INFLUENCE OF SUSPENDED SOLIDS ON SILICA REMOVAL BY COAGULATION WITH ALUMINUM SALTS

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Effluents with high silica content can exceed the discharge limits and/or limit the application of reuse treatments based on reverse osmosis membranes. In these cases, silica removal is usually carried out in the effluent by coagulation. In this work, silica is removed from process waters in dissolved air flotation (DAF) units used as internal treatments. It is hypothesized that the presence of a high content of small suspended solids and colloids in DAF units should favour the rate of precipitation of $Al(OH)_3$ and the orthokinetic flocculation, thus the removal efficiency of contaminants. Results confirmed that the coagulant required for silica removal in the process water is 20-50% lower than in the effluent, especially in DAF2, where the amount of suspended solids is higher and their size is smaller. If the main aim is silica removal, the most efficient coagulants are PAC-HB in DAF1 and PAC-MB in DAF2. If a simultaneous high removal of turbidity and soluble COD is required, the recommended treatment is PANS-PA2.

Keywords: dissolved air flotation, silica, papermaking, coagulation, aluminium

INTRODUCTION

The paper industry is a large consumer of fresh water, being the reduction of water useanissue of growing importance due to the stringent environmental legislation, the increase in water prices, the treatment costs, or simply due to the lack of water resources.[1-4]

The internal reuse of process water after the treatment with dissolved air flotation(DAF) units is the most common alternative used to reduce the fresh water consumption. In recycled newsprint mills, there are up to three or four DAF units in each production line (one in each water loop). In these units, suspended solids are easily removed, but dissolved and colloidal material (DCM) is almost completely recirculated into the process, accumulating in the water circuits, and thus limiting the degree of closure treatment.[5] However, with an adequate coagulation and flocculation, DAF units can also remove finely dispersed and colloidal particles (>0.1-0.2 µm).[6] Dual systems allow the removal of 80-99% suspended solids and, in the best cases,10-30% of soluble COD.[7-10] Inorganic contaminants are usually not removed in DAF units, in fact, the conductivity of the treated waters is normally higher than before the treatment, especially when metal coagulants are used.

A variety of coagulants can be used in DAF systems, including alum, ferric chloride, poly aluminum chloride (PAC), polyamine (PA), poly diallyldimethyl ammonium chloride (PDADMAC), etc. Among them, aluminum based coagulants are probably some of the most versatile and widely used. In addition to alum, many types of polyaluminum coagulants are commercially available for water treatment, such as PAC, aluminium chlorohydrate and poly aluminum sulfates. These products differ in their basicity and strength, and can contain small amounts of other substances, such as sulphate, nitrate, silica and calcium.[11] Furthermore, poly aluminum based coagulants can be combined with cationic polyelectrolytes, such as PA or PDADMAC, in hybrid coagulants to improve their efficiencies.[9,12-13]

Silica is one of the most important salts accumulating in papermaking water circuits. The main origin of silica is the sodium silicate added as process additive for improving thedeinking and bleaching processes, which are the most important

stages to achieve the optical properties required for producing graphic papers.[14] Some attempts have been carried out to replace it,[15,16] however, its variety of functions and low price make it very difficult. There are three main problems derived from high silica contents in the process waters. First, the deposit formation, especially in paper mills with highly closed water circuits, where typical levels are around 150-250 mg/L SiO_2.[17-19] Second, the discharge limit for the effluent set by environmental legislation for silica is more and more stringent, *i.e.* 50 mg/L in Finland, Canada or United States.[18] Finally, reclamation and reuse of the final effluent is an emerging technique to further reduce the fresh water consumption and even substitute it completely. In this case, reverse osmosis (RO) membranes are usually included as a final step to achieve the high quality water necessary to replace fresh water use at critical points of the process. In these cases, silica scaling limits RO recovery to a maximum of a 20%, thus limiting the economic and technical feasibility of the effluent reuse treatment.[3]

Although a great variety of techniques have been used for silica removal, the most common ones are the softening process or the coagulation at high pH.[18,20-26] These techniques obtain high removal efficiencies at low costs, which is a prerequisite to be used in the paper industry. A high initial hardness content, especially magnesium hardness, is usually required for silica removal by softening to avoid the addition of calcium and magnesium salts, which would significantly increase the dissolved solids of the treated waters and also the costs.[25,27] In these cases, but not restricted to them, coagulation is an attractive silica removal technique.

Previous studies have demonstrated that silica removal in the effluent requires high dosages of coagulants and high pHs to achieve the silica removal rates required to avoid silica scaling on RO membranes.[19,23] Without pH regulation (pH 8.3), the removal of silica in the effluent was always lower than 50%, even with the most efficient products at the highest dosage tested (2500 mg/L). This turns to an average of 25-40 mg coagulant per mg SiO_2 removed.[19] Since the effluent has a very low suspended solids content, the rate of precipitation of $Al(OH)_3$ could be improved at higher concentration of small suspended solids and colloids as they can act as nuclei for the formation of $Al(OH)_3$ precipitates.[28] Therefore, it is hypothesized that the coagulant demand, mg of coagulant per mg SiO_2 removed,

would be lower in the inlet of DAF units (with higher suspended solids levels of small size and colloids) than in the effluent. In addition, silica removal in the inlet DAF streams would also contribute to obtaining cleaner water loops and would require less investment (existing DAF units are used).

Therefore, the approach presented in this study is different from previous studies as the objective is to remove silica using two existing DAF units by optimizing their coagulation chemistry with different aluminium based coagulants. In addition, it would be of major importance to determine if in these process streams, due to the high concentration of suspended solids and colloids, it is possible to achieve higher removal of silica per mg of coagulant used, as the dosages required for silica removal in the effluent have been previously determined to be very high, especially at neutral pHs.

EXPERIMENTAL
Materials
Waters

Water samples were taken from the inlet of two DAF units of a newsprint mill, named DAF1 and DAF2. The main characteristics of these waters are shown in Table 1. Additionally, Figure 1 shows the chord size distribution of the waters, measured by the focused beam reflectance measurement (FBRM) technique (1-1000 µm size range), and Table 2 summarizes the main statistics related to the number and size of suspended particles.

Although the level of total solids (TS) and total dissolved solids (TDS) is not very different in both DAF units, there are important differences in terms of total suspended solids (1620 mg/L in DAF1 and 3350 mg/L in DAF2) and their size (see Figure 1). In DAF2, the mean chord size and median chord size of suspended particles are 10.4 µm and 7.1 µm, respectively. Furthermore, 65.3% of the suspended particles are lower than 10 µm and 87.0% lower than 20 µm (Table 2). However, the suspended solids are larger in DAF1: 43.7 µm mean chord size and 34.4 µm median chord size. This higher amount of suspended solids and their lower size result in a considerably higher turbidity in DAF2 waters than in DAF1 waters.

