Combining coagulation, softening and flocculation to dispose reverse osmosis retentates

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A B S T R A C T

The concentrated stream of a reverse osmosis unit was treated by coagulation, softening and flocculation to reduce conductivity and refractory organic matter content. Different polyaluminium chlorides and one ferric salt were used as coagulants, lime was added as softener, and two polymers (anionic and cationic polyacrylamides) were tested as flocculants. Coagulants reduced significantly the presence of refractory compounds by themselves, although conductivity increased. Lime addition decreased conductivity forming precipitates of $CaCO_3$ and $Mg(OH)_2$. When coagulation was combined with flocculation without adding lime, the anionic flocculant was more effective than the cationic one because the specific high hardness of water supplied enough Ca^{2+} and Mg^{2+} to promote the formation of bigger flocs, bridging the slightly negative coagula and anionic groups of the polymer; although they also reduced the efficiency of the cationic polyacrylamide. None of the tested flocculants showed any effect on conductivity and refractory organic matter reduction when lime was added.

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1. Introduction

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

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

There are mainly two options for a further treatment of rejected streams: (1) water removal from the concentrate; and (2) removal of specific components by a selective treatment. In both cases, water can be reused again into the process, or discharged (directly or indirectly via sewage systems) whenever water quality parameters fulfil the requirements established by the corresponding environmental authority [5–7]. Discharge into the sewer system can adversely affect subsequent biological sewage treatment, as microbial growth may be limited by the inhibitory effect of high salinity, or by the refractory character and biotoxicity of typical organic constituents of membrane retentate [8,9].

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

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

On the other hand, Allegre et al. [17] proposed a coagulation–flocculation–decantation train to treat these concentrated streams, paying special attention to the selection of chemicals because the settling velocity and supernatant absorbances were very sensible to the added products. Finally, Dyalinas et al. [18] compared the efficiency of coagulation and activated carbon adsorption with three different advanced oxidation processes (electrochemical treatment, photocatalysis and sonolysis) as alternative treatments to the rejected stream coming from a RO system placed after a membrane biological reactor (MBR), located in a municipal wastewater treatment plant (Chania, Western Crete, Greece). The best results were achieved by activated carbon adsorption, which was able to reach a 91.3% reduction of the dissolved organic carbon (DOC). All the three advanced oxidation methods showed similar results, removing 36%, 34% and 50% of the DOC, respectively. Coagulation with $FeCl_3$ removed 52% of the DOC. Therefore, since the efficiency of the treatment depends on each specific case, nowadays there is not a universal solution to treat these retentates.

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

2. Experimental

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

2.1. Characterization of the reverse osmosis retentate

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

The pilot plant consisted of an initial biological double step (anaerobic + aerobic) in which an important part of the organic material was removed (>80% dissolved COD and 90% BOD_5). Most of the remaining dissolved COD (dCOD) present in the treated wastewater after the biological stages can be considered non-biodegradable; thus it will be referred as refractory COD (rCOD) hereafter. The refractory organic load of wastewater from recovered-paper mills includes high and low molecular weight organic compounds, natural and synthetic polymers, adhesives, coating binders, ink residues, deinking chemicals and wood derivatives [24].

A pressurized UF unit, running in dead-end mode with hollow fibre membranes, was fed with the biologically treated water. UF-filtrated water finally entered the RO plant, which was configured in 1 pass and 3 steps, obtaining a retentate with the quality shown in Table 1. Its main characteristics were the high levels of non-biodegradable matter content (dCOD = 2121 mg/L), conductivity (9.1 mS/cm) and buffer capacity (3224 mg $CaCO_3$/L).

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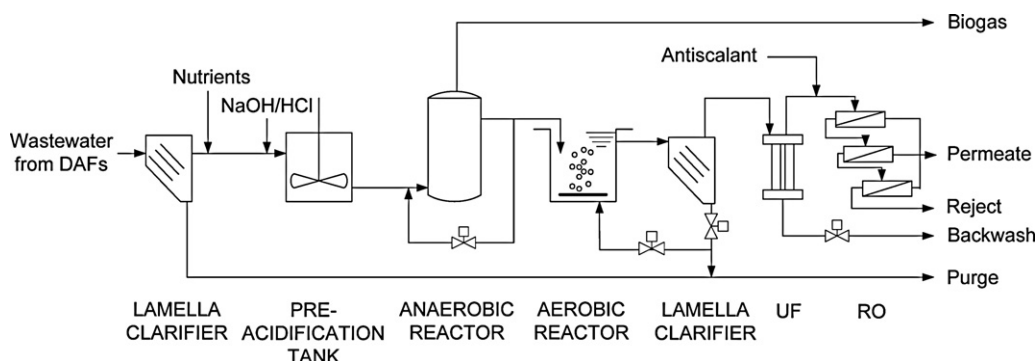

Fig. 1. Diagram of the pilot plant used to reclaim the effluent of the paper mill.

