

pH and Particle Structure Effects on Silica Removal by Coagulation

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Abstract

Coagulation is presented as an efficient alternative to reduce the silica content in effluents from recovered-paper mills that are intended to be recycled by a final reverse-osmosis (RO) step. Coagulation pretreatment by several polyaluminum chlorides (PACls) or FeCl₃ was optimized prior to the RO process. PACls with low alumina content and high basicity achieved almost a 100% removal of silica at pH 10.5. A good reduction of the silica content was attained without regulating the pH by adding one of these PACls. Silica removal was related to the structure of the produced clots in which cylindrical particles produced higher silica removal. All coagulants removed more than 50% of the chemical oxygen demand (COD).

Keywords: Coagulation, Focused beam reflectance, Paper mill effluent, Reverse osmosis, Silica fouling

Introduction

Reverse osmosis (RO) is the preferred final step when an advanced wastewater treatment is implemented to recycle final effluents in paper mills because it ensures the reduction of conductivity and the total removal of pathogens [1–3]. Effluents from recovered-paper mills usually carry an important content of silica (SiO₂), which causes important scaling and fouling in RO membranes [4], leading to lower water production rates, worse quality of the permeate, unsteady-state operation conditions, and serious physical damage to the membranes themselves [5, 6]. This high silica content mainly comes from sodium silicate, which is added during de-inking processes in order to: (i) stabilize hydrogen peroxide added for bleaching pulp in the pulper; (ii) take advantage of its buffering and saponification properties [7, 8]; (iii) assist the dispersion of ink particles and influence their size [9, 10]; (iv) support ink collection [11]; (v) reduce fiber losses; and (vi) avoid flotation of fillers [12].

Silica may be found either in crystalline form or amorphous state. While crystalline silica addresses a solubility of 5–6mg L⁻¹ (25 °C, pH < 9), the solubility of amorphous silica ranges from 120 to 150mg L⁻¹ (25 °C, pH < 8.0–8.5) [13]. Amorphous silica is furthermore classified as dissolved (reactive) silica, colloid (non-reactive) silica, and particulate (suspended) silica [6]. The dissolution process of amorphous silica takes

1 place when silica-oxygen-silica bonds are hydrolyzed forming tetrameric monosilicic
2 acid (H_4SiO_4), the strength of which is weak. The solubility of amorphous silica is
3 mainly affected by temperature (T), pH, and the presence of other ions and organic
4 compounds. The effect of pressure (P) has been demonstrated to be negligible at values
5 up to a few hundred bar at $T < 100\text{ }^\circ\text{C}$ [14]. Specifically, H_4SiO_4 is generally deionized
6 at a neutral pH value, while, as OH^- concentration increases in the solution, the
7 ionization of silicic acid into H_3SiO_4^- and $\text{H}_2\text{SiO}_4^{2-}$ (the most predominant species of
8 dissolved silica under alkaline environments) is facilitated [15], therefore, only 10% is
9 ionized at pH 8.5 and 50% is ionized at pH 10.

10 Dissolved silica interacts with a wide variety of organic and inorganic species, resulting
11 in the formation of complexes that can be deposited on membranes. When Al^{3+} and Fe^{3+}
12 coexist in water feeding the RO system, silica is precipitated even below its saturation
13 point [16]. Al^{3+} and Fe^{3+} contents must be lower than 0.05mg L^{-1} to work safely [5]. In
14 addition, when the Mg^{2+} content is high and magnesium silicate precipitation must be
15 avoided, the product of silica (expressed as $\text{mg SiO}_2\text{ L}^{-1}$) and Mg^{2+} (expressed as
16 $\text{mgCaCO}_3\text{ L}^{-1}$) contents must be kept below $20\ 000\text{mg}^2\text{L}^{-2}$ when the pH is higher than
17 7.5 [17]. In addition to silicate precipitation, silica can also foul RO membranes by
18 polymerization [18]. Silica polymerization increases with water hardness, although
19 polymerization is favored at $[\text{SiO}_2] > 300\text{ mg L}^{-1}$ even in the absence of calcium and
20 magnesium [19].

21 Several technologies have been successfully applied to remove silica from water,
22 namely: (i) those based on increasing the solubility of silica, such as pH and/or T
23 regulation, or the addition of antiscalant products [20, 21]; (ii) addition of chemicals to
24 induce silica coagulation or precipitation; (iii) lime softening [22]; (iv) substitution of
25 antiscalant agents by desupersaturation units, forcing the precipitation of sparingly
26 soluble salts [23], such as calcium carbonate, calcium sulfate, silica, calcium phosphate,
27 and barium sulfate; (v) addition of strong anionic-exchange resins in hydroxide form
28 that assist the removal of silica, which acts as a very weak acid [24, 25]. As the
29 solubility of silica strongly depends on the pH, silica precipitation may be avoided
30 working at $\text{pH} > 10$, at which silica solubility increases up to $300\text{--}350\text{ mg L}^{-1}$ [13],
31 although the generation of carbonate ions is also favored at this pH value, leading to
32 greater calcium carbonate scaling on RO membranes [26, 27].

