have reported  
19 the evolution of particles size distribution when treating synthetic water by each one of  
20 these processes separately [19-21], the combination of these three processes in the  
21 treatment of a real wastewater has not been reported to date. In addition to the removal  
22 of COD and conductivity, the efficiency of this combined system, where different  
23 mechanisms can interact together, will be assessed in terms of the achieved reductions of  
24 absorbance at different wave lengths, which are related to the nature of the refractory  
25 compounds that are affected by the treatment [22,23].

1

## 2 **2. Experimental**

3 The following *nomenclature* has been adopted in order to avoid misunderstandings when  
4 reading the manuscript: (1) *coagulation* is the destabilization phenomenon of dissolved  
5 and colloidal matter (DCM) produced by the addition of coagulation products  
6 (coagulants); (2) *coagula* are the little aggregates ( $>1 \mu\text{m}$ ) formed after coagulation; (3)  
7 *flocculation* refers to the aggregation phenomenon of coagula to form bigger particles by  
8 both the effect of shear stress or the addition of flocculation agents (flocculants); (4)  
9 *flocs* are the big particles resulting from this aggregation.

10

### 11 *2.1. Characterization of the reverse osmosis retentate*

12 The RO retentate to be treated was sampled at a pilot plant placed inside a 100%  
13 recovered-paper mill located in Madrid (Spain). The objective of these pilot trials was to  
14 evaluate the feasibility of reclaiming the current paper mill effluent to up-grade its water  
15 quality allowing its reuse within the process, and thus reduce fresh water consumption.  
16 The pilot plant (Figure 1) treated water flowing out from a dissolved air flotation unit  
17 (DAF) placed in the first water loop of the deinking plant, which is the most  
18 contaminated water in the mill.

19 The pilot plant consisted of an initial biological double step (anaerobic + aerobic)  
20 in which an important part of the organic material was removed ( $> 80\%$  dissolved COD  
21 and  $90\%$  BOD<sub>5</sub>). Most of the remaining dissolved COD (dCOD) present in the treated  
22 wastewater after the biological stages can be considered non-biodegradable; thus it will  
23 be referred as refractory COD (rCOD) hereafter. The refractory organic load of  
24 wastewater from recovered-paper mills includes high and low molecular weight organic

1 compounds, natural and synthetic polymers, adhesives, coating binders, ink residues,  
2 deinking chemicals and wood derivatives [24].

3 A pressurized UF unit, running in dead-end mode with hollow fibre membranes,  
4 was fed with the biologically treated water. UF-filtrated water finally entered the RO  
5 plant, which was configured in 1 pass and 3 steps, obtaining a retentate with the quality  
6 shown in Table 1. Its main characteristics were the high levels of non-biodegradable  
7 matter content (dCOD = 2121 mg/L), conductivity (9.1 mS/cm) and buffer capacity  
8 (3224 mgCaCO<sub>3</sub>/L).

9 All water analyses were performed according to the Standard Methods for  
10 Examination of Water and Wastewater [25].

11

## 12 *2.2. Focused Beam Reflectance Measurement equipment*

13 Flocculation studies were performed with a M500L focused beam reflectance  
14 measurement (FBRM) probe manufactured by Lasentec, Mettler Toledo, Seattle, WA.  
15 The FBRM instrument operates by scanning a highly focused laser beam at a fixed speed  
16 (2000 rpm) across particles in suspension, measuring the time duration of the  
17 backscattered light from these particles. The temporal duration of the reflection from  
18 each particle multiplied by the velocity of the scanning laser results in a characteristic  
19 measurement of the particle geometry, namely chord length. Thousands of chord length  
20 measurements are collected per second, producing a histogram in which the number of  
21 observed counts is sorted in several chord length bins over the range 0.5 to 1000, or  
22 2000 μm [26]. All the experiments with the FBRM device were programmed to obtain a  
23 chord length distribution every 5 seconds. In this way, enough particles are detected to  
24 have a good representative distribution of the size population.

25

1    2.3. *Coagulation*

2    Seven different coagulants were tested: one ferric salt (FeCl<sub>3</sub>), five polyaluminium  
3    chlorides (PAC11, PAC12, PAC13, PAC14, PAC15), supplied by Kemira Ibérica S.A  
4    (Spain), and a polyaluminium nitrate sulphate salt (PNSS), supplied by Sachtleben  
5    Chemie GmbH (Germany). All of them were supplied pure, as a liquid suspension, and  
6    were diluted to the desired concentration with tap water the same day they were used.  
7    Their properties are shown in Table 2 and Table 3, respectively.

8            PAC11, PAC12 and PNSS have the lowest basicity values (42, 43 and 45%,  
9    respectively). The grade of basicity is related to the quantity of Al-polymeric species  
10    formed in the water during coagulation, and it is calculated by equation 1, where [OH<sup>-</sup>]  
11    and [Al<sub>T</sub>] are the amounts of base and aluminium, respectively, present in the chemical  
12    formulation of the coagulant [27].

13    
$$Basicity (\%) = 100 \cdot \left( \frac{1}{3} \frac{[OH^-]}{[Al_T]} \right) \tag{1}$$

14            To determine the optimum dosage of each coagulant, 0.15L of RO retentate was  
15    stirred during one minute at 200 rpm before starting to add 600 mg of coagulant per litre  
16    of water each 10 seconds. The maximum number of counts yielded after adding the  
17    coagulant determined the optimum value of coagulant dosage.

18            Coagula resistance was evaluated by monitoring the evolution of the number of  
19    counts versus the applied stirring intensity. The optimal dosage of coagulant was added  
20    to the water sample and stirred at 200 rpm for 4 minutes. The stirring speed was then  
21    increased up to 400 rpm for 4 additional minutes; and a final 4-minute step was run at  
22    600 rpm. This experiment allowed to simulate the shear stress that coagulated water  
23    could suffer when it is pumped.

24            After finishing the coagulation trials, the water sample was allowed to settle and

1 clear water was sampled and filtered by 0.45  $\mu\text{m}$  before measuring conductivity, dCOD  
2 and absorbances at 254, 284, 310, 350 and 500 nm. Conductivity was measured with a  
3 GLP3 conductivity meter from Crison (Barcelona, Spain), and dCOD and absorbances  
4 were determined with an UV-Visible Spectrometer (Aquamate AQA091801 Model from  
5 Thermo Fisher Scientific, Waltham, MA, USA). The absorbance at 254 nm has been  
6 related to the degree of aromaticity and unsaturation of the compounds present in water  
7 [22]; while absorbances at 284, 310, 350 and 500 nm reflect the amount of: aromatic  
8 compounds (i.e. phenols), restrained conjugated aromatic rings, conjugated aromatic  
9 rings with certain level of resonance, and colored substances presenting a high level of  
10 resonance, respectively [23].

11

#### 12 *2.4. Softening*

13 Lime was added to soften the solution because conductivity increased after using  
14 coagulants alone. The lime-softening step began two minutes after the addition of the  
15 coagulant, stirring at 200 rpm. As a consequence of lime addition, pH increases and  
16 calcium and magnesium are removed from water as precipitates of  $\text{CaCO}_3$  ( $\text{pH}>9.5$ ) and  
17  $\text{Mg}(\text{OH})_2$  ( $\text{pH}>10.0$ ), respectively [28], reducing water hardness [29]. The addition of  
18 lime was therefore studied at pH values of 9.5 and 10.5. Lime was prepared as a  
19 supersaturated solution of  $\text{Ca}(\text{OH})_2$  from Panreac Química S.A.U., Spain.