Table 1
Chemical characterization of the retentated flow from the RO system.

Parameter	Units	RO retentate
pH	–	8.0
Conductivity	mS/cm	9.1
tCOD	mg/L	2365
dCOD	mg/L	2121
Alkalinity	mg CaCO$_3$/L	3224
Turbidity	NTU	8.21
Hardness	mg CaCO$_3$/L	1100

2.2. Focused beam reflectance measurement equipment

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

2.3. Coagulation

Seven different coagulants were tested: one ferric salt (FeCl$_3$), five polyaluminium chlorides (PACl1, PACl2, PACl3, PACl4, PACl5), supplied by Kemira Ibérica S.A (Spain), and a polyaluminium nitrate sulphate salt (PNSS), supplied by Sachtleben Chemie GmbH (Germany). All of them were supplied pure, as a liquid suspension, and were diluted to the desired concentration with tap water the same day they were used. Their properties are shown in Tables 2 and 3, respectively.

PACl1, PACl2 and PNSS have the lowest basicity values (42, 43 and 45%, respectively). The grade of basicity is related to the quantity of Al-polymeric species formed in the water during coagulation, and it is calculated by Eq. (1), where [OH$^-$] and [Al$_T$] are the amounts of base and aluminium, respectively, present in the chemical formulation of the coagulant [27].

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

To determine the optimum dosage of each coagulant, 0.15 L of RO retentate was stirred during 1 min at 200 rpm before starting to add 600 mg of coagulant per litre of water each 10 s. The maximum number of counts yielded after adding the coagulant determined the optimum value of coagulant dosage.

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

After finishing the coagulation trials, the water sample was allowed to settle and clear water was sampled and filtered by 0.45 μm before measuring conductivity, dCOD and absorbances at 254, 284, 310, 350 and 500 nm. Conductivity was measured with a GLP3 conductivity meter from Crison (Barcelona, Spain), and dCOD and absorbances were determined with an UV–Visible Spectrometer (Aquamate AQA091801 Model from Thermo Fisher Scientific, Waltham, MA, USA). The absorbance at 254 nm has been related to the degree of aromaticity and unsaturation of the compounds present in water [22]; while absorbances at 284, 310, 350 and 500 nm reflect the amount of: aromatic compounds (i.e. phenols), restrained conjugated aromatic rings, conjugated aromatic rings with certain level of resonance, and colored substances presenting a high level of resonance, respectively [23].

2.4. Softening

Lime was added to soften the solution because conductivity increased after using coagulants alone. The lime-softening step began 2 min after the addition of the coagulant, stirring at 200 rpm. As a consequence of lime addition, pH increases and calcium and magnesium are removed from water as precipitates of CaCO$_3$ (pH > 9.5) and Mg(OH)$_2$ (pH > 10.0), respectively [28], reducing water hardness [29]. The addition of lime was therefore studied at pH values of 9.5 and 10.5. Lime was prepared as a supersaturated solution of Ca(OH)$_2$ from Panreac Química S.A.U., Spain.

2.5. Flocculation

Finally, the use of flocculants was included in the treatment train [30,31]. Water was flocculated with organic polymers two minutes after lime addition. Two flocculants were evaluated, a 60%-charged medium molecular weight (MMW) cationic polymer (cPAM), and a 15%-charged MMW anionic flocculant (aPAM). Both products were supplied by Nalco Company (Spain) in powder form, and they were prepared at a concentration of 0.5 g/L by dilution of the corresponding powder in tap water, stirring the solution at 400 rpm during 1 h. The chemicals were prepared the same day they were used.

After the coagulation–softening–flocculation treatment, water was led to settle for 30 min and the supernatant was filtered through 0.45 μm before measuring conductivity, dCOD and absorbances at 254 (A_{254}), 284 (A_{284}), 310 (A_{310}), 350 (A_{350}) and 500 (A_{500}) nm.

