Influence of Water Quality in the Efficiency of Retention Aids Systems for the Paper Industry

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ABSTRACT

It has been reported that about 10-15% of the fresh water intake in a paper mill is used for feeding and diluting retention aids, so important savings could be achieved replacing fresh water with process water. Water from different sources and qualities: fresh water (FW), the outflow from an internal ultrafiltration placed in the machine circuit of a paper mill (UFW), and water from a membrane bioreactor used to treat the final effluent of this paper mill (MBRW), were used to prepare a dual retention system consisting of a cationic polyacrylamide (cPAM) and bentonite. While the behaviour of bentonite was not significantly affected by the quality of the water used in its preparation, the efficiency of the cationic polyacrylamide was reduced around the 12%, when it was prepared with water with high anionic trash content and conductivity due to a partial neutralization of the charged groups. The effect of non-ionic chemical oxygen demand on the efficiency of the polymer resulted negligible.

Keywords: closure of water circuits, paper industry, cationic polyacrylamide, bentonite, anionic trash, flocculation

Introduction

Pulp and paper industry has reduced water consumption per tonne of paper produced by one third over the last 10 years, and by about a 90% over the last 20 ones[1]. Water consumption depends on many factors, such as the type of raw material used, the product quality and the technology applied in the manufacturing process[2,3]. Examples of fresh water consumption in some actual paper mills are: paper board (3-10 m^3/t), newsprint (5-15 m^3/t), tissue (15-20 m^3/t) and printing paper (>20 m^3/t)[4]. Fresh water is mainly used as dispersion and transport medium for fibrous raw materials and additives throughout the different stages of the production process, from pulping to forming. It is also used as a heat-exchange fluid, as a sealant in the vacuum systems, for the production of steam, and as a lubricant[4,5].

Papermakers are continuously improving their production process in order to keep their competitiveness in the sector. Achieving a high production rate without affecting the quality of the products is one of the keys for the success in such a competitive industry. The paper machine speed is limited by the rate of water removal in the paper sheet forming section, where the retention of fines, fillers and additives is important. In the last years, widely accepted techniques have been developed aiming to increase the speed of the paper machine, which slowly influence drainage and retention systems[6-9].

A great part of the fresh water intake (10-15%) of a paper mill is used for feeding and diluting wet-end chemicals[10]. As white water (drainage water) is highly re-used, detrimental substances (coming from wood, recycling of paper and chemicals added) accumulate in the water circuit[11], generating the following problems[12]: wet-end deposition (58%), mill odours (55%), foam and corrosion (47%), final product odour (45%), decreased machine operability (38%) and losses in drainage (33%). For all these reasons, the implementation of different internal purification strategies (e.g. chemical coagulation[13], dissolved air flotation[14-16], membrane filtration[17,18], biological[19,21], enzymatical[22] and oxidative[23] treatments, etc.) are necessary to improve the closure of water circuits in the mills.

Nowadays, research pointing to further reduce fresh water consumption in the paper industry, without affecting product quality and paper machine runnability, is mainly performed via two different approaches[24]. The first one covers the study of how detrimental substances, present in the pulp suspension, affect the performance of retention aids[25]. In this context, Pruszynski et al.[26] presented a review where pH, conductivity, cationic demand, quality and quantity of extractives and hardness were highlighted as the most important factors, from the chemical point of view, influencing the wet-end process. In particular, ionic strength is the most significant factor[27-29] because salts produce a shielding effect on charged groups, hence decreasing their activity. In fact, a large increase in salts content in the process water reduces the zeta potential, affecting the chemical flocculation mechanisms (e.g. from bridging to patching). Buontempo et al.[30] compared the effect of conductivity on the charge density of different polymers, both in the presence and in the absence of starch. As conductivity is increased, polymers with low charge density begin to lose effectiveness retaining fines. Polymers with high charge density showed the opposite behaviour, that is, they increase their retention effectiveness at higher conductivity values. This trend resulted the same in the presence or in the absence of starch, but it was more acute when it was added. Finally, according to Huiren et al.[31], water conductivity does not affect either beating or sheet properties; but freeness values (Schopper Riegler) are affected if the water used to dilute the beaten pulps has a conductivity lower than 0.2 mS/cm.

A second approach of current research on saving water in the mills is focused on
analysing the effects of the quality of preparation water on the efficiency of retention 9
chemicals. If fresh water is not used for the feed of the retention aid, the right choice of chemicals is very important. In this sense, different dissolved and colloidal substances present in the water for dilution can interfere with the function of the retention aids[10,32]. Particularly, the presence of anionic substances in the water used for preparing cationic polyelectrolytes has been shown to be the most detrimental factor to its efficiency. In fact, these authors remarked that cationic demands higher than 0.2 mEq/L could make cationic polyacrilamides (cPAM) completely ineffective. But there is a wide lack of information regarding the direct use of different qualities of water for preparing the retention system from powder. In Rÿoso and Manner[10,32], chemicals are initially dissolved with deionised water, and then, they point out that the final dilution may be made using other types of water with mechanical pulp. Moreover, the requirements for the quality of feed water may be much relieved if the contact time with the polyelectrolyte is shortened.

In short, the main objective of this research is to evaluate the effect of different water qualities, outflowing from different water treatments available in a recycling paper mill, on the preparation of the retention aid system from powder. The effectiveness of a possible substitution of fresh water (tap water) in the preparation of retention chemicals is discussed. Results are analyzed in terms of flocculation, drainage and retention efficiency, and the properties of the final paper product.

Materials and Methods

Fresh de-inked pulp (DIP) from a newsprint paper mill in Madrid (Spain) was used in the experiments. This mill uses 100% recycled paper as raw material and tap water coming from "Canal de Isabel II", the regional water utility, as fresh water (FW). 1
The pulp was collected from the de-inked pulp storage silo in order to minimize the amount of treatment chemicals present in the pulp, and it was stored at 4ºC after collection. A sample of the collected pulp was filtered through a 7μm filter and the quality of water was analyzed. Pulp concentration was adjusted to 1% adding fresh water before performing the flocculation and drainage experiment. All water analyses were performed following the Standard Methods for Examination of Water and Wastewater[33].

