SILICA REMOVAL FROM NEWSPRINT MILL EFFLUENTS WITH ALUMINUM SALTS

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ABSTRACT

The main obstacle for the implementation of reverse osmosis (RO) in a treatment chain to reuse the effluent of a newsprint mill as fresh water is the high silica content of the water, which produces severe scaling on the membrane, thus, limiting its recovery. Coagulation is one of the preferred methods to reduce silica concentration. Five aluminum based coagulants have been tested at five dosages (500-2500 ppm) and three pHs (8.3, 9.5 and 10.5). All products showed their best efficiency at the highest dosage and pH, with the exception of alum, that was more efficient at intermediate dosages. A combination of a polyaluminum nitrate sulphate with a cationic quaternary polyamine (PANS-PA2), was the most efficient and versatile coagulant. It removed 97% of silica (5 ppm residual silica) at the optimal conditions (pH 10.5, 2500 ppm) and it was very efficient (76% silica removal) at pH 8.3, avoiding the need of any pH adjustment, and minimizing the conductivity and pH increase of the treated waters as well as obtaining some removal of the organic colloidal matter ($\approx$25%).

Keywords: Reverse osmosis; silica; scaling; effluent reuse; coagulation; aluminum.

Highlights:
► Silica coagulation is necessary for the viability of RO treatments in paper mills.
► Silica removal is favored at high pH and dosages, the drawback is the conductivity increase.
► Polyamine modification of a polyaluminum salt is the most efficient coagulant.
► PANS-PA2 is able to reduce 97% silica concentration at pH 10.5 and 2500 ppm.
► Even without pH regulation, a 76% silica removal is obtained with PANS-PA2.

1. INTRODUCTION

Sustainable water use in the paper industry requires the closure of the water system without affecting paper machine runnability and product quality [1], which can be achieved by reusing the mill effluent after its advanced membrane treatment [2] and/or

by the use of reclaimed water [3], depending on the availability of alternative water sources.

In deinking paper mills the closure of the internal water circuit is limited by the accumulation of recalcitrant organic colloidal matter that alters the process and the paper quality [1]. On the other hand, the reuse of the final effluent is limited by the reverse osmosis (RO) membrane fouling caused by silica. Thus, causing a decline in water production rates, low permeate quality, unsteady-state operation conditions, higher energy consumption and serious damages on the membranes that shorten their lifetime, by doing so compromising the technical and economic feasibility of the whole treatment chain. If silica is not removed the RO recovery is of only around 20% [2].

The main source of silica in deinking paper mills is sodium silicate, used as process additive. It has a variety of functions within the process. In the pulping stage, sodium silicate enhances ink dispersion and facilitates its removal by flotation. In the bleaching process, sodium silicate acts as a peroxide stabilizer by chelation of transition metals and a pH buffer, it controls corrosion and is a surface active agent. Although some attempts have been carried out to reduce the use of sodium silicate during deinking [4], it is still a necessary additive.

Silica can be found in crystalline and amorphous forms, being the first one more stable than the second. The difference of solubility is 6 ppm (as SiO_2) for crystalline silica versus 100-140 ppm (as SiO_2) for amorphous silica, both at 25ºC [5]. Solubility depends on many factors such as pH or the presence of organic and inorganic matter. The solubility of silica polymorphs, both crystalline and amorphous, is essentially constant between pH 2 and 8.5, but increases rapidly from pH 9 onwards [6]. On the other hand, silica solubility is highly affected by temperature, increasing from 100-140 ppm at ambient temperature up to 300 ppm at 70ºC [7].

There are different methods to control silica scaling, which can be grouped in preventive, corrective and cleaning. Prevention and correction of scaling are those preferred as it is very difficult to clean silica deposits. Preventive methods interact and modify silica so as not to allow it to deposit on membranes but they do not remove it. The use of antiscalants is probably the most common method [8, 9], although their efficiency in highly contaminant waters is low. Besides, when treated water is reused in other process stages, as the process conditions can change significantly, scaling problems could appear once again. Regarding corrective methods, there are many silica removal techniques proposed in the literature, but these are usually carried out during softening processes or by coagulation at high pH [10, 11]. These techniques enable the treatment of large volumes of water with high removal rates at low costs, which is a prerequisite for its use in papermaking applications.

When silica removal is carried out during a softening process it is necessary to ensure that there is enough hardness present in the water, especially magnesium hardness. On

the other hand, several studies have been carried out with traditional coagulants such as alum, or ferric chloride, to treat pulp and paper mill effluents [12]. In this case, coagulation with alum has been proved to be more effective for silica removal than ferric chloride. Coagulation and ultrafiltration (UF) have been also successfully used in brackish water RO treatment to avoid silica problems [13, 14]. Alum, ferric chloride and sodium aluminate were also studied to improve silica removal rate in a lime-soda ash process with brackish water [15].

Polyaluminum chlorides are effective at low temperatures in a wider range of pHs, they generate compact flocs easily sedimentable, they are less likely to cause overdosage phenomena and they are less sensitive to water properties fluctuations [16, 17]. As chlorides can cause corrosion problems, sometimes they are partially substituted by other species such as sulphates or nitrates, providing a new range of products: polyaluminum nitrates, polyaluminum sulphates or a combination of them, such as polyaluminum nitrate sulphate. The main differences between these products are their basicity, strength and the content of other species such as silica, calcium or even organic compounds [18-20]. Although the silica removal mechanism of polyaluminum coagulants is not well understood [17, 21], there is a consensus in that they act by two primary coagulation mechanisms [18, 22]: (1) charge neutralization of the negative particles by adsorption of positively charged dissolved aluminum species, and (2) enmeshment of particles in precipitated $Al(OH)_3$.

Previous studies have demonstrated that coagulation with aluminum salts is effective for the treatment of deinked paper mill effluents; however, the required dosages and the conductivity of the treated waters were very high [10]. Therefore, the process was neither economically nor chemically feasible. To avoid these drawbacks, this paper studies the efficiency of new coagulants under several conditions, optimizing the operating pH and the pH regulator. The final objective is to increase RO recovery from 20% to 60-80%, making the effluent reuse process technically and economically feasible.

2.-MATERIALS AND METHODS

2.1.-Water Samples. This research was carried out with the effluent of a Spanish paper mill using 100% recovered paper to produce newsprint. The mill has an integrated wastewater treatment plant consisting of a primary treatment by dissolved air flotation and a secondary treatment based on an aerobic digestion of the waters on a moving bed bioreactor followed by a dissolved air flotation for sludge separation. Water samples were taken before their discharge to an urban waste water treatment plant. Samples were stored at 4ºC for a maximum of five days. Table 1 summarizes the effluent characteristics.

Table 1.- Characteristics of the paper mill effluent.

RAW WATER	
pH	8.3
Conductivity (mS/cm)	2.20
COD (ppm)	635
BOD (ppm)	300
Cationic Demand (meq/L)	0.50
Total Solids (ppm)	1830
Total Suspended Solids (ppm)	125
Turbidity (NTU)	63
Total Alkalinity (ppm $CaCO_3$)	790
DISSOLVED FRACTION	
Silica (ppm SiO_2)	140
COD (ppm)	560
Sulphates (ppm)	200
Chlorides (ppm)	161
Calcium (ppm)	55
Magnesium (ppm)	2.7
Turbidity (NTU)	15

2.2.-Chemicals. Alum ($Al_2(SO_4)_3 \cdot 18H_2O$) and four polyaluminum-based products were used as coagulants. The polyaluminum-based coagulants were two polyaluminum chlorides and two polyaluminum nitrate sulphates-based products. One of the polyaluminum chlorides has a high basicity (PACl-HB) and was supplied by Kemira Ibérica S.A. (Spain); the other has a medium basicity (PACl-MB) and was supplied by SERTEC-20 S.L. (Spain). The polyaluminum nitrate sulphate-based coagulants, named PANS-PA1 and PANS-PA2, were supplied by Sachtleben Wasserchemie GmbH (Germany). These products are obtained from the blending of a polyaluminum nitrate sulphate (PANS) with increased dosages of a cationic quaternary polyamine (PA), with a 17% charge density. Alum, reagent grade, was supplied by PANREAC. Table 2 summarizes their main characteristics. An anionic polyacrylamide with high molecular weight and medium charge density was used as flocculant aid in all tests (supplied by SERTEC-20 S.L., Spain). Two different pH regulators were used: NaOH and $Ca(OH)_2$, both of analytical grade supplied by PANREAC. Coagulants were prepared at 20 wt%, flocculant at 0.1 wt% and pH regulator at 10 wt% with ultrapure water on a daily basis.

Table 2. Characteristics of the coagulants used in this study.