2.6. Experimental design

A faced centered-central composite experimental design with one central point was run to assess the influence of the

Table 2
Chemical specifications of the ferric salt and polyaluminium chlorides coagulants.

Coagulant	Concentration (w/w) (%)	Al$_2$O$_3$ (%)	Basicity (%)	Other
FeCl$_3$	39–47	–	–	–
PACl1	–	17.0 ± 0.5	42 ± 2	–
PACl2	–	17.0 ± 0.5	43 ± 5	High molecular weight
PACl3	–	9.5 ± 1.0	70 ± 5	Contains micropolymers
PACl4	–	9.7 ± 0.3	85 ± 10	–
PACl5	–	9.7 ± 0.3	85 ± 10	Contains micropolymers

Table 3
Properties of the polyaluminium nitrate sulphate salt (PNSS).

Composition(%)			Contents (%)			pH	Basicity
Al	NO₃	SO₄	Monomeric	Oligomeric	Polymeric		
5.2	15	3	22	35	43	2.5	46

independent variables controlling the studied process at lab scale, namely coagulant and flocculant dosages (X_{coag} and X_{floc}), and pH (X_{pH}), together with their interaction. The removal percentages of rCOD, conductivity and absorbances (A_{254}, A_{284}, A_{310}, A_{350} and A_{500}) were considered as dependent variables; and experimental results are fitted to a second-order polynomial model. The total number of experiments required to perform the designed experimental protocol is 15, considering three levels for every independent variable, namely: X_{pH} = without lime (8.0), 9.5 and 10.5, according to hardness removal by $CaCO_3$ and $Mg(OH)_2$ precipitation, respectively; X_{coag} = 2000, 2500 and 3000 mg/L; and X_{floc} = 3, 5 and 7 mg/L.

The type and doses of coagulant were chosen according to the results of preliminary coagulation trials run to test several products (see Section 3.1), as described previously (see Section 2.3); and considering a reasonable treatment cost (personal communication from paper mill managers). Ahmad et al. [31] tested 1–6 mg/L doses of PAMs to improve PACl coagulation treatment of pulp and paper mill wastewater, reporting no effect on COD removal. As only a 10% of the COD is associated to TSS in the RO retentate, in contrast to the 90% in the wastewater treated in Ahmad et al. [31], we have initially selected cost-reasonable higher values for the flocculant dosage to be introduced in the experimental design.

The levels of the independent variables were normalized according to Eq. (2), adopting values from −1 to +1 (centre = 0).

$$X_n = 2\frac{X - \overline{X}}{X_{max} - X_{min}} \tag{2}$$

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

3. Results and discussion

3.1. Coagulation trials

The total number of counts per second registered by the FBRM probe versus the added quantity of coagulant determines the optimal dosage of each one (Fig. 2). Only $FeCl_3$, PACl1, PACl2 and PNSS produced any significant effect on the treated wastewater. As a greater amount of these coagulants were added, DCM destabilized and began to aggregate, resulting in an increase of the number of counts. The other PACl's destabilized DCM, but their effect was comparatively minimal. $FeCl_3$ began to coagulate quicker than PACl1 and PACl2; and all of them achieved, for the same dosage, a higher number of counts per second than PNSS (Fig. 2). A similar behaviour was previously observed by Kim et al. [33]. While $FeCl_3$ required just 5 min to complete the full coagulation treatment, PACl products took 15 min to achieve the same results.

Considering only particle destabilization, two primary coagulation mechanisms can be defined, depending on pH and the concentration of Al or Fe: (1) charge neutralization of negatively
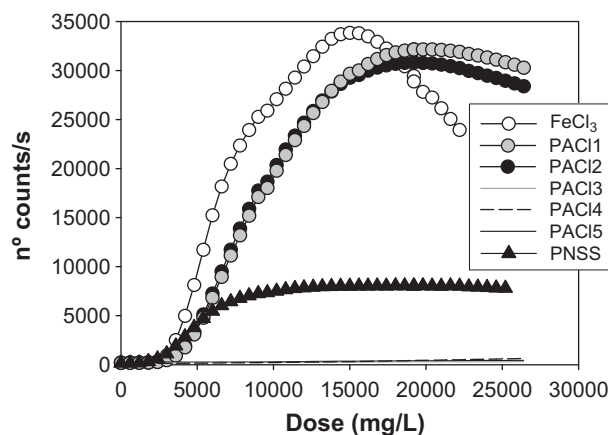

