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Separation of Contaminants from Deinking Process Water by Dissolved Air Flotation: Effect of Flocculant Charge Density

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Abstract: The effect of charge density of 5 cationic polyacrylamides (C-PAMs) and 3 anionic polyacrylamides (A-PAMs) in single and in dual treatments with a coagulant on the flocculation and removal of dissolved and colloidal material by dissolved air flotation (DAF) in papermaking has been studied. In single systems, good results were achieved both with low and high charge C-PAMs (1.0 and 3.0–3.5 meq/g). In dual systems, high charge C-PAMs (3.0–3.5 meq/g) and A-PAMs (1.5 meq/g), were the most efficient. Results show that monitoring flocculation by a focused beam reflectance measurement (FBRM) allows papermakers to optimize the chemical dosages to maximize the separation efficiency of DAF units either with single or dual systems, which is not always possible with traditional methods as charge titration.

Keywords: Charge density, dissolved air flotation, dissolved and colloidal material removal, FBRM, flocculation, papermaking, polyacrylamide

INTRODUCTION

The paper industry is one of the major industrial sectors in terms of water consumption during the manufacturing process, the reduction of water use being an issue of growing importance due to the stringent

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environmental legislation, the increase in water prices, the treatment costs, or simply due to the lack of water resources (1–2). In fact, there are some products, mainly packaging paper/board, in which the runnability of the paper machine is not as sensitive as in printing paper manufacture, and zero liquid effluent has been already achieved with the only fresh water consumed in the process replacing the water evaporated in the drying section (1.0–1.5 m^3/t) (3,4). In closed systems, the reuse of water increases the concentration of suspended, colloidal, and dissolved substances. These substances can be organic, inorganic, or biological in nature. While suspended solids are removed easily in the existing clarification systems, the dissolved and colloidal material (DCM) is almost completely recirculated into the process and, therefore, accumulates and limits the closure of the water circuits. DCM negatively affects the production process (e.g., blockings, scaling, slime formation, breaks, and stickies deposits) and the quality of the final product (by impairing its physical properties or by the presence of dirt and holes) (5–7). The main source of DCM is the recovered paper, although chemical additives used during the manufacturing process also contribute. DCM is mainly released during pulping, refining, and bleaching (8,9). Inorganic salts commonly found in papermaking are calcium, sulphates, chlorides, silicates, and also iron, manganese, and copper; salts are responsible for scaling phenomena, corrosion, odors, or the reduction of the efficiency of some additives (10). Biological DCM, mainly bacteria, is the cause of slime formation, microbiologically-induced corrosion, generation of odors, degradation of some additives, etc. (11). Organic compounds found in the dissolved and colloidal fraction of deinking process water are mainly adhesives, printing inks, coating binders, starches, deinking chemicals, and wood extractives. They are responsible for secondary stickies deposits. These deposits are a key issue for papermakers (12–14).

One of the most common internal treatments used in papermaking is dissolved air flotation (DAF), due to the fact that they can treat large water flows with a wide range of solids content, between 300 mg/L and 5000 mg/L. For example, in recycled newsprint mills there are up to five DAF units (1st loop, 2nd loop, paper machine loop, sludge treatment, and effluent treatment). In principle, DAF efficiently removes 80–98% of suspended solids, e.g., fibers, fines, and fillers as well as a wide variety of contaminants such as ink particles and lipophilic extractives. Besides, with suitable chemicals, also finely dispersed and colloidal organic particles (>0.1–$0.2\,\mu m$), can be agglomerated and removed (15–18). The best reductions of organic DCM obtained by microflotation, measured as COD, are in the range of 10–30%, because COD load is caused mainly by substances smaller than $0.2\,\mu m$ in size (15,19). It is estimated that

85% of the TOC measured in the DCM fraction corresponds to dissolved substances and the remaining 15% to colloidal substances (20). The removal of colloidal substances, measured in terms of cationic demand is a little bit higher, in the range of 10–40% (21). Inorganic and biological DCM is not affected much by DAF, so other water treatment technologies are necessary if these compounds are limiting a further closure of the water circuits.

A variety of chemical additives are used in DAF systems, usually supported by tailor-made chemicals (22). In general, there are three main flocculation strategies. The first is a single cationic flocculant with a low to medium cationic charge, and very high molecular weight, usually a PAM. This approach is attractive due to its simplicity and low cost. The second is a cationic coagulant and an anionic flocculant together. The coagulant has a high cationic charge and low molecular weight, and is usually a poly(diallyldimethylammonium chloride) (polyDADMAC) or a polyamine. The coagulant is used in conjunction with a high molecular weight anionic flocculant (e.g., A-PAM). The coagulant is added first to neutralize the anionic charge and coagulate the sample. Then, a small amount of a long chain anionic flocculant is added to form the main flocs. The third strategy is another dual system: a cationic coagulant and a cationic flocculant together. Usually, the cationic flocculant is used alone but when its efficiency is too low, a cationic coagulant is added to neutralize the anionic trash and increase the flocculation efficiency of the flocculant.

Flocculation is a complex phenomenon in which various processes occur simultaneously: adsorption of polymer molecules on the particle surface, rearrangement (or re-conformation) of adsorbed polymeric chains, collisions between particles forming aggregates (flocs) and break-up of flocs (23). The importance of each process depends on various factors such as (24–26):

1. the flocculant characteristics: structure, molecular weight, charge density and concentration;
2. the characteristics of the suspended particles: size and charge density;
3. the characteristics of the suspending medium: pH, conductivity, and ionic charge; and,
4. the contact time and turbulence intensity, among others.

