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Efficiency of polyaluminum nitrate sulfate–polyamine hybrid coagulants for silica removal

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ABSTRACT

Previous studies have demonstrated the efficiency of commercial polyaluminum–polyamine coagulants for high silica removal from industrial effluents without pH adjustment. This paper studies the efficiency of newly developed tailor-made hybrid coagulants for silica removal, based on the combination of a commercial polyaluminum nitrate sulfate (PANS) and three polyamines (PAs) of different molecular weights. Four hybrids for each polymer, with different proportions of PANS and polyamine (5, 10, 15, and 20%) were tested at two initial pHs (8.4 and 10.5) and five dosages (in the range 500–2,500 mg/L). Results showed that without pH regulation (pH 8.4), all the hybrids were more efficient than PANS on silica removal, 5% of polyamine being the optimum content (>50 vs. 30% silica removal obtained by PANS). For the same level of efficiency (30% silica removal), the required dosages of hybrids are considerably lower than for PANS: 500 vs. 2,500 mg/L. At initial pH of 10.5, higher silica removal rates are obtained (90%) with all the products and the differences in efficiency between hybrid coagulants and PANS were minor. The hybrid coagulants were always more efficient in COD removal: 51 vs. 37% at initial pH 8.4, and especially at initial pH 10.5 (for similar silica removal): 31 vs. 4%. The effect of molecular weight of the PAs was significant for COD removal (higher molecular weight PAs are more efficient for COD removal), while it was not significant for silica removal efficiency. The main flocculation mechanisms and the visual aspect of the flocs for the different treatments have been analyzed. It is concluded that PANS induced a sweep flocculation, while PA hybrids produced flocculation by a combination of sweep flocculation and patch formation.

Keywords: Silica removal; Coagulation; Hybrid coagulant; Aluminum salt; Polyamine

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1. Introduction

Coagulation is widely recognized as an efficient silica removal technique. In this sense, aluminum coagulants are effective for the treatment of high silica loaded waters such as deinking paper mill effluents [1–3]. Among aluminum coagulants, polyaluminum chlorides offer several advantages compared to traditional ones such as alum or sodium aluminate. They are effective in a wider range of pHs and at low temperature, generate more compact and easily sedimentable flocs, are less likely to cause overdosage phenomena and also less sensitive to water properties fluctuations [4,5].

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Although polyaluminum chlorides have been extensively used in the last decades for wastewater treatment, chlorides can cause corrosion problems, thus sometimes, chlorides are partially substituted by other species such as sulfates or nitrates, providing a new range of substituted coagulants. Polyaluminum nitrates, polyaluminum sulfates, or a combination of them, such as polyaluminum nitrate sulfates (PANS), have been developed and tested with success in different applications [6–8]. Besides, these products can also be modified with organic polymers to create inorganic–organic hybrids. The most extensively used organic polymers are cationic polyacrylamides (PAMs), polydimethyldiallylammonium chloride (p-DADMACs), and polyamines (PAs) [9–11]. Hybrid coagulants offer the advantages of allowing high removal rates at lower dosages, broader pH operating range, and smaller sludge production due to the synergy between the individual components [12].

Previous studies carried out by the authors proved that modifications of PANS coagulants with cationic polyelectrolytes improved the efficiency of PANS for silica removal [2,3]. In these studies, commercial hybrids based on a polyamine (PA) and two PAMs were tested. Results showed that PA hybrids were more effective for silica removal than PAM hybrids, allowing intermediate silica removal rates and significant COD removal even without pH adjustment. If pH adjustment was not needed, conductivity increase and pH decrease of the treated water would be lower and the effluent would be able to be treated by ultrafiltration (UF) and reverse osmosis (RO) with a normal recovery (the current limitation is 20% recovery) in order to reuse it in the paper mill [13].

Although commercial PA hybrids allow reducing the treatment cost as no pH regulation is required, these coagulants are expensive. This paper aims to generate new knowledge on the formulation and use of PANS–PA hybrids for industrial applications. Taking into account that PA prices are around double the price of the aluminum salts, one of the main factors to optimize is the percentage of polyamine combined with the aluminum salt. In this sense, the novelty of the paper is that different tailor-made coagulants are prepared combining a commercial PANS coagulant with three PAs of different molecular weights in different ratios (5–20 wt.% of PA) in order to optimize both, the PA type and the PA content. The objective is to obtain a new brand of highly effective products with low PA contents reducing the active content in the hybrids and the dosage needed in the process and thus the cost of the treatment. The effectiveness of the hybrids is studied at two initial pH levels (8.4 and 10.5) and at five dosages (500–2,500 mg/L). The requirements of the treatment are set in reducing silica concentration to around 20–60 mg/L to allow increasing RO recovery from 20% to 60–85%, without silica scaling problems in the RO membrane when reusing the effluent as fresh water in the process. Additionally, COD removal is also considered. Finally, the flocculation mechanism and floc aspect are studied in detail.

2. Materials and methods

2.1. Materials

2.1.1. Source of wastewater

This study was carried out with the effluent of a Spanish paper mill using 100% recovered paper to produce newsprint. This effluent is treated by a combination of a primary treatment by dissolved air flotation, followed by a secondary treatment in a moving bed bioreactor and a secondary dissolved air flotation. Water samples from the final effluent, before its discharge into an urban wastewater treatment plant, were taken. Table 1 summarizes its main characteristics. Dissolved fraction was obtained by filtration through 0.45-μm PTFE filters.