The retention chemicals dual system under evaluation consists of a cationic polyacrilamide (cPAM) and bentonite. The cPAM used (PERCOL®3320, Ciba, Basel, Switzerland. Now part of BASF, Ludwigshafen am Rhein, Germany) is characterized[34] by its high molecular weight ($1\text{-}5\cdot10^6$ g/mol) and low charge (1-10% charged groups, 1.1-1.3 mEq/g). The charge density of the cPAM was measured by titration (Titrator Compact I, Crison Instruments) of 0.5 g cPAM/L with sodium poly(ethene sulfonate) (PesNa) 0.001 N. Bentonite (HYDROCOL®OM2LS, Ciba, Basel, Switzerland. Now part of BASF, Ludwigshafen am Rhein, Germany) contains primarily smectite clay mineral, characterised by its colloidal size, lamellar crystal shape and high negative charge density[35]. It has been demonstrated that this micro-particle improves retention, drainage, pitch control and other properties with relation to using a cationic polymer alone[6,36]. Chord length distribution of this bentonite was determined with a focused beam reflectance measurement (FBRM) probe in a saturated suspension of the product stirred at 400 rpm, as described below for flocculation trials. The result was a normal distribution with a mean chord length value of 9.73 μm. Both cPAM and bentonite are supplied as powder. cPAM suspensions of 1g/L were prepared by adding the powder to the tested waters and mixing the solution for one hour. The bentonite was prepared in the same way at a concentration of 5g/L. Maturation time was 1 day for both chemicals.

Three different qualities of water from different sources inside the mill were used to prepare and compare the behaviour of the retention system: fresh water (FW), the outflow from an internal ultrafiltration (UFW) placed in the machine circuit (process water), and water from a membrane bioreactor (MBRW) used to treat the final effluent of the paper mill. This means that nine different systems have to be tested to cover all the possible combinations of retention chemicals and types of water. All the waters were analysed to compare their quality[33] (Table 1).

Flocculation studies were performed with a M500L focused beam reflectance measurement (FBRM) probe manufactured by Lasentec, Mettler Toledo, Seattle, WA. The FBRM instrument operates by scanning a highly focused laser beam at a fixed speed (2000 rpm) across particles in suspension and measuring the time duration of the backscattered light from these particles. The temporal duration of the reflection from each particle or floc multiplied by the velocity of the scanning laser, which is a known value, results in a characteristic measurement of the particle geometry, known as chord length. Thousands of chord length measurements are collected per second, producing a histogram in which the number of observed counts is sorted in several chord length bins over the range 0.5 to 1000 or 2000 μm. From the data, total counts, counts in specific size regions (population), mean chord lengths, and other statistical parameters can be easily calculated[37,38].

All the experiments with the FBRM were programmed to obtain a chord length distribution every 5 seconds. In this way, enough particles are detected to have a good representative distribution of the population. The optimal dosage of cPAM was determined adding 0.3 mg of polymer per g of dried pulp every 30 seconds, while stirring the suspension at 400 rpm, until the mean chord size reaches a constant value (saturation level). cPAM and bentonite were combined in a 1:1 weight ratio. This equal weight proportion should allow to observe the effect of the quality of water on the efficiency of each retention chemical clearly enough. Previous trials carried out with a model pulp and moderate higher cPAM:bentonite ratios showed non-significant differences in retention and drainage time values[39]. Lower ratios lead to an increasing ineffective excess in the content of bentonite, thus leading to lower mean chord length values due to the presence of a higher proportion of small particles.

Flocculation trials were performed following the scheme showed in Figure 1. Results are analysed in terms of increments of the mean chord length (MCL), expressed as a percentage (Equation 1); and as a function of the re-flocculation ability of the flocs after reducing the stirring speed from 800 to 400 rpm (Equation 2). The first determination (MCL_1) is performed at t=20s, before adding cPAM; and the second value (MCL_2) represents the maximum chord length obtained after the addition o the retention system. The third registration (MCL_3) is the minimum floc size reached before increasing the shear forces to 800 rpm. Finally, the last determination (MCL_4) is performed after reducing the shear forces from 800 to 400 rpm.

$$\Delta MCL\ (\%) = \frac{MCL_2 - MCL_1}{MCL_1} \cdot 100 \qquad (1)$$

$$\mathrm{Ref.}(\%) = \frac{MCL_4 - MCL_3}{MCL_2 - MCL_1} \cdot 100 \qquad (2)$$

Drainage was measured using a MütekTM DFR-04 (BTG) equipment. The pulp suspension (1L at 10g/L) is transferred to a stirring chamber (400 rpm) where it is exposed to shear forces during the addition of chemicals (bentonite is added 30s after CPAM addition). After 1 minute of mixing, the suspension was filtered through a 70µm sieve and the filtrate weight versus the drainage time evolution is determined. Filtrates were collected to measure turbidity and total solids.

The quality of the type of water used to prepare the retention system was also compared in terms of the characteristics of the final paper product. Paper hand sheets of 60 g/m^2 were formed with a FRET Retention Tester (Techpap, Saint Martin D'Heres, France). The fibre suspension was stirred in a jar at 400 rpm when the retention system is added, following the same procedure that with the MütekTM DFR-04. Then, a valve opens and the suspension is transferred into another jar that simulates the wire of a paper machine. After homogenizing the suspension with air, the sheet is formed on a wire (150µm) under vacuum (-0.2 bar) and then dried in an oven before being ready to measure paper properties.