The interaction of polymers with DCM and their effect on flocculation is determined by non-specific electrostatic interactions. Electrostatically stabilized colloids with similar charges can be aggregated by increasing the ionic strength or by adding a polyelectrolyte into the system and, consequently, removed by DAF (27,28). One of the afore-mentioned parameters that most strongly affects flocculation is the charge density of the polyelectrolyte, because it determines its conformation when it is adsorbed on the particle surface, and, therefore, the predominant flocculation mechanism (23–25,29). In general, if the molecular weight is high and the charge density is low, the polymer adsorbs on the particle surface in such a way that tails and loops are extended far beyond the surface interacting with other particles; in this case the flocculation process is dominated by bridging. When the charge density is high, the bridging capability is reduced because the polymer chains adopt a flat conformation on the particle surface, which results in the formation of cationic patches that attract the polymer free surfaces of other particles. In this case, the adsorption rate becomes lower and the conformation rate becomes faster as the cationic charge of the polymer increases (23,30–32). Bridging is the dominating mechanism in the flocculation of DCM with PAMs (30,33,34) and, in general the flocculation efficiency improves when the charge density increases (35). However, there is an optimal charge density depending on the colloidal nature of the system (26,36,37).

Traditional methods for determining the efficiency of chemical treatments in DAF are based on turbidity measurements, determination of lipophilic extractives and carbohydrates by chromatography (chemical oxygen demand (COD) and total organic carbon (TOC) are also often measured), and the determination of cationic demand by polyelectrolyte titration or zeta potential measurement (34). These methods may require time-consuming sampling, sample pre-treatment, and analysis and the interpretation of results. Furthermore, several analytical methods are needed in order to obtain an overall picture of processed water. On the other hand, the Focused Beam Reflectance Measurement (FBRM) technique can reflect the evolution of the flocculation process of suspended particles and DCM in real time (20,29,38–40). This system is able to predict flocculation behavior without the limitations of traditional methods such as charge titration which are not valid when bridging or patching mechanisms dominate the system (23). Recently, FBRM has been used for the chemical optimization of DAF units treating thermomechanical pulp (TMP) waters (28,34).

The principle of FBRM is that a laser beam is directed down the probe and focused at, or near the window at the tip. The optics are rotated around an axis parallel to the probe, so that the beam traces a circular path. When particles intercept its path, the light is reflected and propagated back through the probe window to the detector. The particle will continue to reflect light until the focused beam has reached the opposite edge of the particle. The time duration of the backscattered light pulse allows the particle chord length to be calculated as the time taken for the beam to cross the particle, divided by linear speed of the beam's rotation. This optical length corresponds to a random chord length of the particle, that is, a straight line between any two points on the edge of a particle. The width of the chords will be dependent on the particle's size, shape, and orientation (41,42). Thousands of chord length measurements are collected per second, producing a histogram in which the number of the observed counts is sorted in several chord length channels over the measurement range. From these data, total counts, counts in specific size intervals, mean chord size, and other statistical parameters can be easily calculated.

The objectives of the present study are to first, examine the interaction mechanisms between cationic and anionic PAMs with various charge densities, used in both single and dual systems, and the DCM from the deinking process water; and second, to predict DAF efficiency by monitoring the flocculation induced by different chemical systems at lab-scale with the FBRM technique.

MATERIALS AND METHODS

Materials

Water samples were taken from the inlet of a DAF unit in loop 2 (pulp preparation stages) of a paper mill producing newsprint from 100% recovered paper. All trials and analyses were carried out within 48 hours after the sampling to avoid the possible degradation of the waters.

Several combinations of single and dual flocculation systems were studied. The flocculants studied were five C-PAMs with the same molecular weight but different charge densities, from 1.0 to 3.5 meq/g, and three A-PAMs with the same molecular weight, but with charge densities ranging from 0.75 to 1.5 meq/g. Polymer properties, as reported by the supplier, are listed in Table 1. The coagulant used (SC) is a high molecular weight polyamine type based on blends of cationic copolymers with different charges. All the chemicals were supplied by SERTEC-20 (Spain).

Doses of the products used at lab-scale were suggested by the supplier based on previous tests. Flocculant dosage was fixed to 20 mg/L; this dosage is higher than at industrial scale due to the lower hydrodynamic efficiency of the lab DAF cell compared to the industrial ones. The coagulant dosage was fixed to 500 mg/L to obtain a reduction of approximately 75% of the cationic demand of the feed waters; this dosage is high enough to remove most of the DCM without reaching the isoelectric point and without blocking the particle sites necessary for further flocculation by bridging (20,32,43,44).

Table 1. Characteristics of the flocculants

Polymer	Molecular weight (Da)	Charge density (meq/g)
C1		1.0
C2	$9{\cdot}10^6$	1.5
C3	(High)	2.5
C4		3.0
C5		3.5
A1	$12{\cdot}10^6$	0.75
A2	(Very high)	0.925
A3		1.5

Methodology for DAF Tests

Experiments were carried out in a lab-scale DAF unit (Flottatest FTH3), supplied by Orchidis Laboratoire. Both coagulant and flocculants were added from 1.0 wt% stock solutions to 1 L of sample. A blank was carried out without adding any chemical, to consider the dilution of the samples as a consequence of the addition of air saturated water during flotation (200 mL); this reference sample is named REF. The tests were carried out in duplicate and the average error between replicates was always lower than 5%. All the experiments were carried out at room temperature (20–25°C).