Coagulants

Table 3 summarizes the main properties of the six aluminium coagulants tested. Alum ($Al_2(SO_4)_3 \cdot 18H_2O$), reagent grade, was supplied by Panreac. PAC-MB is a conventional polyaluminum chloride with high aluminum content and intermediate basicity (16.8% Al_2O_3, 37% basicity), supplied by Sachtleben Wasserchemie GmbH, while PAC-HB is a high basicity polyaluminum chloride with intermediate

aluminium content (9.7% Al_2O_3, 85% basicity) with a small amount of silica, supplied by Kemira Ibérica S.A.PANS is a polyaluminum nitrate sulphate with intermediate aluminum content and intermediate basicity (10.2% Al_2O_3, 46% basicity), having a 16.0% NO_3^- and 3.0% SO_4^{2-} contents, and PANS-PA1 and PANS-PA2 are two derivatives obtained by the addition of different dosages of a high charge density and low molecular weight quaternary polyamine to PANS; all these three coagulants were supplied by Sachtleben Wasserchemie GmbH. The active content in PANS-PA1 is around three times lower than in PANS-PA2. All the coagulants were tested in combination with an anionic polyacrylamide of high molecular weight and medium charge used as flocculant, supplied by SERTEC-20 S.L. (Spain).

PANS-PA1was included in the tests with DAF2 waters after the good results obtained by PANS-PA2 with DAF1 waters, to determine if it was possible to reduce the cost of this hybrid coagulant by reducing the polyamine active content.

In DAF1, the dosages of the coagulants were selected according to preliminary tests, varying from 25 to 250 ppm Al_2O_3. As the dosages of the coagulants in terms of commercial products were very different, in the second study all the products were tested at the same dosages of commercial products (100-1250 mg/L), independently of their aluminium content. For a better comparison between the studies, the commercial product dosage has always been used for the discussion of the results.

Table 1
Characteristics of DAF1 and DAF2 inlet waters and DAF1 and DAF2 blanks

	DAF1 inlet	DAF2 inlet	DAF1 blank	DAF2 blank
pH	6.9	7.7	6.8	7.6
Conductivity (25 ºC) (mS/cm)	2.62	2.13	2.12	1.74
Total solids (mg/L)	5520	6590	3394	3520
COD (ppm)	3665	3310	2332	2420
Total suspended solids (mg/L)	1620	3350	183	930
Turbidity (NTU)	680	2400	268	1850
Cationic demand (meq/L)	1.16	1.28	0.99	1.00
Total alkalinity (ppm $CaCO_3$)	856	1425	645	1020
After centrifugation				
Total solids (mg/L)	3898	3240	3211	2590
Dissolved silica (mg/L SiO_2)	273	240	225	200
Dissolved COD (ppm)	2600	2285	2010	1876
Dissolved turbidity (NTU)	21.8	89	18.0	76

Table 2
Average chord sizes of the particles in the raw waters: DAF1 *vs*. DAF2

	DAF1		DAF2	
Mean chord size (1-1000 µm) (µm)	43.7		10.4	
Median chord size (1-1000 µm) (µm)	34.4		7.1	
		%		*%*
Number of particles (1-5 µm) (#/s)	234	10.7	633	33.2
Number of particles (5-10 µm) (#/s)	240	11.0	613	32.1
Number of particles (10-20 µm) (#/s)	282	12.9	413	21.7
Number of particles (20-29.3 µm) (#/s)	213	9.7	160	8.4
Number of particles (29.3-50.1 µm) (#/s)	451	20.6	71	3.7
Number of particles (50.1-100 µm) (#/s)	574	26.3	14	0.8
Number of particles (100-199.5 µm) (#/s)	183	8.4	2	0.1
Number of particles (199.5-1000 µm) (#/s)	11	0.5	0	0.0
Total number of particles (1-1000 µm) (#/s)	2188	100.0	1906	100.0

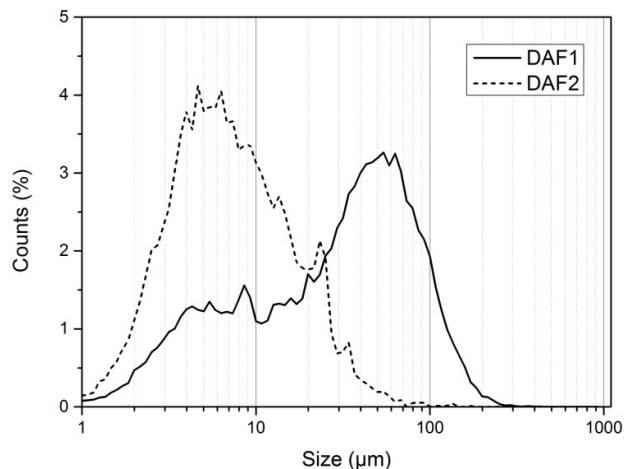Figure 1: Chord size distribution of DAF1 and DAF2 waters

Table 3
Characteristics of the coagulants used in this study

Coagulant	Al_2O_3 (%)	Basicity (%)	Charge density (meq/g)	Density (g/cm^3)	pH	Dry content (%)
Alum	15.3	0	-	-	-	-
PAC-MB	16.8	37	1.77	1.37	< 1	34.1
PAC-HB	9.7	85	1.67	1.22	2.7	29.5
PANS	10.2	46	1.22	1.27	2.6	21.7
PANS-PA1	8.8	-	1.68	1.26	2.0	21.3
PANS-PA2	6.05	-	2.57	1.23	3.0	20.4

Methodology
DAF tests

Experiments were carried out in a lab-scale DAF unit (Flottatest FTH3) supplied by Orchidis Laboratoires. A sample volume of 1 L was used in all the cases. In these tests, first the coagulant was added to the sample from a 10% wt/vol solution and mixed at high speed (180 rpm) during 2.5 min. Next, the flocculant was added from a 0.10% wt/vol and mixed at slow speed (40 rpm) for 10 min. Finally, a 20% tap water (200 mL) saturated in air at 7 bar was added, and after 10 min flotation time, samples were collected from the bottom of the jars.

A number of blanks for each DAF waters were carried out without adding any chemical, to consider the dilution of the samples due to the addition of air-saturated water during flotation (20%) and the physical efficiency of the DAF (without any chemicals). The average values for these blanks are referredto as 0 mg/L dosage and their characteristics are summarized in Table 1. All the experiments were carried out at room temperature (20-25 ºC) by duplicate, and the average error between replicates was around 5%. To avoid the possible degradation of the waters, all trials and analyses were carried out within five days after the sampling and the waters were always kept at 4ºC before use.