33 Both soluble and colloidal silica can be successfully removed from water by co-
34 precipitation with soluble metals, or by adsorption on freshly formed insoluble
35 hydroxides added to water. For example, the removal of dissolved silica through the
36 formation of $\text{Fe}(\text{OH})_3$ has been addressed successfully at $\text{pH} \geq 9.0$ after adding NaOH or
37 $\text{Ca}(\text{OH})_2$ to a solution containing $\text{Fe}_2(\text{SO}_4)_3$ [28]. $\text{Mg}(\text{OH})_2$ has shown a particularly
38 strong tendency to react with silica [29]. On the other hand, the presence of salts
39 reduces the solubility of amorphous silica, and an alkaline environment favors the
40 formation of silicate ion, which reacts with metal ions forming insoluble silicates [30].
41 In addition, alumina (Al_2O_3), aluminum chloride, and sulfate salts are also considered
42 excellent adsorbents for dissolved and colloidal silica. Particularly, the amount of Al^{3+}
43 needed to remove colloidal silica was assessed lower than the corresponding quantity to
44 remove dissolved silica at $\text{pH} 4.1\text{--}4.7$ [31]. Maximum silica adsorption on Al_2O_3 (≈ 90
45 %) was achieved at $\text{pH} 8.0\text{--}8.5$ [32].

46 Considering examples from industrial wastewater treatment, 60% silica content
47 has been reported to be removed by FeCl_3 coagulation in effluents from two different
48 paper mills [33]. The optimal combination of NaOH with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and

1 ZnSO₄·7H₂O reduced the silica content in more than 60% from heavy-oil wastewaters
2 [34]. Although these are good examples of how coagulation has been already
3 successfully applied to reduce the silica content in wastewater, very limited research
4 efforts have been made to monitor the coagulation process itself in relation to particle
5 properties in real industrial wastewater [35].

6 The main objective of this research was to assess the efficiency of different
7 coagulants, including those modified to exhibit high basicity content or containing
8 micropolymers, for removing silica from the final effluent of a recovered-paper mill that
9 is meant to be recycled by a final RO step aiming to reduce freshwater consumption
10 within the mill. Results will be discussed considering coagulation mechanisms,
11 properties of the coagulants, and structure of the formed coagula.

12 13 **2. Materials and Methods**

14 Samples were taken from the effluent of a 100% recovered-paper mill located in
15 Madrid, Spain. This wastewater is previously treated by aerobic digestion and dissolved
16 air flotation to degrade organic matter and remove suspended solids, respectively,
17 before being dumped into the municipal wastewater treatment plant. Samples were first
18 filtered through 150 μm filters and then characterized before being stored at ± 4 °C for
19 four days maximum. Results are summarized in Tab. 1. All analyses were performed
20 following the Standard Methods for Examination of Water and Wastewater [36]. In
21 short, samples were additionally filtered through 1 μm filters before measuring
22 alkalinity, hardness, chloride, iron, calcium, and aluminum contents, and through 0.45
23 μm filters before measuring soluble chemical oxygen demand (COD), sulfate, and silica
24 (as SiO₂). Particularly, reactive SiO₂ to molybdosilicic acid (H₄Mo₁₂O₄₀Si) was
25 measured by flow injection analysis (FIA) and photometric detection, as described in
26 the method DIN EN ISO 16264: 2004/2005, using an FIA compact device (Medizin-
27 und Labortechnik Engineering GmbH, Dresden, Germany).

28 One iron salt (FeCl₃) and five polyaluminum chlorides (PAC11, PAC12, PAC13,
29 PAC14, and PAC15) from Kemira Ibérica S.A. (Spain) were tested as coagulants. Tab. 2
30 summarizes their main properties. All coagulants were delivered as a liquid suspension
31 and diluted to the desired concentration adding tap water the same day they were used.

32 Polyaluminum coagulants are typically characterized by their basicity, which is
33 related to the quantity of Al-polymeric species formed in water during coagulation.
34 Basicity was calculated as follows [37]:

$$35 \quad \text{Basicity}(\%) = 100 \cdot \left(\frac{1}{3} \cdot \frac{[OH^-]}{[Al_T]} \right) \quad (1)$$

36 where [OH⁻] and [Al_T] designate the concentration of base and aluminum,
37 respectively, that are present in the chemical formulation of the coagulant.

38 The optimal dosage of each coagulant was determined by monitoring the process
39 with a commercially available non-imaging scanning laser microscope or focused beam
40 reflectance measurement device (FBRM) [38], manufactured by Auto-Chem, Mettler
41 Toledo (Seattle, WA, USA). The FBRM instrument operates by scanning the particles
42 in suspension with a laser beam at a focal point that describes a circular path. When a
43 particle intercepts this path, the time duration of the backscattered light from this
44 particle is measured and multiplied by the velocity of the scanning laser, which is a

1 known characteristic of the device, resulting in a characteristic dimensional
 2 measurement of the geometry of the particle, namely the chord length. Thousands of
 3 chord length measurements (i.e., number of counts) are collected per second, producing
 4 a histogram in which the number of the observed counts is sorted in several chord
 5 length bins over the range of 0.5–1000 or 2000 μm [38]. All the experiments with the
 6 FBRM were programmed to obtain a chord length distribution every 5 s, so that enough
 7 particles are detected to get a good representative distribution of the population.

Table 1. Characterization of the paper mill effluent.

Parameter	Units	Mean	Std. dev.
pH	[-]	8.6	0.3
Conductivity	[mS cm^{-1}]	3.1	0.4
Total suspended solids (TSS)	[mg L^{-1}]	145	74
Soluble COD	[mg L^{-1}]	505	174
Alkalinity	[$\text{mg}_{\text{CaCO}_3} \text{L}^{-1}$]	400	75
Hardness	[$\text{mg}_{\text{CaCO}_3} \text{L}^{-1}$]	150	2
Turbidity	[NTU]	158	21
SO_4^{2-}	[mg L^{-1}]	582	122
Cl^-	[mg L^{-1}]	110	28
Si	[$\text{mg}_{\text{SiO}_2} \text{L}^{-1}$]	185	31
Fe_{total}	[mg L^{-1}]	0.9	0.1
Ca	[$\text{mg}_{\text{CaCO}_3} \text{L}^{-1}$]	138	25
Al^{3+}	[mg L^{-1}]	0.09	0.06