The efficiencies of the different treatments were evaluated by turbidity, cationic demand, and COD of the feed and the clarified waters, as shown in Fig. 1. These measurements are commonly used for evaluating the removal of detrimental substances in papermaking and DAF systems (17,34). Turbidity measures the amount of suspended solids but in samples with relatively low suspended solids, the measurement indicates the presence of colloidal particles. COD measures a great variety of organic compounds which are detrimental to the process. Charge measurement is also generally accepted as one of the most important indicators of the amount of detrimental substances in papermaking, although not all interfering substances are anionic (45).

Turbidity was measured with a Hanna LP-2100 turbidimeter. Cationic demand was measured with a particle charge detector PCD 03 (Mütek GmbH) and an automatic titrator Compact I (Crison Instruments SA), using poly-DADMAC (0.001 N) as titrant. COD was measured by the Merck Spectroquant® COD 300–3500 method, using an Aquamate Vis spectrophotometer (Thermo Scientific Inc.). The pH and conductivity

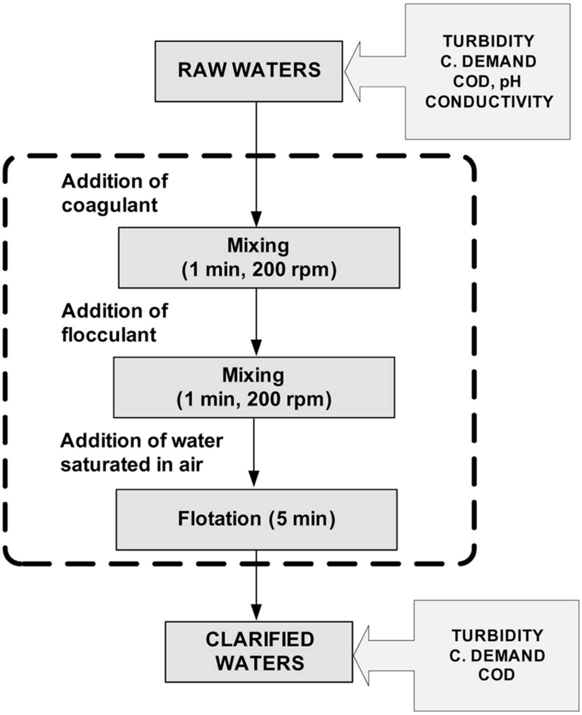

Figure 1. Experimental protocol for the determination of chemical efficiency in a DAF unit.

of the raw waters were also analyzed using a GLP-22 pH-meter and a GLP-32 conductivity meter (both supplied by Crison Instruments, S.A.). Measurements were carried out in duplicate in all cases.

Methodology for Flocculation Tests

Flocculation was monitored using a FBRM device, model M500LF, supplied by Mettler Toledo. The measurement range of this device is 1–1000 μm (31,33). In a typical trial, the probe is submerged into a 150 mL sample being stirred at 400 rpm. After one minute of stirring, the coagulant is added. Then, the system is allowed to evolve for 60 s before addition of the flocculant. The evolution of the system is monitored for 2–3 minutes after flocculant addition. The same procedure is used for single systems, where only the flocculant is added.

RESULTS AND DISCUSSION

The characterization of the waters from the inlet of the industrial DAF unit is shown in Table 2. Figure 2 shows the chord size distribution of the feed water, measured by the FBRM technique. The mean chord size is 2.7 µm. The shape of the chord size distribution also indicates that there is a considerable amount of DCM (<1 µm) in the waters.

The mill has experienced problems with the removal of contaminants with this unit due to the presence of a very stable colloidal system, a consequence of the low but highly concentrated surface charge of the colloids. These colloids are mainly organics, released from the recovered paper in the bleaching stage with hydrogen peroxide and sodium silicate. Bleaching with hydrogen peroxide produces soluble and highly anionic compounds due to the oxidant effect of the peroxides, leading to COD, cationic demand, and colloid concentration increase (46,47). On the other side, sodium silicate, commonly added in the bleaching stage for reducing the hydrogen peroxide decomposition by metal ions, enhances the release of more anionic substances from the recovered paper at the same time that the colloid size is decreased (47), being very detrimental for the clarification of waters. If the amount of silicates is high (>1%), the clarification is very difficult, e.g., waters with a 2% concentration of silicates require a triple concentration of the dose of the coagulant to obtain the same water quality, compared to waters with 1% silicates (21). To achieve the destabilization of the colloidal system two conditions are necessary: a good adsorption of the coagulant and polymers on the particles surface, difficult due to the rather low surface charge of the particles in this system and a good agglomeration of the particles, after the re-conformation of the adsorbed polymeric chains. With the traditional methods of testing, mainly charge-related measurements, it is not easy to know if the process is led by one force or another, but using the FBRM, additional information can be obtained.