20

#### 21 *2.5. Flocculation*

22 Finally, the use of flocculants was included in the treatment train [30,31]. Water was  
23 flocculated with organic polymers two minutes after lime addition. Two flocculants were  
24 evaluated, a 60%-charged medium molecular weight (MMW) cationic polymer (cPAM),  
25 and a 15%-charged MMW anionic flocculant (aPAM). Both products were supplied by

1 Nalco Company (Spain) in powder form, and they were prepared at a concentration of  
2 0.5 g/L by dilution of the corresponding powder in tap water, stirring the solution at 400  
3 rpm during 1h. The chemicals were prepared the same day they were used.

4 After the coagulation-softening-flocculation treatment, water was led to settle for  
5 30 minutes and the supernatant was filtered through 0.45  $\mu\text{m}$  before measuring  
6 conductivity, dCOD and absorbances at 254 ( $A_{254}$ ), 284 ( $A_{284}$ ), 310 ( $A_{310}$ ), 350 ( $A_{350}$ )  
7 and 500 ( $A_{500}$ ) nm.

8

## 9 2.6. *Experimental design*

10 A faced centered-central composite experimental design with one central point was run  
11 to assess the influence of the independent variables controlling the studied process at lab  
12 scale, namely coagulant and flocculant dosages ( $X_{coag}$  and  $X_{floc}$ ), and pH ( $X_{pH}$ ), together  
13 with their interaction. The removal percentages of rCOD, conductivity and absorbances  
14 ( $A_{254}$ ,  $A_{284}$ ,  $A_{310}$ ,  $A_{350}$  and  $A_{500}$ ) were considered as dependent variables; and  
15 experimental results are fitted to a second-order polynomial model. The total number of  
16 experiments required to perform the designed experimental protocol is 15, considering  
17 three levels for every independent variable, namely:  $X_{pH}$  = without lime (8.0), 9.5 and  
18 10.5, according to hardness removal by  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  precipitation, respectively;  
19  $X_{coag}$  = 2000, 2500 and 3000 mg/L; and  $X_{floc}$  = 3, 5 and 7 mg/L.

20 The type and doses of coagulant were chosen according to the results of  
21 preliminary coagulation trials run to test several products (see section 3.1), as described  
22 previously (see section 2.3); and considering a reasonable treatment cost (personal  
23 communication from paper mill managers). Ahmad et al. [31] tested 1-6 mg/L doses of  
24 PAMs to improve PACl coagulation treatment of pulp and paper mill wastewater,  
25 reporting no effect on COD removal. As only a 10% of the COD is associated to TSS in

1 the RO retentate, in contrast to the 90% in the wastewater treated in Ahmad et al. [31],  
2 we have initially selected cost-reasonable higher values for the flocculant dosage to be  
3 introduced in the experimental design.

4 The levels of the independent variables were normalized according to equation 2,  
5 adopting values from -1 to +1 (centre = 0).

$$6 \quad X_n = 2 \cdot \frac{X - \bar{X}}{X_{\max} - X_{\min}} \quad (2)$$

7 Where  $X_n$  is the normalized value of  $X_{coag}$ ,  $X_{pH}$  or  $X_{floc}$ ;  $X$  is the absolute  
8 experimental value of the variable concerned;  $\bar{X}$  is the mean between the extreme  
9 values of  $X$ ; and  $X_{max}$  and  $X_{min}$  are the maximum and minimum values for  $X$ , respectively.  
10 This normalization also results in more accurate estimates of the regression coefficients,  
11 as it reduces inter-relationships between linear and quadratic terms [32].

### 13 **3. Results and Discussion**

#### 14 *3.1. Coagulation trials*

15 The total number of counts per second registered by the FBRM probe versus the added  
16 quantity of coagulant determines the optimal dosage of each one (Figure 2). Only FeCl<sub>3</sub>,  
17 PAC11, PAC12 and PNSS produced any significant effect on the treated wastewater. As  
18 a greater amount of these coagulants were added, DCM destabilized and began to  
19 aggregate, resulting in an increase of the number of counts. The other PACI's  
20 destabilized DCM, but their effect was comparatively minimal. FeCl<sub>3</sub> began to coagulate  
21 quicker than PAC11 and PAC12; and all of them achieved, for the same dosage, a higher  
22 number of counts per second than PNSS (Figure 2). A similar behaviour was previously  
23 observed by Kim et al. [33]. While FeCl<sub>3</sub> required just 5 min to complete the full  
24 coagulation treatment, PACI products took 15 min to achieve the same results.

1           Considering only particle destabilization, two primary coagulation mechanisms  
2 can be defined, depending on pH and the concentration of Al or Fe: (1) charge  
3 neutralization of negatively charged particles by adsorption of the positively charged  
4 dissolved Al-species added within the coagulant; and, (2) colloid enmeshment or  
5 sweeping in  $\text{Al}(\text{OH})_3$  or  $\text{Fe}(\text{OH})_3$  precipitates [27]. The hydrolysis of PACl's implies the  
6 appearance of monomers, dimmers, polymers and amorphous precipitate of aluminium;  
7 and the proportion of high valence species increases with an increasing basicity in the  
8 medium, so products having basicity values higher than 70% (PACl3, PACl4 and  
9 PACl5) contain polymeric species possessing high cationic charges [27, 34].  
10 Considering the initial pH value of the concentrate (Table 1, pH = 8.0) and the important  
11 amount of Al and Fe that is required to destabilize DCM (Table 4), amorphous  
12 precipitate of aluminium ( $\text{Al}(\text{OH})_{3(\text{am})}$ ) would be the main species that is formed after  
13 adding PACls to water [27]. On the other hand, when  $\text{FeCl}_3$  is added to water with a  
14 natural bicarbonate alkalinity,  $\text{Fe}(\text{OH})_{3(\text{s})}$  precipitates coexist with other Fe-hydrated  
15 species. The main species present in water should be  $\text{Fe}(\text{OH})_{3(\text{s})}$  when using  $\text{FeCl}_3$  at pH  
16 8.0 [35]. In short, it could be therefore stated that the main existent coagulation  
17 mechanism for both types of coagulant ( $\text{FeCl}_3$  and PACl's) is sweeping.

18           Although PACl2 produced a very similar good effect on DCM, PACl1 was  
19 chosen to perform the next experimental trials, adding lime softening and flocculation  
20 steps, because it is a cheaper product.  $\text{FeCl}_3$  was discarded as an optimal product  
21 because it turns water colour to intense red-orange at optimal dosage. According to  
22 results shown in Figure 2, 5000, 10000 and 18500 mg/L of PACl1 were chosen as  
23 reference doses to perform floc resistance trials.

24           Time course evolutions of the number of counts (Figure 3a) and the mean chord  
25 length (MCL, Figure 3b) when PACl1 was added at these selected concentrations, and

1 the water sample was stirred at increasing speeds (200, 400 and 600 rpm), showed that,  
2 while the number of counts per second increased during the first minute, the size of the  
3 particles decreased. Although big particles (20-25  $\mu\text{m}$ ) attached each other forming  
4 bigger flocs as the coagulant was added, DCM of  $<1 \mu\text{m}$  was also destabilized, and  
5 small particles got in touch forming small coagula greater than  $1 \mu\text{m}$ . As these particles  
6 are now detected by FBRM, the proportion of small particles led to an overall decrease  
7 in the MCL distribution (Figure 3b). In addition, the number of counts per second was  
8 higher as the coagulant dosage was increased from 5000 mg/L to 10000 mg/L; but  
9 significantly decreased when 18500 mg/L were added. The water solution got saturated  
10 of coagulant when such an amount was used, having a negative effect on the treatment  
11 efficiency [36]. The number of counts was particularly high when 10000 mg/L of PACl1  
12 were used.

13 After increasing the stirring velocity from 200 to 400 and 600 rpm when PACl1  
14 was added at 5000 and 10000 mg/L, fewer particles were detected by FBRM, but MCL  
15 kept more or less constant compared to the values achieved after adding the coagulant at  
16 400 rpm. Finally, when 18500 mg/L were added, the number of FBRM-detected  
17 particles did not decrease up to reaching 600 rpm; and MCL kept a similar performance  
18 as for 5000 and 10000 mg/L (Figure 3b).