Coagulant	Chemical family	Formula	Al_2O_3 (%)	Basicity (%)	Dry content (%)	Charge density (meq/g)	pH
PACl-HB	Polyaluminum chloride	$Al_n(OH)_x(Cl)_y$	9.7	85	29.5	1.67	2.7
PACl-MB	Polyaluminum chloride	$Al_n(OH)_x(Cl)_y$	10.0	65	35.0	1.27	2.6
PANS-PA1	Polyaluminum nitrate sulphate	$Al_n(OH)_x(NO_3)_y(SO_4)_z$	8.8	46*	21.7	1.68	2.0
PANS-PA2	Polyaluminum nitrate sulphate	$Al_n(OH)_x(NO_3)_y(SO_4)_z$	6.0	46*	20.4	2.57	3.0
Alum	Aluminum Sulphate	$Al_2(SO_4)_3 \cdot 18H_2O$	15.3	-	-	-	-

* Basicity of the polyaluminum nitrate used as base in these products.

2.3.-Methodology for jar-tests. For each coagulant, 5 dosages (from 500 to 2500 ppm) were tested, those selected according to preliminary tests [23]. These dosages were tested at 3 different basic pHs: 8.3 (water initial pH), 9.5 and 10.5, as basic pHs are the most effective for the removal of silica by coagulation [11, 24] and pH 10.5 is enough for almost complete removal of silica for this application [23]. First, the best coagulants were selected using NaOH as pH regulator, then, pH regulator was optimized, comparing the efficiency of NaOH and $Ca(OH)_2$.

Figure 1 summarizes the jar-test methodology followed to study the efficiency of the different coagulation treatments. The comparison between different pH regulators was carried out following the same "jar-test" methodology but, in this case, the study was only focused on the most efficient coagulant according to previous results. Three different dosages (500, 1500 and 2500 ppm) of PANS-PA2 were tested with the two pH regulators and using the same flocculant with the same dosage as before. In addition, sedimentation rates were also considered in the comparison of the pH regulators.
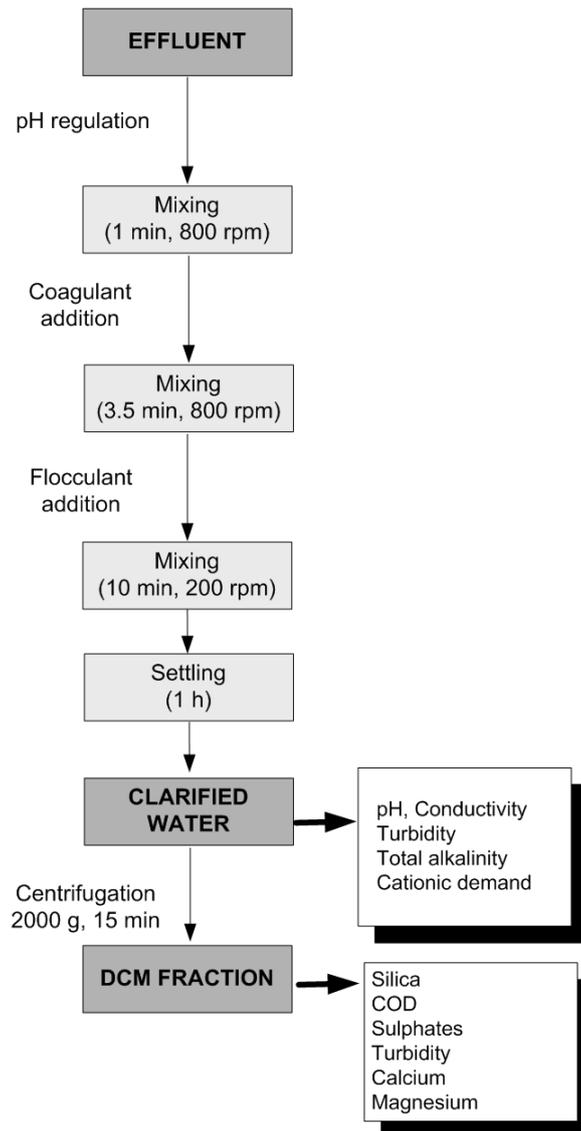
Figure 1.- Jar-test protocol followed to study the efficiency of different coagulants.

Mixing was carried out in a multiposition magnetic stirrer OVAN MulitMix Heat D. All trials were carried out at room temperature (20ºC ±2 ºC) by duplicate, and the average error between replicates was always under 5%. The pH was measured using a model GLP 22 (Crison, S.A), according to Standard Method 4500 [25], and the conductivity was measured with a model GLP 31 (Crison, S.A.), according to the ISO 7888. Reactive silica was measured by flow analysis and photometric detection through silicamolybdate and reduction to molybdenum blue, using a FIA Compact (MLE GmbH) according to DIN EN ISO 16264 and expressed as ppm of SiO_2. COD was measured according to the Standard Method 5220-D [25]. Cationic demand was measured by colloid tritation with poly-diallyldimethylammonium chloride (PDADMAC) using a CAS Charge Analyzing System supplied by AFG Analytic GmbH to measure the end point. Alkalinity was measured by titration with 0.1 N H_2SO_4 according to EPA 310.1 method. Sulphate content was measured using Nanocolor® sulphates method (Macherey-Nagel GmbH). Calcium and magnesium content were measured using a direct air-acetylene flame atomic absorption method according to

ISO-7980:1986. Finally, turbidity was measured with a LP 2000-11 nephelometer, supplied by Hanna Instruments, according to ISO 7027.

2.4.- Methodology for monitoring flocculation behaviour. The coagulation process was studied using a M500L Focused Beam Reflectance (FBRM) probe manufactured by Lasentec (Mettler Toledo, United States). The device generates a laser beam that is focused on a focal point that describes a circular path at high speed (2000 rpm). When particles cross the trajectory of the focal point, the detector measures the time duration of the backscattered light from this particle. This period of time is proportionally related to the size of the particle intercepted under the focal point. Thousands of chord lengths between 1μm and 1000 μm, which are the detection limits of the device, are collected per second. From these data, the total number of counts (TNC), counts in a specific size region, mean chord size (MCS) and other statistical parameters can be calculated. The use of FBRM technique to monitor flocculation has been thoroughly described previously by the authors [26, 27]. In a typical trial, the probe is submerged into a 100 ml and the stirring speed was fixed at 200 rpm. A continuous addition of coagulant was tested: 200 ppm of coagulant were added each 10 s up to a final dosage of 8000 ppm. Whenever necessary (pH 9.5 and 10.5), pH adjustment was carried out by the addition of NaOH 10 wt.% just after the 30 s stabilization time, the coagulant started to be added after 30 s of adding the caustic soda.

3.- RESULTS AND DISCUSSION

3.1.- Selection of pH and coagulant dosage. For all the coagulants but alum, silica was reduced by increasing the coagulant dosage and the pH (figure 2). In the case of alum, higher pHs also improved its efficiency but the most efficient dosage was found to be around 500-1000 ppm. Comparing all products, PANS-PA2 was clearly the most efficient. At the highest dosage, silica removal ranged from 73% (pH 8.3) to 78% (pH 9.5) and 97% (pH 10.5), achieving a residual silica of only 5 ppm at the best conditions. One important difference between this product and the others was its efficiency at pH 8.3: a 73% silica removal could be achieved at 2500 ppm, and even with a dosage of 500 ppm, 42% silica removal could be obtained. The other coagulants yielded very similar efficiencies, with only slight differences related to their different nature, aluminum content and final pH after the treatment (governed by their aluminum content and basicity). PACl-MB removed around 50% silica at the highest dosage and pHs 8.3 and 9.5, and an important increase in efficiency was observed at pH 10.5 (85% removal). The same high increase of efficiency at pH 10.5 was observed with PANS-PA1. In this case, the removal efficiency at 2500 ppm increased from 50-55% at pH 8.3 and 9.5 to 92% removal at pH 10.5. Removal efficiencies obtained with the highest dosage of PACl-HB varied largely from pH 8.3 (45% removal) to the highest (72% removal). Finally, the use of alum at the optimal dosages (500-1000 ppm) achieved a35% removal at pH 8.3, 58% at pH 9.5 and 73% at pH 10.5. Although the removal efficiencies of alum can be higher than those of PANS-PA2 at pH 10.5, only with PANS-PA2 high efficiencies can be achieved without any pH adjustment. Probably

because of its high charge density and the effect of the quaternary polyamine added to the polyaluminum salt, which is efficient even at pH 8.3. However, the dosage of polyamine in the coagulant must be high enough, as in the case of PANS-PA2, because at lower dosages of polyamine (PANS-PA1), only 53% removal was achieved at initial pH. The dosage of polyamine in PANS-PA2 was around three times higher than in PANS-PA1. On the other hand, the high efficiency of alum could be related to its high aluminum content, around 2.5 times higher than the coagulant with the lowest aluminum content (PANS-PA2). The explanation for why its efficiency was decreased at higher dosages than 1000 ppm is a combination of two factors, its high aluminum content and the 0% basicity of the product, which caused the highest alkalinity consumption and an important pH decrease, making the formation of the active species of the aluminum salts difficult. In summary, PANS-PA2 and alum were found to be the most promising treatment options.