Table 2. Characterization of the water sample from the inlet of the DAF unit

pH	7.8
Conductivity (25°C)	1662 µS/cm
Turbidity	1200 NTU
Cationic demand	0.83 meq/L
COD	1461 ppm

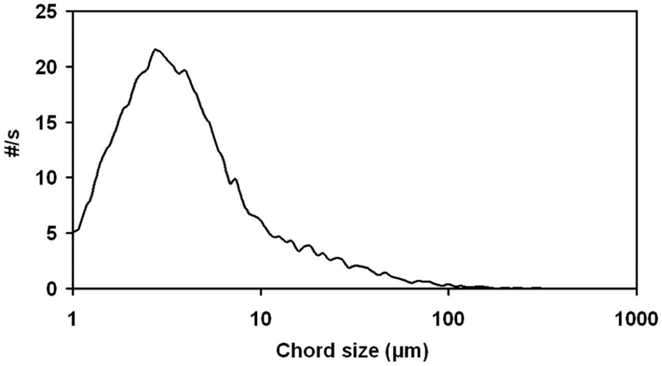

Figure 2. Chord size distribution of the sample from the inlet of the DAF unit.

Single Systems

The effect of flocculant addition was studied to determine the suitability of these systems for cleaning the feed waters, and for a subsequent comparison with dual systems. If the contaminants are mainly suspended solids, single systems are usually enough for obtaining good clarification levels (48,49), but if the removal of finely dispersed and colloidal particles is required, dual systems are necessary (16,17). Figure 3 summarizes the results of turbidity, cationic demand and COD of the clarified waters obtained in the DAF tests. As it was expected, anionic flocculants are not able to interact with the contaminants present in the waters, mainly

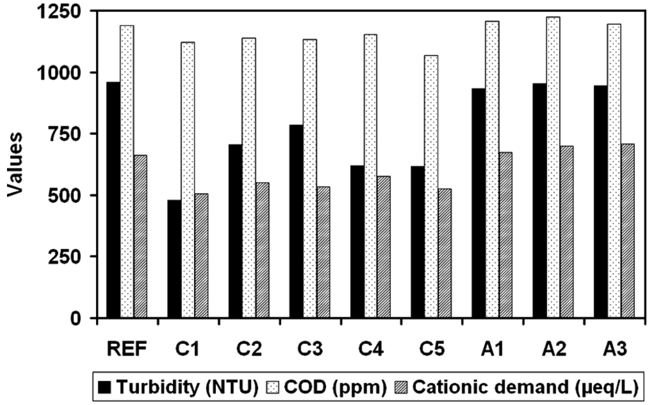

Figure 3. Turbidity, COD and cationic demand of clarified waters in DAF tests (single systems).

DCM, because the DCM is characterized as the main carrier of the anionic charge (8). Cationic flocculants reduced the turbidity by 20–50%, and the flocculant with the lowest charge (C1) was the most efficient. COD reductions were very low (<5%), except with the flocculant with the highest charge (C5), which obtained a 10% reduction. Similar reductions of cationic demand were achieved with the different C-PAMs, ranging from 13 to 23%. C1 and C5 were the most efficient ones (>20% reduction).

The results show that there is not a clear relationship between the charge density of the flocculant and its efficiency in DAF. Previous studies, focused on the destabilization of DCM in TMP process waters, have shown that high charge C-PAMs achieve a better removal of contaminants than low charge C-PAMs (mainly related to the wood extractives content) (28,37,50). In general, high charge C-PAMs are usually preferred to the low charge ones, although there is a limit, because a very high charge density may be detrimental, causing a slight reduction in the adsorption of contaminants (51). However, in this study, the most efficient C-PAMs are both the lowest charged one (C1) and the highest charged one (C5). Only a few authors have reported that a C-PAM with low charge density was more efficient in removing DCM than high charge C-PAMs. M. Nurmi et al. (25) tested two C-PAMs with the same molecular weight ($7 \cdot 10^6$ g/mol) and different charge densities: 1.0 and 1.5 meq/g, and found that the C-PAM with the lowest charge density was more effective. Something similar was observed by Wagberg et al. (52), who found that a high charge density C-PAM (1.89 meq/g) was more efficient at lower levels of polymer addition, but C-PAMs with lower charge densities (0.36 and 0.62 meq/g) had a higher flocculation ability over a large range of polymer dosage; the low charge C-PAMs being the most efficient flocculants at high dosages, such as those used in this study.

The possible explanation of a higher efficiency of the low charge C-PAMs can be related to the bridging mechanism, recognized to be the dominating mechanism in the flocculation of deinked and TMP waters with C-PAMs (33,34). Figure 4 shows the proposed scheme of the flocculation mechanism induced by C1, case A, and by one of the higher charged C-PAMs, case B. The anionic charge of colloids in this system is low but can be concentrated in some zones on the particle surface. Attractive electrostatic forces between C1 and the particle surface are weak because of the low charge of the polymer. Therefore, adsorbed chains keep a highly extended conformation. Because of this, and due to the low polymer charge, the number of chains that can interact with each particle is higher than it is in case B (25,52). Therefore, more bridges can exist between each particle