2.1.2. Chemicals

Different inorganic–organic hybrids have been prepared using PANS as the base product. PANS is a commercial PANS with an intermediate aluminum content and basicity (5.5% Al, 46% basicity), with 16.0% NO_3^- and 3.0% SO_4^{2-} contents. Hybrids were prepared by direct blending of PANS with three PAs of different molecular weights at ambient temperature, their molecular weight following the order:

Table 1
Characteristics of the effluent (raw water and dissolved fraction)

Raw water		
Parameter	Mean	Std. dev.
pH	8.4	0.1
Conductivity (25°C) (mS/cm)	1.8	0.1
Total solids (mg/L)	1,990	50
Turbidity (NTU)	11.4	0.7
Cationic demand (meq/L)	0.52	0.07
Dissolved fraction		
Total solids (mg/L)	1,890	40
COD (mg/L)	256	7
Silica (mg/L SiO_2)	145	11
Calcium (mg/L)	33.7	0.3
Magnesium (mg/L)	2.8	0.1

PA1 < PA2 < PA3. PANS and PA2 were supplied by Sachtleben Wasserchemie GmbH, while PA1 and PA3 were supplied by Kemira Oyj. Table 2 shows the main characteristics of these coagulants.

For each polyamine type, four different addition levels were tested. These levels were 5, 10, 15, and 20% wt% of commercial solutions (48–52% dry solids), the rest being PANS. Higher polyamine contents were also prepared, but the blends were unstable as evidenced by the appearance of turbidity within 24 h after its preparation. Additionally, PANS was also tested alone to evaluate its efficiency compared to the hybrid materials. Hybrids are noted as PANS–PAx-Z where PAx is PA1, PA2, and PA3 (depending on the polyamine used) and Z is the polyamine weight content in the hybrid. The aluminum content and the cationic charge of these hybrid coagulants, grouped by the commercial polyamine solution content, are shown in Table 3. Finally, all the hybrids and PANS were tested in combination with the same flocculant: an anionic polyacrylamide of high molecular weight and medium charge, supplied by Ciba (Switzerland).

2.2. Methods

For each coagulant, five dosages (500, 1,000, 1,500, 2,000, and 2,500 mg/L) were tested, those that were selected according to preliminary tests [2]. These dosages were tested at two pHs 8.4 (initial pH of the effluent) and 10.5, as silica removal increases at basic pHs and is almost removed completely at pH around 10.5 [2,3]. Higher pHs would increase significantly both the conductivity of the treated waters and the treatment costs, without further significant silica removals. Flocculant dosage was fixed at 10 mg/L in all the tests. A sample volume of 200 mL was used in all the experiments.

First, in the case of initial pH 10.5, the pH of the samples was adjusted by adding NaOH (10 wt./vol.%). After 30 s of high speed mixing at 200 rpm, the coagulant was added to the sample from a 10% wt./vol. solution and mixed at high speed (200 rpm) during 2.5 min. Next, the flocculant was added from a 0.10% wt./vol. solution and was mixed for 10 min at slow speed (40 rpm). Finally, the sample was allowed to settle during 60 min and the supernatant was characterized by pH, conductivity, cationic/anionic demand, and turbidity. Furthermore, reactive silica and chemical oxygen demand (COD) were measured in the dissolved fraction of the supernatant, obtained by centrifugation at 2,000*g* during 15 min in a Hettich Zentrifugen Universal 32. Jar tests were carried out in a multiposition magnetic stirrer OVAN MultiMix Heat D at room temperature (20 ± 2˚C) by duplicate, and the average error between replicates of the analytical measurements was always under 5%. Coagulants, the flocculant, and the pH regulator solutions were prepared on daily basis. To avoid the possible degradation of the wastewater, all trials were carried out within 5 d after the sampling and the waters were always kept stored at 4˚C until its used.

The pH was measured using a GLP 22 pH meter (Crison, S.A), according to Standard Method 4500 [14] and conductivity was determined with a GLP 31 conductivity meter (Crison, S.A.), according to the ISO 7888. Cationic and anionic demand was measured by colloidal titration using 0.001 N poly-diallyldimethylammonium chloride (p-DADMAC) and 0.001 N polyethylene sulfonic acid sodium salt (PES-Na) as titrants, respectively, in a CAS Charge Analyzing System supplied by AFG Analytic GmbH. Turbidity was measured with a LP 2000–11 nephelometer, supplied by Hanna Instruments, according to ISO 7027. Total solids were measured according to the Standard Method 2450 B [14]. Reactive silica was measured by flow analysis and photometric detection through silicomolybdate and reduction to molybdenum blue, using a FIA Compact (MLE GmbH), according to DIN EN ISO 16264 and expressed as mg/L of SiO_2. COD was photometrically measured by the Nanocolor® COD 1500 Method from Macherey-Nagel GmbH, according to ISO 15705:2003 in an Aquamate UV–vis spectrophotometer supplied by Thermo Scientific Inc. Finally, calcium and magnesium content was measured using a direct air-acetylene flame atomic absorption method, according to ISO-7980:1986 in a SpectraA 220 spectrophotometer supplied by Varian.

Table 2
Characteristics of the coagulants used for the hybrid formulations

Coagulant	Cationic charge (meq/g)[a]	Molecular weight
PANS	0.8	–
PA1	3.2	Low
PA2	3.4	Medium
PA3	3.8	High

[a] Expressed in g of commercial solution, measured through colloidal titration.

3. Results and discussion

3.1. Removal of contaminants

3.1.1. Silica

Fig. 1 shows silica removal rates obtained with different hybrid coagulants at initial pH 8.4 and 10.5.

Table 3
Characteristics of the hybrid coagulants

Coagulant	Polyamine content (wt.%)	Al (%)	Cationic charge (meq/g)
PANS	–	5.5	0.8
PANS–PAx-5	5	5.2	≈0.9–1.0
PANS–PAx-10	10	5.0	≈1.1
PANS–PAx-15	15	4.7	≈1.2
PANS–PAx-20	20	4.4	≈1.3–1.4

At initial pH 8.4, all coagulants were more effective than the base commercial polyaluminum salt (PANS). With PANS, silica removal obtained varied between 12 and 31% with 500 and 2,500 mg/L, respectively.