Although the most critical parameter in this application was silica removal, COD removal has to be considered as well since it contributes to the organic fouling of the membranes. First, it is important to note COD removal followed just the opposite trend to silica removal: it was higher at lowest pH (8.3) than at the highest pHs (pH 9.5 and 10.5) (figure 3). This fact can be explained by the competition between silica and the organic matter (mainly anionic) for the neutralizing capacity of the coagulant. This reverse relationship has also been described by D. Hermosilla *et al.* (2012) [10]. Higher dosages of the coagulants were always more efficient in COD removal, however, the effect of high dosages on COD removal was more evident at pH 8.3 and 9.5, while at pH 10.5 it was less significant. In general, the effect of dosage on COD removal was higher at the lowest dosages of the coagulant and remained almost constant at the highest (1500-2500 ppm).

PANS-PA1 was the most efficient product in COD removal, independently of pH and dosage. At pH 8.3, the maximum COD removal was obtained (39%), and the removal decreased to 30% at pH 9.5 and to 18% at pH 10.5. Alum was the second most efficient product removing COD, with very similar efficiency than PANS-PA1 at the highest dosages, but slightly lower efficiency at the lowest dosages. Maximum removal rates with alum were 36%, 32% and 20% at pH 8.3, pH 9.5 and pH 10.5, respectively. PACl-MB and PACl-HB were the least efficient products removing COD: at pH 8.3 the highest removals were 25-27%, and at pH 10.5, were 8%. PANS-PA2 showed an intermediate efficiency, its removal efficiency varying from 27% at pH 8.3 to 23% at pH 9.5 and 11% at pH 10.5. Although there was an inverse trend in the removal efficiencies of silica and COD, PANS-PA2 was able to maintain an intermediate COD removal while being the most efficient product in silica removal.
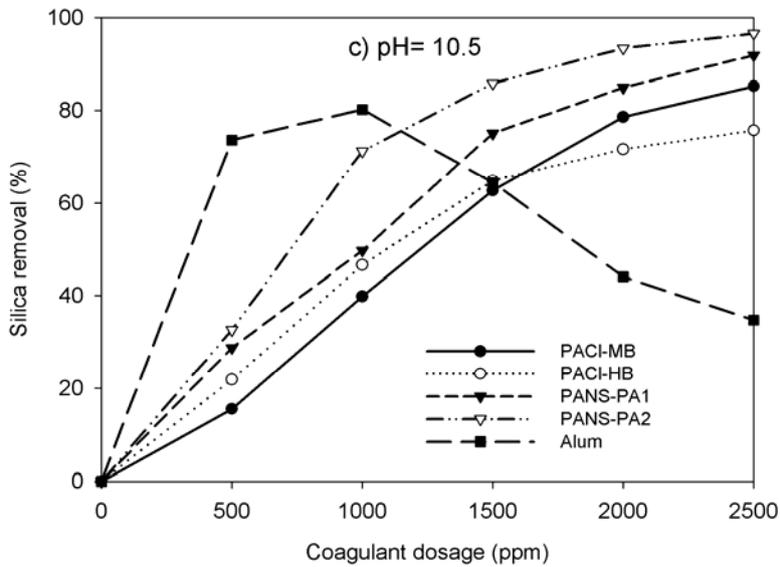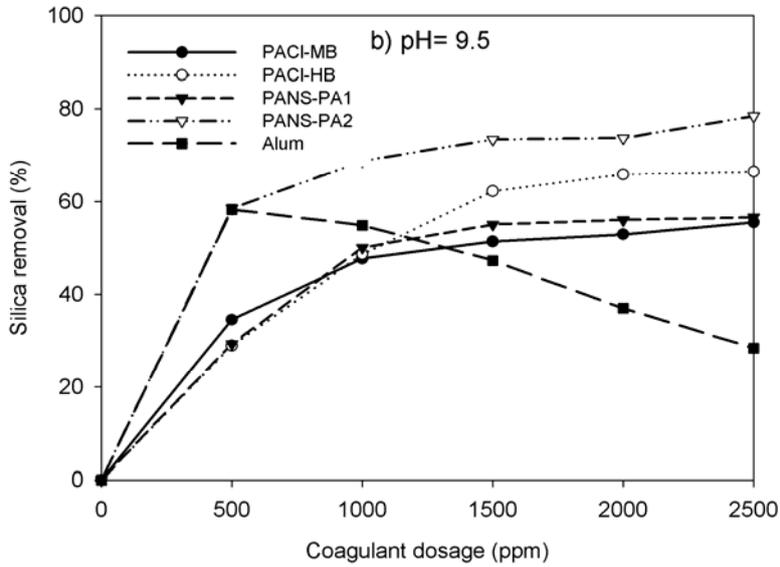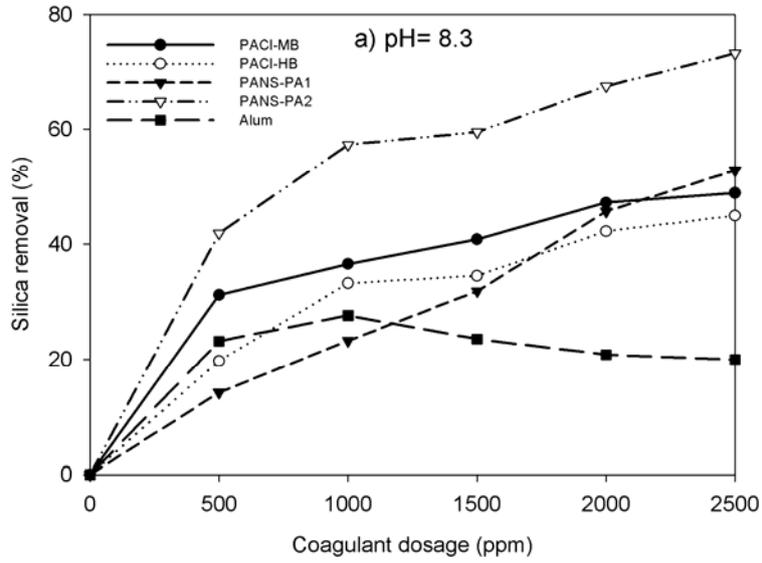
Figure 2.- Silica removal vs. coagulant dosage at different initial pHs: (a) pH=8.3; (b) pH=9.5; (c) pH= 10.5.
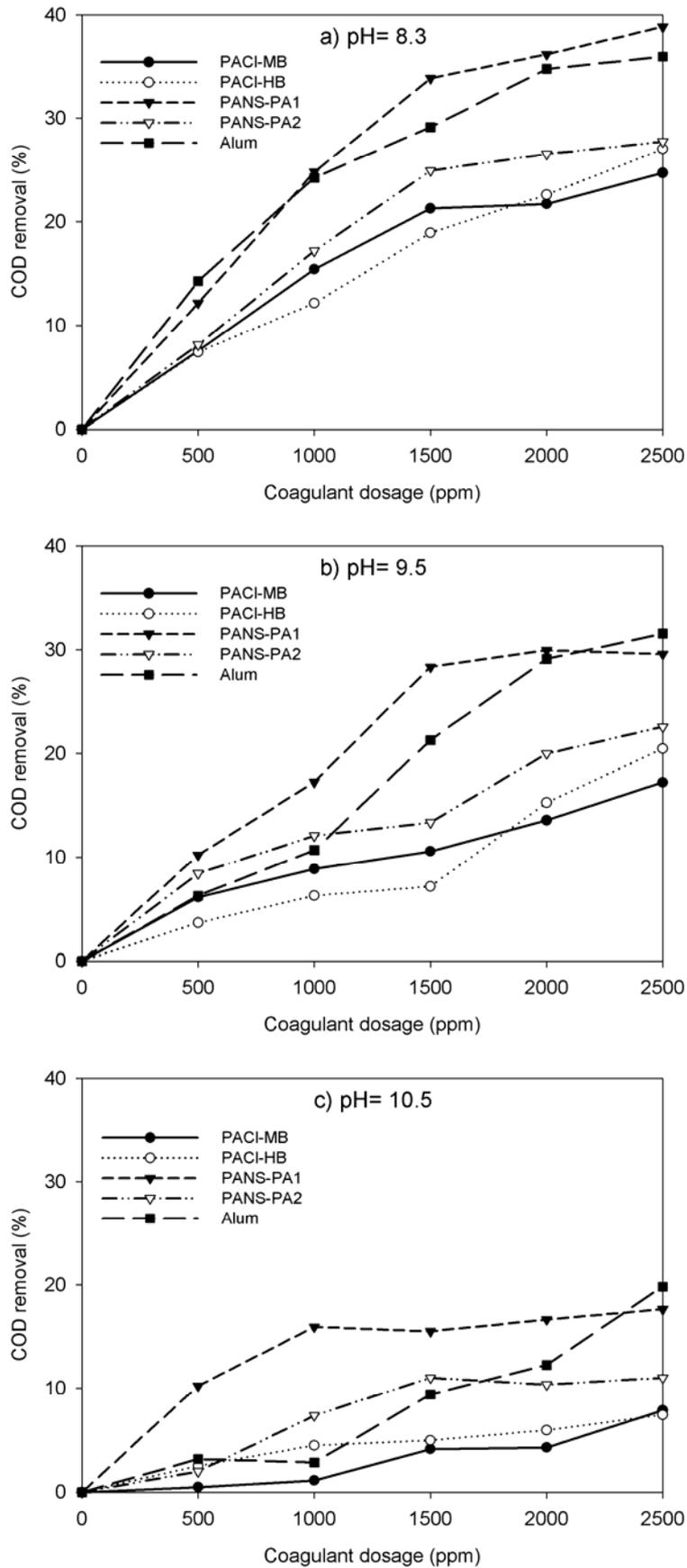
Figure 3.- COD removal vs. coagulant dosage at different initial pHs: (a) pH=8.3; (b) pH=9.5; (c) pH= 10.5.