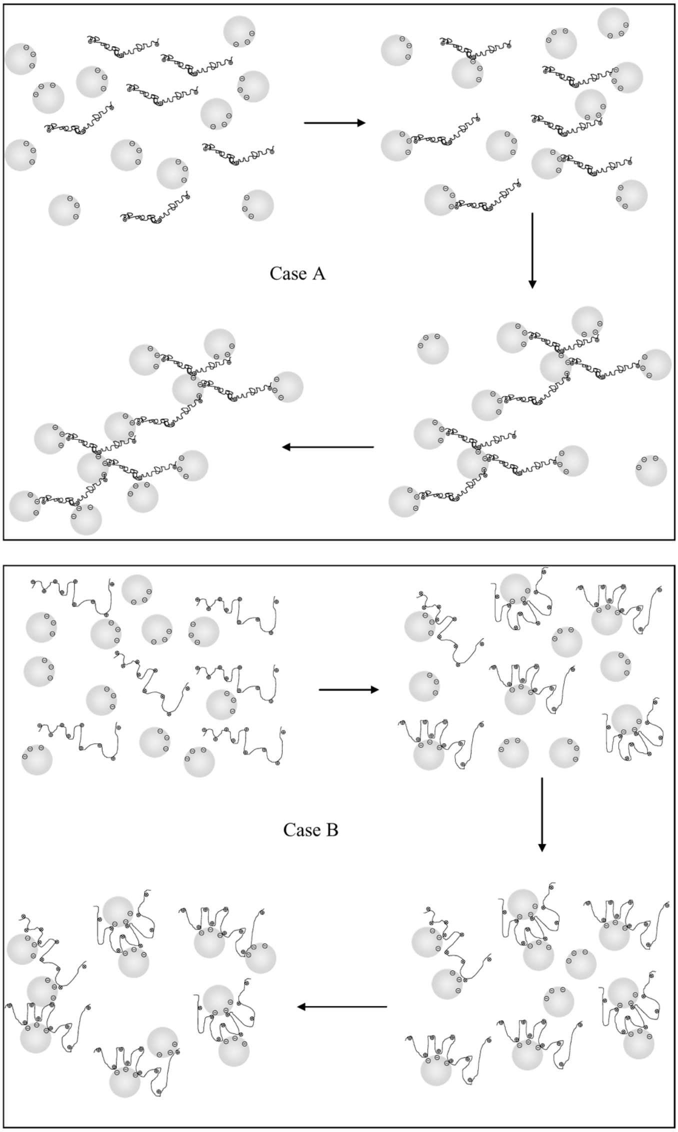

Figure 4. Proposed scheme of the flocculation mechanism. Case A: C1. Case B: a high charge C-PAM.

and the adjacent ones, forming large flocs that aggregate slowly to form very large flocs. Floc density is low because bridges among particles in these flocs are long, and flocs are therefore easy to remove by flotation.

In case B, electrostatic forces between particles and the chains are stronger, and therefore:

1. the conformation of adsorbed chains is less extended;
2. a fewer number of chains can interact with each particle due to the repulsion between the charged groups, and consequently, a lower number of bridges can be formed among particles and the flocs are smaller (53);
3. the bridges are shorter than in case A, so the flocs are more compact and dense, and thus, more difficult to float.

However, the higher neutralization ability of the highly charged C-PAMs increases the efficiency of anionic colloids' neutralization, when C4 and C5 are used at the same dosage than the other C-PAMs (37). In the case of C5, the charge density could be high enough to induce the evolution of the bridging flocculation mechanism towards patching (23).

Figure 5 shows the chord size distribution obtained by the FBRM 10 s after the addition of the different flocculants, when the degree of flocculation is maximum. In general, flotation is promoted by large flocs, although, in some cases, a low mean chord size with a higher number of counts mean that DCM has been destabilized and aggregated to form small flocs that can be also subsequently removed by flotation (27). A chord size distribution obtained with A-PAMs is similar to that of raw waters (RW) because they did not interact with the detrimental material.

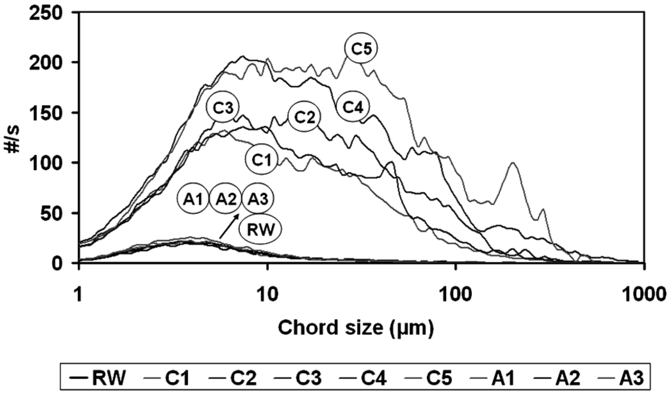

Figure 5. Chord size distribution of the waters after 10 s of the flocculant addition (single systems).

Addition of C-PAMs increases the area of chord size distribution and shifts it towards larger chord sizes, indicating a flocculation of colloids smaller than 1 µm. The area of the chord size distribution increases with polymer charge density, with C5 being the one that forms more and larger flocs from colloids smaller than 1 µm in 10 s. Flocs aggregate in a second stage, around 20 s after flocculant addition, with a strong decrease in the number of chords between 1 and 10 µm when C1 was used, as shown in Fig. 6. A sharp decrease in the number of counts was also observed in all the higher chord sizes intervals, indicating the formation of flocs larger than 1000 µm (the upper measurement range of the FBRM device), which are easily removed in the DAF unit. This second stage, however, takes place in a short time span, being unable to detect of the exact maximum degree of flocculation for C1. Consequently, the chord size distribution shown in Fig. 5 does not exactly represent the moment at which the flocculation of C1 is maximum due to the longer time required for aggregation to begin (after 20 s of flocculant addition), which permits the differentiation between the nucleation and growth of flocs (23), and the fast aggregation kinetics to produce very large flocs, outside of the measurement range of the FBRM device.

