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New range of natural products for pre-treatment of water desalination plants

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ABSTRACT

Water desalination plants performance and time evolution of its main operational parameters may be influenced by the presence of certain substances both in solution and in suspension in natural waters. Within these substances, humic acids, which percentage may rise up to 50% of total organic matter, could lead to film formation on membranes surface if removal treatments are not properly implemented. Moreover, contact with disinfectant agents such as chlorine can cause the formation of trihalomethanes (THMs) as undesirable reaction side products. Synthetic coagulant and flocculant dosing programs are included as pre-treatments in water desalination plants as a first stage on water processing in order to remove colloidal matter, from both organic and inorganic sources. However, coagulant and flocculant overdosing not only may be null from the treatment effectiveness point of view but also might lead to recalcitrant fouling phenomena. ADIC GR102, a natural polymer, was used as a flocculant agent in natural organic matter removal processes leading to similar organic matter removal yields and Flocculation Index values to those obtained with currently marketed products. Several assays performed at 80% of coagulant requirement to destabilize the suspension and relatively low dosage of ADIC GR102 opened the doors to a promising future water treatment strategies.

Keywords: Coagulation; Flocculation; Organic matter; Natural polymers

1. Introduction

1.1. Coagulation and flocculation

Coagulation and flocculation processes have ever been a basic process on drinking water treatment. Removal of natural organic matter (NOM) (polycarboxylic acids and aromatic-rich humic substances), responsible for giving water certain degree of color, as well as colloidal particles, is achieved by using a range of products that promote pollutant aggregation to be easily separated from water through mechanical operations like filtration, decantation, or flotation[1,2].

NOM and colloidal particle's presence in water treatment plant's feedwater stream line may lead to healthy risky disinfection by-products formation when they react with chlorine and recalcitrant fouling phenomena on reverse osmosis membrane systems [1–4].

In this context, coagulation is defined as a process of increasing particle's aggregation kinetics of a stable suspension to start forming flocs. Coagulation is based on particle's surface charge neutralization through the use of an ionic coagulant to overcome the balance

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between electrostatic and Van der Waals forces that avoid its aggregation. Focusing on NOM, negative surface charge is highly dependent on water pH and has its origin mainly in ionization reaction of carboxylic groups (Eq. (1)).

$$\text{R–COOH} \leftrightarrow \text{R–COO}^- \tag{1}$$

On the other hand, colloidal particles as silica (SiO_2) can acquire negative surface charge through silicon atom substitution on the solid structure [1,2,5]. Fig. 1 shows the integration of an aluminum atom on the tetrahedral structure of SiO_2.

Flocculation, besides, is defined as a massive aggregation of previously destabilized particles. Flocculant agents provide binding points with these particles, increasing its strength and shear resistance.

1.2. Coagulants and optimal coagulant dosage

Aluminum and iron hydrolyzing metal salts (HMS) ($Al_2(SO_4)_3$, $AlCl_3{\cdot}6H_2O$, $NaAlO_2$, $Fe_2(SO_4)_3{\cdot}8H_2O$, $FeSO_4{\cdot}7H_2O$, $FeCl_3$) are the most widely used coagulant agents in water treatment [1,2,6]. Despite the introduction of both synthetic (often tailor-made) and natural products [1,4] in the chemical market to be used as coagulants, dosage of HMS prevails due to their low cost and availability.

HMS addition in water treatment plants is not a trivial issue, since its overdosage may lead to serious operational problems in some stages of water processing. Relatively low levels of iron (Fe^{3+}) and aluminum (Al^{3+}) after pre-treatment process could cause the supersaturation of certain salts and its precipitation as colloidal matter on reverse osmosis membrane, diminishing plant's global yield. Moreover, there are suspects that remaining aluminum residual in drinking water may be associated with neuropathological diseases including presenile dementia and Alzheimer's disease [7].