With PANS–PA1, maximum silica removal obtained was 47% with 2,500 mg/L of PANS–PA1–20. The other PA1 hybrids yielded very similar maximum efficiencies (around 40%) but at different dosages: 1,000 mg/L of PANS–PA1–5, 1,500 mg/L of PANS–PA1–10, and 2,000 mg/L with PANS–PA1–15.

At initial pH 8.4, PANS–PA2 hybrids showed slightly higher silica removal rates than PANS–PA1 hybrids (around 50%), with 2,500 mg/L of PANS–PA2–5 and PANS–PA2–10. With 500 mg/L, maximum silica removals of 39, 35, 26, and 23% were obtained with active contents of 5, 10, 15, and 20%, respectively. The addition of PA2 considerably improved silica removal especially at low dosages.

Silica removal efficiencies with PANS–PA3 hybrids were slightly lower than with PA2 but still higher than with PA1. In this case, maximum removal rates were achieved with 2,500 mg/L of the different hybrids and varied between 51% with PANS–PA3–5 and 40% with PANS–PA3–20. With 500 mg/L of PANS–PA3–5, 42% silica removal was obtained compared to 12% at the same dosage using PANS. On the other hand, silica removals obtained with 20% PA3 were lower than with the other three hybrids.

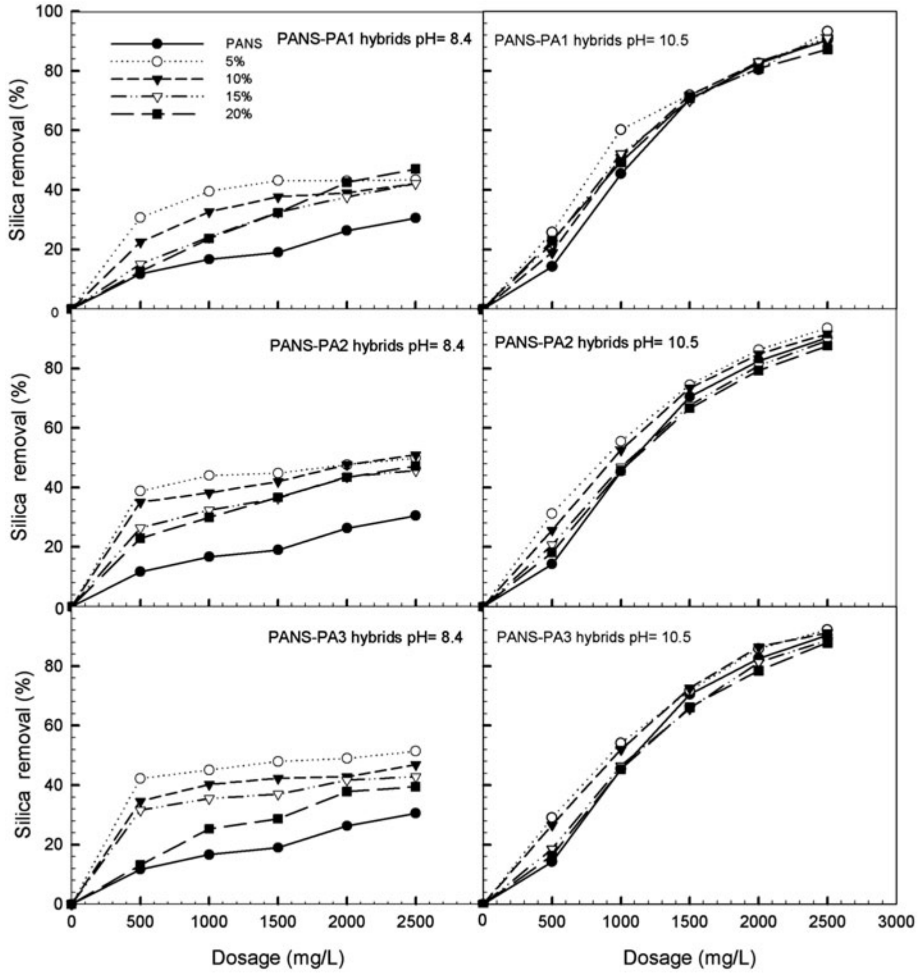

Fig. 1. Silica vs. hybrid coagulant dosage at different initial pHs.

As a general trend, it was observed that silica removal increased mainly at the lower dosages, while silica removal values remained almost constant at the highest dosages. This could be explained as at initial pH 8.4 only part of total silica is ionized, thus only a certain fraction of silica could be removed by coagulation. The higher alkaline pH, the higher ionization of silica, and hence higher removal rates could be achieved [15–17]. Very efficient products, such as the hybrids tested, removed most of silica ionized at low dosages. On the contrary, with a less efficient product such as PANS, silica removal continuously increased with the dosage and, even at the highest dosage tested; its efficiency was still far from those obtained with the hybrid coagulants. It was also observed that silica removal decreased with increasing polyamine content at the lower dosages. One of the factors affecting this behavior could be the lower aluminum content in the hybrid coagulant. In this sense, with the highest dosage of the hybrid coagulant (2,500 mg/L), where the aluminum content is high enough, the removal rates obtained with the hybrids were very close and the addition of the increased dosages of PAs did not have a detrimental effect on silica removal. It was also observed that, at lower dosages, high molecular weight polyamine was better for silica removal.

The synergy between the PAs and the aluminum salt allows achieving similar silica removal rates with 500 mg/L than with 2,500 mg/L of PANS, with only 5% of polyamine in the hybrids. Another advantage of using hybrid coagulants is that maximum 50% silica removal could be achieved compared to 31% with PANS, at 2,500 mg/L dosages.