The total number of counts increases with destabilization of DCM because most of the colloidal material is initially below the detection limit but reaches a final value (without figure) that could be related to the global flotation efficiency. In our study, a large increase in the total number of counts from around 500 to 7000 #/s was observed for all the C-PAMs, except for C5 (11000 #/s), and no increase in the number of counts was observed for A-PAMs. After the initial increase in the

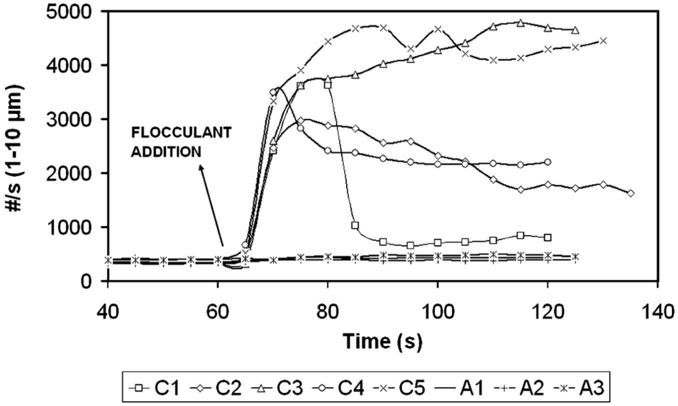

Figure 6. Evolution of the number of chords/s in the range 1–10 µm along the flocculation process (single systems).

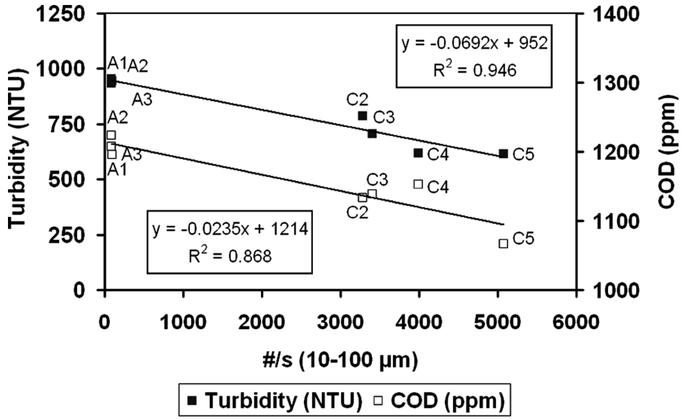

Figure 7. Relationship between turbidity and COD of the clarified waters by DAF and the number of counts/s between 10–100 µm, measured by FBRM, at the moment of maximum flocculation.

number of particles, these can increase, decrease, or remain stable. The final value of the number of the counts is in the following order: C5 > C4 > C3 > C2 > C1, similar to the efficiency obtained in the DAF tests except for C1. The same results were observed analyzing the mean chord size.

In the case of single systems, both the cationic demand of the clarified waters and different FBRM statistics can predict the efficiency of DAF. The coefficients of determination between the cationic demand and the turbidity and COD are, respectively, $R^2 = 0.733$ and $R^2 = 0.815$. Comparable results, and even better if C1 is not considered due to its different flocculation behavior, are found with different FBRM statistics. The coefficients of determination between the number of counts per second in the range of 10–100 µm are $R^2 = 0.946$ for turbidity and $R^2 = 0.868$ for COD (Fig. 7). If the mean chord size (1–1000 µm) is considered, the coefficients of determination are $R^2 = 0.900$ for turbidity and $R^2 = 0.756$ for COD. With the total number of counts (1–1000 µm), the coefficients of determination are $R^2 = 0.733$ for turbidity, and $R^2 = 0.844$ for COD.

Dual Systems

Figure 8 summarizes the efficiency of dual systems in DAF tests; the results obtained for the only addition of coagulant are also included. The coagulant combined with A-PAMs reduced turbidity by 70–90%, COD by 15–20% and cationic demand by 70–75%. If C-PAMs are used,

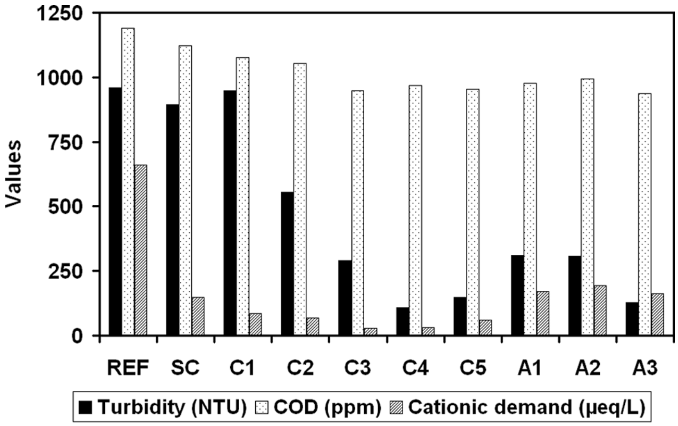

Figure 8. Turbidity, COD and cationic demand of clarified waters in DAF tests (coagulant alone and dual systems).

the reductions vary between 1% and 90% for turbidity, 10–20% for COD, and 90–95% for the cationic demand. Results obtained with the best A-PAM (A3) and the best C-PAMs (C4 and C5) are similar, except for the cationic demand, due to the contribution of the charge of the polymers to the total charge measured by colloidal titration. The coagulant caused very little aggregation by itself (only a 7% reduction of turbidity and 6% of COD), but induced an important increase in the aggregation achieved by a subsequent PAM addition. A coagulant induces the neutralization of the anionic charge, facilitating the destabilization of DCM and increasing the amount of free C-PAM available to flocculate the aggregates (20,46). However, there is a limit to the dosage of coagulant: if too much coagulant is added, particles start to repel each other due to steric and electrostatic stabilization. This occurs near the isoelectric point of the waters. In our study, the dosage of coagulant was fixed to obtain a reduction in the cationic demand of around 75% of the feed water in order to avoid the total neutralization of the waters (especially considering that C-PAMs are used in conjunction with the coagulant), but still enough to obtain a good removal of DCM (20).