19 This behaviour may be explained by the fact that a higher stirring speed yields a  
20 higher number of particle-particle collisions, reducing the number of small particles as  
21 they attach each other after colliding. This phenomenon was reflected by FBRM by a  
22 reduction of the number of counts per second when speeding up from 200 to 400 rpm  
23 (Figure 3a). On the other hand, this phenomenon also decreases the rate of formation of  
24 very large flocs as they break up after been collided. Therefore, rather than provoking  
25 big particles to break, increasing the stirring speed favored particle-particle collisions,

1 and its further attachment forming bigger particles, at lower doses of coagulant (i.e. 5000  
2 mg/L), resulting in the observed increase of MCL at 600 rpm (Figure 3b). At higher  
3 coagulant doses, large particles formation was still prevailing over big particles  
4 breakage, as fewer particles are detected in the water sample (Figure 3a); while MCL  
5 decreased slowly as the stirring velocity was increased (Figure 3b). Although there were  
6 fewer particles in the water, big flocs broke up into smaller particles (but bigger than  
7 1  $\mu\text{m}$ ) that are bigger than the aggregates formed by small particles, which collision was  
8 enhanced by faster stirring rates.

9 A higher coagulant dosage produced a higher reduction in rCOD, reaching  $\approx 80\%$   
10 when 18500 mg/L were added; but it increased conductivity as well (Figure 4a), as more  
11 Al is added to the medium. The mechanisms to remove this kind of organic compounds  
12 are similar to DCM ones [36]: (1) binding metal species to anionic sites neutralizing  
13 charges; and (2) adsorption on amorphous metal hydroxide precipitate. Although many  
14 studies have reported flocculation experiences, it is however very difficult to distinguish  
15 between both mechanisms, which depend mainly on pH and coagulant concentration  
16 [37].

17 On the other hand, better absorbance removals at all the measured wavelengths  
18 were achieved when 10000 mg/L of PAC11 were added, while lower reductions were  
19 yielded at lower and higher dosages (Figure 4b); denoting a selective removal of  
20 refractory organic matter. Particularly, coloured compounds with a high level of  
21 resonance ( $A_{500}$ ) were not removed at all when 18500 mg/L of coagulant were used. Yan  
22 et al. [38] detected a similar trend for  $A_{254}$ , which is related to the presence of  
23 hydrophobic and high molecular weight natural organic matter, such as humic  
24 substances.

25

1 3.2. Coagulation, softening and flocculation. Treatment modelling from experimental  
2 design

3 The final aim of the experimental design was to study the influence of the three  
4 independent variables ( $X_{coag}$ ,  $X_{floc.}$ ,  $X_{pH}$ ) controlling the combined treatment process in  
5 terms of conductivity and recalcitrant organic matter content in water. 2500 mg/L of  
6 PAC11 were set as the reference level ( $X_n=0$ ) of the experimental design as it produced a  
7 significant treatment effect (COD removal >30%; conductivity increase >5%) at a  
8 reasonable industrial cost. In fact, lime was added to soften the solution; while a  
9 flocculation step was thought to reduce the quantity of coagulant to be added. Two  
10 experimental designs, one per each tested flocculant (aPAM and cPAM), were  
11 performed. Results in terms of the achieved reductions of dCOD, conductivity and  
12 absorbances are shown in Table 5 (aPAM) and Table 6 (cPAM).

13 Second-order polynomial models fitted from experimental results for every  
14 considered dependant variable (removal percentages of dCOD, conductivity and  
15 absorbances) as a function of the defined independent ones ( $X_{coag}$ ,  $X_{pH}$ ,  $X_{floc}$ ) show that  
16 only  $X_{coag}$  and  $X_{pH}$  are explaining the results of the defined treatment; that is, the  
17 variation of both variables and the interaction between them ( $X_{coag} \cdot X_{pH}$ ) are really  
18 determining the reductions of dCOD, conductivity and absorbances (Table 7). Despite  
19 the regressions for the removal of  $A_{254}$ , which showed poorer  $R^2$  values (0.740 for  
20 aPAM; and 0.677 for cPAM), the variation of the results was explained over the 85% for  
21 all the second-order polynomial equations ( $R^2=0.857-0.997$ ). The estimations provided  
22 by these modelled equations reproduced the experimental values with errors lower than  
23 10% and 6.5% when adding aPAM and cPAM, respectively.

24 Particularly, the addition of lime ( $X_{pH}$ ) was the main factor affecting the  
25 reduction of conductivity for both flocculants (Table 7). As a greater amount of lime is

1 added,  $Mg(OH)_2$  precipitates ( $pH \geq 10$ ) in addition to  $CaCO_3$  ( $pH \geq 9.5$ ), thus more  $Ca^{2+}$   
2 and  $Mg^{2+}$  ions are removed from the water, decreasing conductivity. Softening also  
3 affected very positively the reduction of  $A_{350}$  for both flocculants,  $A_{310}$  for the aPAM,  
4 and  $A_{254}$ ,  $A_{350}$ , and  $A_{500}$  for the cPAM. On the other hand, PAM dosage ( $X_{floc}$ ) did not  
5 produce any significant variation in the properties of the treated wastewater.

6 When flocculant was added without lime, the FBRM probe detected significant  
7 differences in the number of counts from when a previous soften step is performed  
8 (Figures 5 and 6). While the number of particles decreased as aPAM was added; no  
9 effect was observed in the distribution of particles when cPAM was used (Figure 5).  
10 Two possible mechanisms may explain this performance: (1) aggregates formed by  
11 PAC11 and lime have a slightly positive surface charge, so cPAM would repeal them  
12 [39]; and (2) negatively-charged surfaces may be adsorbed on aPAM despite  
13 electrostatic repulsion whenever there is enough concentration of divalent metal ions in  
14 the solution [40].

15 Due to the pH value of the concentrated stream (8.0), and the amount of  
16 coagulant added, it is more reasonable to think that the surface of the aggregates formed  
17 from PAC11 and lime are slightly negatively charged; so the second explanation maybe  
18 most suitable to what it is really happening. As hardness of the retentate was really high  
19 (1100 mg $CaCO_3$ /L; Table 1), important amounts of  $Ca^{2+}$  and  $Mg^{2+}$  should be present,  
20 enhancing flocculation processes bridging anionic groups of the aPAM to negative sites  
21 on the surface of particles. On the other hand, these cations would interfere with the  
22 positively charged groups of the cPAM, repealing each other, and making the polymer  
23 lose its extended structure. Therefore, the efficiency of this polymer is limited [39].

24 When lime was added, more particles were detected in the solution (Figure 6), as  
25  $CaCO_3$  and  $Mg(OH)_2$  precipitates are formed. When a constant number of particles was

1 achieved, the flocculant was added. No significant effect on the number of particles was  
2 appreciated after the addition of the flocculants when lime was previously added.  $\text{Ca}^{2+}$   
3 and  $\text{Mg}^{2+}$  ions are removed from the water when lime is added, so there are not such  
4 intermediates in the water solution to form bridges between slightly negative particles  
5 and the aPAM, driving its addition ineffective. On the other hand, it could be thought  
6 that cPAM would be able to flocculate the new aggregates, but it begins to hydrolyze  
7 when pH gets to 8.5, thus becoming ineffective as well. This hydrolysis process does not  
8 only result in the loss of cationic sites, but also in a change in the conformation of the  
9 chain structure because the appearance of carboxylate groups reduces the length of the  
10 polymer [39].