Trends observed at initial pH 10.5 were very different to those obtained without pH regulation. At initial pH 10.5, silica removal continuously increased with the coagulant dosage. This could be explained by two simultaneous factors. The first one is that at this pH, silica was ionized in a larger extent than at pH 8.4, therefore more silica could be removed by coagulation. The second one is that at pH 10.5, there was more alkalinity available for aluminum coagulants to form the different aluminum hydroxides which are the active species in coagulation. At pH 10.5, the differences on silica removal rates between the hybrids and PANS were lower than at pH 8.4. On the other hand, the molecular weight of the polyamine or the percentage of polyamine in the hybrids had no significant effect. PANS was able to obtain 90% removal with 2,500 mg/L dosage. Moreover, still high removal rates of 71 and 83% were also obtained with lower PANS dosages: 1,500 and 2,000 mg/L, respectively. In the case of hybrid materials, silica removal rates were around 50, 70, 80, and 90% with 1,000, 1,500, 2,000, and 2,500 mg/L, respectively, for all the hybrids tested. At 500 mg/L, differences between the different hybrids were higher. In this sense, silica removal varied between 16% obtained with PANS–PA3–20 and 31% obtained with PANS–PA2–5, while with PANS was 14%.

As observed in previous studies, conventional and hybrid coagulants have large differences at lower pHs, while have similar efficiencies if the pH is high enough [2]. This is because aluminum coagulants are usually more efficient at high pHs as they require high alkalinity to form the aluminum hydroxides which are the active species on coagulations. Therefore, high pHs (and high alkalinities) can render better efficiency. On the other hand, PA polyelectrolytes do not require alkalinity consumption, allowing working efficiently in a wider pH range than aluminum products such as PANS. Therefore, although higher silica removals were expected at higher pHs due to ionization of silica, these increases would be higher in the case of PANS (as its efficiency is also increased) than in the case of PA hybrids (which has a similar efficiency in a wider pH range).

The use of the hybrid coagulants would not be justified at initial pH 10.5, since the marginal increase in silica removal would not compensate the increase in treatment costs due to the use of the organic polymers. This is completely different to what occurs at initial pH 8.4, where the use of hybrid coagulants would be clearly recommended. At initial pH 8.4, silica removal did not increase by increase in the polyamine content in the hybrid, showing the best results with 5% active content, which is also very beneficial for the treatment costs.

Taking into account the solubility of silica, to work at regular recoveries of 60–80% in RO membranes it would be necessary to decrease silica from 145 mg/L initial content to around 20–60 mg/L (60–85% removal). This objective could be achieved at pH 10.5 with all the hybrids and PANS, with dosages of 1,500 mg/L or higher. If higher removals were necessary it would be possible even to achieve a 94% silica removal with 2,500 mg/L of PANS–PA2–5 at initial pH 10.5. With no pH regulation, it was not possible to meet these stringent criteria as a maximum 50% removal rate was obtained. However, it could be an interesting option to reduce silica content in the effluent to achieve the necessary removal rates to meet SiO_2 limit for discharge (50 mg/L in Finland, Canada, or United States) [16] or to work at recoveries of 60–80% in RO membranes in paper mill effluents with around 100 mg/L initial SiO_2 content.

3.1.2. Chemical oxygen demand

Although the most critical parameter for effluent reuse in this paper mill is silica content, COD is also of interest to minimize the possible organic fouling on the membranes. Previous studies have demonstrated that there is a certain competition between COD and silica removal for a fixed dosage of coagulant, therefore silica and COD removals usually show opposite trends [1,2].

Fig. 2 shows the COD removal vs. dosage at initial pH 8.4 and 10.5. Opposite to silica, COD removal was lower at higher initial pH. At initial pH 8.4, the maximum COD removal was obtained at the highest dosage tested (2,500 mg/L) for all the hybrids. With the reference product (PANS), COD removals of 0, 12, 23, 31, and 37% were obtained with 500, 1,000, 1,500, 2,000, and 2,500 mg/L. At initial pH 8.4, PANS–PA1–10, among PA1 hybrids, was the best product at all the dosages. COD could be reduced from 270 to 160 mg/L (43% removal) either with 2,500 mg/L of PANS–PA1–5 or PANS–PA1–10. At initial pH 8.4, a maximum 44% COD removal was achieved with PANS–PA2–5. With PA2, maximum COD and silica removal were achieved under the same conditions of 2,500 mg/L of PANS–PA2–5. With PANS–PA3 hybrids, maximum COD removal of 51% was achieved with 2,500 mg/L PANS–PA3–15.

According to these results, COD removal increased with the active content of polyamine, but there was a maximum active content over which COD removal decreased. It was also observed that the higher the molecular weight of the polyamine the higher the removal rates. Additionally, the higher molecular weight of the polyamine the higher PA active content could be used in the hybrid before the efficiency decreased. In this sense, with 2,500 mg/L and 20% of active content, COD removals obtained were 8, 28, and 43% obtained with PA1, PA2, and PA3, respectively.