The results show a clear relationship between the turbidity removal and the charge density of the flocculants. High charge A-PAM (A3) is more efficient than low charge A-PAMs (A1 and A2) due to the higher interaction with the coagulant adsorbed on colloids. In the case of C-PAMs, the optimum charge density is 3.0–3.5 meq/g (C4 and C5). In the presence of a coagulant, electrostatic forces among C-PAM and particles are lower due to the lower remaining charge of the particle surface. Therefore, adsorption of C1 is too weak to form useful flocs while flocculants with a higher charge density can adsorb with an extended conformation and form larger flocs. Previous studies, focused on the removal of wood extractives in TMP waters, have demonstrated that the point of charge reversal and the point of optimal flocculation differed considerably from each other in bridging flocculation, as occurred in single systems. But if dual systems are used, the maximum DCM removal was obtained for a coagulant dosage close to the isolectrical point (25,50,54,55).

Figure 9 shows the chord size distributions of the suspension 10 s after the addition of the flocculant. The best treatments (C4, C5, and A3) caused a very broad, almost flat, chord size distribution, with a high number of particles with chord sizes larger than 100 µm. These kinds of distribution curves are typically obtained when flocs larger than 1000 µm are formed because they lie outside of the measurement range of the FBRM probe. These types of chord size distributions cannot be characterized properly by the mean chord size. If the rest of the chemical treatments are considered, it is observed that the efficiency of DAF systems is related to the maximum of the mean chord size distribution.

The total number of counts can also be analyzed to obtain further information about the flocculation process (Fig. 10). The addition of the coagulant induced a very sharp increase in the total number of counts from around 500 #/s to 9500–10000 #/s (more than 70% of this increase is in the 1–31.6 µm size range). This value remained almost constant until the addition of the flocculant. Then, more efficient products sharply reduced the number of counts to around 1000 #/s (C4 and C5), and to 2000 #/s for A2 and A3. Products with an intermediate efficiency, such

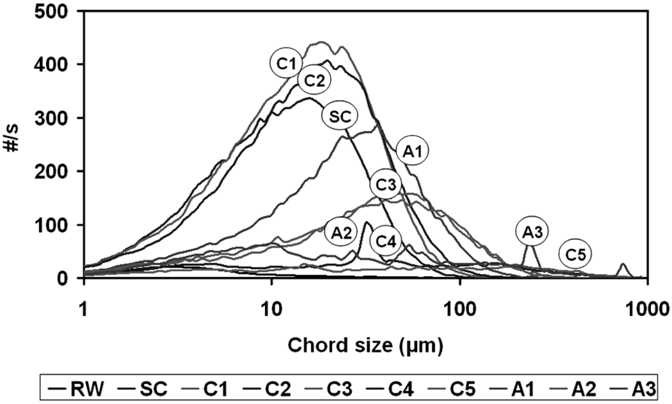

Figure 9. Chord size distribution of the waters after 10 s of the flocculant addition (dual systems).

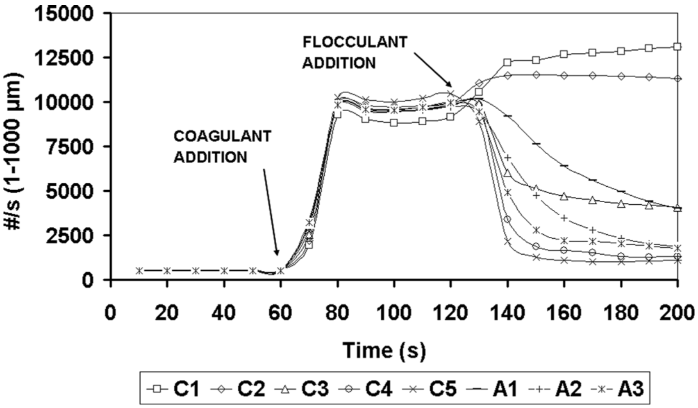

Figure 10. Evolution of the total number of chord/s (1–1000 µm) along the flocculation process (dual systems).

as A1 and C3, reduced the number of counts to around 3000–4000 #/s and increased the number of counts for particles larger than 100 µm. C1 and C2, however, increased the number of counts to over 11000 #/s and all of the flocs were smaller than 100 µm. This corroborates the fact that these flocculants are not able to form larger flocs from the destabilized DCM and, consequently, their efficiency for removing contaminants by DAF is low.