Another important parameter in coagulation processes is the water cationic demand. The neutralization capacity of the different aluminum-based products is mainly governed by the charge density of the products, which varies depending on the characteristics of the water (pH, conductivity, cationic demand, etc.). The initial cationic demand of water samples is higher at higher initial pHs because of the higher content of hydroxide ions and, in a lower extent, due to the ionization of species such as carboxylic or fatty acids.

PANS-PA2 is the coagulant with the highest charge density and the most efficient product reducing the cationic demand of waters. At the three studied pHs, the highest dosages (2000-2500 ppm) achieved complete neutralization of waters. Alum and PANS-PA1 obtained very similar neutralization efficiencies. Alum achieved complete neutralization at 2000-2500 ppm dosages at pH 8.3, almost neutralization at pH 9.5 and 2500 ppm (0.02 meq/L), and an important decrease at pH 10.5 and 2500 ppm (0.14 meq/L). On the other hand, PANS-PA1 obtained almost complete neutralization at pH 8.3 and 9.5 (0.03 meq/L) and 0.34 meq/L at pH 10.5 and 2500 ppm dosage. Finally, PACl-MB and PACl-HB had similar efficiencies. At pH 8.3, 9.5 and 10.5 and 2500 ppm dosage, PACl-MB reduced, respectively, the cationic demand to 0.12, 0.19 and 0.41 meq/L; and PACl-HB to 0.21, 0.30 and 0.48 meq/L.

Although the reduction in cationic demand is beneficial for the removal of contaminants by coagulation, its effect must be addressed together with the main flocculation mechanisms involved. If the removal of contaminants takes place by charge neutralization, the maximum removal rate is close to the isoelectrical point and overdose is possible (restabilization occurs at charge reversal). However, with high dosages of aluminum salts, the main flocculation mechanism can be "sweep flocculation", where the contaminants are removed by enmeshment in the fresh precipitated flocs of $Al(OH)_3$. In this case, optimum dosage of coagulant does not occur at the isoelectric point and there will not be overdose phenomena although reaching charge reversal [17]. It is very interesting to notice that although higher cationic demand removals are beneficial to obtain higher removal efficiencies, a direct relationship between silica removal and cationic demand does not occur in all the cases. In some of them, reverse charge occurred, but silica removal efficiency even increased in these conditions. Therefore, flocculation by sweep flocculation predominates.

Aluminum reacts with hydroxyl groups to form different aluminum hydroxides, which are the active species in coagulation. The required alkalinity in the media is directly related to the dosage, aluminum content and basicity of the coagulants [28]. The results show that all coagulants had the same tendency. Alkalinity of the water decreased with the coagulant dosage and increased at higher initial pHs due to pH adjustment. Alkalinity of the treated waters was similar for all products but alum. At the highest dosage (2500 ppm), the final alkalinity was around 500 ppm $CaCO_3$ at pH 8.3, 600 ppm $CaCO_3$ at pH 9.5 and 750 ppm $CaCO_3$ at pH 10.5. The consumption of alkalinity for 2500 ppm dosage was around 300 ppm $CaCO_3$ at pH 8.3, 350 ppm $CaCO_3$ at pH 9.5 and 550 ppm $CaCO_3$ at pH 10.5. The highest decrease in alkalinity was in parallel with

a higher silica removal at the highest pHs, especially at pH 10.5. Another factor influencing alkalinity consumption is the precipitation of calcium carbonate. For all the coagulants but alum, calcium in the treated waters remained in the 45-55 ppm range at pH 8.3 and 9.5 and decreased to around 10 ppm at pH 10.5, which is in agreement with the highest consumption of alkalinity at this pH 10.5 due to calcium carbonate precipitation. On the other hand, alum caused the highest alkalinity consumption. At 2500 ppm dosage, alkalinity of the treated waters was 0 ppm $CaCO_3$ at initial pH, 30 ppm $CaCO_3$ at pH 9.5 and 300 ppm $CaCO_3$ at pH 10.5. This is explained because this product was the one with the highest aluminum content and the lowest basicity (0%); therefore, alum was the product consuming more alkalinity from waters and, as described next, the one causing the highest pH decrease after the treatment.

To avoid any pH "shock" when mixing the tested water with process waters which could cause scaling phenomena and organic deposit formation, the treated waters must have a pH of 7.5 ±1.0. Besides, according to the discharge limits of the newsprint mill, the RO rejects should have a pH between 6.5 and 9.5 to avoid the need of a final pH-adjustment. Final pH was determined by two factors: the pH adjustment before coagulation and the pH decrease caused by the alkalinity consumption of the coagulants.

PANS-PA2 was the product least affecting the pH of treated waters, while alum was the one causing the highest pH decrease, due to its highest aluminum content and lowest basicity. Without pH adjustment (pH 8.3) at the highest dosage (2500 ppm), pH of treated waters with PANS-PA2 decreased from 8.3 to 8.2, while in the case of alum, decreased to 4.3. The other three coagulants showed a similar trend, decreasing the pH from 8.3 to around 7.4. Their differences in aluminum content and basicity were not so large to observe important differences among them. When initial pH of waters was adjusted to pH 9.5 and using 2500 ppm dosage, the final pH of the water was in the range 7.7-8.3 for all the products but alum (pH 4.6). At initial pH 10.5 and 2500 ppm dosage, the final pH of treated waters was around 9.3-9.4 for all the coagulants but alum (pH 6.9).

The conductivity of the treated waters is also important as it affects the performance of RO membranes and the need to treat the RO rejects, which is a determinant factor in the economic feasibility of the full treatment chain. As regular recoveries in RO systems for this application are usually in the 60-80% range, the conductivity of RO rejects will be from 2 to 4 times higher than the inlet to the RO membranes. The boundary condition in this case is that it cannot exceed 7.5 mS/cm which is the limit for direct effluent discharge to the sewage system without post-treatment.

Conductivity of the treated waters was always higher than before the treatment, being the initial pH adjustment and the nature and dosage of the coagulants the two most determining effects. The increase in conductivity caused by the pH regulation was around 0.19 mS/cm to achieve pH 9.5 and 0.41 mS/cm for pH 10.5. In these studies,

caustic soda was the pH regulator. The coagulation treatment also affects the conductivity of the waters, therefore, some differences were observed depending on the coagulant used. At the three pHs tested, alum was the product causing a higher increase in the conductivity of the waters, between 0.4 and 0.6 mS/cm at 2500 ppm dosage (excluding conductivity increase by pH adjustment). With PACl-MB and PACl-HB, this increase was 0.3-0.5 mS/cm. On the other hand, PANS-PA1 and PANS-PA2 are the coagulants causing the smallest increases in the conductivity (around 0.2 mS/cm for both products).

Apart from the problems caused by the high pH decrease and conductivity increase when the waters were treated with alum, the increase in sulphates content was also a factor to be considered. In this case, high sulphate concentration can cause calcium sulphate scaling on the RO membranes; in addition, sulphate content is limited to 1000 ppm for direct discharge of the RO rejects without any pre-treatment. Although PANS-PA1 and PANS-PA2 have sulphates in their composition a very small increase of sulphates was observed in the treated waters (from 200 to 230-250 depending on the initial pH). However, when alum was used, the concentration of sulphates increased up to 1050-1150 ppm. These levels cause scaling phenomena in RO membranes.