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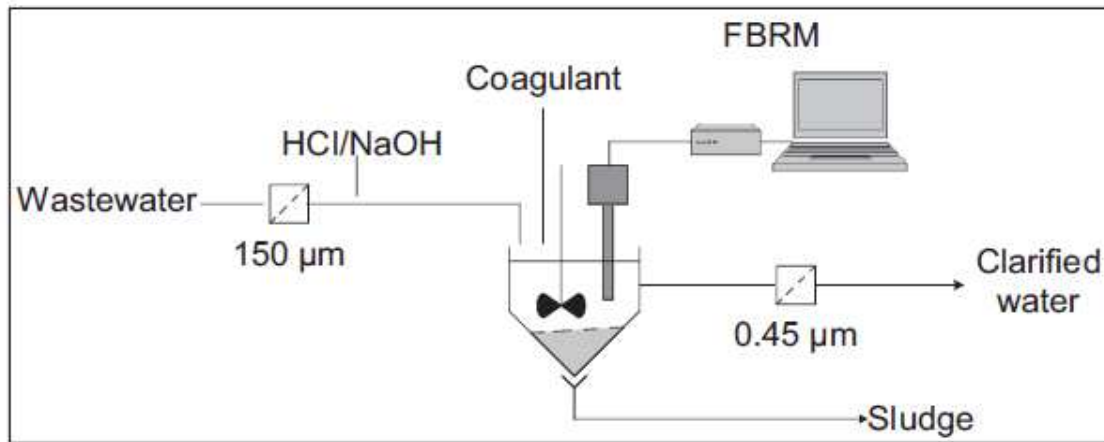
Table 2. Chemical specifications of the coagulants.

Coagulant	Concentration [wt-%]	Al_2O_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

9

10 Coagulant (100 mg L^{-1}) was added to water samples of 0.15 L every 10 s under
 11 stirring at 270 rpm. Each dosage optimization experiment finished when water was
 12 saturated with the coagulant reaching a constant value for both, the mean chord length
 13 (MCL) and the total number of counts (TNC) per second. Since pH affects the
 14 coagulation process, experiments were run at three different initial pH values: 5.5
 15 (acidic), 8.6 (typical for the wastewater sample, Tab. 1; no pH regulation was required),

1 and 10.5 (basified); 0.1M HCl was used to adjust the pH to 5.5 and 1M NaOH was
2 added to reach pH 10.5. The flow diagram of the installation used to perform these
3 coagulation trials is presented in Fig. 1.



5
6 **Figure 1.** Flow diagram of the installation used to perform the coagulation trials

7
8 Each coagulation trial was repeated three times. After performing every
9 coagulation treatment, clarified water was timely filtered for measuring conductivity,
10 soluble COD, silica, chloride, iron, and aluminum contents, as described above. The
11 type and size of coagulated particles were determined by analyzing images taken by an
12 optical microscope (Olympus BX41). Scanning electron microscopy-energy dispersive
13 X-ray spectroscopy (SEM-EDS) was applied to determine the atomic composition of
14 the aggregates formed by the coagulants using a Jeol JSM-6400 scanning electron
15 microscope.

16 Sedimentation rates were calculated for the most efficient treatments. After
17 addition of the coagulant to a jar containing 0.5 L of water, the sample was stirred at
18 180 rpm for 5 min before slowing down the agitation rate to 45 rpm for 10 min. Finally,
19 the solution was allowed to settle for 120 min, along which the height of the sediment
20 was periodically measured.

21 Analysis of variance was performed to test the effects of pH and coagulant type
22 on the removal efficiency of silica content and COD. Tukey's test was used for all
23 pairwise comparisons of mean values ($P < 0.05$). Nonlinear regression was applied to
24 explain the relationship between some measured results.

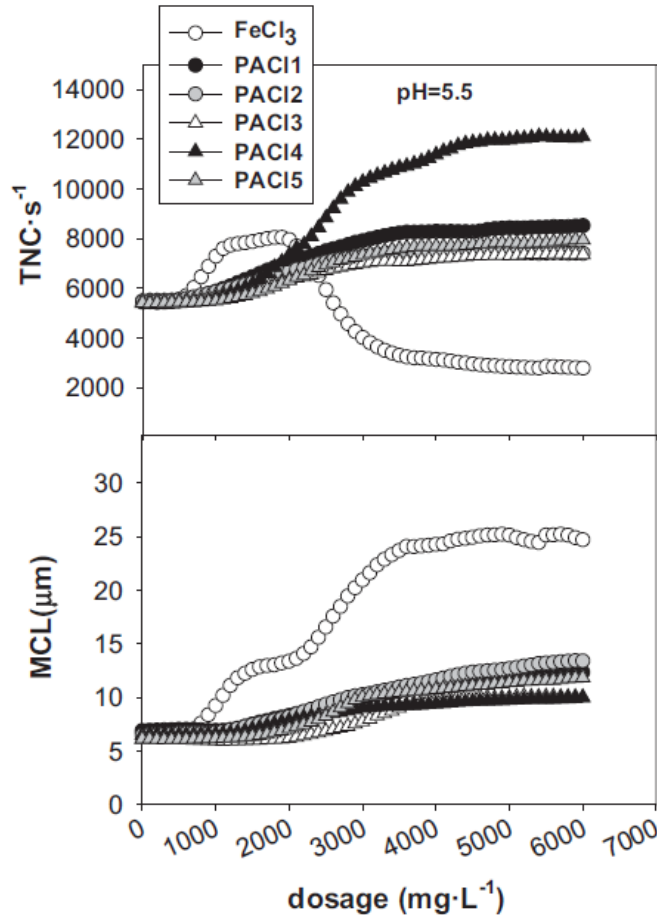
25 **3 Results and Discussion**

26 The optimal dosage of each coagulant at every tested pH value was determined
27 as the minimum required coagulant addition that maximized the TNC per second and
28 the MCL determined by the FBRM probe (Figs. 2–4). In general, no effect was detected
29 before reaching a certain dosage threshold, and a steady state was achieved when no
30 cumulative effect was observed after increasing the dosage.