Fig. 2. Evolution of the number of counts versus coagulant dose.

charged particles by adsorption of the positively charged dissolved Al-species added within the coagulant; and, (2) colloid enmeshment or sweeping in $Al(OH)_3$ or $Fe(OH)_3$ precipitates [27]. The hydrolysis of PACl's implies the appearance of monomers, dimmers, polymers and amorphous precipitate of aluminium; and the proportion of high valence species increases with an increasing basicity in the medium, so products having basicity values higher than 70% (PACl3, PACl4 and PACl5) contain polymeric species possessing high cationic charges [27,34]. Considering the initial pH value of the concentrate (Table 1, pH 8.0) and the important amount of Al and Fe that is required to destabilize DCM (Table 4), amorphous precipitate of aluminium ($Al(OH)_{3(am)}$) would be the main species that is formed after adding PACls to water [27]. On the other hand, when $FeCl_3$ is added to water with a natural bicarbonate alkalinity, $Fe(OH)_{3(s)}$ precipitates coexist with other Fe-hydrated species. The main species present in water should be $Fe(OH)_{3(s)}$ when using $FeCl_3$ at pH 8.0 [35]. In short, it could be therefore stated that the main existent coagulation mechanism for both types of coagulant ($FeCl_3$ and PACl's) is sweeping.

Although PACl2 produced a very similar good effect on DCM, PACl1 was chosen to perform the next experimental trials, adding lime softening and flocculation steps, because it is a cheaper product. $FeCl_3$ was discarded as an optimal product because it turns water colour to intense red-orange at optimal dosage. According to results shown in Fig. 2, 5000, 10,000 and 18,500 mg/L of PACl1 were chosen as reference doses to perform floc resistance trials.

Time course evolutions of the number of counts (Fig. 3a) and the mean chord length (MCL, Fig. 3b) when PACl1 was added at these selected concentrations, and the water sample was stirred at increasing speeds (200, 400 and 600 rpm), showed that, while the number of counts per second increased during the first minute, the size of the particles decreased. Although big particles (20–25 μm) attached each other forming bigger flocs as the coagulant was added, DCM of <1 μm was also destabilized, and small particles got in touch forming small coagula greater than 1 μm. As these particles are now detected by FBRM, the proportion of small

Table 4
Iron and aluminium concentrations (mol/L) for some doses of $FeCl_3$ and PACl's selected from Fig. 2.

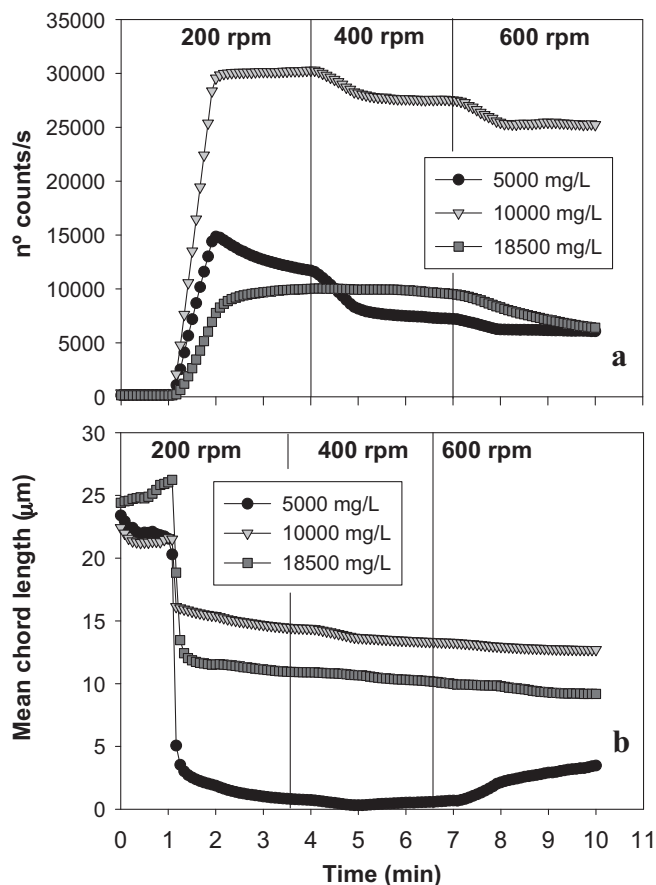| Doses, mg/L	[Fe], mol/L	[Al], mol/L		
	$FeCl_3$	PACl1 and PACl2	PACl4 and PACl5	PACl3
2500	0.0060–0.0070	0.0021	0.0012	0.0012
5000	0.0120–0.0145	0.0042	0.0024	0.0023
10,000	0.0024–0.0289	0.0083	0.0048	0.0047
18,500	0.0444–0.0536	0.0154	0.0088	0.0086