Several parameters were analysed to characterize the quality of the paper hand sheets made in the laboratory, according to normalized trials. Tensile strength, which is the force required to produce a rupture in a strip of paperboard (ISO/FDIS 1924-3:2005), is indicative of the strength, bonding and length of the fibers Furthermore, it is considered an indicator of the resistance to web breaking during printing or covering. Complementarily, the percentage of elongation (ISO/FDIS 1924-3:2005) refers to the maximum elasticity that a strip of paperboard can resist before breaking. On the other hand, ISO Brightness (UNE 57062:2003) is defined as the percentage reflectance of blue light at 457 nm. It must not be confused with whiteness, which refers to the extent that paper diffusely reflects light of all wavelengths throughout the visible spectrum. These three parameters (tensile strength, percentage of elongation and ISO Brightness) were measured with an Autoline 300 (Lorentzen & Wettre, Kista, Sweden). In addition, formation is an indicator of how uniformly the fibers and fillers are distributed in the sheet. A poorly formed sheet will be weaker, thinner and may show thick spots. Formation was measured with a Beta Formation Analyzer (Ambertec, Espo, Finland). Finally, ash content, that is, the residue left after the complete combustion of paper at high temperature, was also determined (UNE 57050:1994). This parameter is an estimate of the amount of fillers the paper has retained.

Results and Discussion

Theoretically, when the cPAM is added to the pulp, suspended particles are flocculated. Flocs are slowly broken down by shear forces and, when bentonite is added, a three-dimensional micro-floc structure is formed, which favours drainage and retention of fines and fillers without affecting formation.

The optimum dosage of cPAM resulted 1.5 mg/g for the three types of water used to prepare the retention chemicals (Figure 2). As more polymer is added to the suspension, flocs increase in size gradually until a certain value, which is kept at higher additions of the chemical,, as the pulp is already saturated. This dosage was adopted to perform the flocculation experiments. Water quality did not affect the optimal dosage of cPAM, but it reduced the MCL obtained for each dosage. When UF or MBR waters were used to dissolve the cPAM, the ratio between the anionic compounds content and the cPAM is higher. Although anionic trash does not cause an extra consumption of cPAM chains, it affects to some cationic groups of each chain leading to a slight reduction of the efficiency of the polymer.

The quality of the water used to prepare the bentonite did not influence flocculation (Figures 3 and 4) or drainage (Figure 5) significantly. The specific surface of bentonite is very high and anionic. Therefore, electrostatic repulsive forces are acting between this surface and the anionic trash contained in the water used to disperse the bentonite[41]. Furthermore, the adsorption of this anionic trash does not modify a significant part of the surface of the bentonite because the ratio between anionic trash content and this surface is low.

According to Figure 3, the highest MLC values were obtained when the cPAM was prepared with fresh water; and the lowest floc size was achieved when the cPAM was dissolved in MBR water. The reflocculation ability or reversibility of the flocs was nearly the same for all the studied cases (Figure 4). However, the quality of water affected significantly the efficiency of the cPAM, as shown by the different MCL results obtained after adding cPAM in the flocculation experiments (Figure 3). MCL of the cPAM prepared with MBR water was lower than when it was prepared with fresh water. In terms of drainage, the best results were shown when the cPAM was prepared with fresh water (Figure 5). The use of UF or MBR waters to prepare the cPAM reduced drainage rate and increased turbidity and solids content of the filtrate (Figure 6).

Cationic demand (CD), conductivity, hardness, COD and sulphates content were found to be the parameters presenting the most significant differences among the three types of water (Table 1). Anionic substances contents measured by CD shows a partial polymeric character that makes them sparingly soluble in water and able to interact with the cationic groups of the cPAM, reducing its effective cationic charge density. Therefore, the interaction with fibres, fines, fillers, bentonite, and other colloids in pulp suspensions will be weaker. This reduces the collision efficiency[42] and, thus, the bridging ability of the cPAM. As a result, flocculation and floc sizes are reduced by the use of UF or MBR waters, as shown by the increment of MCL registered after flocculation (Figure 3). Consequently, the retention of solids decreases, as reflected by the increase in turbidity and solids content of the filtrate (Figure 6). In fact, Ryösö and Manner[10,32] recommended not to use waters with a CD higher than 0.2 mEq/L for the dilution of cationic retention polymers.

Furthermore, as a result of the weaker interaction of the cPAM with the bentonite, a higher amount of bentonite does not interact with the cPAM and behaves as a filler, passing through the wire during water drainage and increasing the turbidity of the filtrate. The reduction in floc size and the increase of the amount of non-flocculated fillers and fines result in a closer mat structure than the one obtained when fresh water was used to prepare the flocculant, which reduces the drainage rate. Non-retained fines and fillers pass through the sheet, increasing the turbidity and the solid content of the filtrate (Figure 6).

The lower electrostatic repulsion between cPAM chains segments, due to the neutralisation of some cationic groups of the chains and to the higher conductivity of the water used in its preparation, affects its conformation, which becomes less extended in the solution. This could reduce its efficiency to form long bridges. However, some authors have found that the effect of the conductivity of the makedown water used to prepare the cationic flocculant is negligible[43]. The effect of water conductivity on the conformation of the polymer is faster than the flocculation process. Therefore, and as soon as the cPAM solution is added to the pulp, the conformation of polymer chains changes according to the conductivity of the pulp suspension.

Another important consideration is that COD seems to be non-relevant in the role of the retention aid. This fact corroborates the observations described above, because it demonstrates that the effect of water quality on the efficiency of the cPAM is not related to the content of organic compounds; but it is related to the anionic charge, which is the responsible of the neutralization of cationic groups in the chains of the cPAM[27].

As the behaviour of bentonite was not influenced by the quality of the water used for its preparation, the studies analysing the final paper quality were performed preparing the bentonite with fresh water.

Results related to paper quality are shown in Figure 7. Both ISO brightness and grammage were not different for the three types of water used. All the other studied parameters resulted similar for fresh water and UF water, but were very different for MBR water. As it has been already commented when analysing drainage results, if MBR water is used, the retention of fines and fillers is reduced considerably, so the paper sheet shows a lower ash content. On the other hand, a higher tensile strength and elongation percentage is attributed to a lower amount of fillers[44,45] and to a lower formation index. It is important to consider that, although fillers reduce the strength of the paper sheet, they are also used to reduce the cost of raw materials and to increase the quality of the paper. This remarks the importance of having a good filler retention when paper is formed optimizing the benefits. Moreover, when flocs are large enough, the attachment of fillers to them is favoured. If flocs are small, the aggregation of colloidal particles themselves is improved[46], forming small flocs that are not easily retained.