31 At the beginning of the experiments, dissolved and colloidal material (DCM)
32 might have not been detected because particles were smaller than 1 μm , which is the
33 detection size limit of the FBRM. DCM destabilized as more coagulant was added, thus,
34 the incipient formation of aggregates was detected by FBRM as an increase of the TNC
35 [39]. The size of these aggregates usually increases as well along the coagulation trial

1 resulting in a corresponding increase of the MCL. The main source of DCM in the
 2 mill's wastewater is recovered paper, although some chemical additives used during the
 3 manufacturing process may also contribute. Stickies, salts and organic compounds
 4 released during pulping, dispersing, and bleaching, are substances that may be included
 5 within this fraction [40].

6



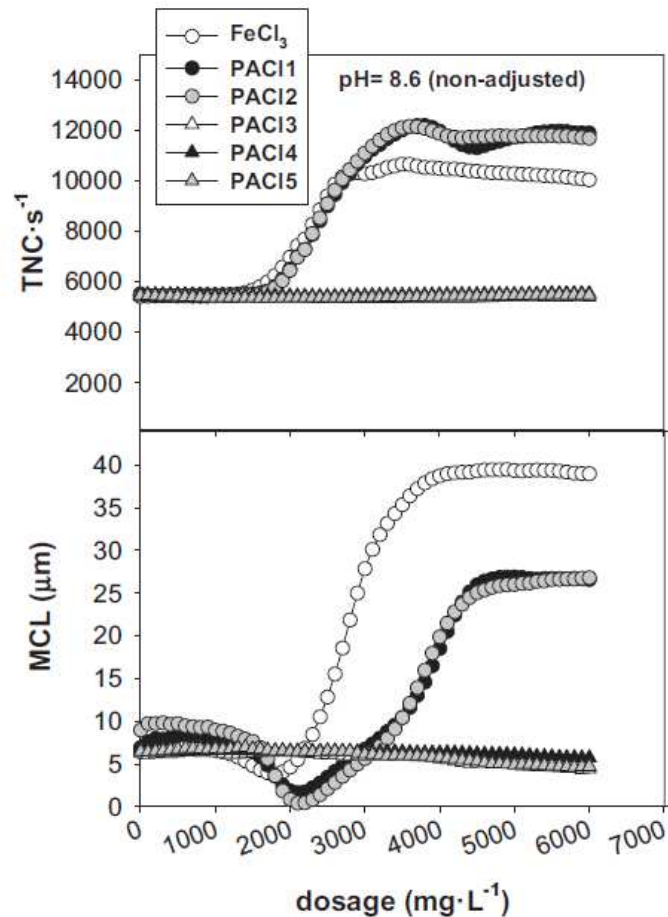
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8 Figure 2. Evolution of the total number of counts (TNC) per second and mean chord
 9 length (MCL) as the coagulant dosage increases at pH 5.5.

10 Particularly, the addition of FeCl₃ was apparently able to generate bigger
 11 coagula than PACIs under all tested pH conditions, as detected by FBRM (Figs. 2–4).
 12 The optimal dosage of FeCl₃ maximizing TNC and MCL increased from acid to basic
 13 condition of the solution from 1500 to about 2500 mg L⁻¹. In general, the formation of
 14 aggregates was detected at lower concentration thresholds than in the case of low-
 15 basicity PACIs. The observed decrease in the TNC in the presence of FeCl₃ at pH 5.5
 16 (Fig. 2) denotes that doses higher than 2500 mg L⁻¹ cause the predominant coagulation
 17 of particles and aggregates larger than 1 μm.

18 In addition, both low-basicity PACIs (PACI1 and PACI2, Tab. 2) exhibited some
 19 similar performance patterns to FeCl₃ trials, i.e., the TNC progressively increased to a
 20 maximum when a higher coagulant dose was added at any pH value of the solution
 21 (Figs. 2–4), and MCL increased at higher coagulant doses at pH 5.5 (Fig. 2) and 10.5
 22 (Fig. 4). In addition, MCL decreased to a minimum value more pronouncedly than in
 23 the case of FeCl₃ when the pH was not regulated (pH 8.6, Fig. 3), even though the TNC
 24 began to increase. At this point, the coagulant dosage was lower than 2000 mg L⁻¹ for

1 all these three coagulants (FeCl_3 and both low-basicity PACIs). The coagulation of the
 2 smallest DCM particles that were not initially detected by the FBRM ($< 1 \mu\text{m}$) may
 3 explain why MCL decreases as the TNC increases at a dosage below 2000 mg L^{-1} . The
 4 addition of a higher dose of these coagulants resulted in the generation of enough larger
 5 particles to make MCL finally increase. In general, the coagulant dosage at which MCL
 6 remained more or less constant was higher for the trials performed at higher pH values
 7 (Figs. 2–4).