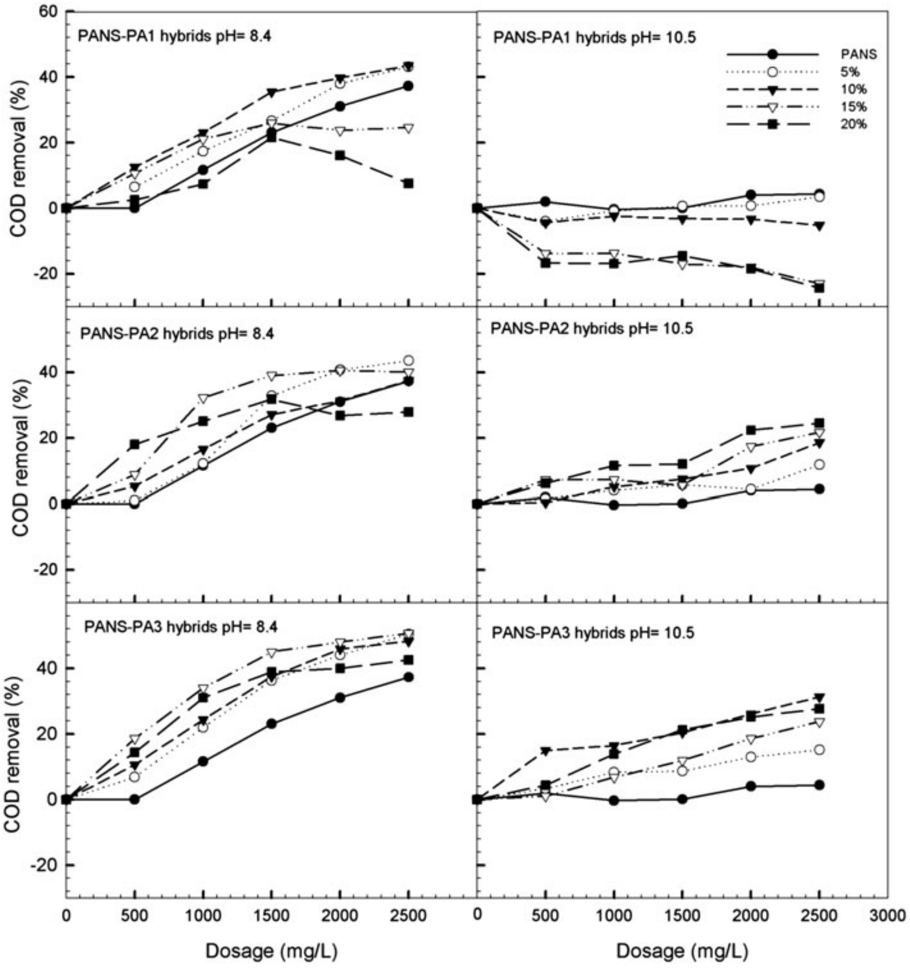

Fig. 2. COD vs. hybrid coagulant dosage at different initial pHs.

Moreover, COD removal rates obtained with PANS–PA3 hybrids were higher than with the reference product even with high silica removal rates which is of great interest. At pH 8.4, the optimum condition for silica and COD removal was obtained with 2,500 mg/L of PANS–PA3–5. Under these conditions, 50% silica removal and 50% of COD removal were achieved. As commented before, at initial pH 8.4, only part of the silica was ionized thus silica removal achieved a maximum at low dosages and then, remained constant. This did not occur with COD. In this case, the higher the dosage the higher the COD removal.

At pH 10.5, COD eliminations were lower than at initial pH 8.4. PANS obtained COD removal rates lower than 4% at the five dosages tested. This means that PANS had clearly more affinity for silica than for organic matter. PANS–PA1 hybrids did not remove COD, moreover, final COD values increased with the increase in the active content. The reason could be that the organic part of the hybrid coagulant could be measured as COD. COD removals with PA2 hybrids increased compared to PA1 hybrids. With PANS–PA2 hybrids, COD removal increased with the dosage and the active content, maximum removal of 24% was obtained with 2,500 mg/L of PANS–PA2–20. This maximum COD removal was not achieved under the same conditions of maximum silica removal. The decline in silica removal at the highest PA2 content was accompanied by an improvement in COD removal. Under the conditions of maximum silica removal (92%) at 2,500 mg/L of PANS–PA2–10, 19% COD removal was obtained. PANS–PA3 hybrids showed higher removal rates than other polymers and achieved a maximum COD removal of 31% with 2,500 mg/L of PANS–PA3–10, where the maximum silica removal of 91% was achieved. With 5% of active content, COD removal rates were slightly lower than with the rest of the PA3 hybrids tested. It seems that higher molecular weights of the polyamine (for a similar charge density) improve COD removal.

Based on the results obtained, it can be concluded that COD removal increased with the dosage of the hybrid and, opposite to silica removal, it decreased at higher initial pH. In general, it seems that high active contents impaired COD removal at pH 8.4, while enhanced COD removal at pH 10.5, probably due to the highest cationic demand at this pH which is still far from neutralization even at the highest active contents and dosages used. Finally, higher molecular weight PAs seem to be more efficient for COD removal.

3.1.3. Cationic demand

Another important parameter in coagulation processes is the cationic demand, which measures the surface charge of anionic particles in a suspension. A high reduction in the cationic demand is usually necessary to destabilize the contaminants of the waters.

The neutralization capacity of the different treatments is mainly governed by the charge density of the products, which can vary depending on the characteristics of the water such as pH or conductivity. As shown in Fig. 3, the three PAs had a considerable higher charge density than PANS (3.2–3.8 vs. 0.8 meq/g, Table 1). Additionally, it is important to notice that charge density of the aluminum salt was 0 meq/g at pHs over 9. Taking into account that high pHs are necessary for the ionization of silica, there is a need to find other type of products that do not lose their charge at alkaline pHs. In this sense, as it is observed in Fig. 3, the addition of the PAs to PANS made the charge of the products more independent of the pH. It is also important to consider that the initial cationic demand is higher at higher initial pHs because there is a higher content of hydroxide ions and, in a lower extent, some ionization of species such as carboxylic or fatty acids, which are present in the waters. Thus, to achieve charge neutralization at higher pHs, higher dosages of the coagulants are necessary.