As formation refers to the uniformity in the spatial distribution of fibres, fines and fillers in the paper sheet, large fibre flocs deteriorate formation due to the relatively large diameter of the pores formed in the wet sheet[47]. Figure 7 shows that formation index decreases when the cPAM is prepared with MBR water. Moreover, the use of fresh water and UF water in the preparation of the cPAM leads to a worse formation. These results were expected, as the flocculation efficiency shown by the cPAM prepared with MBR water was lower than in the other cases. As a consequence, the sheets of paper manufactured when MBR water was used for the preparation of the cPAM showed better mechanical properties (tensile strength and elongation), but lower ash content and grammage.

Conclusions

The optimum dosage of the cPAM was the same for the three different types of water quality tested. But the use of UF and MBR waters to dissolve the cPAM produce a reduction of the flocs sizes and, therefore, a decrease in flocculation efficiency. MBR water contains the highest anionic trash, which results in a partial neutralisation of the charged groups of the cPAM. Consequently, a reduction of its efficiency is observed, as reflected by the lower retention of solids and drainage rate and the improvement of formation that are shown. Thus, tensile strength and elongation show higher values. The effect of non-ionic COD on cPAM efficiency was negligible. Therefore, the reuse of water from the mill to prepare cPAM solutions requires the previous neutralization and removal of anionic trash. On the other hand, bentonite was not significantly affected by the type of water used in its preparation in any case.

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Table 1. Chemical characterization of the water used to prepare the retention system.

Parameter	Units	Pulp suspension	Fresh water	UF water	MBR water
pH		8.04	7.58	7.50	7.65
Conductivity	mS/cm	1.16	0.11	2.30	3.19
TSS	g/L	-	0	0	0
VSS	g/L	-	0	0	0
Cationic demand	mEq/L	0.216	0	0.340	0.988
Turbidity	NTU	-	0	4.22	1.77
Alkalinity	mEqCaCO$_3$/L	8.49	0.45	12.47	15.29
Hardness	mEq/L	2.0	1.2	2.8	5.6
Total COD	mg/L	701	0	972	436
Soluble COD	mg/L	586	0	952	431
BOD$_5$	mg/L	250	0	360	20
SO_4^{2-}	mg/L	276	<10	130	375
Cl^-	mg/L	69	8	164	159
Ca^{2+}	mg/L	38	21	40	75
Disolved SiO_2	mg/L	80	<0.2	140	100
Mn^{2+}	mg/L	0.9	<0.1	<0.1	0.9
Fe^{2+}	mg/L	0.18	0.03	0.20	0.22

Figure 1. Procedure followed in the flocculation trials.

Figure 2. Mean chord length versus cPAM dosage considering different make-up water qualities.

Figure 3. Evolution in time of the mean chord length after flocculating the pulp with the retention aid system prepared with different water qualities (e.g. FW-MBRW means cPAM prepared with fresh water and bentonite with MBR water).

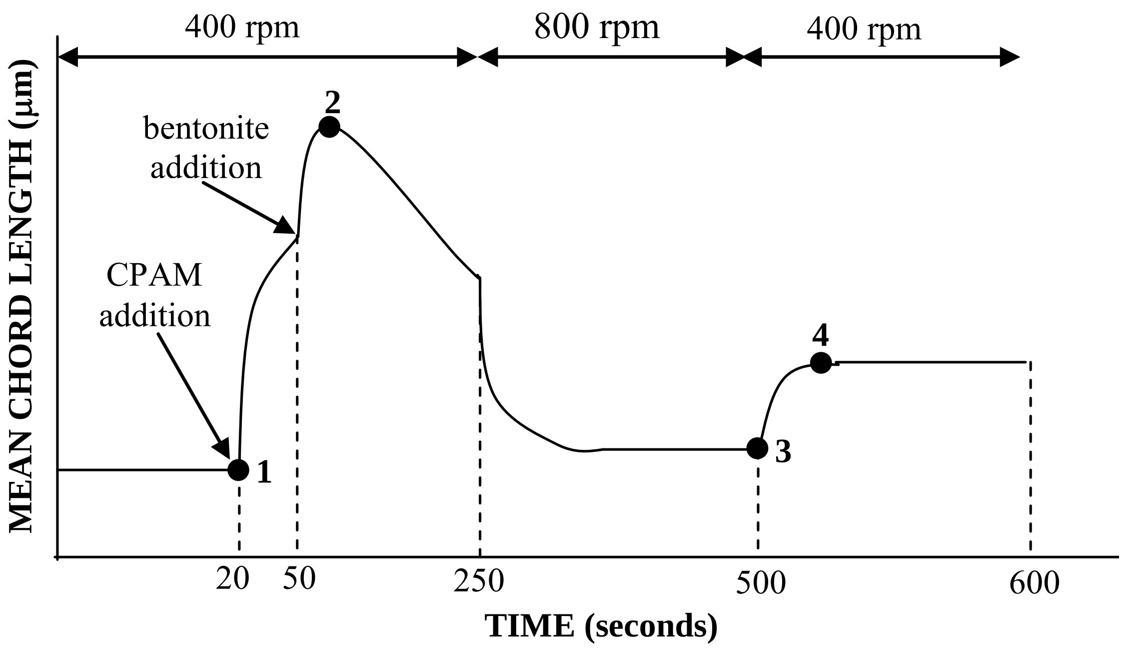
Figure 4. Increment of mean chord length (MCL) and re-flocculation ability of the flocs for every combination of water qualities used to prepare the retention aid (e.g. FW-MBRW means cPAM prepared with fresh water and bentonite with MBR water).

Figure 5. Drainage trials, expressed as filtrate weight versus time for every combination of water qualities used to prepare the retention system (e.g. FW-MBRW means cPAM prepared with fresh water and bentonite with MBR water).