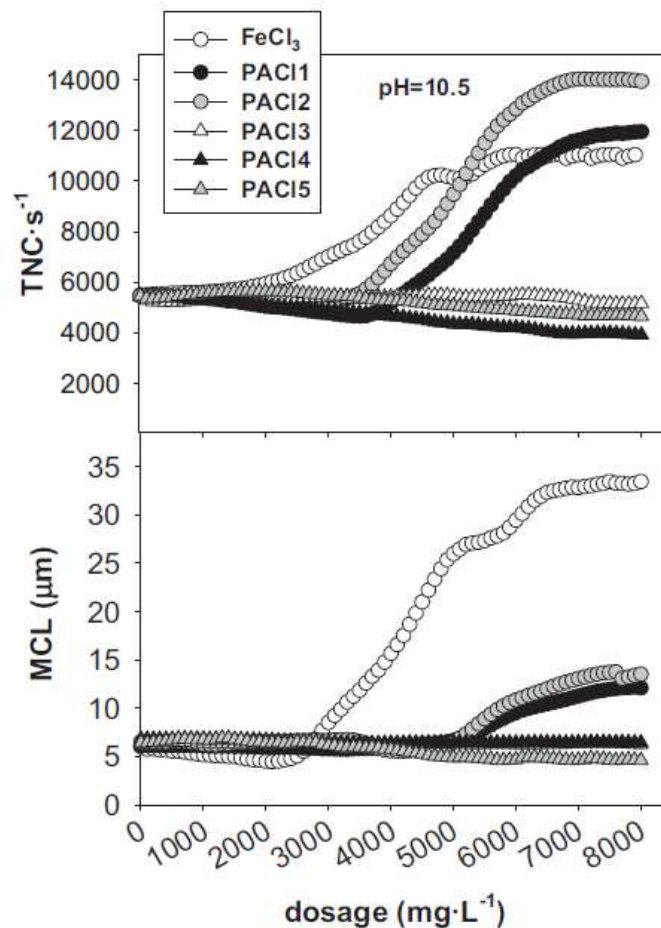


8
 9 Figure 3. Evolution of the TNC per second and MCL as the coagulant dosage increases
 10 without pH regulation (pH 8.6).

11 In contrast, the behavior of high-basicity PACIs (PACI3, PACI4, and PACI5)
 12 was totally different from that of FeCl_3 and low-basicity PACIs (PACI1 and PACI2)
 13 under alkaline conditions. MCL kept constant and TNC decreased very slightly,
 14 indicating that these coagulants did not induce a significant amount of measurable
 15 particle aggregation at these pH values. Changes in the morphology of suspended
 16 particles were, however, observed under the microscope. Coagulation phenomena took
 17 place despite the FBRM did not properly detect what occurred. Particles were
 18 aggregated linearly, generating cylindrical coagula with the same diameter than the
 19 original particles, but much longer (Fig. 5). This kind of particle aggregation slightly
 20 diminished the TNC at an increasing coagulant dosage but the shape of the aggregates
 21 did not make the MCL increase because the probability that the focal point of the
 22 FBRM probe covered these particles lengthwise was very low.

23 The decrease of the TNC due to the aggregation of measurable particles might
 24 have been compensated by the increase of the TNC caused by the coagulation of

1 particles smaller than 1 μm , thus resulting in no significant change of the TNC when
 2 more coagulant was added at pH 8.6. Coagulation of DCM $<1\mu\text{m}$ should have been
 3 predominant at pH 5.5, therefore producing an increase of the TNC and generating
 4 larger coagulated particles than the current mean coagula size which in turn results in
 5 higher MCLs. Finally, the aggregation of coagulated particles larger than 1 μm was
 6 predominant at pH 10.5, so the TNC correspondingly decreased.



7
 8 Figure 4. Evolution of the TNC per second and MCL as the coagulant dosage increases
 9 at pH 10.5.

10 As it was previously demonstrated, the addition of FeCl₃ apparently generated
 11 bigger coagula than PACIs at all tested pH values (Figs. 2–4). Photographs taken by
 12 optical microscopy indicated that FeCl₃ really produced larger and more spherical
 13 aggregates than PACIs (Fig. 5). These results agree with previous research reporting
 14 that FeCl₃ and TiCl₄ produced larger and more spherical aggregates than aluminum salts
 15 (aluminum and one PACI) [41]. They also flocculated faster, i.e., while 5 min were
 16 enough to perform an optimal coagulation by FeCl₃, 15 min were required by the tested
 17 PACI. As a result, high-basidity PACIs produced longer and more defined structured
 18 aggregates than low-basidity ones (Fig. 5), and these aggregates were able to remove a
 19 significantly higher silica content (Tab. 3).

20 The optimal doses of each coagulant at different pH conditions were considered
 21 as the non-saturating ones producing maximum TNC (Figs. 2–4). At a constant TNC,
 22 MCL may still increase due to the aggregation of smaller particles that have already
 23 been formed, but the coagulation treatment would not perform further significant
 24 removal of silica and COD. When the TNC was constant or slightly decreasing

1 regardless increasing the coagulant dosage (e.g., PACls at pH 8.6 and 10.5), the
 2 maximum dosage added to the sample was chosen to assess the efficiency of the
 3 treatment. For the same coagulant, a higher amount of silica was removed with a higher
 4 initial pH value of the solution (Tab. 3) but the required dosage of the coagulant was
 5 also much higher. In short, the best efficiencies (> 95 %) in removing the dissolved
 6 silica content were obtained after adding high doses of high-basicity PACls at pH 10.5.

Table 3. Coagulation treatment efficiency in terms of dissolved silica and COD removals, and conductivity. Letters (a–e) label heterogeneous groups of mean values by Tukey's test ($P < 0.05$; $n = 3$), as the interaction of factors resulted significant.