The analysis of the mean chord size evolution corroborates these observations (Fig. 11). The addition of the coagulant yielded little

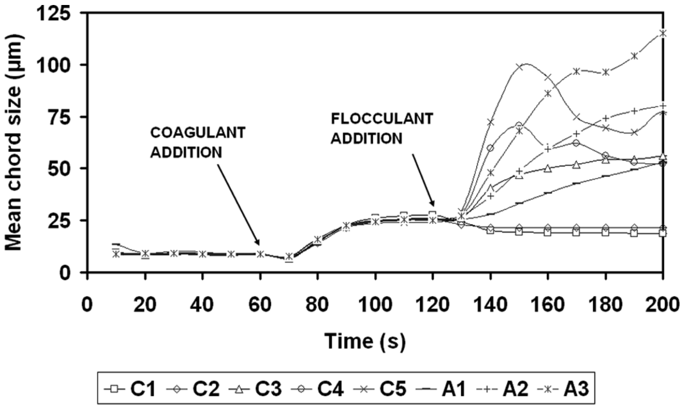

Figure 11. Evolution of the mean chord size (1–1000 µm) along the flocculation process (dual systems).

increase in this statistic (from 10 µm to 25µm), as was already observed by A.J. Dunham et al. (20). After the flocculant addition, the most efficient products showed a sharp increase of the mean chord size (up to 110 µm). Intermediate efficient products such as A1 and C3 produced a progressive increase in the mean chord size, although the final values were lower. In the case of less efficient products (C1 and C2) the mean chord size showed only a small increase after flocculant addition.

In contrast to the observations made with single systems, the efficiency of the dual systems can not be successfully correlated with the final cationic demand of the clarified waters. If neutralization would be the main flocculation mechanism, the optimal removal efficiency should be at the isoelectric point, but this is not the case. This fact indicates that, although a coagulant acts by the neutralization mechanism, the flocculants do not. For this reason, relatively low differences in cationic demand, e.g., 90 µeq/L (C1) and 60 µeq/L (C5), led to great differences in the reduction in turbidity: 1% (C1) and 85% (C5).

Therefore, other measurements, different than traditional methods, are necessary to predict and control the efficiency of the flocculation process. In this sense, FBRM is a valuable tool that can be used independently if single or dual systems are tested. Good correlations have been obtained for different FBRM statistics as the number of counts in the 10–100 µm size range (Fig. 12), the total number of counts or the mean chord size in 1–1000 µm size range (Table 3).

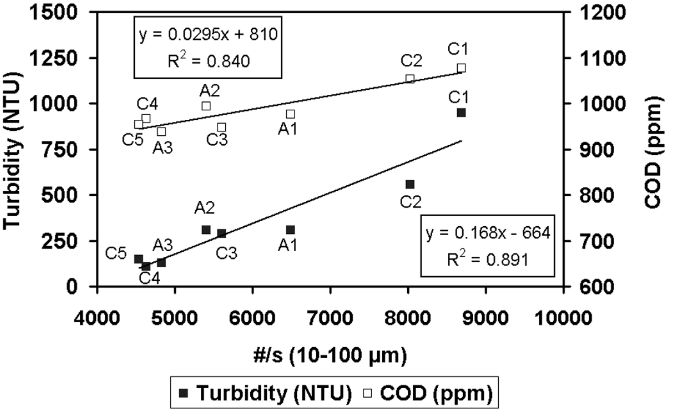

Figure 12. Relation between turbidity and COD of the clarified waters by DAF and the number of counts/s between 10–100 µm, measured by FBRM, at the moment of maximum flocculation.

Table 3. Correlation of DAF efficiency with cationic demand and FBRM statistics. Dual systems

	R^2	
	Turbidity	COD
Cationic demand	0.001	0.003
Number of counts/s (10–100 μm)	0.891	0.840
Total number of counts (#/s)	0.888	0.835
Mean chord size (1–1000 μm)	0.617	0.664

CONCLUSIONS

Dual systems are necessary for the clarification of deinking process waters with DAF due to the high stability of this colloidal system. A maximum reduction of 50% of turbidity and 10% of COD is achieved by C-PAMs alone. Dual systems, either based on C-PAMs or A-PAMs, achieved reductions of 90% in turbidity and 20% in COD.

Although it is generally believed that C-PAMs with a high charge density are more efficient when they are used as single systems in DAF units, it has been demonstrated that low charge C-PAMs can be efficient in DAF treatments for deinking process waters due to their capacity to form more and larger bridges between particles, giving larger and less dense flocs. However, recharging of particles increases with a higher charge density of the flocculant, and therefore leads to DCM destabilization, which explains also the high efficiency of the highest charge C-PAM tested.

The advantages of low charged flocculants become a drawback when the coagulant is added before in dual systems. In this case, the efficiency increases with increased charge density of the flocculant, as it was expected.

For single systems, although the dominating flocculation mechanism is bridging, the flocculation efficiency can be predicted based on charge measurements as cationic demand or zeta potential. On the contrary, these measurements do not correlate with the efficiency of DAF in dual systems, although coagulation takes place by charge neutralization.

Monitorization of chemical flocculation by FBRM gives us valuable information to predict the efficiency of different chemical treatments in DAF for both single and dual systems. The number of counts per second in the 10–100 μm size range represents a useful parameter to correlate flocculation monitoring and the efficiency of DAF systems. Coefficients of determination of this statistic with turbidity and COD in dual systems are, respectively, $R^2 = 0.891$ and $R^2 = 0.840$. In the case of single systems, if C1 is not considered due to its different flocculation behavior, the coefficients of determination are $R^2 = 0.946$ for turbidity and $R^2 = 0.868$ for COD.

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