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

particles led to an overall decrease in the MCL distribution (Fig. 3b). In addition, the number of counts per second was higher as the coagulant dosage was increased from 5000 mg/L to 10,000 mg/L; but significantly decreased when 18,500 mg/L were added. The water solution got saturated of coagulant when such an amount was used, having a negative effect on the treatment efficiency [36]. The number of counts was particularly high when 10,000 mg/L of PACl1 were used.

After increasing the stirring velocity from 200 to 400 and 600 rpm when PACl1 was added at 5000 and 10,000 mg/L, fewer particles were detected by FBRM, but MCL kept more or less constant compared to the values achieved after adding the coagulant at 400 rpm. Finally, when 18,500 mg/L were added, the number of FBRM-detected particles did not decrease up to reaching 600 rpm; and MCL kept a similar performance as for 5000 and 10,000 mg/L (Fig. 3b).

This behaviour may be explained by the fact that a higher stirring speed yields a higher number of particle–particle collisions, reducing the number of small particles as they attach each other after colliding. This phenomenon was reflected by FBRM by a reduction of the number of counts per second when speeding up from 200 to 400 rpm (Fig. 3a). On the other hand, this phenomenon also decreases the rate of formation of very large flocs as they break up after been collided. Therefore, rather than provoking big particles to break, increasing the stirring speed favored particle–particle collisions, and its further attachment forming bigger particles, at lower doses of coagulant (i.e. 5000 mg/L), resulting in the observed increase of MCL at 600 rpm (Fig. 3b). At higher coagulant doses, large particles formation was still prevailing over big particles breakage, as fewer particles are

detected in the water sample (Fig. 3a); while MCL decreased slowly as the stirring velocity was increased (Fig. 3b). Although there were fewer particles in the water, big flocs broke up into smaller particles (but bigger than 1 μm) that are bigger than the aggregates formed by small particles, which collision was enhanced by faster stirring rates.

A higher coagulant dosage produced a higher reduction in rCOD, reaching $\approx$80% when 18,500 mg/L were added; but it increased conductivity as well (Fig. 4a), as more Al is added to the medium. The mechanisms to remove this kind of organic compounds are similar to DCM ones [36]: (1) binding metal species to anionic sites neutralizing charges; and (2) adsorption on amorphous metal hydroxide precipitate. Although many studies have reported flocculation experiences, it is however very difficult to distinguish between both mechanisms, which depend mainly on pH and coagulant concentration [37].

On the other hand, better absorbance removals at all the measured wavelengths were achieved when 10,000 mg/L of PACl1 were added, while lower reductions were yielded at lower and higher dosages (Fig, 4b); denoting a selective removal of refractory organic matter. Particularly, coloured compounds with a high level of resonance (A_{500}) were not removed at all when 18,500 mg/L of coagulant were used. Yan et al. [38] detected a similar trend for A_{254}, which is related to the presence of hydrophobic and high molecular weight natural organic matter, such as humic substances.