Figure 6. Turbidity (vertical bars) and total solids content (circles) of the filtrate obtained in drainage trials performed for every combination of water qualities used to prepare the retention system (e.g. FW-MBRW means cPAM prepared with fresh water and bentonite with MBR water).

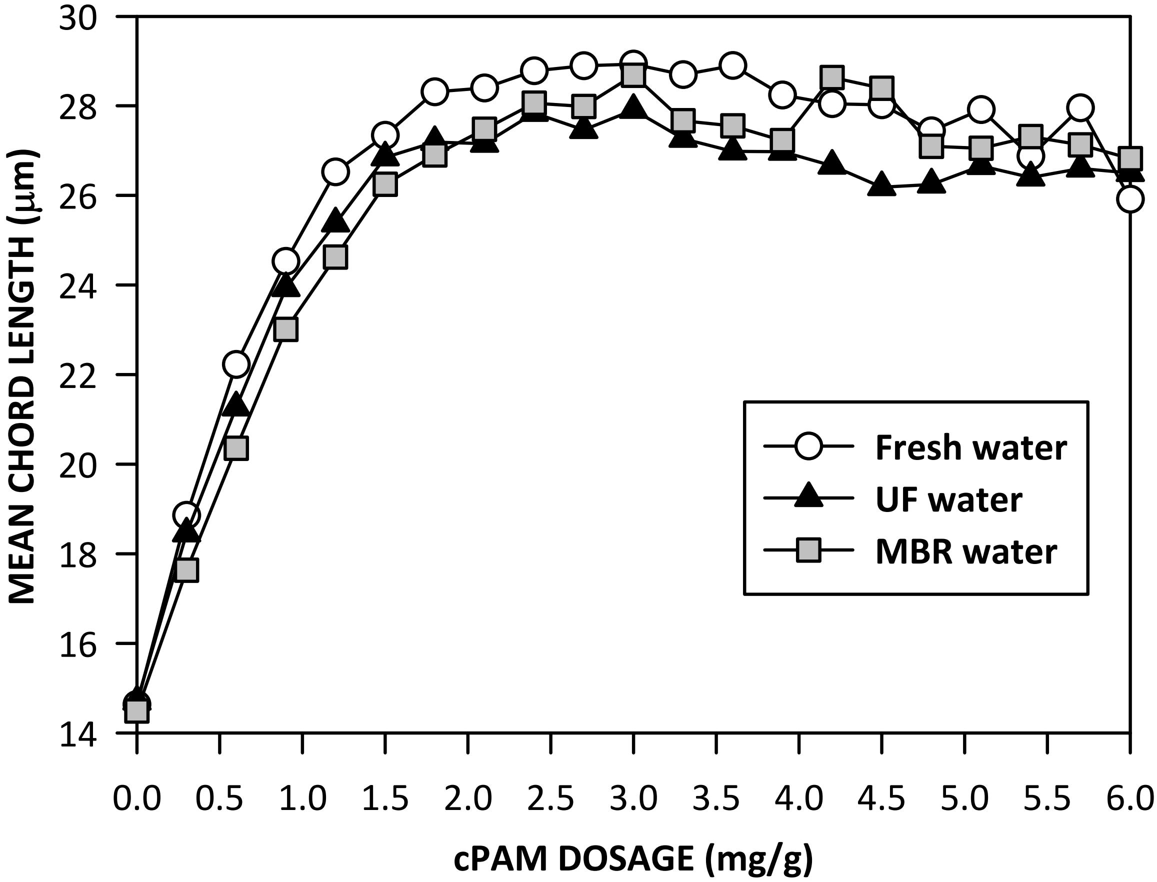
Figure 7. Final paper properties related to the water quality used in the preparation of the retention system (e.g. FW-MBRW means cPAM prepared with fresh water and bentonite with MBR water).

FIGURE 1



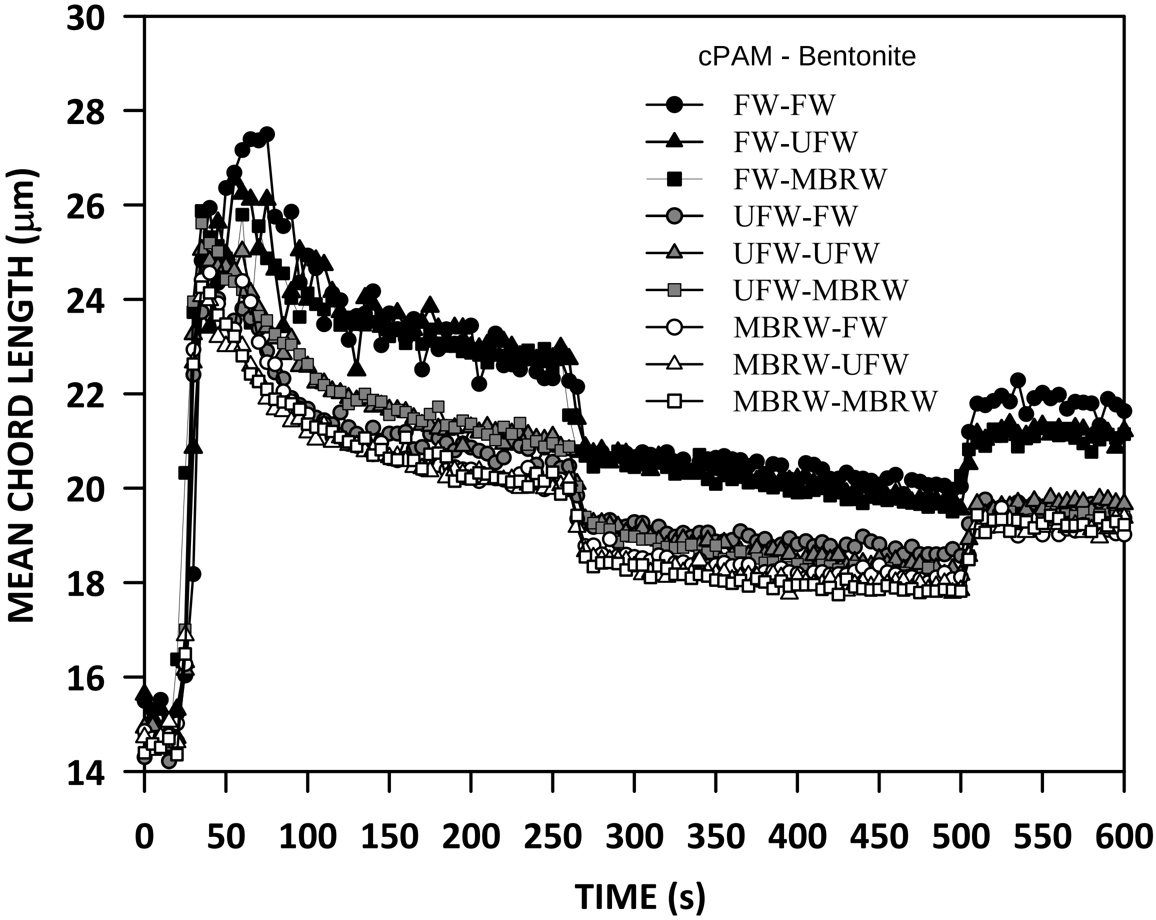
400 rpm
800 rpm
400 rpm
MEAN CHORD LENGTH (µm)
bentonite addition
CPAM addition
1
2
3
4
20
50
250
500
600
TIME (seconds)