11

#### 12 **4. Conclusions**

13  $\text{FeCl}_3$  and low basicity PACl's (PACl1 and PACl2) were the best coagulants to  
14 destabilize DCM in RO retentate.  $\text{FeCl}_3$  turned water colour to intense red-orange at  
15 optimal dosage and PACl2 is more expensive than PACl1.

16 The coagulation treatment with PACl1 efficiently removed refractory COD,  
17 particularly coloured compounds with a high level of resonance. In fact,  $A_{500}$  was  
18 reduced more than 95% with the addition of 10 g/L of PACl1. The main drawbacks of  
19 this treatment were that conductivity increased as more coagulant is added, and that the  
20 high doses of coagulant that are required to achieve reductions of the dCOD higher than  
21 60% would make the process economically unfeasible.

22 Lime-softening resulted to be a good alternative to reduce conductivity, as  $\text{Ca}^{2+}$   
23 and  $\text{Mg}^{2+}$  are removed from the water through the precipitation of  $\text{CaCO}_3$  ( $\text{pH} \geq 9.5$ ) and  
24  $\text{Mg}(\text{OH})_2$  ( $\text{pH} \geq 10.0$ ). As these precipitates are formed, organic matter is adsorbed on  
25 their surface and could be additionally removed in part by this precipitation process.

1           Anionic PAM resulted to be the best option to aid coagulation with PAC11 when  
2 no lime was added because  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, which are present in the medium  
3 yielding high water hardness, bridge slightly negative aggregates that PAC11 formed  
4 previously. On the other hand, these cations affected cPAM performance driving its  
5 addition inefficient when no lime was used.

6           When flocculants were combined with previous coagulation and lime-softening  
7 steps, no additional effect was observed on the reduction of dCOD, conductivity and  
8 absorbances at different wave lengths; which is explained by the efficient removal of  
9  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the solution, and the high pH value at which the treatment was  
10 performed.

11

## 12 **Acknowledgements**

13           This research was developed in the framework of projects “PROLIPAPEL I and  
14 II” (S-0505/AMB-0100; P-2009/AMB-1480), funded by the Regional Government of  
15 Madrid (Comunidad Autónoma de Madrid), Spain; “AGUA Y ENERGÍA” (CTM2008-  
16 06886-C02-01), funded by the Ministry of Science and Innovation of Spain (Ministerio  
17 de Ciencia e Innovación); and “AquaFit4Use” (211534), funded by the European Union.  
18 We would like to thank HOLMEN Paper staff for technical advice and discussion of the  
19 results; and Kemira Ibérica (Spain), Sachtleben Chemie GmbH (Germany) and Nalco  
20 Company (Spain) for supplying the chemicals used in this study.

21

## 22 **References**

23 [1] A. Blanco, C. Negro, C. Monte, E. Fuente, J. Tijero, Environ. Sci. Technol. 38  
24 (2004) 414A-420A.

- 1 [2] R. Ordóñez, D. Hermosilla, E. Fuente, A. Blanco, *Ind. Eng. Chem. Res.* 48 (2009)  
2 10247-10252.
- 3 [3] *Integrated Pollution Prevention and Control (IPPC): Reference Document on Best*  
4 *Available Techniques in the Pulp and Paper Industry*, European Commission,  
5 Brussels, 2001.
- 6 [4] R.Y. Ning, T.L. Troyer, *Desalination* 208 (2007) 232-237.
- 7 [5] D. Squire, J. Murrer, P. Holden, C. Fitzpatrick, *Desalination* 108 (1996) 143-147.
- 8 [6] M. Mickley, *Membrane Concentrate Disposal: Practices and Regulations*, U.S.  
9 Department of the Interior, Bureau of Reclamation, Technical Service Center, Water  
10 Treatment Engineering and Research Group, 2004.
- 11 [7] S. Sethi, S. Walker, J. Drewes, P. Xu, *Florida Water Res. J.* June (2006) 38-48.
- 12 [8] D. Squire, *Desalination* 132 (2000) 47-54.
- 13 [9] M. Ahmed, W.H. Shayya, D. Hoey, J. Al-Handaly, *Desalination* 133 (2001) 135-  
14 147.
- 15 [10] R.Y Ning, T.L. Troyer, *Desalination* 237 (2009) 238-242.
- 16 [11] T. Nandy, P. Manekar, R. Dhodapkar, G. Pophali, S. Devotta, *Resour. Conserv.*  
17 *Recycl.* 51 (2007) 64-77.
- 18 [12] K. Ranganathan, K. Karunagaran, D.C. Sharma, *Resour. Conserv. Recycl.* 50 (2007)  
19 306-318.
- 20 [13] R. Rautenbach, T. Linn, *Desalination* 105 (1996) 63-70.
- 21 [14] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, *Water Res.* 43  
22 (2009) 2317-2348.
- 23 [15] E. Balanosky, J. Fernández, J. Kiwi, A. López, *Water Sci. Technol.* 40 (1999) 417-  
24 424.
- 25 [16] K. van Hege, M. Verhaege, W. Verstraete, *Electrochem. Comm.* 4 (2002) 296-300.

- 1 [17] C. Allegre, M. Maisseu, F. Charbit, P. Moulin, J. Hazard. Mat. B116 (2004) 57-64.
- 2 [18] E. Dialynas, D. Mantzavinos, E. Diamadopoulos, Water Res. 42 (2008) 4603-4608.
- 3 [19] E. Barbot, S. Moustier, J.Y. Botterob, P. Moulin, J. Memb. Sci. 325 (2008) 520-527.
- 4 [20] W. Yu, L. Guibai, Y. Xu, X. Yang, Powder Technol. 189 (2009) 439-443.
- 5 [21] J.A. Nason, D.F. Lawler, J. Environ. Eng. 136 (2010) 12-21.
- 6 [22] M.F. Sevimli, C. Kinaci, Water Sci. Technol. 45 (2002) 279-286.
- 7 [23] M. Boroski, A.C. Rodrigues, J.C. Garcia, A.P. Gerola, J. Nozaki, N. Hioka, J.  
8 Hazard. Mat. 160 (2008) 135-141.
- 9 [24] R. Miranda, A. Balea, E. Sanchez de la Blanca, I. Carrillo, A. Blanco, Ind. Eng.  
10 Chem. Res. 47 (2008) 6239-6250.
- 11 [25] Standard Methods for the Examination of Water and Wastewater, 21st Edition,  
12 APHA, AWWA and WEF, Washington DC, 2005.
- 13 [26] A. Blanco, E. Fuente, C. Negro, J. Tijero, Can. J. Chem. Eng. 80 (2002) 1-7.
- 14 [27] D.J. Pernitsky, J.K. Edzwald, J. Water Supply: Res. Technol. - AQUA 55 (2006)  
15 121-141.
- 16 [28] M. Scholz, in: M.Scholz (Eds.), Wetland Systems to Control Urban Runoff, 1<sup>st</sup>  
17 Edition, Elsevier, The Netherlands, 2006, pp. 135-139.
- 18 [29] E. Yildiz, A. Nuhoglu, B. Keskinlerb, A. Akay, B. Farizoglu, Desalination 159  
19 (2003) 139-152.
- 20 [30] M.I. Aguilar, J. Sáez, M. Lloréns, A. Soler, J.F. Ortuño, V. Meseguer, A. Fuentes,  
21 Chemosphere 58 (2005) 47-56.
- 22 [31] A.L. Ahmad, S.S. Wong, T.T. Teng, A. Zuhairi, Chem. Eng. J. 137 (2008) 510-517.
- 23 [32] D.C. Montgomery, Diseño y análisis de experimentos, Grupo Editorial  
24 Iberoamericana, Mexico, 1991.
- 25 [33] S.-H. Kim, J.-S. Yoon, S. Lee, Desalination Water Treat. 10 (2009) 95-100.