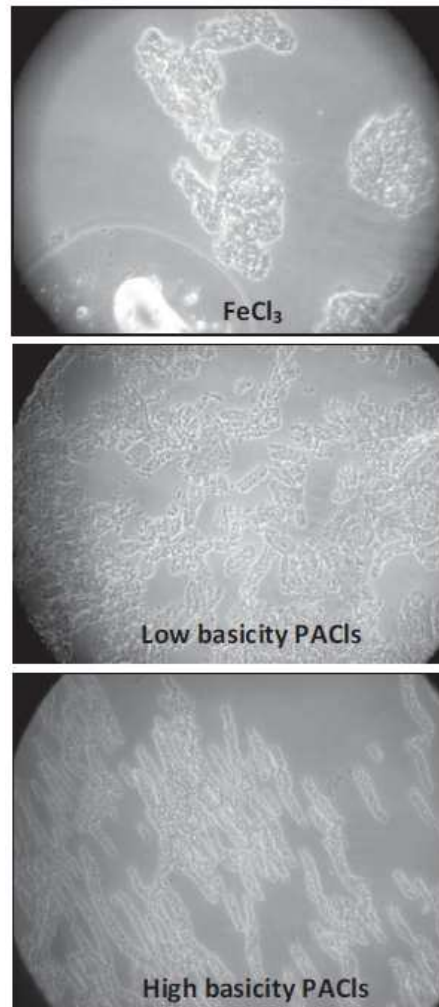
Coagulant	pH	Optimal dosage [mg L ⁻¹]	SiO ₂ [% removal]		COD [% removal]		Conductivity [mS cm ⁻¹]	
			Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
FeCl ₃	5.5	2000	17 ^e	2	77 ^{b,c}	3	4.75	0.31
	8.6	3000	25 ^{d,e}	3	87 ^a	3	4.09	1.02
	10.5	6000	27 ^{d,e}	5	85 ^{a,b}	1	6.49	0.91
PAC11	5.5	3500	32 ^{d,e}	1	64 ^{b,c,d}	6	4.20	0.76
	8.6	4000	30 ^{d,e}	3	76 ^{b,c}	1	3.93	0.98
	10.5	7000	57 ^{b,c}	4	76 ^{a,b,c}	8	6.16	1.62
PAC12	5.5	3000	41 ^{c,d}	4	63 ^{c,d}	1	4.69	1.65
	8.6	4000	38 ^{c,d}	7	75 ^{a,b,c}	8	3.99	1.17
	10.5	7000	65 ^b	1	83 ^{a,b}	6	5.16	0.39
PAC13	5.5	4500	25 ^{c,d,e}	6	72 ^{a,b,c}	7	4.81	0.33
	8.6	6000	67 ^b	7	58 ^{c,d}	1	4.35	0.23
	10.5	8000	96 ^a	1	56 ^{c,d}	5	5.09	0.06
PAC14	5.5	4500	28 ^{d,e}	1	78 ^{b,c}	1	3.98	0.95
	8.6	6000	54 ^{b,c}	6	62 ^{c,d}	2	4.65	0.36
	10.5	8000	97 ^a	1	53 ^d	1	4.95	0.65
PAC15	5.5	4000	25 ^{d,e}	5	78 ^{b,c}	1	4.01	0.78
	8.6	6000	74 ^b	5	58 ^{c,d}	2	4.49	0.33
	10.5	8000	96 ^a	1	64 ^{b,c,d}	5	5.30	0.21

7

8 Depending on the pH and the concentration of aluminum and iron in the
 9 solution, two primary coagulation mechanisms can be defined [42]: (i) adsorption of
 10 cationic-charged species onto anionic particles, neutralizing its charge and enabling
 11 their aggregation, and (ii) enmeshment or sweeping of colloids in Al(OH)₃ or Fe(OH)₃
 12 precipitates.

13 PACls hydrolyze when they are added to water, which implies the generation of
 14 monomers (Al³⁺, Al(OH)²⁺), dimers (Al₂(OH)₂(H₂O)₈⁴⁺), and polymers (Al₆(OH)₁₂⁶⁺,
 15 Al₁₃O₄(OH)₂₄(H₂O)₁₂⁺⁷). As the pH increases, the amount of these cationic species
 16 decreases, and other anionic species appear, such as Al(OH)₄⁻. The first coagulation
 17 mechanism will be active as soon as these cationic species are present in the solution.
 18 For the same coagulant dosage, the proportion of these high-valence species increases if

1 the basicity of the added PACl is higher. Therefore, chemicals with basicity values of
2 >70% (PACl3, PACl4, and PACl5) produce polymeric species with a high cationic
3 charge, among which $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{+7}$ (also known as Al_{13}^{7+}) has been reported
4 to be an especially predominant species [37]. Al_{13}^{7+} particles form aggregates whose
5 size and structure depend on its surface charge which is also pH-dependent. While the
6 charge of the aggregates is high at pH4.5 and they exhibit an open structure, the surface
7 charge is lower at higher pH values, driving the structure denser and affecting the
8 performance of coagulation [43]. As a result, the production of well-defined cylindrical
9 coagula was observed (Fig. 5).



10

11 Figure 5. Optical microscope images (20×) of particles formed after adding different
12 types of coagulant at alkaline pH.