The different treatments were evaluated for turbidity, total solids, chemical oxygen demand (COD), cationic/anionic demand, alkalinity, pH and conductivity in the clarified waters, and turbidity, silica, total solids and sulphates in the dissolved fraction of clarified waters. The dissolved fraction was obtained after centrifugation of clarified waters at 2000 g during 15 min in a Universal 32 centrifuge (Hettich Zentrifugen GmbH). Total solids and turbidity were measured according to Standard Methods 2540B and 2130B, respectively,[29] using a Hanna LP-2100 turbidimeter for turbidity. COD was measured by the Nanocolor® COD 1500 method from Macherey-Nagel GmbH, using an Aquamate Vis spectrophotometer (Thermo Scientific Inc.), according to ISO 15705:2003. Cationic/anionic demand was measured by colloidal titration using a Charge Analyzing System (CAS) supplied by AFG Analytic GmbH and poly-diallyldimethylammonium chloride (PDADMAC

(0.001 N) and polyethylene sulfonic acid sodium salt (PES-Na) (0.001 N) as titrants, depending on the sample charge. Silica was measured by ISO standard 16264:2002 "Water quality – Determination of soluble silicates by flow analysis (FIA and CFA)". In this method, silica reacts with molybdate under acidic conditions to form yellow beta-molybdosilic acid; this acid is subsequently reduced with stannous chloride to form a heteropoly blue complex that has an absorbance maximum at 810 nm. Total alkalinity was measured by titration of the sample to pH = 4.5 with H_2SO_4 0.1 N, using an automatic titrator (Compact I model, supplied by Crison) connected to a pH probe, according to EPA 310.1 method. Sulphates were measured by the Nanocolor® Sulphate 200 or Sulphate 1000 methods from Macherey-Nagel GmbH, using an Aquamate Vis spectrophotometer (Thermo Scientific Inc.). Finally, the pH and conductivity of the samples were analyzed using a GLP-22 pH-meter and a GLP-32 conductivity meter (both supplied by Crison Instruments, S.A.).

RESULTS AND DISCUSSION
Removal of contaminants
Turbidity and solids

DAF1waters had a turbidity of 680 NTU. DAF1 blank, without chemicals, had a turbidity of 268 NTU (60.6% removal, including the 20% removal due to the dilution of the raw waters with water saturated in air). This indicates the size of suspended solids is large enough to be significantly removed without the addition of any chemical.The addition of 10 mg/L flocculant further reduced the turbidity to 196 NTU (71.2% removal referred to raw waters, 27% removal referred to blank). When coagulants were used, turbidity removal increased continuously with the dosage up to around 1500 mg/L, with only marginal increases at higher dosages (Figure 2a). While PANS-PA2, PAC-HB and PANS decreased turbidity to a maximum of 55-60 NTU

(80-85% removal) at around 1500 mg/L, alum and PAC-MB decreased turbidity to a maximum of 80-90 NTU (65-70% removal), at around 1000 mg/L. Dissolved turbidity (data not shown) also decreased at higher dosages of coagulant, with no significant differences at dosages higher than around 1000mg/L. In this case, PANS-PA2, PAC-HB and PANS decreased the dissolved turbidity from around 22 NTU to 9.5-10.5 NTU (50-60% removal), while in the case of alum and PAC-MB, the minimum dissolved turbidity obtained was around 10 NTU (alum) and 13.5 NTU (PAC-MB).

In the case of alum and PAC-MB, an increase in turbidity and dissolved turbidity was observed at dosages >1000 mg/L, indicating that restabilization by charge reversal could have taken place. Although alum and PAC-MB werethe products with the highest aluminum content (15.3-16.8% Al_2O_3), the same aluminum dosages were tested for all the coagulantsand this effect was not observed for any of them. The explanation of this behavior is related to the higher pH decrease after the treatment with these coagulants due to their low basicities (final pH around 5.4 for alum and 6.0 for PAC-MB). The pH of minimum solubility of $Al(OH)_3$, which produces the larger amount of $Al(OH)_3$ precipitates and the lower residual aluminum concentration, is around 6.0 for alum and 6.2-6.4 for PACs.[30] For these reasons, the lower pH at which aluminum salts can be used is limited to around 5.5-5.8, depending on the temperature and the presence of other species, *i.e.* sulphates, phosphates, etc.[31] In these industrial waters, this pH limit seems to be slightly lower: around 5.8 for alum and 6.0 for PAC-MB.
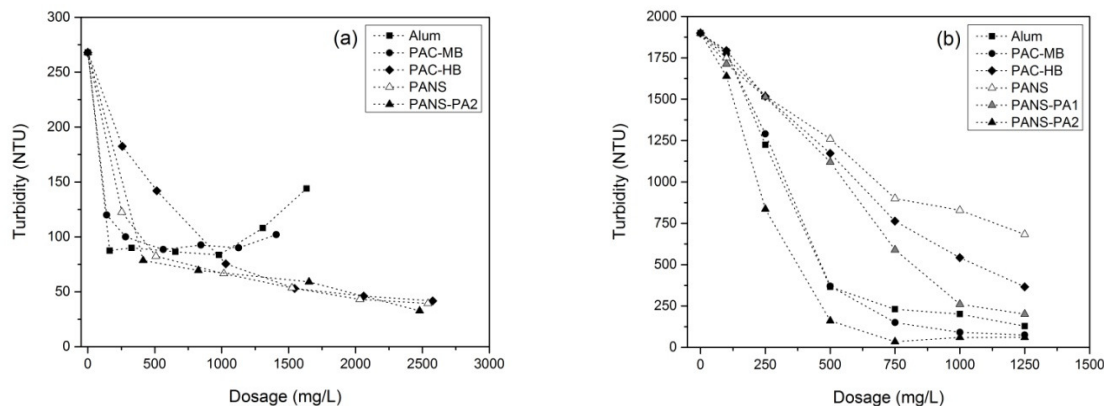

Figure 2: Turbidity of clarified waters from (a) DAF1 and (b) DAF2 *vs.* dosage of coagulants

Although around 50% of total solids were suspended solids in DAF2 waters, these suspended solids had a very small size to be efficiently removed without any previous coagulation, especially for a DAF laboratory cell with worse hydrodynamics than industrial DAF units. Without chemicals or using only flocculant, there was no significant removal of turbidity, the decrease in turbidity from 2400 NTU (inlet DAF2 waters) to 1850 NTU (DAF2 blank) or 1750 NTU (DAF2 with 10 mg/L flocculant), was mainly justified by the 20% saturated in air-tap water used for flotation. However, aluminium salts resulted to be very efficient in reducing turbidity (Figure 2b). The most efficient products were PANS-PA2, PAC-MB and alum. At the highest dosages of these products, the turbidity of the clarified waters could be reduced to 60-120 NTU (93-97% removal) and even at intermediate dosages, i.e. 500 mg/L, 90% removal could be achieved (150-350 NTU residual turbidity). On the other hand, PANS and PAC-HB were the lowest efficient products, with turbidity removals varying in the range 65-80% (350-700 NTU residual turbidity), even at 1250 mg/L dosage. The efficiency of PANS-PA1 was intermediate. The dissolved turbidity in DAF2 waters was not reduced by DAF without previous coagulation (data not shown). The dissolved turbidity of the blank and after adding 10 mg/L of flocculant (both 76 NTU) was practically the same as the dissolved turbidity of the raw waters (89 NTU) after considering the 20% dilution with tap water. When coagulants were used, the most efficient products were again PANS-PA2, PAC-MB and alum, reducing dissolved turbidity to 5-10 NTU (≈90% removal). The other products had similar efficiency, which was very low compared to the previous three coagulants; dissolved turbidity is 25-50 NTU (35-70% removal).