- 1 [34] A. Torra, F. Valero, J.L. Bisbal, J.F. Tous, *Tecnol. Agua* 177 (1998) 58-67.
- 2 [35] C.J. Gabelich, T.I. Yuna, B.M. Coffey, I.H. Suffet, *Desalination* 150 (2002) 15-30.
- 3 [36] J. Duan, J. Gregory, *Adv. Colloid Interface* 100 (2003) 475-502.
- 4 [37] X.C. Wang, P.K. Jin, J. Gregory, *Water Sci. Technol.: Water Supply* 2 (2002) 99-
- 5 106.
- 6 [38] M. Yan, D. Wang, J. Nia, J. Qu, C.W.C. Chow, H. Liu, *Water Res.* 42 (2008) 3361-
- 7 3370.
- 8 [39] B. Bolto, J. Gregory, *Water Res.* 41 (2007) 2301-2324.
- 9 [40] C. Negro, L.M. Sánchez, E. Fuente, A. Blanco, J. Tijero, *Chem. Eng. Sci.* 61 (2006)
- 10 2522-2532.
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**Table 1**

Chemical characterization of the retentated flow from the RO system.

| <b>PARAMETER</b> | <b>UNITS</b>            | <b>RO<br/>RETENTATE</b> |
|------------------|-------------------------|-------------------------|
| pH               | -                       | 8.0                     |
| Conductivity     | mS/cm                   | 9.1                     |
| tCOD             | mg/L                    | 2365                    |
| dCOD             | mg/L                    | 2121                    |
| Alkalinity       | mg CaCO <sub>3</sub> /L | 3224                    |
| Turbidity        | NTU                     | 8.21                    |
| Hardness         | mg CaCO <sub>3</sub> /L | 1100                    |

**Table 2**

Chemical specifications of the ferric salt and polyaluminium chlorides coagulants.

| <b>Coagulant</b>  | <b>Concentration (w/w)<br/>(%)</b> | <b>Al<sub>2</sub>O<sub>3</sub><br/>(%)</b> | <b>Basicity<br/>(%)</b> | <b>Other</b>              |
|-------------------|------------------------------------|--|-------------------------|---------------------------|
| FeCl <sub>3</sub> | 39-47                              | -  | -                       | -                         |
| PAC11             | -                                  | 17.0 ± 0.5                                 | 42 ± 2                  | -                         |
| PAC12             | -                                  | 17.0 ± 0.5                                 | 43 ± 5                  | High molecular weight     |
| PAC13             | -                                  | 9.5 ± 1.0                                  | 70 ± 5                  | Contains<br>micropolymers |
| PAC14             | -                                  | 9.7 ± 0.3                                  | 85 ± 10                 | -                         |
| PAC15             | -                                  | 9.7 ± 0.3                                  | 85 ± 10                 | Contains<br>micropolymers |

**Table 3**

Properties of the polyaluminium nitrate sulphate salt (PNSS).

| <b>Composition (%)</b> |                 |                 | <b>Contents (%)</b> |            |           | pH  | Basicity |
|------------------------|-----------------|-----------------|---------------------|------------|-----------|-----|----------|
| Al                     | NO <sub>3</sub> | SO <sub>4</sub> | Monomeric           | Oligomeric | Polymeric |     |          |
| 5.2                    | 15              | 3               | 22                  | 35         | 43        | 2.5 | 46       |

**Table 4**

Iron and aluminium concentrations (mol/L) for some doses of FeCl<sub>3</sub> and PACl's selected from Figure 2.

| <b>Doses, mg/L</b> | <b>[Fe], mol/L</b>      | <b>[Al], mol/L</b>       |                          |              |
|--------------------|-------------------------|--------------------------|--------------------------|--------------|
|                    | <b>FeCl<sub>3</sub></b> | <b>PACl1 &amp; PACl2</b> | <b>PACl4 &amp; PACl5</b> | <b>PACl3</b> |
| 2500               | 0.0060-0.0070           | 0.0021                   | 0.0012                   | 0.0012       |
| 5000               | 0.0120-0.0145           | 0.0042                   | 0.0024                   | 0.0023       |
| 10000              | 0.0024-0.0289           | 0.0083                   | 0.0048                   | 0.0047       |
| 18500              | 0.0444-0.0536           | 0.0154                   | 0.0088                   | 0.0086       |

**Table 5**

Experimental design results combining PAC11 + lime + aPAM to reduce conductivity and dCOD.

| Xcoag | Xfloc | XpH | % removal    |      |                  |                  |                  |                  |                  |
|-------|-------|-----|--------------|------|------------------|------------------|------------------|------------------|------------------|
|       |       |     | Conductivity | dCOD | A <sub>254</sub> | A <sub>284</sub> | A <sub>310</sub> | A <sub>350</sub> | A <sub>500</sub> |
| 0     | 0     | 0   | 48.1         | 60.4 | 43.8             | 37.6             | 65.8             | 68.7             | 79.4             |
| 1     | 1     | 1   | 59.8         | 70.3 | 51.1             | 44.8             | 44.5             | 66.6             | 89.2             |
| -1    | 1     | 1   | 52.0         | 61.8 | 41.6             | 31.2             | 64.8             | 65.0             | 74.1             |
| 1     | 1     | -1  | 0.0          | 34.8 | 41.2             | 41.3             | 15.6             | 41.6             | 84.8             |
| -1    | 1     | -1  | 0.0          | 40.0 | 47.4             | 38.2             | 41.7             | 48.4             | 84.7             |
| 1     | -1    | 1   | 59.6         | 69.2 | 51.6             | 45.9             | 44.0             | 66.5             | 90.8             |
| -1    | -1    | 1   | 50.7         | 58.6 | 41.2             | 29.9             | 62.3             | 61.9             | 72.1             |
| 1     | -1    | -1  | 0.0          | 31.9 | 37.4             | 34.5             | 13.6             | 34.8             | 77.7             |
| -1    | -1    | -1  | 0.0          | 38.5 | 50.4             | 39.7             | 42.7             | 49.0             | 87.4             |
| 0     | 1     | 0   | 48.0         | 61.6 | 47.3             | 40.8             | 66.4             | 70.2             | 80.9             |
| 0     | -1    | 0   | 45.9         | 60.0 | 50.4             | 40.1             | 65.8             | 68.7             | 84.9             |
| 0     | 0     | 1   | 54.0         | 62.8 | 47.1             | 38.1             | 66.8             | 69.4             | 79.6             |
| 0     | 0     | -1  | 0.0          | 41.5 | 49.6             | 40.3             | 56.7             | 62.4             | 88.4             |
| 1     | 0     | 0   | 54.6         | 65.2 | 51.6             | 46.1             | 72.6             | 67.1             | 87.3             |
| -1    | 0     | 0   | 38.6         | 52.8 | 38.3             | 28.6             | 59.4             | 59.6             | 73.1             |

Xcoag = 2000 (-1), 2500 (0), and 3000 (+1) mg/L ; XpH = without lime-pH=8.0 (-1), pH=9.5 (0), and pH=10.5 (+1); Xfloc = 3 (-1), 5 (0), and 7 (+1) mg/L.