FIGURE 2



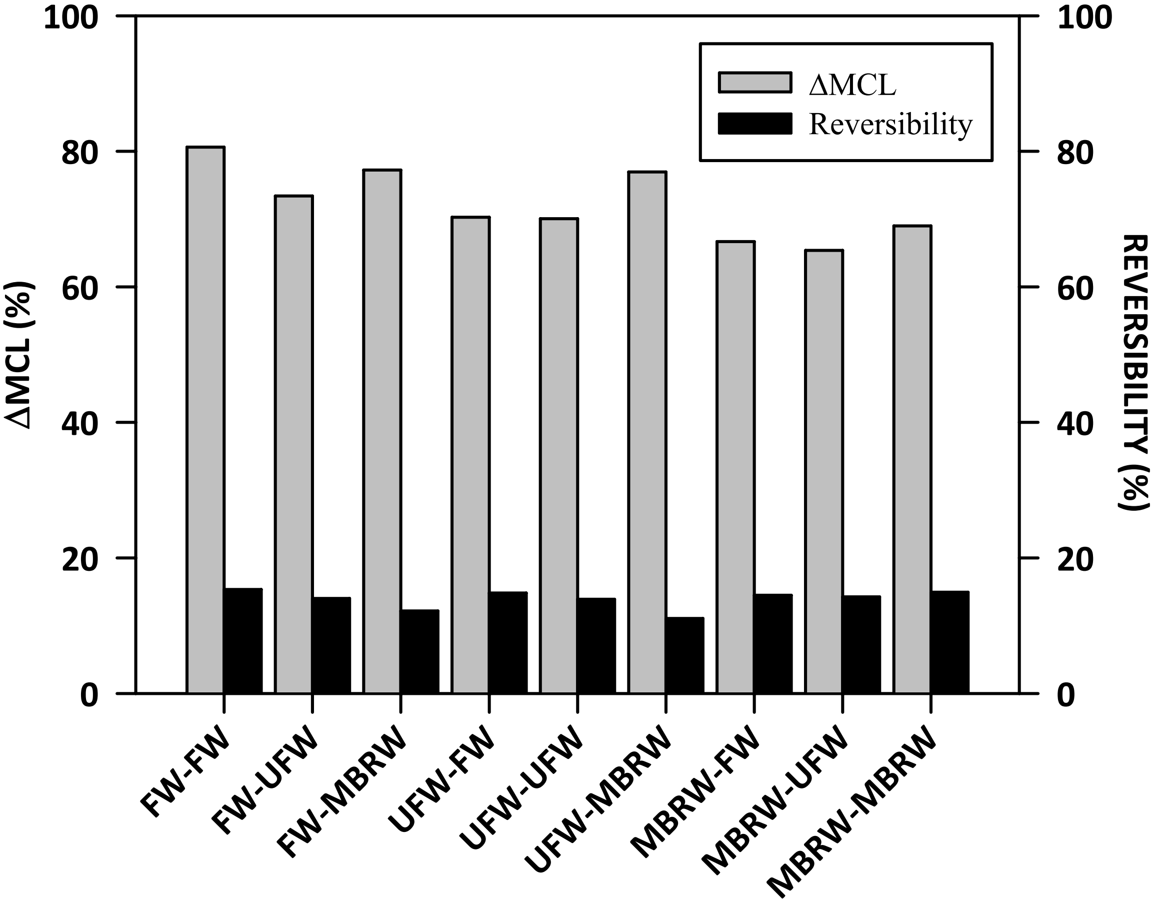
MEAN CHORD LENGTH (μm)
30
28
26
24
22
20
18
16
14
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
cPAM DOSAGE (mg/g)
Fresh water
UF water
MBR water