For all these reasons, many efforts have been put on optimizing coagulant load to a particular type of water focusing on HMS mechanisms of action. Considering NOM removal, two main mechanisms can be distinguished [1,2,6]:

- Surface charge neutralization. Adsorption of positively charged coagulant species (Al^{3+} and Fe^{3+}, hydrolysis products) on anionic sites of organic pollutants can take place by means of simple electrostatic forces, leading to the precipitation of metal–humic complexes.
- Enmeshment on hydroxide precipitate. When working at higher coagulant dosage, aluminum or ferric hydroxide ($Al(OH)_3$ and $Fe(OH)_3$) precipitation occurs at intermediate pH values sweeping pollutant particles and metal–humic complexes.

Sweep flocculation or enmeshment provides better organic matter removal rates but required coagulant dosage is somewhat higher than that in charge neutralization mechanism of action. Moreover, hydroxide precipitation is a relative difficult-to-control process. On the other hand, charge neutralization mechanism requires lower coagulant dosage but coagulant optimal load must be determined since an excess on it may cause a reverse on particles' charge sign and suspension restabilization leading to poor removal yields. Therefore, some techniques aimed to determine optimal coagulant load have been developed. Among them, analysis of potential at the plane of shear between moving particle and surrounding liquid (potential Z) when titrating the sample with a coagulant agent allows to determine coagulant demand to satisfy charge neutralization at zero zeta potential.

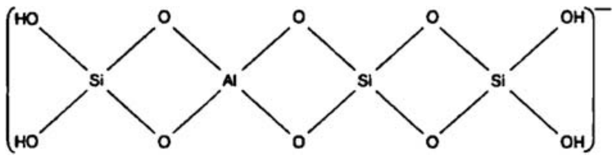

Fig. 1. SiO_2 structure negatively charge.

1.3. Flocculants

Flocculants are compounds mainly used to increase flocculation rate of flocs formed during the coagulation stage of the process. Although there are lots of compounds from different sources, natural polymers addition is widely spread due to non-toxicity, biodegradability, and readily availability from renewable sources [1,2,4]. Despite its own benefits sometimes turn into drawbacks, when referring to low storage life, the use of natural polymers as flocculant agents may represent an interesting water treatment alternative from water quality and waste handling point of view. Furthermore, some citations on the literature reported savings of up to 20% of HMS coagulants when using natural polymers as flocculant aids [1,8].

2. Objectives

The aim of this work is to develop a coagulation–flocculation process strategy based on the use of both HMS coagulant and a natural polymer as a flocculant to reduce the amount of coagulant required to remove NOM contaminated water when the process is driven by the charge neutralization mechanism. It is intended to combine two mechanisms of action to efficiently remove the pollutants from real case water. The first one, as described, based on the precipitation of metal–humic complex by means of electrostatic forces, and the second one based on the interaction of hydrophobic sites of pollutants with the natural polymer used.

3. Materials and methods

3.1. Real case water

Elemental composition of water used in this work simulates a real case water from a river source used as a feedwater stream line to a water treatment plant. Elemental composition is shown in Table 1.

Contribution to TOC is carried out by means of commercial humic acid powder (humic acid sodium salt, Cat. No. H1675-2, Sigma–Aldrich) while other elements are introduced by using shelf reagents.

Assays were performed using iron-based and aluminum-based coagulants and ADIC GR101, ADIC GR102, and ADIC 828 AF (currently marketed product) as flocculant agents.

Table 1
Elemental composition of real case water from river source fed into a water treatment plant

Parameter	Value
pH	7.3
Calcium (mg Ca/L)	104
Magnesium (mg Mg/L)	31
Sodium (mg Na/L)	158
Potassium (mg K/L)	31
Barium (mg Ba/L)	0.055
Strontium (mg Sr/L)	1.7
Iron (mg Fe/L)	0.008
Aluminum (mg Al/L)	0.24
Manganese (mg Mn/L)	0.026
Sulphate (mg SO_4/L)	204
Chloride (mg Cl/L)	320
Fluoride (mg F/L)	0.180
Bicarbonate (mg HCO_3/L)	294
Nitrate (mg NO_3/L)	9.0
Silica (mg SiO_2/L)	2.57
Phosphate (mg PO_4/L)	0.35
TOC (mg C/L)	3

3.2. Analytical methods

3.2.1. Zeta potential monitoring

To determine optimal coagulant load, a Coagulant Charge Analyzer CCA3100 (Chemtrac) was used. The device allowed monitoring zeta potential when titrating with a coagulant agent. Optimal coagulant load was established as the amount of coagulant that yielded a value of zero on zeta potential.