Comparing DAF1 and DAF2 treatments, the optimum ones for the removal of turbidity were opposite. In DAF1, the coagulants with the highest basicities (PAC-HB and PANS) plus PANS-PA2 were the most efficient, independently of their aluminium content. However, in DAF2, the most efficient products werethose with the highest aluminium content (PAC-MB and alum), which were the least efficient coagulants in DAF1, and again PANS-PA2. In principle, at the same commercial dosage, PAC-MB and alum could produce a larger amount of $Al(OH)_3$, thus a higher removal of contaminants. Nevertheless, in DAF1, the pH wasthe most critical parameter, and due to the lower basicity of these products, a large pH decrease was observed, which impaired its efficiency due to the rapid increase of solubility of aluminium at pH values lower than 5.8-6.0. On the other hand, PANS-PA2 wasthe coagulant with the lowest aluminium content but including a polyamine in its composition, which also contributes to the destabilization of the contaminants. The combination of PANS with polyaminewasvery efficient in reducing turbidity independently of the water tested.

Similar conclusions could be obtained from the analysis of total and dissolved solids of the clarified waters from DAF1 and DAF2 waters (data not shown). In DAF1, PANS-PA2 and PAC-HB reduced total solids from 3.39 g/L of the DAF1 blank to 3100-3150 mg/L, which means around 10% TS removal and 3% TDS removal (TDS in DAF1 blank is 3210 mg/L). Although PANS-PA2 and PAC-HB increased the level of inorganics in waters due to their inorganic nature (a higher final conductivity in treated waters was observed), final TDS were lower than the DAF blank as they also removed an important amount of DCM. On the other hand, PAC-MB and PANS-PA increased slightly the total dissolved solids, indicating a lower removal of DCM. Finally, alum increased up to 8% the TDS due to the important amount of sulphates released to waters, however, some DCMwas removed as the increase in TDSwaslower than expected by the sulphates content in alum (540 mg/L sulphates at 1250 mg/L alum dosage).

In DAF2 waters, higher solid removals for similar levels of total and dissolved solids were achieved. Even the DAF blank achieved an important removal of suspended solids, from 3.35 g/L to 0.93 g/L (72.2% removal), although only a 22.9% removal of turbidity was achieved. This apparent controversy could be explained because in DAF blank the biggest size particles were removed predominantly, which contributes most to the total weight of suspended solids, while the smallest size particles, contributing less to the total weight of suspended solids, but being the main origin of turbidity, were not removed. In DAF2 waters, the most efficient products were PANS-PA2 and PAC-MB (2200-2300 mg/L). PANS-PA2 removed 38% TS and 15% TDS, while PAC-MB removed 35% TS and around 10% TDS. The next products in terms of efficiency were PANS-PA1, PAC-HB and alum, with TS ranging between 2.55-2.67 g/L (24-30%

TS removal) and almost no removal of dissolved solids (TDS in DAF2 blank is around 2.59 g/L). As occurs in DAF1, if the sulphates theoretical release were subtracted to final TS, the TDS would be around 1.99 g/L, i.e. 23% dissolved solids removal, a value that is in agreement with the high turbidity and dissolved turbidity removals obtained.

Silica

Without coagulation treatment, silica was not removed at all by DAF. The 20% reduction of silica in DAF1 and DAF2 blanks (225 and 200 mg/L SiO_2, respectively), compared to the raw waters (273 and 240 mg/L SiO_2, respectively), was caused by the dilution of the sample after the addition of water saturated in air during the flotation process. Similar results were obtained when adding 10 mg/L flocculant (223 mg/L SiO_2 in DAF1 and 197 mg/L in DAF2). The use of aluminum salts increased significantly the removal of silica (Figure 3). As shown, there was a continuous improvement of silica removal with the coagulant dosage, independently of the coagulant tested, similar to what was observed for COD.

In the treatment of DAF1 waters, only small differences among the coagulants were observed, the main difference was observed between PAC-HB and PANS-PA2 (the most efficient coagulants) and PANS (the least efficient coagulant). PAC-HB and PANS-PA2 obtained 27-28% removal at around 1500 mg/L (residual 162-164 mg/L SiO_2) and 37-41% at around 2500 mg/L (residual 133-142 mg/L SiO_2). On the other side, PANS obtained an 18% removal at around 1500 mg/L (184 mg/L SiO_2) and 35% removal at around 2500 mg/L (residual 154 mg/L SiO_2). The other coagulants (alum and PAC-MB) achieved intermediate removal efficiencies, around 22% at 1500 mg/L (residual 175 mg/L SiO_2). According to silica removal rates, the following ratios (mg of coagulant required per mg of SiO_2 removed) were obtained (0-1500 mg/L): 25 for PAC-HB, 27 for PANS-PA2, 28 for PAC-MB, 29 for alum and PANS-PA2, and 37 for PANS.

For the treatment of DAF2 waters, PAC-MB, alum and PANS-PA2 were the most efficient products, achieving a maximum of 30-35% removal (residual 130-140 mg/L SiO_2) at 1250 mg/L. The other coagulants (PANS, PANS-PA1 and PAC-HB) obtained similar efficiencies, varying in the 20-25% range (residual 150-160 mg/L residual SiO_2) at the same dosage 1250 mg/L. In this case, the following ratios (mg of coagulant per mg of SiO_2 removed) were obtained (0-1250 mg/L): 19-20 for alum, PAC-MB and PANS-PA2 and 26-29 for PANS, PAC-MB and PANS-PA1.

In general, the higher the aluminum content, the higher the possibility of producing larger amounts of $Al(OH)_3$ precipitates, therefore, the higher the efficiency ofthe sweep flocculation mechanism. This was also observed by Chuang *et al.*[21] for the treatment of brackish water where the silica removed by mg of aluminum both for alum and a PAC was the same.
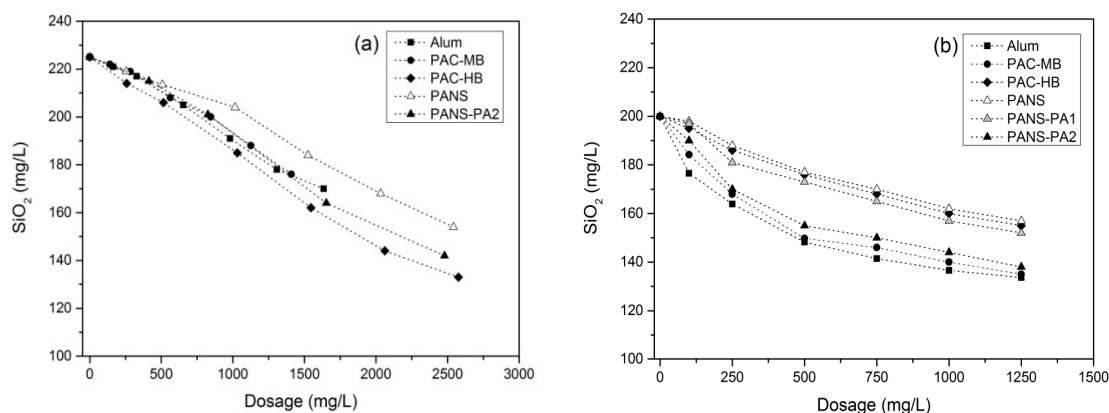