FIGURE 3



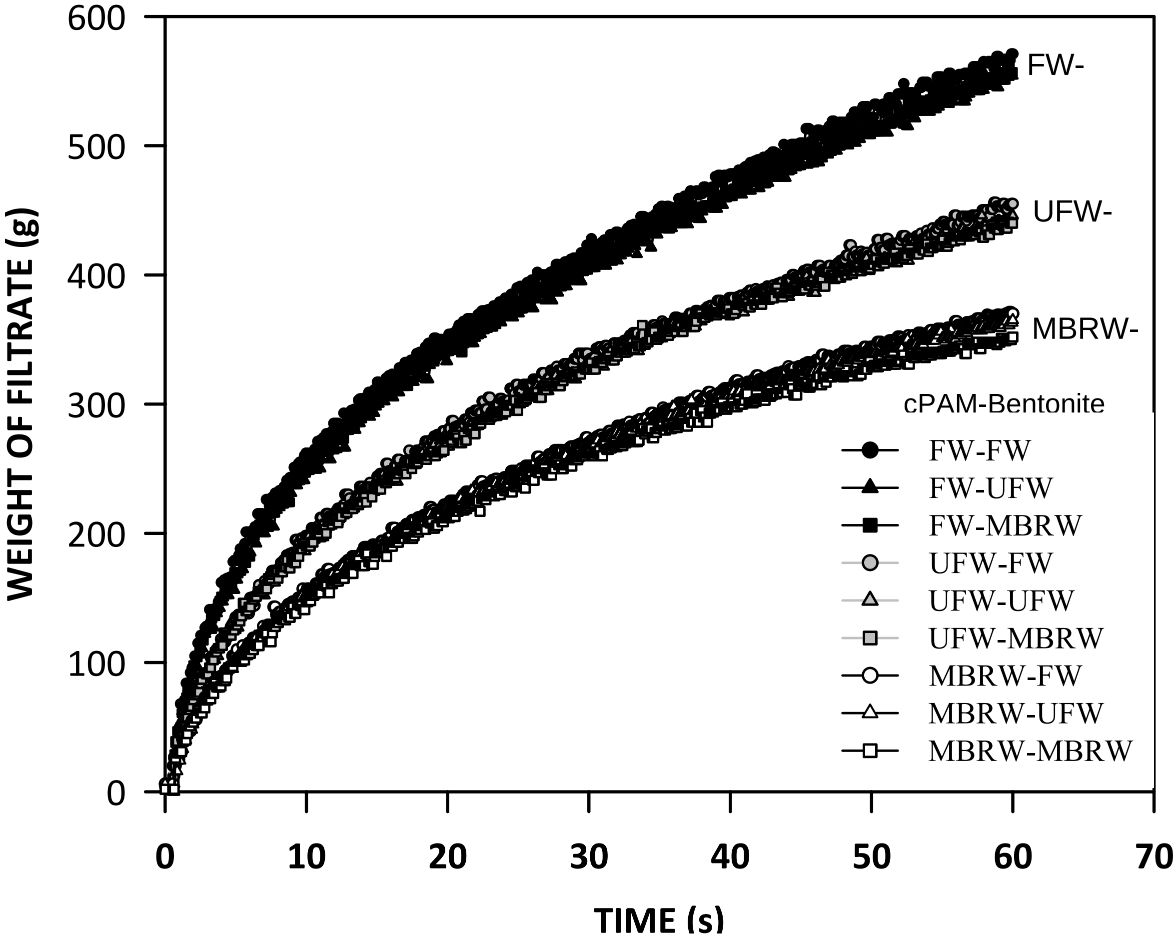
30
28
26
24
22
20
18
16
14
0
50
100
150
200
250
300
350
400
450
500
550
600
MEAN CHORD LENGTH (μm)
TIME (s)
cPAM - Bentonite
FW-FW
FW-UFW
FW-MBRW
UFW-FW
UFW-UFW
UFW-MBRW
MBRW-FW
MBRW-UFW
MBRW-MBRW

FIGURE 4



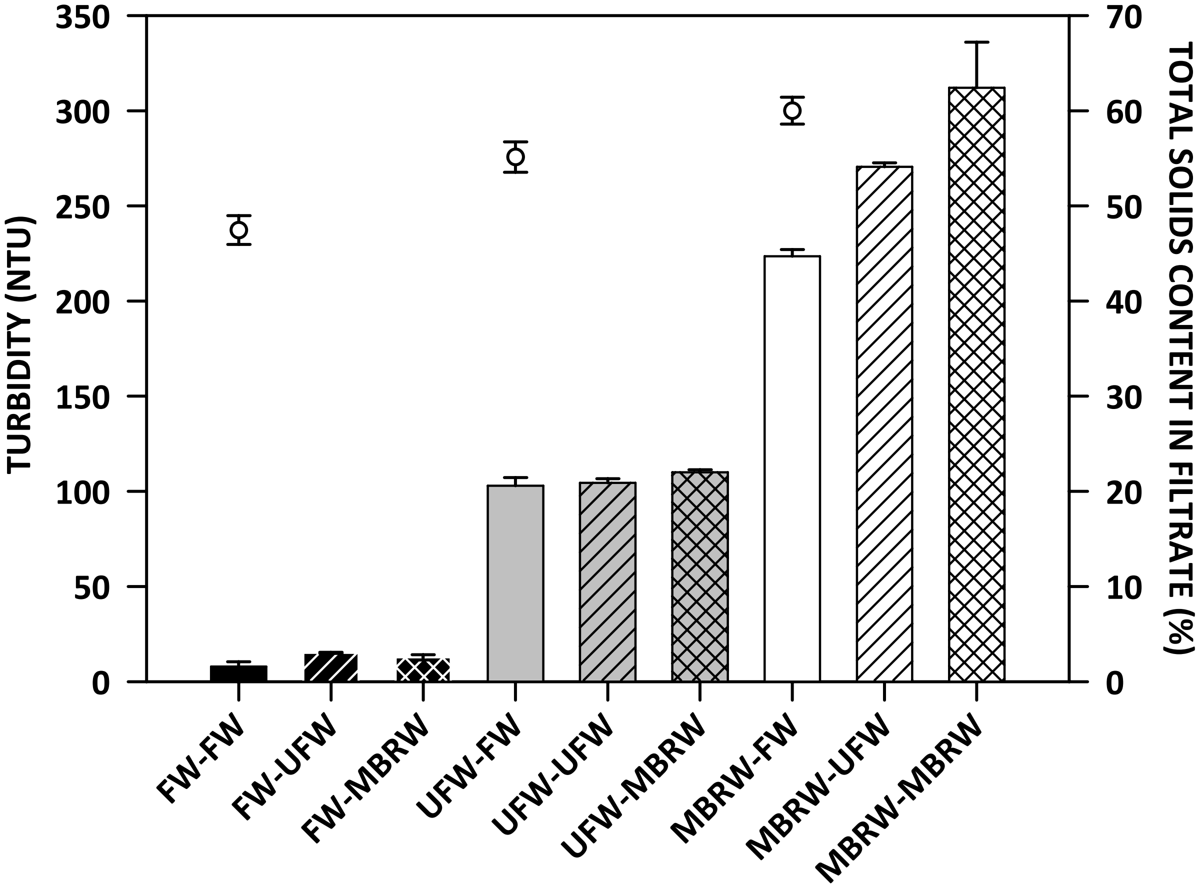
100
80
60
40
20
0
ΔMCL (%)
REVERSIBILITY (%)
ΔMCL
Reversibility
FW-FW
FW-UFW
FW-MBRW
UFW-FW
UFW-UFW
UFW-MBRW
MBRW-FW
MBRW-UFW
MBRW-MBRW