Finally, the turbidity of the waters decreased from 63 NTU (raw water) to 9 NTU (86% removal) with all the products at the three pHs at the maximum dosage. On the other hand, the dissolved turbidity of the waters was reduced from 15 NTU (raw water) to 3 NTU (80% removal). The same 3 NTU could be achieved with alum, however only at the optimal dosage of 1000-1500 ppm. At higher dosages than those, the turbidity increased up to 35 NTU (at 2500 ppm).

3.2.- Selection of the best pH regulator. To improve the coagulation process, the convenience of using lime instead of caustic soda as pH regulator was studied. The main advantages of lime are that it is cheaper and could help to reduce the conductivity of the treated waters (as it is a sparingly soluble salt). Both pH regulators were tested in the same conditions: three different dosages (500, 1500 and 2500 ppm) of the most efficient coagulant (PANS-PA2) and two pHs as previously tested (pH 9.5 and 10.5). First of all, the dosages required for pH adjustment were determined. To achieve pH 9.5 140 ppm NaOH or 312 ppm $Ca(OH)_2$ were necessary, while to achieve pH 10.5, 460 ppm NaOH or 800 ppm $Ca(OH)_2$ were required.

First, it was tested if silica removal was affected by the pH regulator used. It was concluded that silica removal was not significantly affected and the differences between them were always within the experimental error of SiO_2 measurements. However, conductivity of the treated waters was higher when caustic soda was used instead of lime. At pH 9.5, the conductivities of treated waters were 2.5-2.8 mS/cm and 2.1-2.7 mS/cm for caustic soda and lime, respectively. These conductivities vary depending on the dosage of coagulant. At pH 10.5, when the dosage of pH regulator is higher, the

differences are even higher: final conductivity of 3.0-3.2 mS/cm with caustic soda compared to 2.0-2.1 mS/cm with lime.

Although the use of lime can increase the turbidity of the waters, this effect was not relevant in these tests, presenting very similar turbidities with both pH regulators. This is probably due to the flocculant addition after pH adjustment and coagulation. Regarding COD removal, there were minor differences at pH 9.5; however, these differences became larger at pH 10.5: 23% COD removal with lime compared to 13% removal when caustic soda was used.

Another important factor to consider is the effect of the pH regulator on sedimentation rates (figure 4a, 4b). At initial pH 9.5, sedimentation rates with lime were higher than in the case of caustic soda, especially in the first minutes. After that, sedimentation rate decreased and remained practically constant. The final height of the flocs was very similar for both pH regulators. The higher the coagulant dosage used, the lower sedimentation rate, as the production of flocs is higher and the settling is impeded. For 500 and 1500 ppm dosages, most of the sedimentation occurred during the first 5 minutes for both pH regulators. At 2500 ppm dosage, most of the sedimentation process took place in the first 10 minutes in the case of lime, whereas it took another 5 minutes in the cause of caustic soda.

At pH 10.5 (figure 4c and 4d), the differences in sedimentation rates became more evident. Sedimentation with lime was faster than with caustic soda: the sedimentation is almost finished in 5 minutes with lime but around 10 minutes in the case of caustic soda. Compared to the sedimentation rates obtained at pH 9.5, the sedimentation rates at pH 10.5 were faster as the lime flocs are heavier.
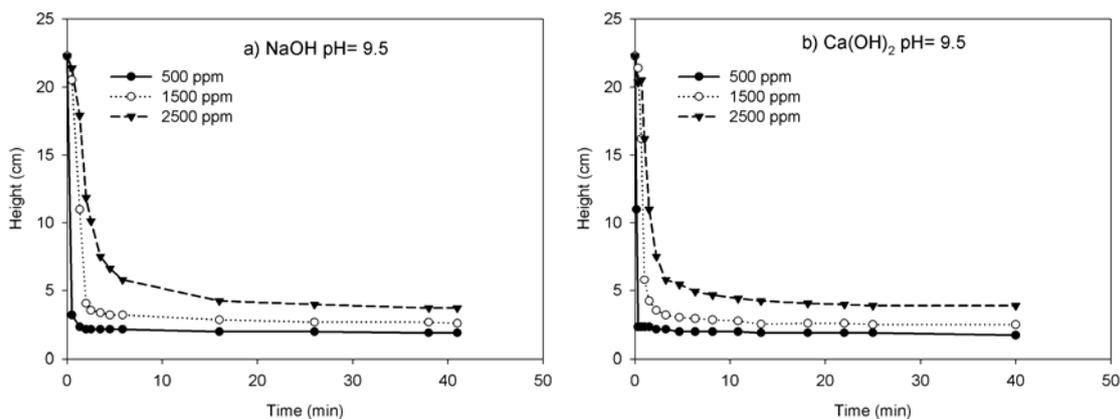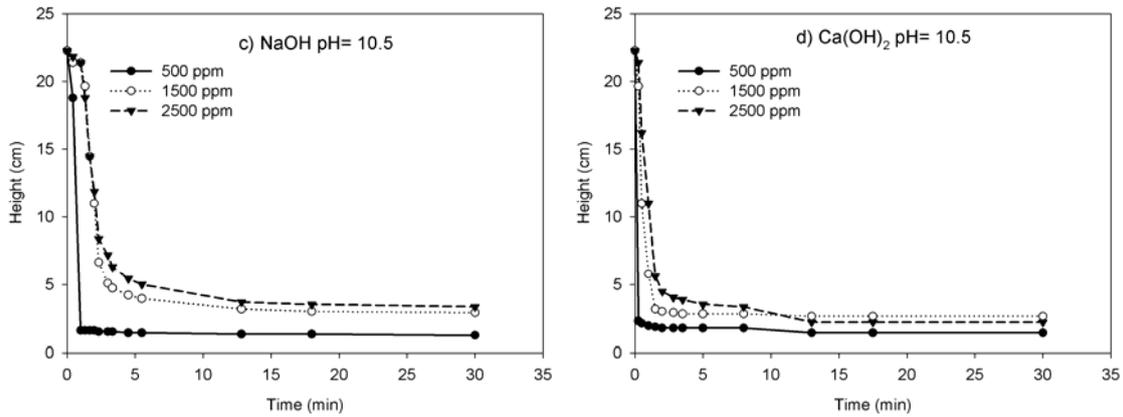
Figure 4.- Sedimentation rates at pH 9.5 and 10.5, with NaOH and Ca(OH)$_2$ and different dosages of PANS-PA2. (a) NaOH, pH=9.5 (b) Ca(OH)$_2$, pH=9.5 (c) NaOH, pH=10.5 (d) Ca(OH)$_2$, pH=10.5.