3.2.2. Jar test experiments

Certain volume of coagulant stock solution (aluminum or iron based) was added to a 1-L glass beaker containing 1 L of synthetic water (Table 1). Stirring speed was set at 200 rpm (Portable floculator FP4—Velp Scientifica) for 10–20 s in order to get a rapid mixing of the coagulant in the sample. The stirring speed was then set at 20 rpm and a certain volume of a natural polymer solution was added to the sample to increase the rate of flocculation. After 10 min of contact, the stirrer was switched off and the flocs were allowed to settle.

3.2.3. Percentage of organic matter removal

Flocs formed in Section 3.2.2 were allowed to settle for 60 min. Supernatant turbidity (Iso turbidimeter HI 98713—Hanna Instruments) was determined every 10 min until a constant value was achieved. Certain volume of supernatant was filtered at 0.45 µm, and optical density was measured at 254 nm (OD_f^{254nm}). Results were compared with the optical density measured before chemicals addition (OD_0^{254nm}), and NOM removal percentage was calculated as follows (Eq. (2)):

$$(\%\ \text{NOM removal}) = \frac{\left((\text{OD})_0^{254\text{nm}} - (\text{OD})_f^{254\text{nm}}\right)}{(\text{OD})_0^{254\text{nm}}} \cdot 100 \qquad (2)$$

3.2.4. Floc size monitoring

Jar test experiments were coupled to Photometric Dispersion Analyzer (PDA) device (Rank Brothers Ltd, UK) to monitor floc size after flocculant dosage [9]. During the flocculation stage of the NOM removal process, a peristaltic pump was used to establish an approximate volumetric flow of 20 mL/min of treated water through the device where the suspension was

Table 2
Jar test experiments performed with aluminum-based coagulants

Coagulant	Coagulant dose (mg Fe/L)	Flocculant	Flocculant dose (mg/L)
Aluminum based	5.95	–	–
Aluminum based	5.95	ADIC GR101	2
Aluminum based	5.95	ADIC GR102	2
Aluminum based	5.95	ADIC 828 AF	2

illuminated by means of a high-intensity light-emitting diode. The variation of floc's characteristics caused a fluctuation in the intensity of transmitted light. Mathematical treatment of the data allowed determining a Flocculation Index (FI) (related with floc size and flocs' state of aggregation) that could be used not only to asses for the best flocculant type for the process but for its optimal dose.

4. Results and discussion

4.1. *Optimal coagulant dosage*

By using Coagulant Charge Analyzer CCA3100, optimal coagulant dosage was found. Fig. 2(A) and (B) shows *Z* potential monitoring when titrating with aluminum-based and iron-based coagulants. For the specific type of water evaluated, surface charge neutralization required higher amounts of aluminum-based coagulant than iron-based coagulant. Although certain citations on the literature reported higher iron-based coagulants for comparable water quality, coagulation and flocculation processes need to be considered on a case-by-case basis.

4.2. *Jar test experiments*

Coagulant dosage for surface charge neutralization lead to a decrease in water pH since complexes of metal ions in water act as weak acids. Given the fact that NOM removal is largely dependent on the pH, experiments carried out both with iron-based coagulants and aluminum-based coagulants were set at the optimum conditions for this to occur. Bearing in mind that coagulation is driven under two main mechanisms, surface charge neutralization and enmeshment on hydroxide precipitate, pH was adjusted at the metal hydroxide ($Al(OH)_3$, $Fe(OH)_3$) minimum solubility value. On the one hand, since aluminum-based coagulation has its optimum at pH 6.6–6.8, addition of required aluminum-based coagulant to null zeta potential and aluminum–water coordination compound hydrolysis ($[Al(H_2O)_6]^{3+}$) provides necessary decrease in pH. On the other hand, on iron-driven coagulation experiments, pH was adjusted at 8 after coagulant dosage as ferric hydroxide reaches its minimum solubility.