FIGURE 5



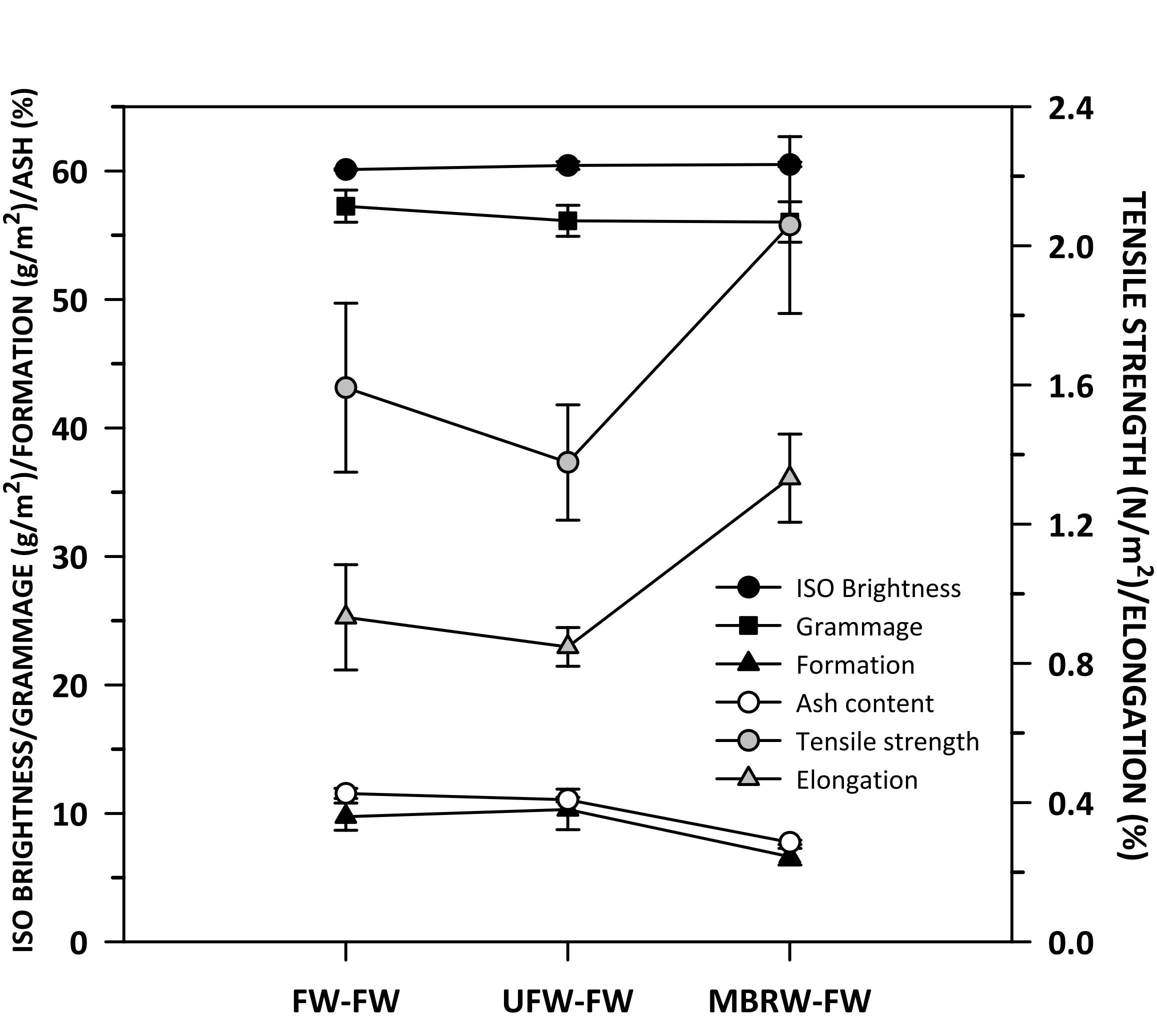
600
500
400
300
200
100
0
0
10
20
30
40
50
60
70
TIME (s)
WEIGHT OF FILTRATE (g)
FW-
UFW-
MBRW-
cPAM-Bentonite
FW-FW
FW-UFW
FW-MBRW
UFW-FW
UFW-UFW
UFW-MBRW
MBRW-FW
MBRW-UFW
MBRW-MBRW

FIGURE 6



TURBIDITY (NTU)
TOTAL SOLIDS CONTENT IN FILTRATE (%)
0
50
100
150
200
250
300
350
0
10
20
30
40
50
60
70
FW-FW
FW-UFW
FW-MBRW
UFW-FW
UFW-UFW
UFW-MBRW
MBRW-FW
MBRW-UFW
MBRW-MBRW

FIGURE 7



ISO BRIGHTNESS/GRAMMAGE (g/m2)/FORMATION (g/m2)/ASH (%)
TENSILE STRENGTH (N/m2)/ELONGATION (%)
0
10
20
30
40
50
60
0.0
0.4
0.8
1.2
1.6
2.0
2.4
FW-FW
UFW-FW
MBRW-FW
ISO Brightness
Grammage
Formation
Ash content
Tensile strength
Elongation