3.3.- Flocculation monitoring by FBRM. The sequential additions of coagulant showed that at initial pH all products but alum decreased the total number of counts (TNC) at increasing coagulant dosages (figure 5) which is in agreement with a regular flocculation process where a number of particles are aggregated in larger flocs. PANS-PA2 was the product with the highest decrease in the TNC. On the other hand, alum showed an important increase (220%) in the TNC with around 2700 ppm of coagulant that coincides with a decrease in the mean chord size (MCS) as explained below. After that, TNC decreased to approximately initial counts range. Although all products but alum showed a decrease in the TNC, the extent of this decrease and the coagulant dosage at which the minimum was reached was different, depending on the tested coagulant and the pH. Regarding MCS coagulants showed also three different behaviors. PACl-MB, PACl-HB and PANS-PA1 showed an increase in the MCS smaller than 20%. These products also showed intermediate silica removal rates. PANS-PA2 was the product with the highest increase of 70% in the MCS and it was also the product with the highest silica removal rate. This maximum MCS was achieved with around 2500 ppm of coagulant that was in accordance with the maximum removal of silica obtained. On the other hand, alum was the only product that caused a decrease of 20% in the MCS.
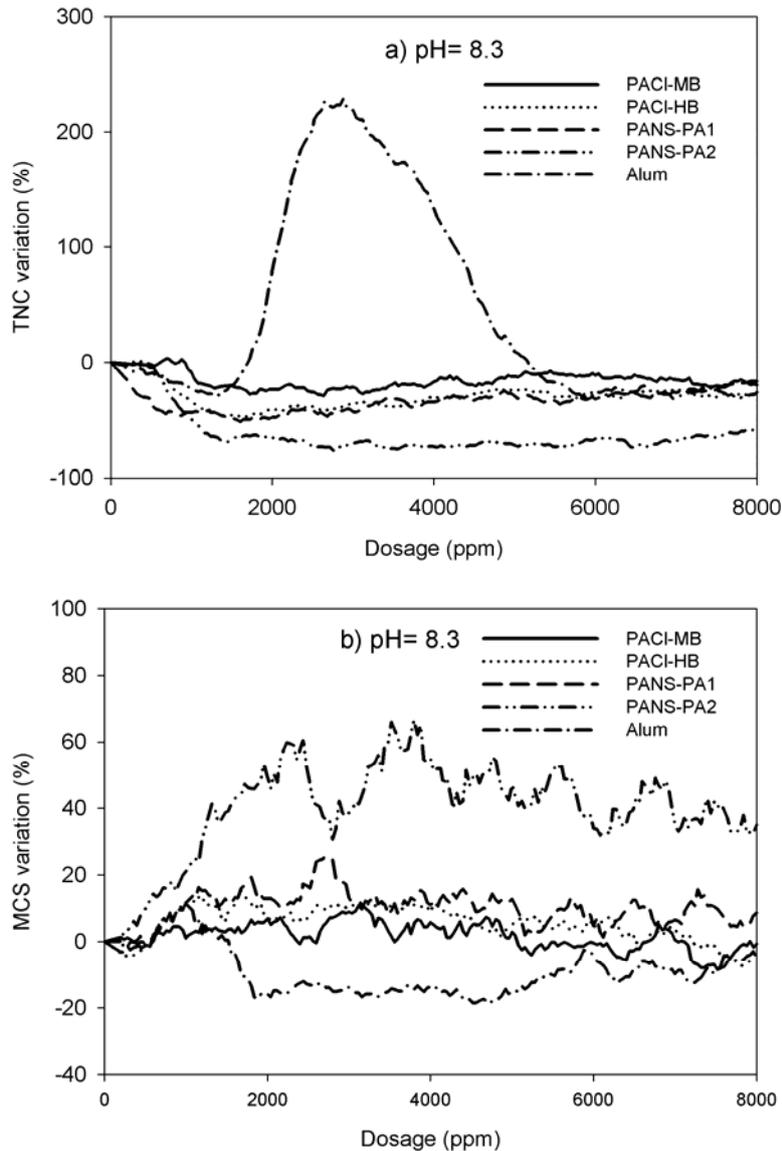
Figure 5.- TNC (a) and MCS (b) variation at pH= 8.3.

At pH 9.5 all products showed the same tendency as at initial pH (figure 6). At this pH PANS-PA2 caused again the highest decrease in the TNC and consequently the highest increase in the MCS. For these four products, the decrease in the TNC appeared at higher coagulant dosages, around 2000 ppm, than at pH 8.3, because there was more alkalinity of the water at this pH. For that reason higher coagulant dosages could be added to the water without reaching charge reversal. The behavior of alum was the same than at pH 8.3. First, TNC decreased, then it increased with the coagulant dosage, but in this case, the maximum increment TCS achieved was 180%. That value was smaller than at initial pH and it was achieved with a higher dosage of coagulant (3800 ppm) (figure 8). Regarding MCS evolution, PANS-PA2 is again the one with the maximum increase in the particle size, but the differences with PACl-HB, PACl-MB and PANS-PA1 were smaller than at pH 8.3. At pH 9.5 these three products showed high silica removal rates and the differences with PANS-PA2, the most efficient product, became smaller. Again alum was the only product that caused a decrease in the MCS (around

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25%). In this case, the decrease in MCS occurred at higher dosages higher (2400 ppm) than at initial pH 8.3 (around 1000 ppm).
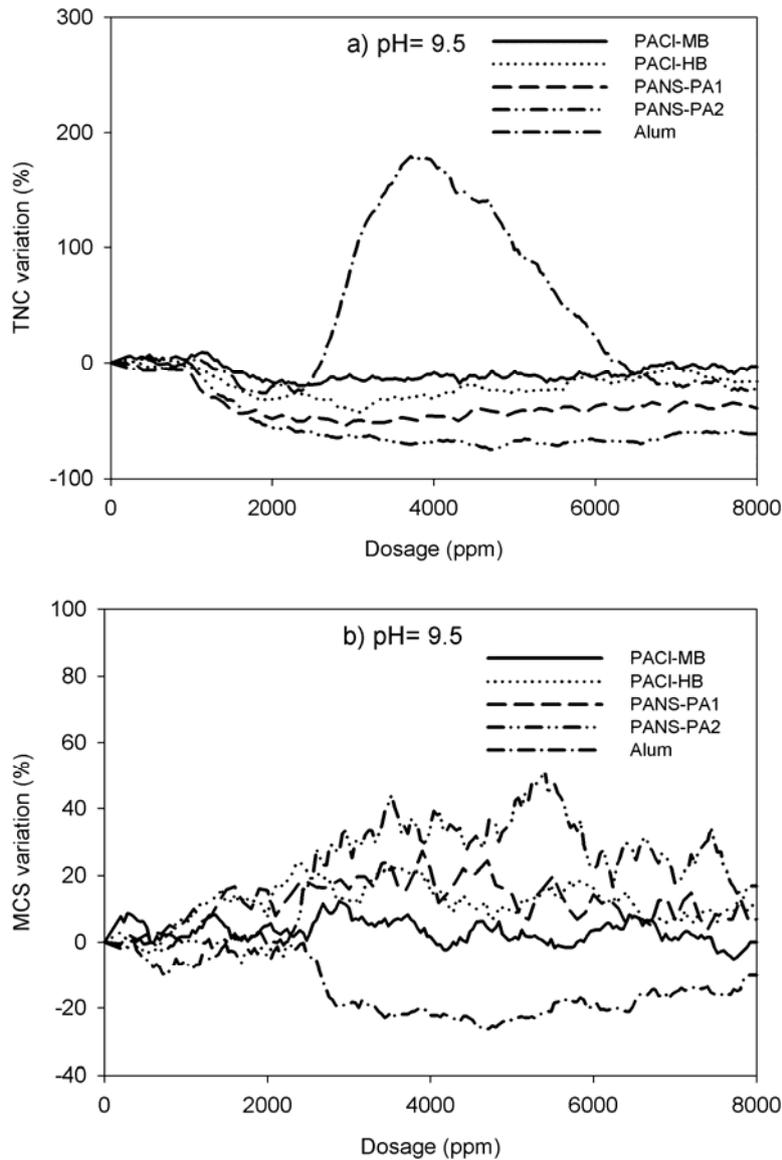
Figure 6.- TNC (a) and MCS (b) variation at pH= 9.5.

At pH 10.5, there were differences in TNC compared with initial pH and 9.5 (figure 7). With all products TNC decreased up to a minimum value and then increased. PANS-PA2 showed the minimum value in the TNC with a dosage of 2300 ppm. With PACl-MB, PACl-HB and PANS-PA1 there was also a minimum in the TNC that appeared around 2000-2500 ppm. In the case of alum, TNC showed almost the same tendency as at the other pHs, TNC decreased 30% with 1700 ppm of alum and remained constants for a longer period of time than with the other two pHs. Then the TNC increased up to 30%. Regarding MCS evolution all products but alum showed similar tendencies. At this pH the increase in the MCS obtained with PANS-PA2 was smaller than the one

obtained at pH 8.3 and 9.5 and was closer to the ones obtained with the rest of the products but alum. This fact is also in agreement with the differences on silica removal rates which became also smaller compared with pH 8.3 and 9.5. With alum, MCS started to decrease at a dosage of 4800 ppm.
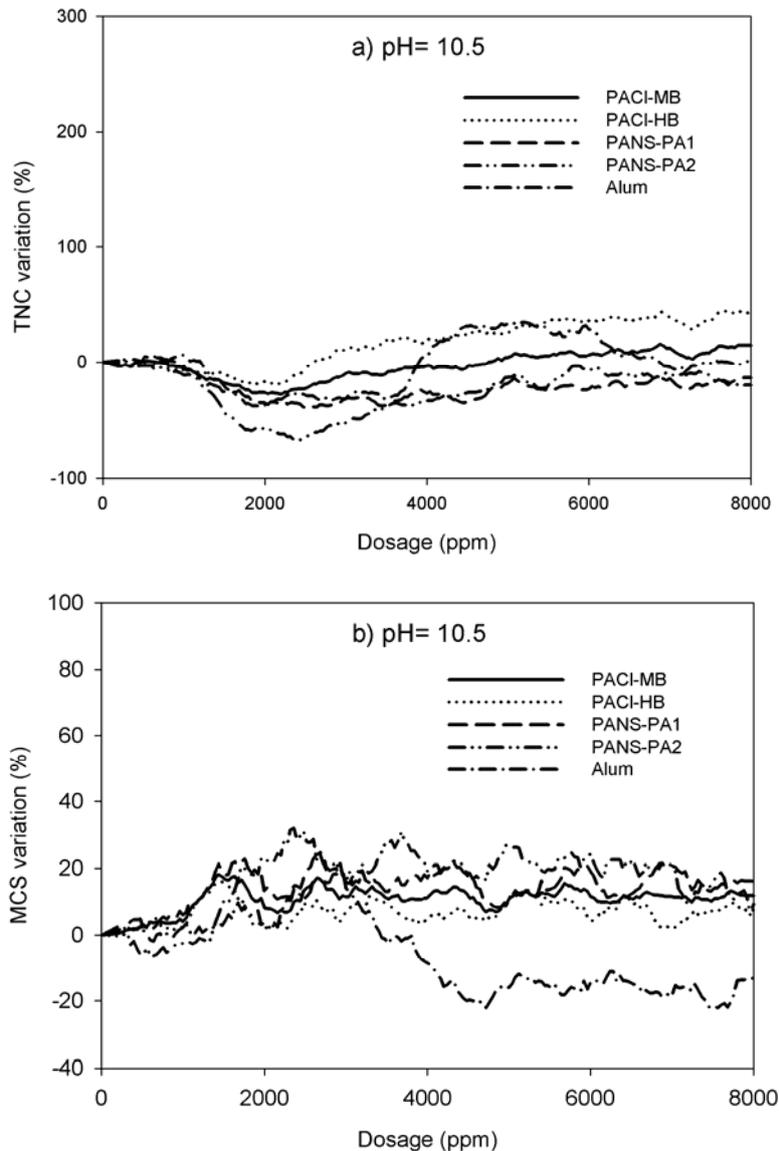
Figure 7. –TNC (a) and MCS (b) variation at pH= 10.5.