**Table 6**

Experimental design results combining PAC11 + lime + cPAM to reduce conductivity and dCOD.

| Xcoag | Xfloc | XpH | % removal    |      |                  |                  |                  |                  |                  |
|-------|-------|-----|--------------|------|------------------|------------------|------------------|------------------|------------------|
|       |       |     | Conductivity | dCOD | A <sub>254</sub> | A <sub>284</sub> | A <sub>310</sub> | A <sub>350</sub> | A <sub>500</sub> |
| 0     | 0     | 0   | 45.0         | 53.2 | 58.9             | 46.4             | 58.6             | 73.2             | 89.4             |
| 1     | 1     | 1   | 54.8         | 62.3 | 44.9             | 40.9             | 46.5             | 67.4             | 85.8             |
| -1    | 1     | 1   | 52.1         | 57.0 | 43.8             | 29.1             | 35.8             | 56.1             | 78.0             |
| 1     | 1     | -1  | 0.0          | 42.0 | 49.7             | 44.4             | 37.4             | 62.7             | 91.6             |
| -1    | 1     | -1  | 0.0          | 23.9 | 37.1             | 23.9             | 18.4             | 41.6             | 74.5             |
| 1     | -1    | 1   | 62.0         | 68.9 | 53.8             | 47.8             | 54.7             | 72.6             | 87.8             |
| -1    | -1    | 1   | 52.7         | 57.1 | 45.4             | 25.6             | 32.8             | 53.2             | 73.9             |
| 1     | -1    | -1  | 0.0          | 43.6 | 52.2             | 45.4             | 38.2             | 62.2             | 90.7             |
| -1    | -1    | -1  | 0.0          | 22.4 | 34.1             | 21.9             | 16.1             | 37.8             | 76.4             |
| 0     | 1     | 0   | 43.9         | 50.3 | 57.7             | 43.5             | 57.9             | 72.7             | 88.3             |
| 0     | -1    | 0   | 43.6         | 54.3 | 53.8             | 44.4             | 55.3             | 70.9             | 87.5             |
| 0     | 0     | 1   | 56.0         | 53.9 | 52.7             | 43.9             | 55.3             | 70.2             | 88.2             |
| 0     | 0     | -1  | 0.0          | 21.0 | 47.4             | 35.2             | 27.2             | 50.5             | 85.9             |
| 1     | 0     | 0   | 45.5         | 58.7 | 52.1             | 46.2             | 48.0             | 68.4             | 89.3             |
| -1    | 0     | 0   | 37.3         | 49.1 | 60.8             | 26.4             | 28.2             | 50.5             | 77.7             |

Xcoag = 2000 (-1), 2500 (0), and 3000 (+1) mg/L ; XpH = without lime-pH=8.0 (-1), pH=9.5 (0), and pH=10.5 (+1); Xfloc = 3 (-1), 5 (0), and 7 (+1) mg/L.

**Table 7**

Models resulting from the resolution of the experimental design. Reduction percentages of conductivity, dCOD and absorbances are expressed as a function of the defined independent variables.

| <b>PAC11+LIME+aPAM</b>   |                      |                  |
|--|----------------------|------------------|
| <b>Equations</b>   | <b>R<sup>2</sup></b> | <b>Error (%)</b> |
| $\%Conductivity = -19.43 \cdot X_{pH}^2 + 2.09 \cdot X_{Coag} \cdot X_{pH} + 3.27 \cdot X_{Coag} + 27.61 \cdot X_{pH} + 47.04$ | 0.997                | 2.5              |
| $\%dCOD = 13.60 \cdot X_{pH} + 53.96$  | 0.884                | 6.3              |
| $\%A_{254} = 4.89 \cdot X_{Coag} \cdot X_{pH} + 46.00$   | 0.740                | 3.5              |
| $\%A_{284} = 4.50 \cdot X_{Coag} + 3.96 \cdot X_{Coag} \cdot X_{pH} + 38.47$   | 0.889                | 2.7              |
| $\%A_{310} = -11.77 \cdot X_{Coag}^2 - 16.02 \cdot X_{pH}^2 - 8.06 \cdot X_{Coag} + 11.21 \cdot X_{pH} + 70.71$                | 0.891                | 9.8              |
| $\%A_{350} = -9.18 \cdot X_{Coag}^2 - 6.63 \cdot X_{pH}^2 + 3.40 \cdot X_{Coag} \cdot X_{pH} + 9.32 \cdot X_{pH} + 70.53$      | 0.943                | 4.4              |
| $\%A_{500} = 5.42 \cdot X_{Coag} \cdot X_{pH} + 3.84 \cdot X_{Coag} + 82.29$   | 0.857                | 3.4              |
| <b>PAC11+LIME+cPAM</b>   |                      |                  |
| <b>Equations</b>   | <b>R<sup>2</sup></b> | <b>Error (%)</b> |
| $\%Conductivity = -15.30 \cdot X_{pH}^2 + 2.2 \cdot X_{Coag} + 27.76 \cdot X_{pH} + 43.06$                                     | 0.996                | 2.4              |
| $\%dCOD = 6.60 \cdot X_{Coag} + 14.63 \cdot X_{pH} + 47.85$  | 0.919                | 6.3              |
| $\%A_{254} = 10.55 \cdot X_{pH}^2 + 56.66$   | 0.677                | 5.8              |
| $\%A_{284} = -7.52 \cdot X_{Coag}^2 + 9.78 \cdot X_{Coag} + 42.68$   | 0.947                | 3.3              |
| $\%A_{310} = 9.78 \cdot X_{Coag} + 37.67$  | 0.866                | 4.9              |
| $\%A_{350} = -7.58 \cdot X_{Coag}^2 - 6.68 \cdot X_{pH}^2 + 9.41 \cdot X_{Coag} + 6.47 \cdot X_{pH} + 70.17$                   | 0.962                | 3.8              |
| $\%A_{500} = 5.29 \cdot X_{Coag}^2 + 6.47 \cdot X_{Coag} - 1.21 \cdot X_{Coag} \cdot X_{pH} + 87.86$                           | 0.973                | 1.6              |

**Figure 1.** Diagram of the pilot plant used to reclaim the effluent of the paper mill.

**Figure 2.** Evolution of the number of counts versus coagulant dose.

**Figure 3.** Evolution in time of the number of counts per second (a), and mean chord length (b) after adding different doses of PACl1.

**Figure 4.** Effect of PACl1 dosage on dCOD removal and conductivity increase (a), and the reduction of the absorbance of refractory compounds (b).

**Figure 5.** Evolution in time of the number of counts per second when PACl1 (2000 and 3000 mg/L) and PAMs (anionic or cationic, 3 and 7 mg/L) are added without lime.

**Figure 6.** Evolution in time of the number of counts per second when 3000 mg/L PACl1 and PAMs (anionic or cationic, 3 and 7 mg/L) are added after the lime at pH = 10.5.