Figure 3: Soluble silica of clarified waters from (a) DAF1 and (b) DAF2 *vs.* dosage of coagulants

Although the consumption of alkalinity washigh and similar pH decreases after coagulation were obtained in DAF2 compared to DAF1, the initial pH in DAF2 washigher, therefore, virtually all the coagulants work under the best conditions and there is a low amount of silica ionized. For this reason in DAF2, the most efficient products were alum and PAC-MB, the coagulants with the highest aluminum content (15.3-16.8% Al_2O_3), and PANS-PA2, the coagulant with the lowest aluminum content (6.0% Al_2O_3), but with the highest active content of polyamine in its formulation, which compensated for the lower aluminum content. The least efficient products, PANS and PAC-HB, were the coagulants with the lowest aluminum content (9.7-10.2% Al_2O_3) and finally, PANS-PA1 was slightly more efficient than PANS due to the PA addition, however, still far from PANS-PA2 due to their lower active content.

In DAF1 waters, however, differences in silica removal werenot correlated with the aluminum content of the coagulants. For example, the most and the least efficient coagulants had similar aluminum contents (9.7% Al_2O_3 for PAC-HB and 10.2% Al_2O_3 for PANS), and these aluminum contents were intermediate among the coagulants tested. In this case, the most important factor in silica removal was the final pH of the treated waters and it was more affected by the basicity than by the aluminum content of the coagulant. It is important to notice that the most efficient product in the removal of silica for the treatment of DAF1 waters (PAC-HB) was the less efficient for the removal of silica in DAF2 waters. The reason is that a low pH decrease is not critical in DAF2 waters (higher initial pH and higher initial

alkalinity), then the aluminum content became more important (9.7% Al_2O_3 of PAC-HB vs. 15.3-16.8% Al_2O_3 for alum and PAC-MB). As commented earlier, the products with lower basicities (alum and PAC-MB) obtained a lower efficiency in DAF1 due to the rapid increase of solubility of aluminum at pH values lower than 5.8-6.0.

Soluble COD

Soluble COD was not removed by DAF1 without coagulants or using only flocculant, the value of 2050 ppm (around 20% lower than DAF1 inlet waters) could be entirely explained by the dilution of the waters in flotation. For all the coagulation treatments, the higher the coagulant dosage, the higher the COD removal, up to around 1500 mg/L (Figure 4a). The most efficient products were PAC-MB, alum and PANS-PA2. They achieved a maximum reduction of soluble COD in the range 19-21% (final soluble COD 1580-1615 ppm). PANS and especially PAC-HB showed lower efficiency in the removal of soluble COD: 13% removal for PANS (1675 ppm) and 6% removal for PAC-HB (1890 ppm).

The same occurred when the inlet DAF2 waters were treated without chemicals or only 10 mg/L flocculant. No removal of soluble COD was achieved (1876 ppm soluble COD). PANS-PA2 and PAC-MB are the most efficient products, removing 28% and 24% of soluble COD, respectively, at 1250 mg/L (Figure 4b). Next, alum and PANS-PA1 had similar efficiency (20% removal soluble COD). Finally, the least efficient products (PAC-HB and PANS) achieved 9-12% soluble COD removal.
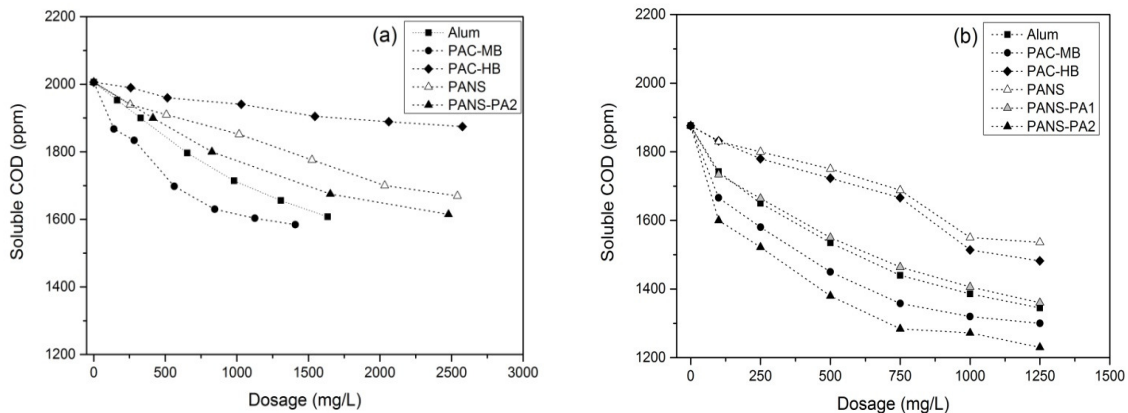

Figure 4: Soluble COD of clarified waters from (a) DAF1 and (b) DAF2 *vs.* dosage of coagulants

Comparing DAF1 and DAF2, the maximum removals of soluble COD in DAF2 were higher than in the case of DAF1 (24-28% *vs*. 20%). The most efficient products in silica removal in DAF1 waters were the least efficient in removing COD, *i.e*. PAC-HB (6% soluble COD removal). In DAF2 waters, however, alum and PAC-MB still had intermediate soluble COD removals. Finally, PANS-PA2 was the only coagulant that maintained a high removal of soluble COD even for high silica removals (20% in DAF1 waters and 28% in DAF2 waters).

Cationic demand

Both DAF1 and DAF2 blankshave similar cationic demand (around 1.0 meq/L) and neither DAF without chemicals nor the addition of 10 mg/L flocculant reduced the cationic demand more than the 20% expected due to the addition of tap water, as the main origin of cationic demand lies in the dissolved and colloidal fraction. When treating waters from DAF1, there are important reductions of cationic demand (Figure 5a). According to the reduction of cationic demand, three groups couldbe distinguished among the coagulants tested. The first group was PANS-PA2, which produced charge reversal at dosages higher than 2500 mg/L (data not shown), however, this charge reversal did not affect soluble COD or silica removal, indicating that other different flocculation mechanisms than

charge neutralization weretaking place. The second group wasformed by PAC-MB and alum, with final cationic demand at the highest dosages tested of 0.07-0.10 meq/L (90-93% removal). The third group was formed by PAC-HB and PANS, achieving around 75% removal (0.24-0.25 meq/L final cationic demand).