As shown in Fig. 3, the charge density of the different hybrids was always higher than PANS and their charge was higher at increased polyamine active contents. On the other hand, there were no important differences on the charge density of the

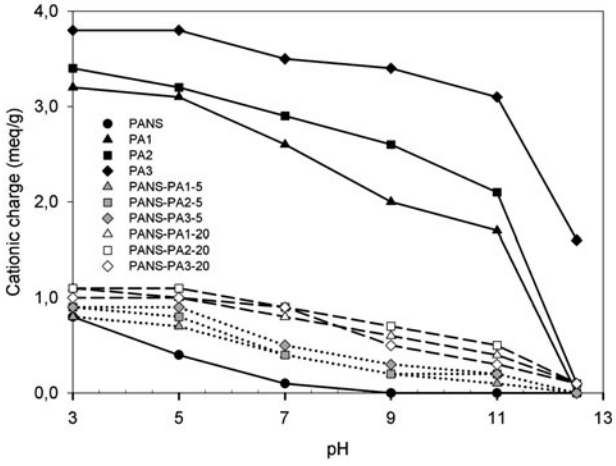

Fig. 3. Cationic charge vs. pH for the different coagulants.

different hybrids with the same percentage of polyamine. With the 20% hybrids, charge density was around 0.5–0.7 meq/g at pH 9 and around 0.3–0.5 meq/g at pH 11. Besides, for the 5% polyamine hybrids, charge density was around 0.1–0.2 meq/g at pH 9 and 11.

Fig. 4 shows final cationic demand with the different treatments. At initial pH 8.4 and 10.5, no charge reversal was achieved with the reference product (PANS), final cationic demand varied between 0.54 and 0.16 meq/L at pH 8.4 and 0.73–0.64 meq/L at pH 10.5. The decrease in cationic demand was higher at pH 8.4 than at pH 10.5 probably due to the lowest charge density of PANS at higher pHs. PA1 was the product with the lower charge density and its hybrids neither at pH 8.4 nor 10.5 achieved charge neutralization. Cationic demand of the treated water ranged 0.47–0.09 meq/L at pH 8.4 and 0.89–0.35 meq/L at pH 10.5.

With PA2 hybrids and at initial pH 8.4, charge neutralization occurred with PANS–PA2–15 and PANS–PA2–20 with dosages over 2,000 mg/L and over 1,500 mg/L, respectively. However, at pH 10.5, charge reversal did not occur. The cationic demand of the treated water varied between 0.8 meq/L with 500 mg/L of PANS–PA2–5 and 0.1 meq/L with 2,500 mg/L of PANS–PA2–20. PANS–PA3 also achieved charge reversal with the 15 and 20% hybrids but in this case at dosages higher than 2,000 mg/L. At pH 10.5, cationic demand varied between 0.72 meq/L with 500 mg/L of PANS–PA3–5 and 0.11 meq/L with 2,500 mg/L of PANS–PA3–20.

Although the reduction in cationic demand means the destabilization of anionic matter, it can be either inorganic (i.e. silica) or organic (i.e. COD). Therefore, a direct relationship between silica removal and cationic demand did not occur in all the cases, but it is clear that reduction in cationic demand is one of the main

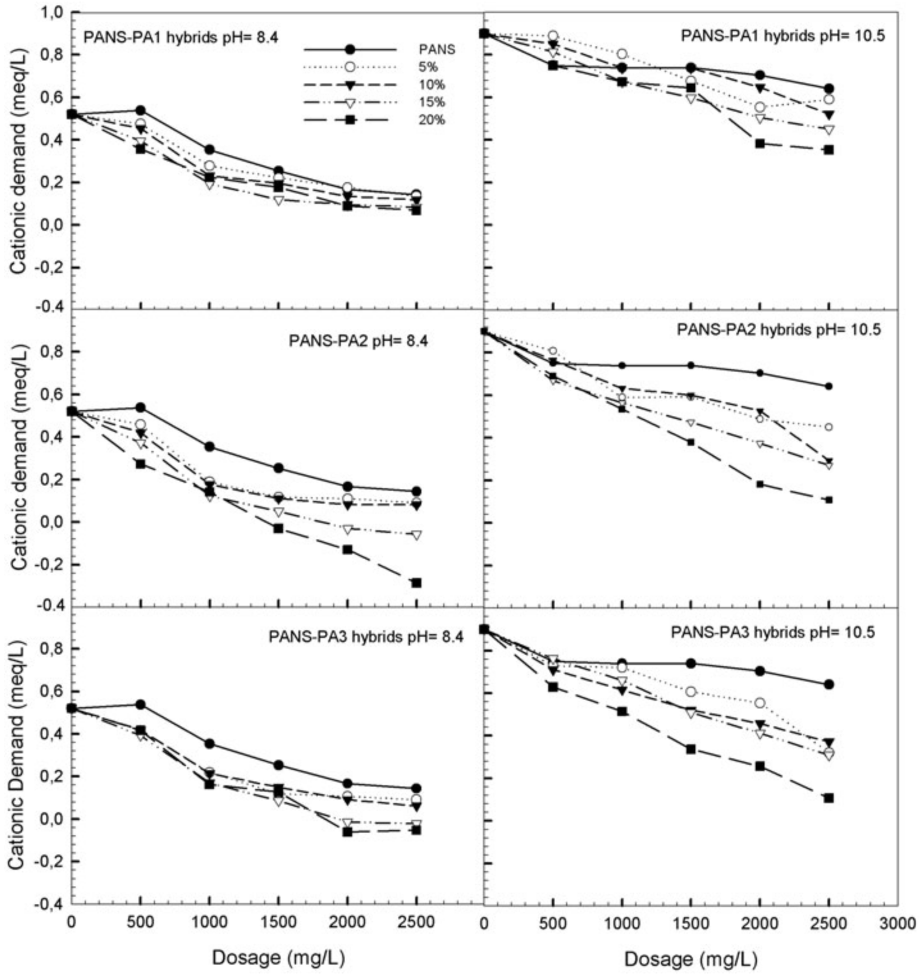

Fig. 4. Cationic demand vs. hybrid coagulant dosage at different initial pHs.

parameters affecting silica removal. It is very important to notice that charge reversal occurred for some hybrids (Fig. 4), however, this fact did not impair silica removal. This fact may be caused by the contribution of other coagulation–flocculation mechanisms apart from charge neutralization as explained in Section 3.2. It is also of interest that the higher the initial pH the higher the cationic demand. Consequently, when using coagulants with constant and even decreasing charge, the decrease in cationic demand would be lower. Moreover, higher initial pHs favor silica ionization, thus silica is removed by coagulation and/or precipitation [15–17].