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

The final aim of the experimental design was to study the influence of the three independent variables (X_{coag}, X_{floc}, X_{pH}) controlling the combined treatment process in terms of conductivity and recalcitrant organic matter content in water. 2500 mg/L
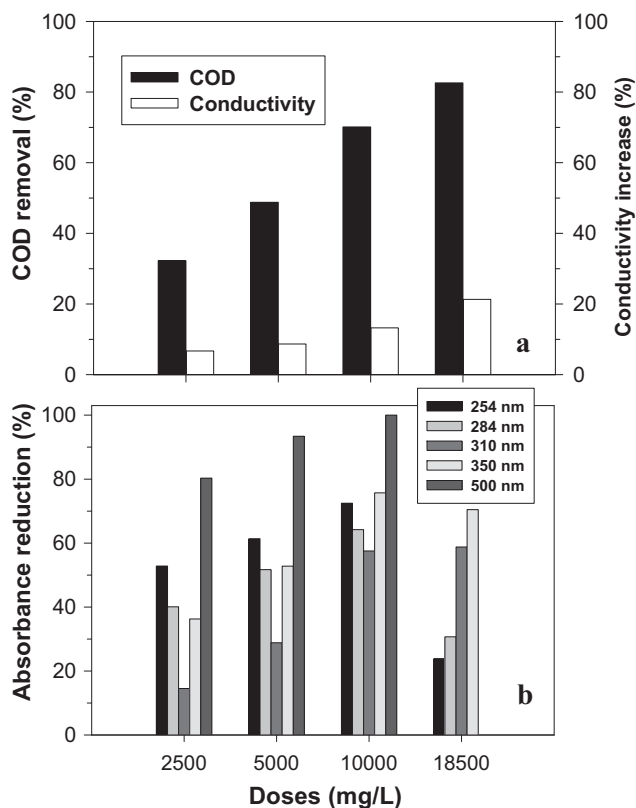

Fig. 4. Effect of PACl1 dosage on dCOD removal and conductivity increase (a), and the reduction of the absorbance of refractory compounds (b).

Table 5
Experimental design results combining PACl1 + lime + aPAM to reduce conductivity and dCOD.

X_{coag}	X_{floc}	X_{pH}	% Removal						
			Conductivity	dCOD	A_{254}	A_{284}	A_{310}	A_{350}	A_{500}
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

X_{coag} = 2000 (−1), 2500 (0), and 3000 (+1) mg/L; X_{pH} = without lime-pH = 8.0 (−1), pH = 9.5 (0), and pH = 10.5 (+1); X_{floc} = 3 (−1), 5 (0), and 7 (+1) mg/L.

of PACl1 were set as the reference level (X_n = 0) of the experimental design as it produced a significant treatment effect (COD removal >30%; conductivity increase >5%) at a reasonable industrial cost. In fact, lime was added to soften the solution; while a flocculation step was thought to reduce the quantity of coagulant to be added. Two experimental designs, one per each tested flocculant (aPAM and cPAM), were performed. Results in terms of the achieved reductions of dCOD, conductivity and absorbances are shown in Table 5 (aPAM) and Table 6 (cPAM).

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

Particularly, the addition of lime (X_{pH}) was the main factor affecting the reduction of conductivity for both flocculants (Table 7).

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

When flocculant was added without lime, the FBRM probe detected significant differences in the number of counts from when a previous soften step is performed (Figs. 5 and 6). While the number of particles decreased as aPAM was added; no effect was observed in the distribution of particles when cPAM was used (Fig. 5). Two possible mechanisms may explain this performance: (1) aggregates formed by PACl1 and lime have a slightly positive surface charge, so cPAM would repeal them [39]; and (2) negatively charged surfaces may be adsorbed on aPAM despite electrostatic repulsion whenever there is enough concentration of divalent metal ions in the solution [40].

Due to the pH value of the concentrated stream (8.0), and the amount of coagulant added, it is more reasonable to think that the surface of the aggregates formed from PACl1 and lime are slightly negatively charged; so the second explanation maybe most suitable to what it is really happening. As hardness of the retentate was really high (1100 mg $CaCO_3$/L; Table 1), important amounts of Ca^{2+} and Mg^{2+} should be present, enhancing flocculation processes bridging anionic groups of the aPAM to negative sites on the

Table 6
Experimental design results combining PACl1 + lime + cPAM to reduce conductivity and dCOD.

X_{coag}	X_{floc}	X_{pH}	% Removal						
			Conductivity	dCOD	A_{254}	A_{284}	A_{310}	A_{350}	A_{500}
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

X_{coag} = 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); X_{floc} 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.