FIGURE 1

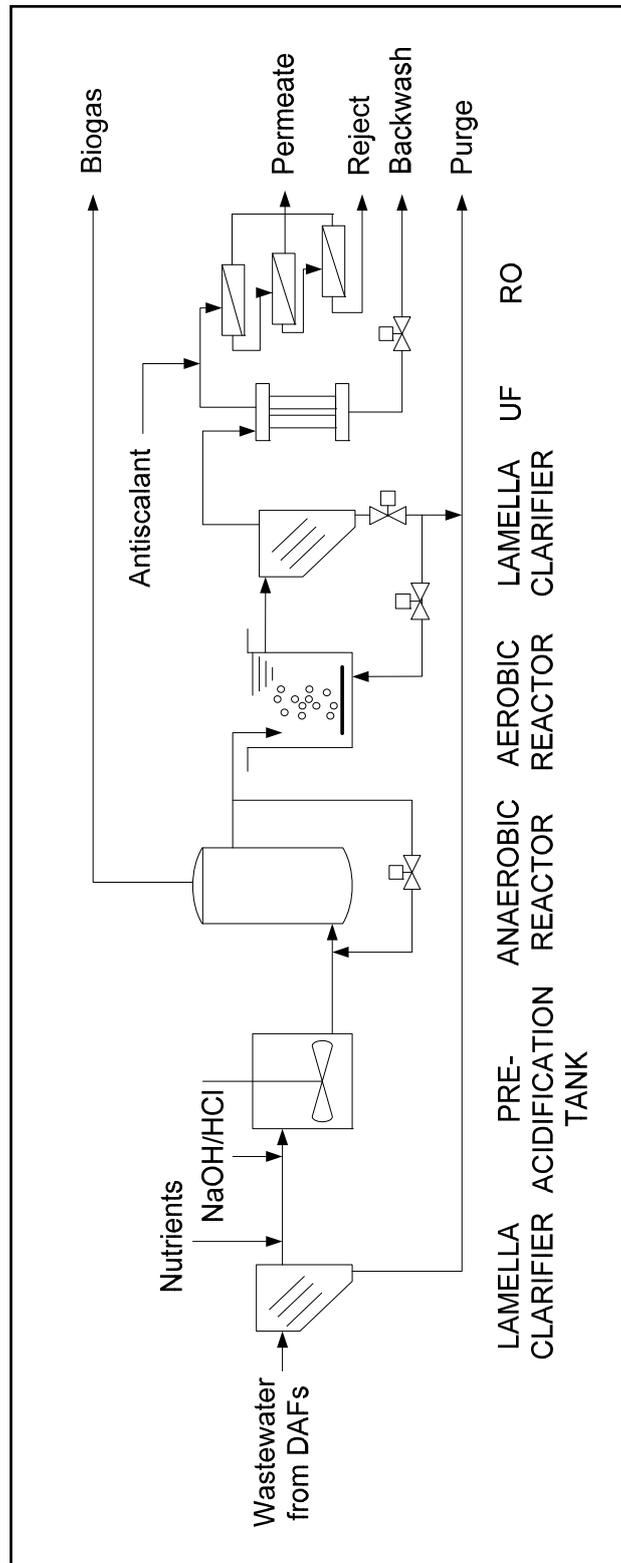


FIGURE 2

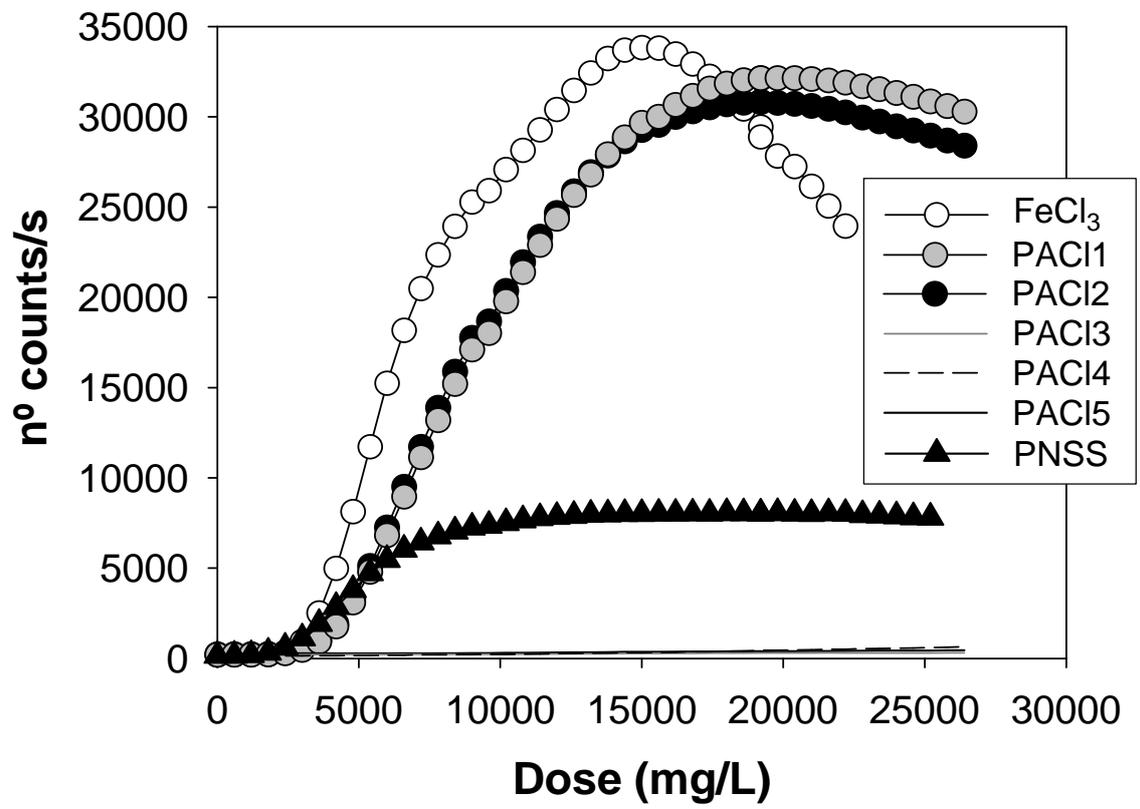


FIGURE 3

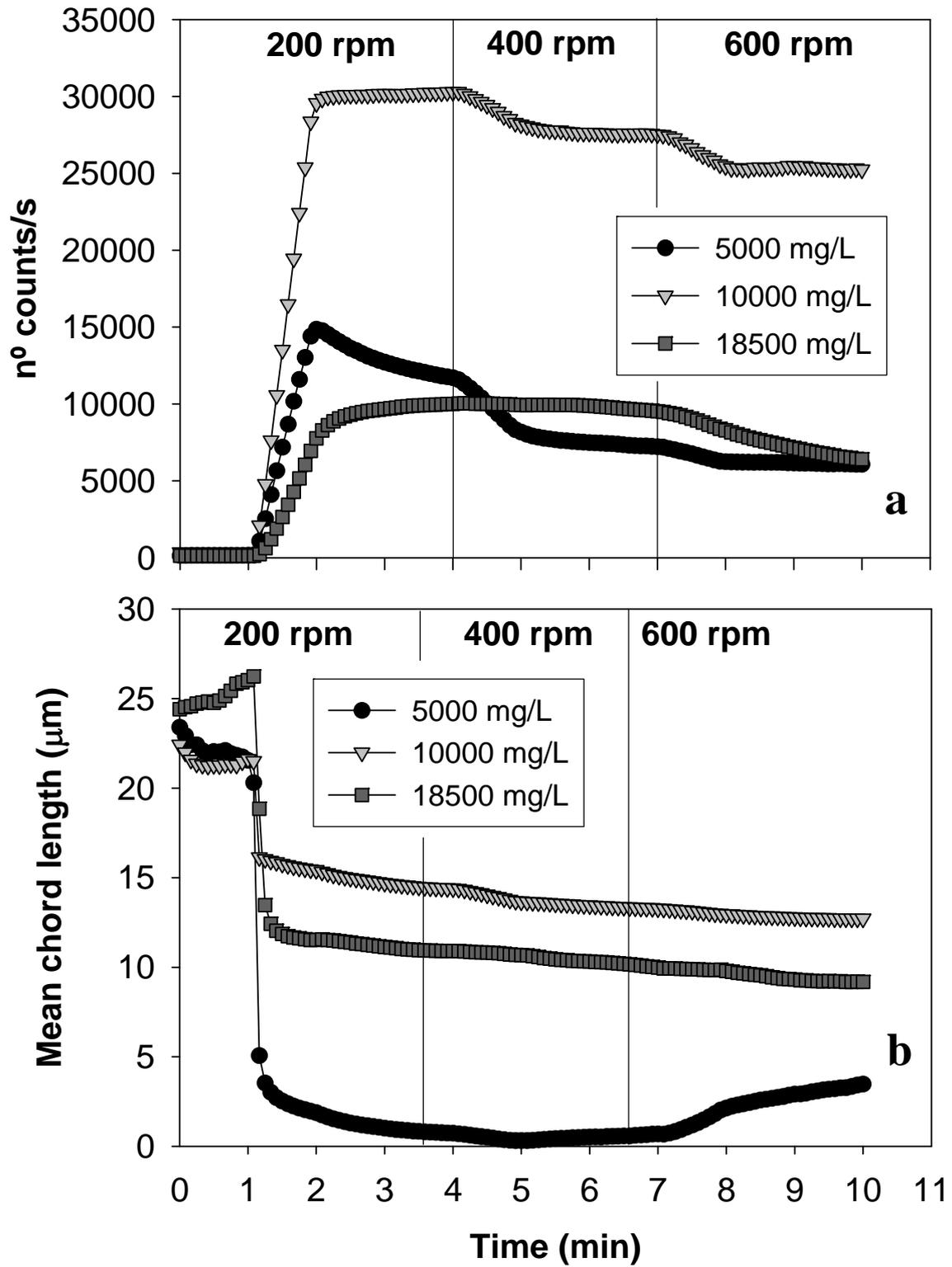