3.1.4. Conductivity

Conductivity of the treated waters is also an important issue on this application for two reasons: (a) an important increase in the conductivity of the treated waters could increase scaling problems on RO membranes, which is exactly what is tried to be avoided and (b) a high conductivity of the treated waters could not make possible the direct discharge of RO rejects (discharge limit for this specific mill is 7.5 mS/cm), increasing the treatment cost and thus the economic feasibility of the whole effluent reuse treatment.

Final conductivity of the water is determined mainly by the pH adjustment and the nature and dosage of the coagulants used. At initial pH 10.5, the increase in conductivity caused by the pH regulation with NaOH was around 1 mS/cm compared to initial pH 8.4, i.e. conductivity of the water was 1.8 mS/cm at pH 8.4 vs. 2.8 mS/cm at initial pH 10.5. The coagulation treatment also affects the final conductivity but in a lower extent. Conductivity increases with the coagulant dosage, but this increase was in all the cases lower than 0.2–0.3 mS/cm at pH 8.4, and lower than 0.1 mS/cm at pH 10.5. The final conductivity with the reference product PANS was in the same range as the hybrid materials, as polyamine proportions are relatively low to observe significant changes.

3.1.5. pH

Metal salts such as aluminum salts consume alkalinity to form their active flocculation species, i.e. $Al(OH)_3$. This alkalinity consumption causes a pH decrease in the treated waters and its extent depends on the dosage of the product, their aluminum content, and basicity. In this study, the same dosages of the products were used, thus the differences were related to the aluminum content of the products and their basicity, which depends on the proportion of PANS in the hybrid materials. Theoretically, the higher the aluminum content and the lower basicity of the chemical, the higher the alkalinity consumption and hence, the higher pH decrease observed.

The pH after the treatment is also an important parameter to take into account when the water is going to be reused. To avoid any pH "shock" when mixing the treated effluent with process waters, which could cause several scaling phenomena, the pH should be around 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: the pH adjustment before coagulation and the pH decrease caused by the alkalinity consumption of the coagulants. With the reference product (PANS), the highest pH decreases were obtained: 1.5 at initial pH 8.4 (final pH 6.9) and 0.9 at initial pH 10.5 (final pH 9.6). With the different hybrids, although the higher pH decrease was observed at the highest dosages, variations among the different hybrids were low, as the polymer content used was similar. With all the hybrids, pH decreased 1.2–1.5 units (final pH 6.9–7.2) at initial pH 8.4 and between 0.5 and 0.9 (final pH 9.6–10.0) at initial pH 10.5.

3.1.6. Turbidity

Turbidity varied depending on the treatment used. At initial pH 8.4, turbidity of the treated water decreased with the coagulant dosage. At this pH, with all the products tested including PANS, final turbidity lower than 3 NTU could be achieved. On the other hand, at pH 10.5, turbidity increased with the pH regulation from 10.4 NTU up to 30.0 NTU. At this pH, final turbidity also decreased with the coagulant dosage. PANS was able to reduce turbidity to 2.2 NTU. With the hybrids turbidity varied between 2.0 and 30.0 NTU.

3.2. Flocculation mechanism and flocs aspect

As commented before, high reduction in cationic demand is necessary to achieve high removal rates, however, other flocculation mechanisms, different to charge neutralization, are also possible. If the removal of the contaminants took place by charge neutralization, the maximum removal rate would be close to the isoelectric point and overdose would be possible (restabilization occurs at charge reversal). Charge neutralization is the main flocculation mechanism at low dosages of aluminum. However, at high dosages of aluminum salts, where the solubility of $Al(OH)_3$ is exceeded, the main flocculation mechanism is usually "sweep flocculation". In this flocculation mechanism, the contaminants are removed by enmeshment in fresh precipitated flocs of $Al(OH)_3$. In this case, the optimum dosage of coagulant does not occur at the isoelectric point and no overdose phenomena are observed, even reaching charge reversal [5]. Generally, both mechanisms are also present. Due to the high dosages used in the present study, sweep flocculation seemed the predominant which is corroborated by the increased removal of contaminants at dosages exceeding the isoelectric point.

In the case of the PAs, other coagulation–flocculation mechanisms such as patch or bridging formation are common [18]. For polyelectrolytes of low to medium molecular weight and high charge density, as the PAs used in this study, patch model is usually the main flocculation mechanism. In this case, the maximum in the flocculation efficiency does not take place in the isoelectric point. This maximum is dependent on the charge of the local patches but occurs at ~50% coverage of surface particles. In the case of the hybrid coagulants, the flocculation mechanism would be the result of a combination of the flocculation mechanism of the aluminum salt (mainly sweep flocculation) and the polyamine (patch formation).

In this study, polyacrylamide was also added in a low dosage (10 mg/L) after coagulation. In this case, bridging formation is the typical flocculation mechanism for this high molecular weight and intermediate charge density polymer. However, depending on the initial pH and the nature of the coagulants, different aspect of the flocs were observed, especially when PANS and hybrid materials are compared. Figs. 5 and 6 show the aspect of the flocs obtained with PANS and the hybrids at initial pH 8.4 (Fig. 5) and initial pH 10.5 (Fig. 6). Pictures were taken just after flocculation and after 1 h settling.