4.2.1. *Aluminum-based coagulant*

Several Jar test experiments were performed using aluminum-based coagulants and natural polymers as flocculant agents. In this study, we present the results obtained when treating water as described in Table 2. Coagulant addition was set according to Section 4.1,

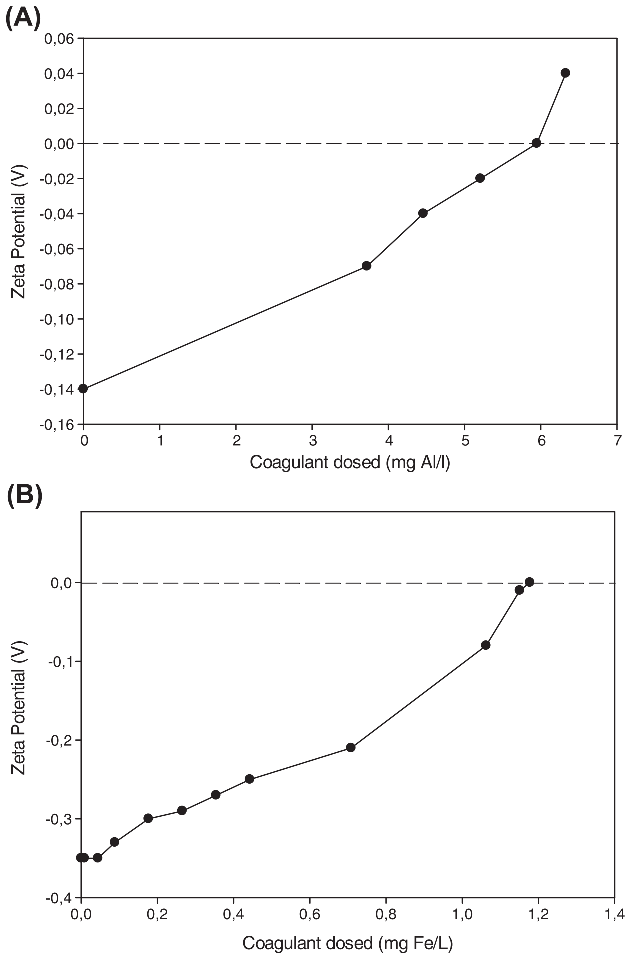

Fig. 2. Synthetic water titration with metal-based coagulant for zeta potential monitoring.

that is, the required dosage to null the zeta potential of the suspension. On the other hand, flocculant dosage was arbitrary.

After proceeding as described in Sections 3.2.2 and 3.2.3, NOM removal percentage was measured. For all the experiments performed, NOM removal percentage ranged between 96% and 97% even without flocculant addition.

Differences were noticeable when coupling Jar test experiments with PDA, where flocs' state of aggregation (FI) was monitored. Since initial turbidity of the suspension (after chemicals addition) was not the same in all the experiments performed, FI provided more useful information about floc size and their resistance to shear stress. Fig. 3(A)–(D) shows FI evolution after coagulant and flocculant addition. All experiments were carried out under the same stirring conditions: before and after chemicals dosage.

All four figures allow distinguishing the main stages of the coagulation and flocculation process:

- From time 0 to 100–150 s, untreated water was flowing through the PDA device. This sets the baseline of the monitoring since no particles were detected by the optical sensor of the equipment.
- At time 100–150 s, stirrer speed was set at 200 rpm and water treatment chemicals were added on the suspension. This is revealed by a sharp peak on the figure.
- After additives dosing, stirrer speed was set at 20 rpm allowing flocs aggregation. Increasing values of the FI were related to an increase in the flocs size.