| Equations	R^2	Error (%)
PACl1 + LIME + aPAM		
%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
PACl1 + LIME + cPAM		
%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
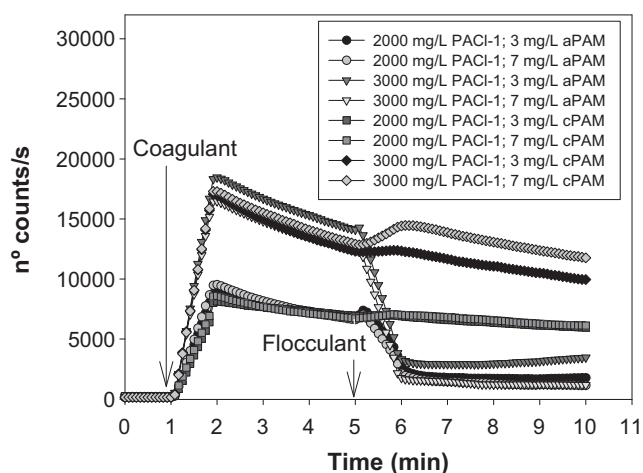
Fig. 5. Evolution in time of the number of counts per second when PACl1 (2000 and 3000 mg/L) and PAMs (anionic or cationic, 3 and 7 mg/L) are added without lime.

surface of particles. On the other hand, these cations would interfere with the positively charged groups of the cPAM, repealing each other, and making the polymer lose its extended structure. Therefore, the efficiency of this polymer is limited [39].
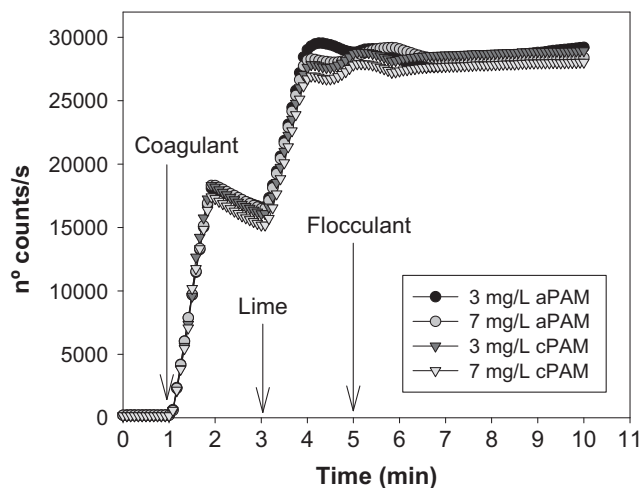

Fig. 6. Evolution in time of the number of counts per second when 3000 mg/L PACl1 and PAMs (anionic or cationic, 3 and 7 mg/L) are added after the lime at pH 10.5.

When lime was added, more particles were detected in the solution (Fig. 6), as $CaCO_3$ and $Mg(OH)_2$ precipitates are formed. When a constant number of particles was achieved, the flocculant was added. No significant effect on the number of particles was appreciated after the addition of the flocculants when lime was previously added. Ca^{2+} and Mg^{2+} ions are removed from the water when lime is added, so there are not such intermediates in the water solution to form bridges between slightly negative particles and the aPAM, driving its addition ineffective. On the other hand, it could be thought that cPAM would be able to flocculate the new aggregates, but it begins to hydrolyze when pH gets to 8.5, thus becoming ineffective as well. This hydrolysis process does not only result in the loss of cationic sites, but also in a change in the conformation of the chain structure because the appearance of carboxylate groups reduces the length of the polymer [39].

4. Conclusions

$FeCl_3$ and low basicity PACl's (PACl1 and PACl2) were the best coagulants to destabilize DCM in RO retentate. $FeCl_3$ turned water colour to intense red-orange at optimal dosage and PACl2 is more expensive than PACl1.

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

Lime-softening resulted to be a good alternative to reduce conductivity, as Ca^{2+} and Mg^{2+} are removed from the water through the precipitation of $CaCO_3$ (pH $\geq$ 9.5) and $Mg(OH)_2$ (pH $\geq$ 10.0). As these precipitates are formed, organic matter is adsorbed on their surface and could be additionally removed in part by this precipitation process.

Anionic PAM resulted to be the best option to aid coagulation with PACl1 when no lime was added because Ca^{2+} and Mg^{2+} ions, which are present in the medium yielding high water hardness, bridge slightly negative aggregates that PACl1 formed previously. On the other hand, these cations affected cPAM performance driving its addition inefficient when no lime was used.

When flocculants were combined with previous coagulation and lime-softening steps, no additional effect was observed on the reduction of dCOD, conductivity and absorbances at different wave lengths; which is explained by the efficient removal of Ca^{2+} and

Mg^{2+} from the solution, and the high pH value at which the treatment was performed.

Acknowledgements

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