As alum showed a totally different trend, its behavior will be explained in more detail. At the three pHs tested there was a maximum in TNC curve (figure 8). This maximum appeared when the pH of the water was around 4. As commented before, alum is the coagulant with both the highest aluminum content and lowest basicity and, consequently, the product with the highest alkalinity consumption. Even at the tested dosages in jar-tests (up to 2500 ppm) at initial pH=8.3 final alkalinity was zero and almost zero at pH=9.5. At high dosages of alum sweep flocculation occurred increasing the TNC as $Al(OH)_3$ precipitates. After that, when pH decreased to around 4.5 and there was not hydroxyl groups to form more $Al(OH)_3$, a dissolution of the fresh $Al(OH)_3$ precipitated

occurred as at pH < 6 aluminum solubilizes in a high extent, causing a decrease in the TNC and MCS. The maximum in the TNC curves appeared at higher dosages at higher initial pHs, because with a higher initial pH there is a higher alkalinity which allow the formation of more Al(OH)$_3$ precipitates.
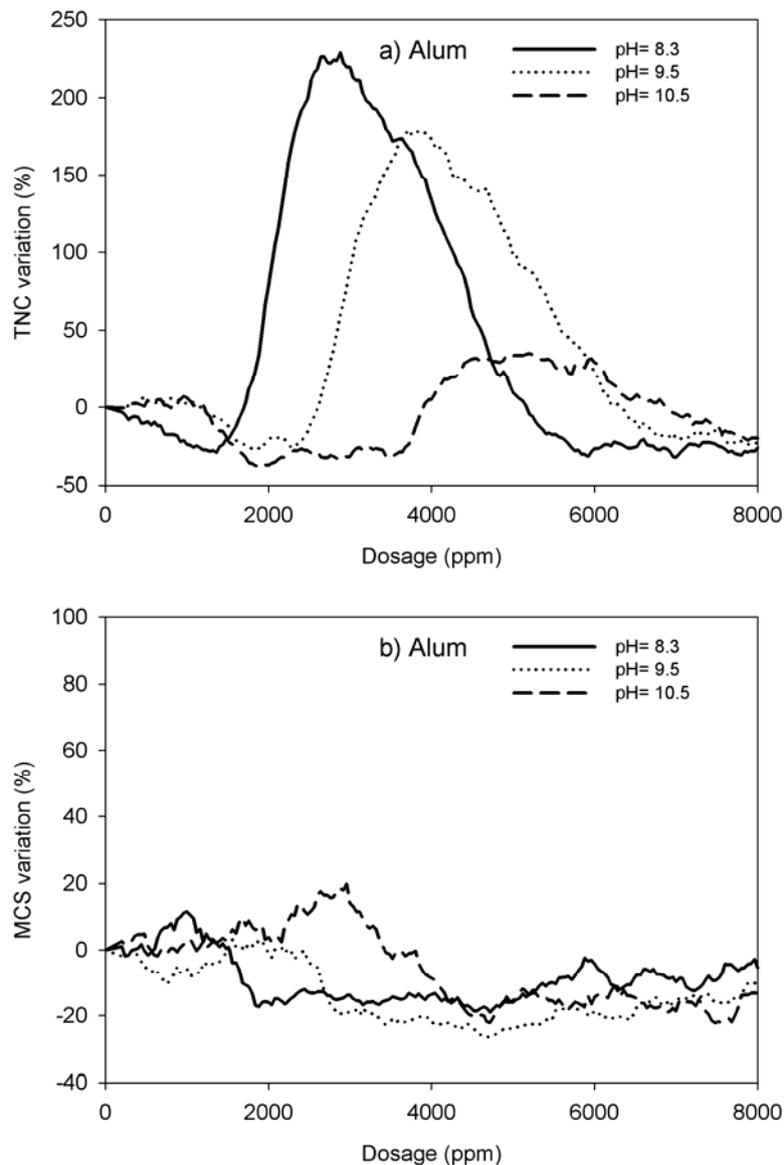
Figure 8. TNC (a) and MCS (b) variation of alum at pH 8.3, 9.5 and 10.5.

3.4. Optimum treatment option. To work at regular recovery rates in RO membranes (60-80%), it is necessary to decrease silica level down to 20-60 ppm. For an initial silica content of 140 ppm SiO$_2$ it was necessary, therefore, to achieve 60-85% silica removal. All the coagulants tested could reduce silica levels to at least 50 ppm. However, they did it at the highest initial pH tested (pH 10.5) and with high dosages, which implies high conductivity of the treated waters, slightly high final pH and high treatment costs. Final conductivity of the water has to be, at least, lower than 3.0 mS/cm. This conductivity is enough to work at 60% recovery in RO membranes, avoiding the need

of a further treatment of the RO rejects before discharge (<7.5 mS/cm) which would affect significantly the economic feasibility of the process. All the coagulants achieved the required silica removal at pH 10.5, PACl-HB also achieved the required silica removal at pH 9.5 and the highest dosage (2000-2500 ppm). Without any doubt, PANS-PA2 is the product recommended for this application. It has a great versatility as it achieved the highest silica removal efficiencies (up to 97%) but, even more important in this application, it could achieve high silica removal rates even without pH adjustment of the water. At this pH final silica concentrations were 45.4 and 37.5 ppm with dosages of 2000 and 2500 ppm, respectively. In these treatments the conductivity increased only from 2.2 mS/cm up to 2.4-2.5 mS/cm, and the COD removal rates are at the same time, the highest (26.5% and 27.7%, respectively). PANS-PA2 could be also used at pH 9.5 and dosages >1000 ppm to achieve the required silica removal, which would reduce the cost of the coagulation in the treatment, but slightly decreasing the other additional benefits. If the same dosage is used higher pH would improve the silica removal. For example, at 2500 ppm dosage, the pH adjustment to 9.5 increased the silica removal from 73.2% to 78.5% (compared to no pH adjustment), however, the conductivity increased from 2.5 mS/cm to 2.7 mS/cm and COD removal decreased from 28% to 22.3%. At initial pH 10.5 and 1500 ppm of coagulant, final silica concentration in water was 19.2 ppm, which was around half that at pH 9.5, and would be enough to work at 80% recovery in the RO process. However, conductivity was higher and COD removal was lower. In other different applications, the highest initial pHs and high dosages could be of interest, to achieve silica removals as high as 97% but in this application, a slightly lower silica removal is preferred if the quality of the waters is less affected.

Other possible solution, although with some drawbacks, could be the treatment with 500-1000 ppm of alum at pH 10.5. At these conditions, the silica concentration was reduced to 36.9 ppm (74% removal) and 27.7 ppm (80% removal), respectively. The drawbacks of using alum, previously mentioned, are partially minimized because it was used at very low dosages. In these conditions, the final conductivity was moderate, around 3.0 mS/cm, as well as the sulphates increase, from 200 ppm to 430-560 ppm. However, it is important to notice that a fine control of alum dosage is required, as overdose can occur, reducing significantly silica removal rates and in, some cases, increasing the turbidity of the treated waters. For example, at pH 10.5, silica removal could decrease from 80% to 44% when using 2000 ppm instead of 1000 ppm. Other drawback is the limited COD removal achieved, around 3%.