At initial pH 8.4, flocs obtained with the PANS and the hybrids presented similar aspect. At this pH, the highest COD removal rates and the lowest silica removal rates were obtained, thus these flocs are mainly composed by organic matter. These flocs were very large and considerably light, presenting a higher tendency to float. On the other hand, at initial pH 10.5, silica removal increased, while COD removal decreased. As observed in Fig. 6, the flocs were clearly heavier than at pH 8.4 and settled very easily due to the higher density of flocs removing silica than those removing organic matter. Moreover, at pH 10.5, significant differences in the flocs obtained with PANS and with the hybrids were observed. Flocs obtained with PANS were small and homogeneously dispersed, which is in agreement with a predominant sweep

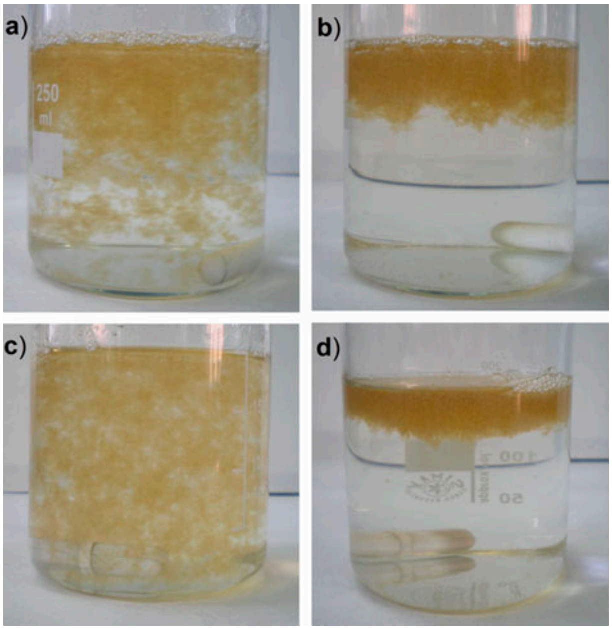

Fig. 5. Flocs formed at initial pH 8.4: (a) PANS after flocculation, (b) PANS after settling, (c) Example of hybrid material after flocculation, and (d) Example of hybrid material after settling.

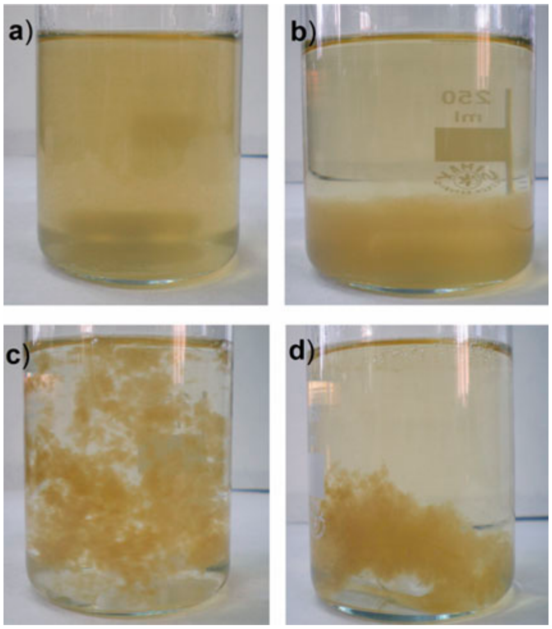

Fig. 6. Flocs formed at initial pH 10.5: (a) PANS after flocculation, (b) PANS after settling, (c) Example of hybrid material after flocculation, and (d) Example of hybrid material after settling.

flocculation mechanism. In the case of hybrids, the aspect of the flocs was similar to the one obtained at initial pH 8.4 but heavier and denser due to the higher presence of inorganic matter in the flocs. These flocs were larger than those obtained by PANS, therefore a partial patch flocculation mechanism enhanced the formation of larger flocs than those of sweep flocculation.

There were two factors affecting the behavior and aspect of the flocs, both conditioned by the initial pH. The first factor affecting the floc aspect is silica ionization. When silica is ionized, it is preferably removed compared to organic matter. In this case heavy flocs which settle easily are formed. Second, the flocculation mechanism is dependent on pH and the nature of the coagulants. As observed in Figs. 5 and 6, the aspect of the flocs obtained with the hybrid coagulants was similar at both operational pH indicating that the flocculation mechanism was the same. However, flocs formed by PANS were very different due to the higher extent of sweep flocculation at initial pH 10.5 than at pH 8.4.

4. Conclusions

(1) Hybrid coagulants are always more efficient than PANS, especially at lower pHs, being 5% the optimum polyamine content. This active content allows simultaneous high silica and COD removal rates and lower treatment cost.

(2) At initial pH 8.4, all the hybrid coagulants are more efficient than PANS in silica removal (50% maximum removal vs. 32% at 2,500 mg/L). Furthermore, the same silica removal (around 30%) is obtained with considerably lower dosages of the hybrids compared to PANS (500 vs. 2,500 mg/L).

(3) At initial pH 10.5, higher silica removal can be obtained (90%), however, differences between hybrids and PANS are lower than at initial pH 8.4. Therefore, in this case, hybrid coagulants would not be recommended.

(4) Hybrid coagulants are also more efficient for COD removal than PANS, 51 vs. 37% at initial pH 8.4 and 31 vs. 4% at initial pH 10.5. PAs of higher molecular weight are more efficient for COD removal.

(5) At initial pH 8.4, flocs are mainly composed by organic matter which form large and loose flocs with a higher tendency to float. At initial pH 10.5, flocs are mainly composed by inorganic matter (silica). These flocs are still large (especially those of the hybrid coagulants), but they are heavier and with a tendency to settle.

(6) The main flocculation mechanism for PANS is sweep flocculation, while for PANS–polyamine hybrids it is a combination of sweep flocculation and patch formation.

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