The same three groups of products couldbe distinguished in DAF2 waters (Figure 5b). PANS-PA2, which was the most efficient product, achieved a final cationic demand of only 0.04 meq/L at 1250 mg/L (96% removal), very close to neutralization of the charge of the particles. The second group was formed by PANS-PA1, alum and PAC-MB. These products had an intermediate efficiency in removing the cationic demand (73-76% at 1250 mg/L) with final values of 0.26-0.27 meq/L. Finally, PANS and PAC-HB decreased cationic demand to 0.48-0.52 meq/L (48-52% removal) at 1250 mg/L.

The trends observed in cationic demand are related to the charge density of the coagulants although the correlation is not perfect as the flocculation active species for aluminum-based products are formed after the coagulant is added to waters. If we consider the aluminum content of the coagulants, as PAC-MB and alum have similar aluminum content (15.3-16.8% Al_2O_3), their neutralization capacity should be very similar, as observed.
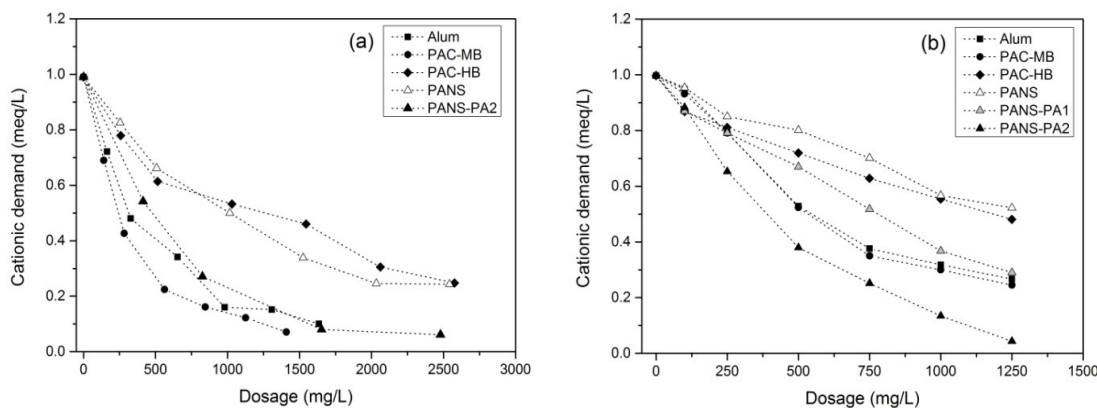

Figure 5: Cationic demand of clarified waters from (a) DAF1 and (b) DAF2 *vs*. dosage of coagulants

On the other hand, PANS and PAC-HB have an intermediate aluminum content of 9.7-10.2% Al_2O_3, therefore they are less efficient products in reducing the cationic demand, as was also

observed. For hybrid coagulants, such as PANS-PA1 and PANS-PA2, there are also cationic polyelectrolytes (PA) contributing to the charge neutralization of the particles apart from

aluminum. Therefore, although with lower aluminum contents, PANS-PA2 is the most efficient product in removing cationic demand and PANS-PA1 has a similar efficiency to those of PAC-MB and alum. Furthermore, it is necessary to consider the pH depression after coagulation treatment as the cationic demand decreases at lower pHs. Comparing the cationic demand removals in DAF1 and DAF2 waters, very similar removals were achieved, the slightly lower reduction with DAF2 waters justified by the lower dosages of coagulants tested. This indicates the neutralization capacity of the coagulants tested was similar, although there was a slightly different contamination load and pH in the waters.

pH

When alum or PAC is added to waters, aluminium hydrolyzes forming a variety of Al species or Al-hydroxide precipitants. In the present study, due to the high dosages used, $Al(OH)_3$ was the predominant formed species and sweep flocculation the main flocculation mechanism.[11] Due to the formation of $Al(OH)_3$, there was a consumption of alkalinity and a parallel pH decrease, which depends on the coagulant dosage, its aluminum content and basicity. The addition of 1 mg/L of alum, for example, resulted in the consumption of 0.5 mg/L $CaCO_3$ of alkalinity, while a PAC with 50% basicity would consume half, 0.25 mg/L $CaCO_3$. As the clarified waters would be reused directly within the process without any pH adjustment, the pH decrease should be as low as possible to avoid pH shocks, which could result in the formation of deposits and operational problems in the process. Although the initial alkalinity of the waters is high, the dosages of coagulant were also high, therefore a significant pH decrease was observed.

The initial pH of the DAF1 inlet and DAF1 blank was 6.8-6.9, while these values were 7.6-7.7 for DAF2. In the tests with DAF1 waters, again three groups could be distinguished in terms of pH decrease after the treatment (Figure 6a): PAC-HB and PANS-PA2 decreased less the pH (<0.3 pH units, final pH 6.5-6.6 at the highest dosage), PANS had an intermediate effect (0.5 pH units decrease, final pH 6.8), and alum and PAC-MB were those decreasing most the pH (pH decrease <0.8-1.0 units, final pH 5.8-6.0). In the tests with DAF2 waters, PAC-HB decreased pH only by 0.2 pH units, PANS-PA1 and PANS-PA2 decreased by around 0.3-0.4 pH units, PANS and PAC-MB decreased pH by around 0.5 units and finally, alum, by around 0.8 pH units, all at the highest dosage tested (Figure 6b).
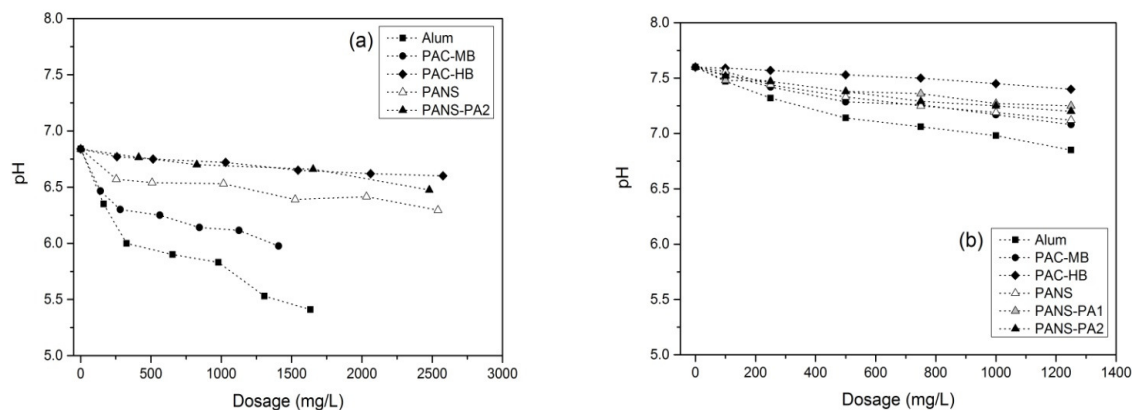

Figure 6: pH of clarified waters from (a) DAF1 and (b) DAF2 *vs*. dosage of coagulants

Alum and PAC-MB were the products causing higher pH decrease because they were the coagulants with the highest aluminum content and with the lowest basicities. This is especially important when treating DAF1 waters, where the initial pH of waters is lower than in DAF2, as commented earlier. The products that decreased less the pH of the waters were PAC-HB and PANS-PA2; PAC-HB due to the intermediate aluminium content (9.7% Al_2O_3) but the highest basicity (85%), and PANS-PA2 due to the lowest aluminum content (6.05% Al_2O_3) and intermediate basicity (46%). Finally, PANS and PANS-PA1 resulted in intermediate pH

decreaseas they have intermediate aluminum contents and basicities. Although the pH decrease was always lower than 1.0 pH unit, the coagulants decreasing the pH to a lower extent are those preferred. At similar dosages of commercial products, the pH decreasein DAF1 waters was higher due to the lowest alkalinity compared to DAF2 (1425 *vs*. 856 ppm $CaCO_3$), *i.e.* the pH decrease with 1250 mg/L of alum is around 1.3 pH units in DAF1, while it was around 0.8 pH units in DAF2.