PACl-HB could achieve final 66-67% removal of silica (47-48 ppm residual silica) with an intermediate pH adjustment (pH 9.5). In this case, the final conductivity would be 2.8-3.0 mS/cm and the COD removal could be the 15-20% range. Higher removals could be obtained at pH 10.5 (72-76%) but the conductivity would increase to 3.3 mS/cm and the COD removal decrease to 6-8%. On the other hand, PANS-PA1 could achieve final 75-92% removals at initial pH 10.5 and dosages ranging 1500-2500 ppm. Conductivity of the treated waters would be around 3.0 mS/cm and the COD removal would be in the 15-20% range.

Finally, lime is preferred to caustic soda as pH regulator. The silica removal efficiency with both pH regulators was the same but using lime, the conductivity of the treated waters was lower, the COD removal was higher and the sedimentation rates were faster. In addition, lime is considerably cheaper than caustic soda.

4.-CONCLUSIONS

The bottleneck of deinking paper mills for reusing their effluent after advanced membrane technologies is high silica content of the water. It can be removed by coagulation; however, this treatment has to be optimized in terms of pH, nature and dosage of coagulant and chemical used for pH adjustment. The research proves that at higher pHs and dosages, the coagulation of silica is more efficient, reaching 97% silica removal with the best treatment. However, these high dosages and pHs, apart from the high costs, can produce an increase in the conductivity of the waters treated which could not be assumed for RO performance and probably, a final pH adjustment after the treatment would be necessary before water reuse.

The results demonstrate that PANS-PA2 was the most efficient and versatile coagulant. This product enables high enough silica removal efficiencies to operate at regular recoveries in RO processes (60-80%) with the advantage of an additional COD removal and a very limited conductivity increase. FBRM results showed that this product also generates the largest flocs. For the present application, a dosage of 2000 ppm without pH adjustment could be the optimum solution. Silica removal was around 70%, conductivity 2.4 mS/cm, final pH 8.1 and COD removal was 26%. For applications in which silica removal requirements are higher, higher pHs should be used.

The use of low dosages of alum (500-1000 ppm) at pH 10.5 could be another feasible alternative, as alum has a lower cost compared with the other products tested. In these conditions, a 75% silica removal could be achieved, however, the conductivity increase was higher than in the case of using PANS-PA2 (3.0 mS/cm) and there was a significant increase of sulphates in the treated waters (from 200 to 430-560 ppm). Final pH was higher than the required (8.6-9.7, depending on the dosage) and only a very low COD removal was achieved (3%). In addition, overdosing problems could occur, as the alkalinity consumption was very high and it could produce a pH decrease which could solubilize the previously formed $Al(OH)_3$ precipitates as it was demonstrated by FBRM studies.

LITERATURE

[1] R. Miranda, C. Negro, A Blanco, Accumulation of dissolved and colloidal material in papermaking- Application to simulation, Chem. Eng. J. 148 (2009) 385-393.

[2] R. Ordoñez, D. Hermosilla, I. San Pío, A. Blanco, Replacement of fresh water use by final effluent recovery in a highly optimized 100% recovered paper mill, Water Sci. Technol. 62 (2010) 1694-1703.

[3] R. Ordoñez, D. Hermosilla, I. San Pío, A. Blanco, Evaluation of MF and UF as pretreatments prior to RO applied to reclaim municipal wastewater for freshwater substitution in a paper mill: A practical experience, Chem. Eng. J. 166 (2011) 1694-1703.

[4] H. Hamäläinen, R. Aksela, J. Rautiainen, M. Sankari, I. Renvall, R. Paquet, Silicate-free peroxide bleaching of mechanical pulps: Efficiency of polymeric stabilizers, Proceedings TAPPI of International Mechanical Pulping Conference, (2007) 215−236, May 6-9, Minneapolis, United States.

[5] R. Sheikholeslami, S. Tan, Effects of water quality on silica fouling of desalination plants, Desalination 126 (1999) 267-280.

[6] J. T. Cornellis, D. Delvaux, R. B. Georg, Y. Lucas, J. Ranger, S. Opfergelt, Tracing the origin of dissolved silicon transferred from various soil-plant systems towards the river: a review, Diogeosci. 8 (2011) 89-112.

[7] Z. Amjad, J.F. Zibrida, R.W. Zuhl, A new antifoulant for controlling silica fouling in reverse osmosis systems, In International Desalination Association World Congress on Desalination and Water Reuse, (1997) October 6–9, Madrid, Spain.

[8] E. Neofotistou, K. D. Demandis, Use of antiscalants for mitigation of silica (SiO2) fouling desposition: fundamentals and applications in desalination systems, Desalination 167 (2004) 257-272.

[9] E. G. Darton, RO plant experiences with high silica waters in the Canary Islands, Desalination 124 (1999) 33-41.

[10] D. Hermosilla, R. Ordóñez, L. Blanco, E. de la Fuente, A. Blanco, pH and particle structure effects on silica removal by coagulation, Chem. Eng. Technol. 35 (2012) 1632-1640.

[11] T. S Huuha, T. A. Kurniawan, M. E. T. Sillanpää, Removal of silicon from pulping whitewater using integrated treatment of chemical precipitation and evaporation. Chem. Eng. J. 158 (2010) 584-582.

[12] E. El-Bestawy, I. El-Sokkary, H. Hussein, A. F. Abu Keela, Pollution control in pulp and paper industrial effluents using integrated chemical–biological treatment sequences, J. Ind. Microbiol. Biotechnol. 35 (2008) 1517-1529.

[13] S. Chen, H. Cheng, S. Yang, In-line Coagulation/Ultrafiltration for silica removal from brackish water as membrane pretreatment, Sep. Purif. Technol. 70 (2009) 112-117.

[14] W. Ma, Y. Zhao, L. Wang, The pretreatment with enhanced coagulation and a UF membrane for seawater desalination with reverse osmosis, Desalination 203 (2007) 256-259.

[15] A. M. Al-Rehaili, Comparative chemical clarification for silica removal from RO groundwater feed, Desalination. 159 (2003) 21-31.

[16] M. I. Aguilar, J. Saez, M. Llorens, A. Soler, J. F. Ortuño, Physico-chemical treatments of wastewaters. Coagulation-flocculation, First ed., University of Murcia, Murcia, 2002.

[17] C. Ye, D. Wang, B. Shi, J. Yu, J. Qu, M. Edwards, H. M. Tang, Alkalinity effect of coagulation with polyaluminum chlorides: Role of electrostatic patch, Colloids Surf. A. 294 (2007) 163-173.

[18] R. Miranda, C. Negro, A. Blanco, Internal treatment of process waters in paper production by dissolved air Flotation with newly developed chemicals. 2. Field trials, Ind. Eng. Chem. Res. 48 (2009) 3672-3677.

[19] D.J. Pernitsky, J.K. Edzwald, Selection of alum and polyaluminum coagulants: principles and applications. J. Water Supply Res. Technol.- AQUA 55 (2006) 88-98.

[20] K. E. Lee, N. Morad, T. T. Teng, B. T. Poh, Development, characterization and application of hybrid materials in coagulation/flocculation of wastewater: a review, Chem. Eng. J. 203 (2012) 370-386.

[21] X. Wu, X. Ge, D. Wang, H. Tang, Distinct coagulation mechanism and model between alum and high Al_{13}-PACl, Colloids Surf. A 305 (2007) 89-96.

[22] A. L. Ahmad, S. S. Wong, T. T. Teng, A. Zuhairi, Improvement of alum and PACl coagulation by polyacrylamides (PAMs) for the treatment of pulp and paper mill wastewater, Chem. Eng. J. 137 (2008) 510-517.

[23] R. Miranda, I. Latour, M. Sánchez, A. Blanco, Removal of silica in a paper mill effluent with enhanced aluminum salts coagulants, 12th Mediterranean Congress of Chemical Engineering, 15th-18th November (2011), Barcelona (Spain).

[24] S. H. Chuang, T. C. Chang, C. F. Ouyang, J. M. Leu. Colloidal silica removal in coagulation processes for wastewater reuse in a high-tech industrial park, Water Sci. Technol. 55 (2006) 187-195.

[25] Standard Methods for the Examination of Water and Wastewater. (2005) American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), United States. 21st ed.

[26] A. Blanco, E. Fuente, C. Negro, J. Tijero, Flocculation monitoring: focused beam reflectance measurement as a measurement tool, Can. J. Chem. Eng. 80 (2002) 734-740.

[27] A. Blanco, E. Fuente, C. Negro, C. M. Monte, J. Tijero, Focused beam reflectance measurement as a tool to measure flocculation, Tappi J. 10 (2002) 14-20.

[28] D.J. Pernitsky, J.K. Edzwald, Solubility of polyaluminum coagulants, J. Water Supply Res. Technol.-AQUA 52 (2003) 395-406.