FIGURE 4

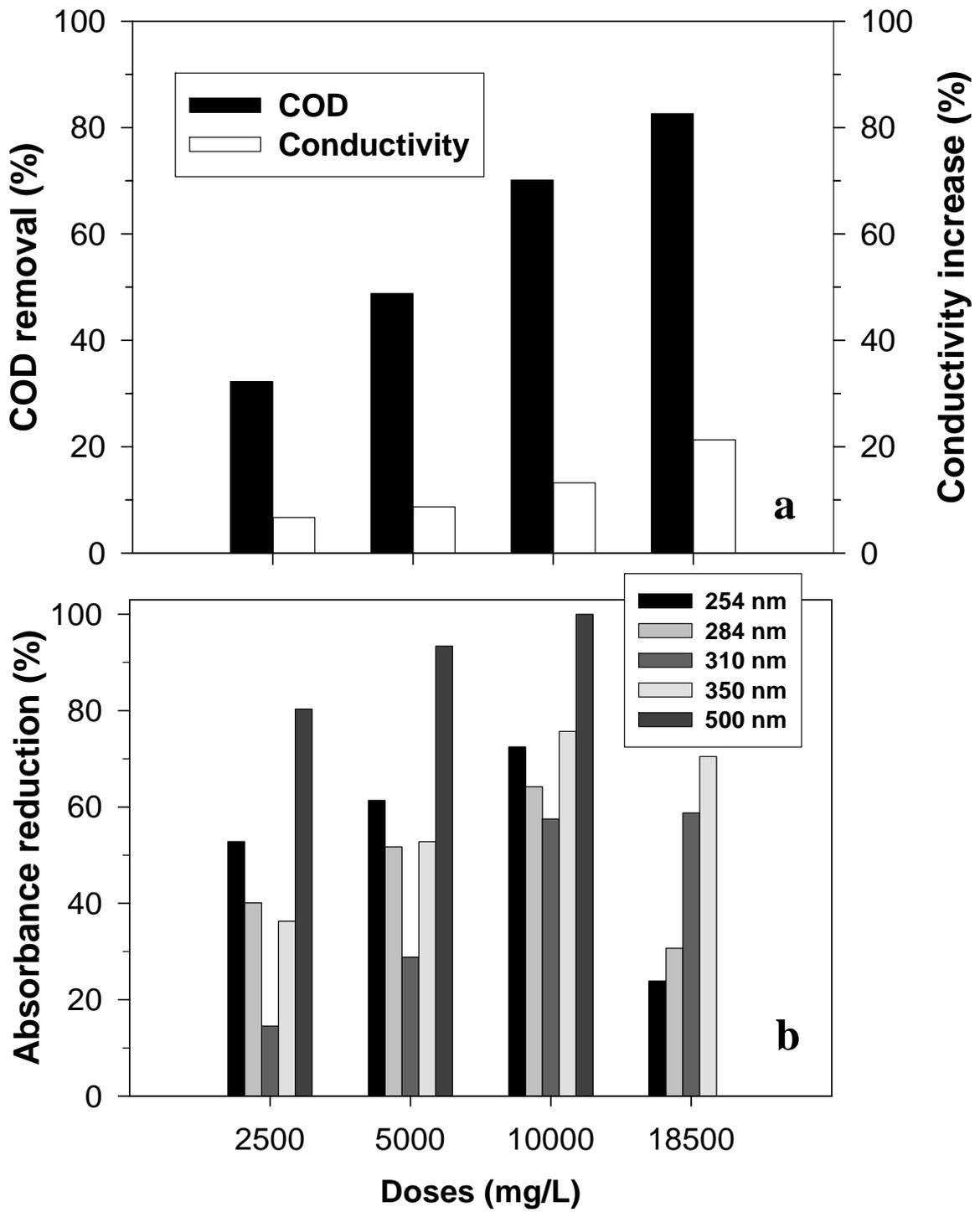


FIGURE 5

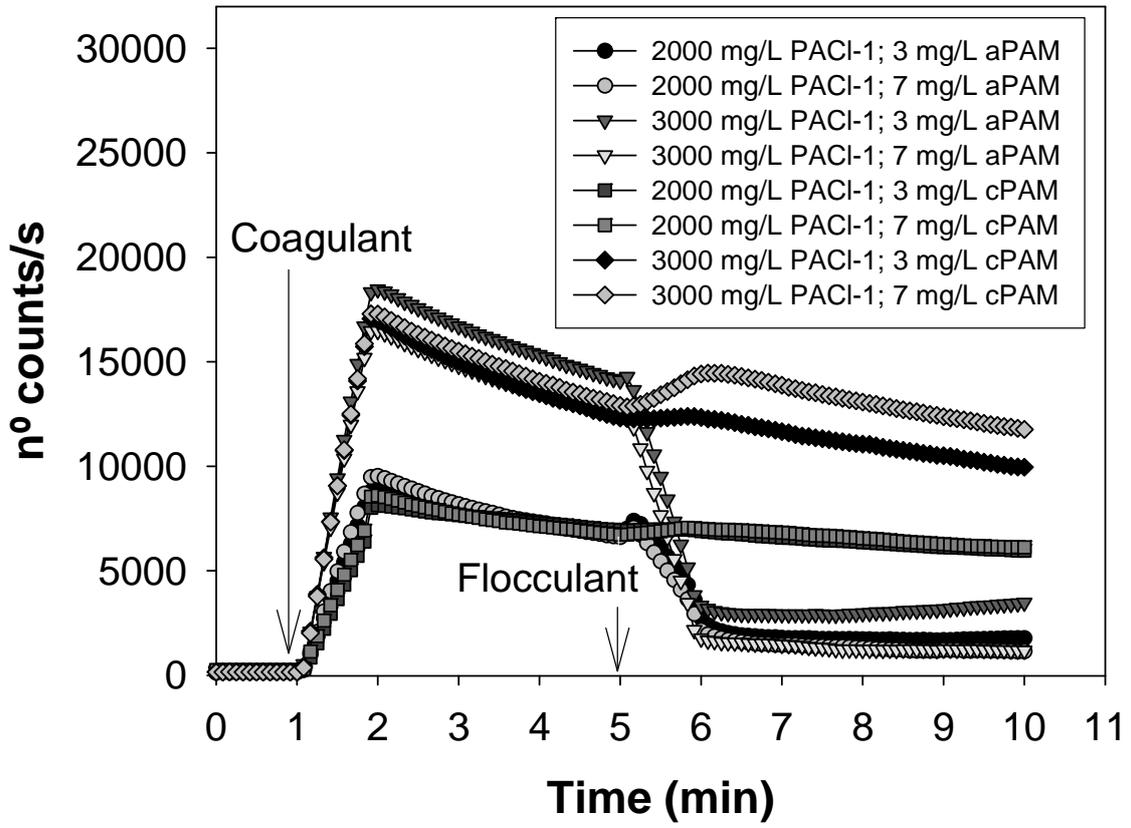


FIGURE 6