Conductivity

The conductivity of raw waters from DAF1 was 2.6 mS/cm and the conductivity of blank was 2.1 mS/cm (19.1% removal). In the same sense, the conductivity of raw waters from DAF2 was 2.13 mS/cm and the conductivity of blank 1.74 mS/cm (18.3% difference). This means DAF is not able to remove inorganics, at least without chemicals. In fact, all the treatments produced an increase in the conductivity of the waters, this increase being higher at higher dosages, which is in agreement with the inorganic nature of all the coagulants tested (Figure 7).
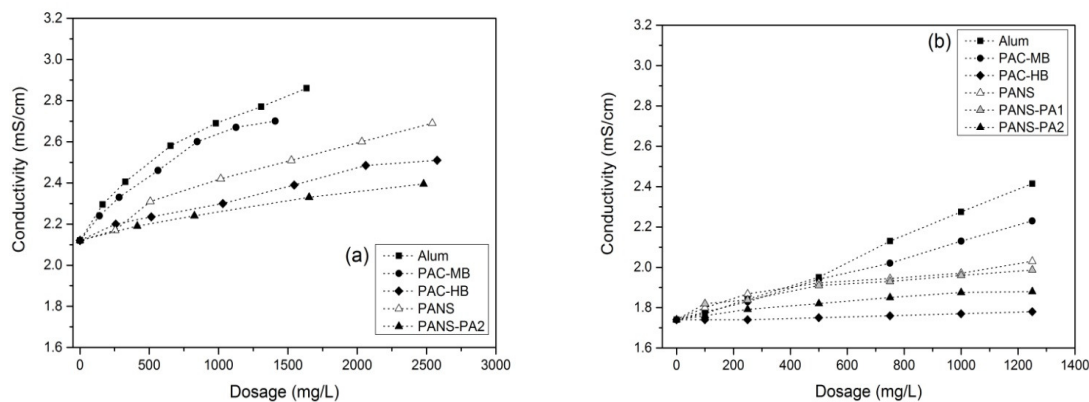
In DAF1 tests, PAC-HB and PANS-PA2 were the products increasing less the conductivity of the waters. With these products, even at the highest dosage tested, the conductivity increased from 2.1 mS/cm up to 2.4-2.5 mS/cm. With the other coagulants, a final conductivity of 2.7-2.8 mS/cm was obtained at the highest dosages tested. One of the most important drawbacks of using alum, which is the cheapest coagulant, is the increase of the conductivity of treated waters due to sulphates release (2.9 mS/cm). With the other coagulants, although some of them have a small amount of sulphates in their composition (*i.e.* PANS or PANS-PA), the increase in sulphates was always lower than 10-15 mg/L. In DAF2 waters, similar trends were obtained. PAC-HB was the coagulant that increased the least the conductivity of the waters, from 1.74 to 1.80 mS/cm at the highest dosage. PANS, PANS-PA1 and PANS-PA2 showed a very similar behaviour, increasing the conductivity of the clarified waters to 1.90-1.95 mS/cm. Finally, PAC-MB increased the conductivity to 2.2-2.3 mS/cm, and alum, to 2.42 mS/cm.

Figure 7: Conductivity of clarified waters from (a) DAF1 and (b) DAF2 *vs*. dosage of coagulants

Totally comparable results were obtained for the two DAF units. There was an important increase of conductivity in the treated waters, but in the case of PANS-PA2 and PAC-HB, which is a very important advantage compared to other products due to the high dosages necessary for efficient silica removal. A lower final conductivity of the treated water constitutes an additional advantage for the chemical treatments tested as, depending on the final conductivity, the

RO rejects must be treated or not before discharge (conductivity limit is 7.5 mS/cm).

Comparison of silica removal efficiency in different process streams with different levels of suspended solids

As it was hypothesized before, the presence of a high concentration of suspended solids (especially those of smaller size) and colloids could be beneficial for the removal of

contaminants, as they could act as precipitation nuclei for $Al(OH)_3$ and promote orthokinetic flocculation. In a previous study carried out by the authors, some of the coagulants tested in the present work (alum, PAC-HB, PANS-PA1 and PANS-PA2) were used to remove silica from the effluent of the same paper mill at three different initial pHs (8.3, 9.5 and 10.5) and dosages up to 2500 mg/L commercial product.[19] In this study, the following ratios (mg of coagulant required per mg of silica removed) were obtained: 35 for alum (although an optimum dosage was observed at dosages lower than 2500 mg/L), 39 for PAC-HB, 34 for PANS-PA1 and 24 for PANS-PA2 at initial pH 8.3. From another study with the same effluent (unpublished), a ratio of 45 was obtained for PANS. Table 4 shows the comparison of these results with those obtained in the present study with DAF1 and DAF2 waters.

The main differences in the contaminant load of the different process water streams (DAF1, DAF2 and effluent) are summarized in Table 5. Although the lowest pH tested (pH 8.3) is slightly higher than the pH of DAF1 and DAF2 waters (pH 6.8 and 7.6, respectively) and silica removal is enhanced at higher pHs, the results obtained clearly demonstrate that a higher efficiency for silica removal in terms of mg of coagulant required per mg SiO_2 removed are obtained if silica is removed from process water in the internal DAF treatments. These higher efficiencies were obtained even in waters that are more contaminated in terms of cationic demand, COD or conductivity than in the effluent,

conditions which usually turn in higher coagulant requirements. Obviously, it is easier to remove a contaminant when the initial content is higher, however, the differences in silica content werenot so large (140 mg/L SiO_2 in the effluent compared to 200-225 mg/L SiO_2 in DAF blanks).