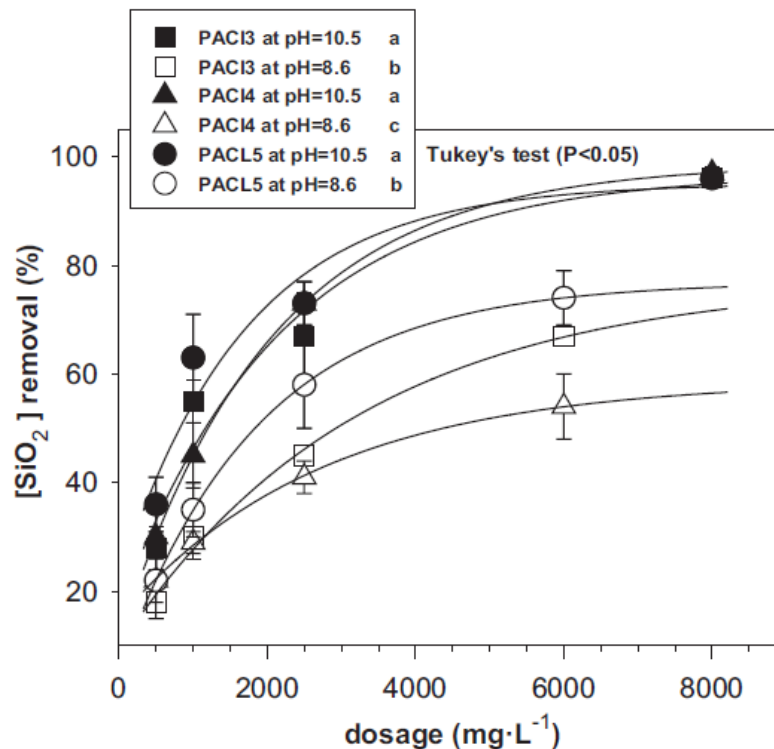
13 In addition, the presence of cationic species in the solution also decreases as the
14 pH increases, which implies that a higher amount of coagulant is required to reach
15 optimum coagulation results (Figs. 2–4). On the other hand, the coagulant concentration
16 added to the solution determines the extent of the second coagulation mechanism
17 mentioned above, so the enmeshment of the colloids will be predominant at higher
18 ratios of $Al(OH)_{3(am)}$ (a solid-amorphous state of the coagulant) to ionized species
19 contents [44]. At pH values ranging from 2.5 to 7.5, silica is present in the solution as
20 SiH_4 species, which do not have ionic charge and are unstable in aqueous solution. At a
21 pH value >7.5, the OH^- concentration increases and facilitates ionization of silicic acid
22 ($H_4SiO_4^0$) into $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ [15]. Furthermore, diverse polymeric species of

1 silica may be present in the solution (e.g., $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$ and $\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$), and,
 2 moreover, polymerization is thought to be catalyzed by hydroxyl anions as well, i.e., it
 3 is a very fast process at neutral or slightly alkaline pH values, whereas it is retarded
 4 under acid environments [45]. As a consequence of these ionization and polymerization
 5 processes, a higher amount of silica may be removed by higher-basicity PACls under
 6 basic condition, even more when they contain micropolymers.

7 On the other hand, the behavior of FeCl_3 is very different. When FeCl_3 is added
 8 to water at natural bicarbonate alkalinity, $\text{Fe}(\text{OH})_3$ precipitate is generated and coexists
 9 with other hydrated species like Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, and $\text{Fe}(\text{OH})_2^+$, although the
 10 concentration of these cationic species is reduced when the pH is >8.0 [44].

11 In order to reduce scaling potential hazard, the concentration of silica in feed
 12 water must be reduced below its saturation limit ($\approx 120\text{mg L}^{-1}$), thus membranes could
 13 work at a recovery rate higher than 85% without problems due to silica precipitation.
 14 The coagulant doses required to achieve the best silica removal are too high to be
 15 feasible at industrial scale. Therefore, additional experiments were performed at pH
 16 values of 8.6 and 10.5 using lower doses of high-basicity PACls

17 ($500\text{--}2500\text{ mg L}^{-1}$) aiming to assess if good silica reductions could be achieved
 18 as well (Fig. 6). These experiments also enabled the performance of further comparisons
 19 among coagulation efficiencies at different dosages.



20
 21 Figure 6. Silica removal using different doses of high-basicity PACls ($> 70\%$) at basic
 22 pH (letters label homogeneous groups among maximum silica content removal values
 23 by Tukey's test; $P < 0.05$; $n = 3$).

24 As a result, the silica content was reduced up to 65–75% using 2500 mg L^{-1} of
 25 these high-basicity PACls at pH 10.5 (Fig. 6), thus ensuring that the RO system may
 26 work safely if a recovery rate higher than 50% is pretended. The main drawback of
 27 performing these coagulation treatments increasing the pH value of the solution is that
 28 the conductivity also increases (Tab. 3). Current legislation of the Region of Madrid sets

1 a maximum limit of 7.5mS cm^{-1} for the conductivity of industrial effluents that are
2 going to be discharged into municipal water lines [46], a consideration that has to be
3 also taken into account when setting the recovery rate of RO units in this case.

4 If high-basicity PACls are added at the same lower concentrations, but without
5 regulating the pH in the solution, thus avoiding the increase of conductivity, a 60%
6 silica content was removed when adding 2500 mg L^{-1} of PACl5, while PACl3 and
7 PACl4 removed only about 40% at this dosage (Fig. 6). These results are, however
8 better than the best efficiencies achieved by even higher doses of low-basicity PACls
9 and FeCl_3 ($3000\text{--}4000\text{ mg L}^{-1}$; Tab. 3). Coagulated particles were analyzed by SEM-
10 EDX, with their main components found as aluminum, oxygen, and silica (Tab. 4). The
11 percentage of the silica content was slightly higher in the particles formed using PACl5.

Table 4. Atomic composition (SEM-EDX) of the coagulated particles formed using high-basicity PACls.