As can be seen in Table 4, the coagulant demand in DAF units is around 20-50% lower than the same treatment applied on the effluent. The main differences in coagulant demand are for alum, PAC-HB and PANS, while the differences in efficiency of PANS-PA1 and PANS-PA2 are less important as their flocculation efficiency is not coming only from their aluminum content, but also from the polyamine included in their formulation. The removal of silica in DAF2 is clearly better than in DAF1 due to the higher concentration of suspended solids and their considerably lower size, even for a similar contamination load in DAF1 and DAF2 waters, including similar total dissolved solids and silica contents. It seems that a higher concentration of suspended solids is more important than total dissolved solids for promoting the flocculation of contaminants either by increasing the rate of precipitation of $Al(OH)_3$ or by improving orthokinetic flocculation. The slightly higher pH in DAF2 compared to DAF1 (around 1.0 pH unit) could also be relevant, however, the pH in DAF2 is still far from pK 9.5, where the ortho silicic acid (H_4SiO_4) is transformed to $H_3SiO_4^-$ and pK 12, when $H_3SiO_4^-$ is transformed in $H_2SiO_4^{2-}$, which would improve the removal of silica by coagulation due to higher silica ionization.[18,20,23]

Table 4

Ratio mg of coagulant required per mg of silica removed in DAF1 waters, DAF2 waters and the effluent

	Alum	PAC-MB	PAC-HB	PANS	PANS-PA1	PANS-PA2	Dosage range
DAF1	29	29	25	37	-	27	0-1500 mg/L
DAF2	19	19	28	29	26	20	0-1250 mg/L
Effluent	35	-	39	45	34	24	0-2500 mg/L

Table 5

Contamination load of DAF1 waters, DAF2 waters and the effluent

	pH	Cat. demand (meq/L)	SiO_2 (mg/L)	TSS (mg/L)	Conductivity (mS/cm)	Soluble COD (ppm)	TDS (mg/L)
DAF1 blank	6.8	0.99	225	1620*	2.12	2050	3211
DAF2 blank	7.6	0.99	200	3350*	1.74	1876	2590
Effluent	8.3	0.50	140	125	2.20	560	1705

* Values from the raw water.

Table 6
Ratio mg of coagulant required per mg of soluble COD removed in DAF1 waters, DAF2 waters and the effluent

	Alum	PAC-MB	PAC-HB	PANS	PANS-PA1	PANS-PA2	Dosage range
DAF1	4.1	3.3	15.3	6.6	-	5.0	0-1500 mg/L
DAF2	2.3	2.2	3.2	3.7	2.4	1.9	0-1250 mg/L
Effluent	10	-	12.4	-	8.8	19.8	0-2500 mg/L

If silica removal rates obtained in this study are compared to other studies from the literature, the removal efficiency is considerably higher. For example, S.H. Chuang et al.[21] obtained silica removal ratios (mg of coagulant per mg SiO_2 removed) around 25 with a polyaluminum chloride (30% Al_2O_3) and 48 with alum. In this study, they treated wastewater from a high-tech industrial park with initial 25-30 mg/L SiO_2, using coagulant dosages of 100-500 mg/L commercial PAC and 200-1000 mg/L alum, at initial pH 7.5. The level of TDS was around 1800 mg/L and the conductivity of 17-1.9 mS/cm, similarly to the values for the present study, but the levels of suspended solids and COD were considerably lower: 10-30 mg/L suspended solids (2-5 NTU of turbidity) and 20-25 ppm COD. The silica removal ratios obtained were very similar to those obtained when the effluent of the paper mill was tested,[19] where the suspended solids were also very low compared to DAF inlet waters (Table 2).

On the other hand, in the treatment of brackish water with 21 mg/L SiO_2, using up to 180 mg/L of a PAC, S. Chen et al.[20] obtained a ratio of 25 mg of coagulant per mg of silica removed at around pH 7. Although the suspended solids or turbidity of the waters were not given, it is expected that the suspended solids would be considerably lower than those of DAF1 and DAF2 waters, very similar to that of the effluent of the paper mill, as usually occurs with brackish waters. The ratio of 25 would mean a higher efficiency in silica removal than in the effluent of the paper mill, however, it is important to notice these brackish waters had a high level of initial hardness (90 mg/L Ca, 80 mg/L Mg), which also promotes silica removal either by the adsorption on $CaCO_3$ or $Mg(OH)_2$ or by co-precipitation as calcium and magnesium silicates. Other references have been analyzed, but it is difficult to make a direct comparison with the results obtained in the present study due to the different conditions tested and the lack of some analytical parameters of the waters tested (initial hardness, total suspended solids, etc.), which are of great importance for comparison purposes.

Although the most important parameter considered in this study is silica, it is necessary to comment that the same decrease in coagulant demand has been also observed for soluble COD removal (see Table 6). A direct comparison between the effluent and the results obtained with DAF waters can not be carried out as there is a large difference in soluble COD (1876-2050 ppm in DAF blanks compared to 560 ppm for the effluent), however, large differences have been also found. DAF1 and DAF2 results could be compared together as the values of soluble COD are similar. Again, there is a clear improvement in the soluble COD removal when treated waters from DAF2 are compared to DAF1 waters (around 50% lower mg of coagulant per mg soluble COD removed). This confirms that the presence of a high amount of suspended solids of small size promotes the removal of COD by sweep flocculation, as previously observed for silica.

CONCLUSION

Without chemicals or using only flocculant, the removal of contaminants is almost negligible in DAF units, especially in DAF2s, due to the small size of suspended solids. In DAF1, the pH decrease after coagulation is the most critical factor for silica removal, therefore, PAC-HB and PANS-PA2 (<0.3 pH units decrease) are the recommended treatment options. PAC-HB is selected when the most important contaminant is silica (40% silica removal, 6% soluble COD removal), while PANS-PA2 is recommended for high silica removals together with high turbidity and COD removals (35% silica removal, 20% soluble COD removal). In DAF2, the most efficient products in silica removal are those with the highest aluminum content, i.e. alum and PAC-MB, plus PANS-PA2. However, the use of alum is not recommended as it largely increases the conductivity of the waters and produces the largest pH decrease. Therefore, the use of PAC-MB and PANS-PA2 are the recommended treatment options. For DAF2 waters, PAC-MB should be used if the most important requirement

is silica removal (35% silica removal, 24% soluble COD removal) and PANS-PA2 if high silica removals are necessary, but also high turbidity and COD removals (30% silica removal, 28% soluble COD removal).

The results obtained indicate that the coagulant demand for silica removal in the effluent can be reduced significantly by treating the inlet of DAF units, especially in DAF2. The coagulant demand can be reduced to 35-50% for the coagulants with the highest aluminum contents (alum and PAC-HB) and around 20% with PANS, PANS-PA1 and PANS-PA2, apart from contributing to having cleaner water circuits compared to silica removal on the effluent. The reason is the presence of a higher concentration of suspended solids of a small size and colloids, which improves the removal of contaminants by sweep flocculation as they can act as precipitation nuclei for $Al(OH)_3$ and also promotes orthokinetic flocculation.

Depending on the initial silica content and the objectives of the treatment (direct discharge or effluent reuse treatments with RO membranes), a post-treatment in the effluent for silica removal could be necessary or not. The most important finding of this study is that silica removal should be carried out preferentially in DAF units used as internal treatments for process waters, avoiding as much as possible the removal of silica from the effluent due to the considerably larger coagulant demands for similar silica and COD removals.

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