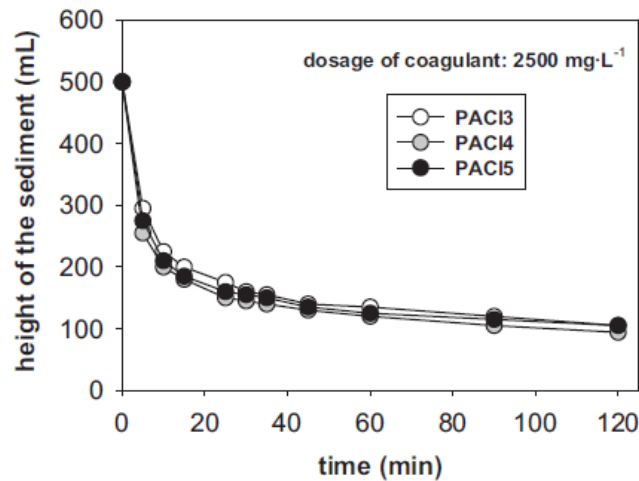
Element	Atomic composition [%]		
	PACl3	PACl4	PACl5
O	55	58	50
Al	35	30	36
Si	8	10	12
Cl	1	1	1
Ca	1	1	1

12
13 The results clearly indicated that a similar dosage of high-basicity PACls
14 significantly removes more silica than low-basicity ones at under basic pH conditions
15 (Tab. 3). The size and structure of the aggregates is different by the effect which the pH
16 exerts on its surface charge, affecting the performance of coagulation [43]. In addition,
17 the presence of cationic species is lower at higher pH values. As a consequence of a
18 higher presence of polymerized species, the removal of silica was improved using high-
19 basicity coagulants, whether by increasing its dosage without modifying the pH or by
20 increasing the pH value of the solution while keeping the same coagulant dosage (Fig.
21 6).

22 The final objective of reaching high silica removal results must be balanced with
23 a good sedimentation velocity, which is related to the area of the clarifier needed to
24 separate the slurry from the clarified water. Sedimentation capacity was also measured
25 for PACl3, PACl4, and PACl5 after coagulating the samples with 2500 mg L^{-1} of each
26 product at pH 8.6. The sediment compacted more than 300mL after 15 min (Fig. 7),
27 which is considered as a high sedimentation velocity [47]. Most of the sediment was
28 close to be totally compacted after 1 h.

29 More than 50% of the COD was removed by all considered coagulants at all
30 tested pH values (Tab. 3). In general, a significant significant higher removal of the
31 COD was achieved when the formed aggregates were more spherical (Fig. 5), and, in
32 particular, when a lower silica content was removed from the solution within the trials
33 performed using high-basicity PACls (Fig. 8). Higher pH values enabled higher doses
34 of these coagulants to achieve the highest reductions of silica content despite pulling
35 down the removal of COD. Good reductions of both silica content and COD could be,

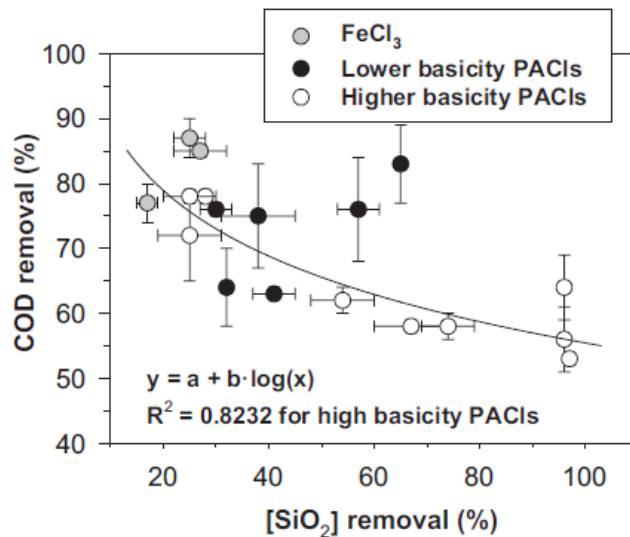
1 however, achieved together in some cases.



2

3

Figure 7. Sedimentation velocity after adding 2500mgL^{-1} of high-basidity PACIs.



4

5

Figure 8. COD and SiO₂ removal for high-basidity PACIs.

6

7 4. Conclusions

8

pH modification to increase the solubility of silica is not recommended whenever there is a risk of carbonate scaling. In such case, coagulation represents a feasible alternative for removing the silica content. The efficiency of the selected coagulants on the reduction of silica content was related to the structure of the formed particles rather than to the size of the aggregates or to DCM destabilization to form larger coagula. Cylindrical particle morphologies were identified to be formed in the cases achieving higher silica removal efficiencies. The use of FeCl₃ induced the formation of the largest and most spherical aggregates, resulting in the achievement of the highest COD removal and the lowest silica removal values (< 30 %).

17

A high silica removal efficiency (> 90 %) was obtained by performing coagulation treatments with high-basidity PACIs (PAC13, PAC14, and PAC15) increasing the pH of the final paper mill effluent up to 10.5, although the required

19

1 coagulant doses were very high. Furthermore, the conductivity of the solution increased
2 as well, which represents another potential limitation for water recovery from RO
3 systems.

4 About 60% reduction of the silica content of wastewater was achieved using
5 2500 mg L⁻¹ of one high-basicity PACl without regulating the pH. This coagulant is
6 characterized by its high basicity value (85 %) and its content of micropolymers. All
7 coagulants achieved reductions in COD > 50% at all tested pH values, although high-
8 basicity PACls tended to decrease their COD removal efficiency at higher pH and
9 dosage, achieving in contrast an almost total removal of the silica content

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18
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21 **Symbols used**

22 COD: [mg L⁻¹] chemical oxygen demand

23 MCL: [μm] mean chord length

24 T: [°C] temperature

25 **Abbreviations**

26 DCM: dissolved and colloidal material

27 FBRM: focused beam reflectance measurement

28 FIA: flow injection analysis

29 PACls: polyaluminum chlorides

30 RO: reverse osmosis

31 SEM-EDS: scanning electron microscopy-energy dispersive X-ray spectroscopy

32 TNC: total number of counts

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