When no flocculant was added in the suspension (Fig. 3(A)), FI increased slightly compared with the baseline. When aluminum-based coagulant was the only additive dosed in the suspension, flocs started forming but aggregation did not significantly occur.

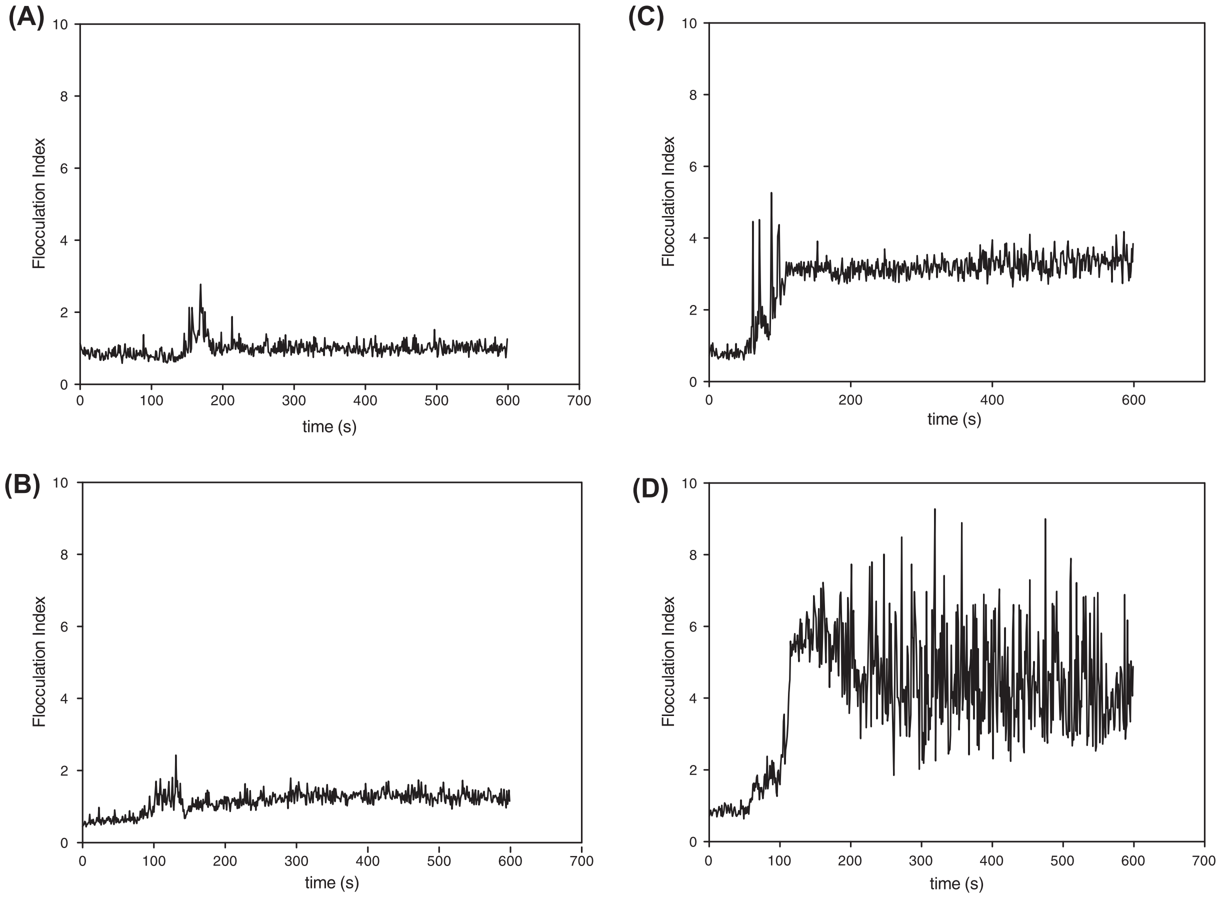

Fig. 3. FI monitoring. (A) Treatment with aluminum-based coagulant. (B) Treatment with aluminum-based coagulant and ADIC GR101 as flocculant agent. (C) Treatment with aluminum-based coagulant and ADIC GR102 as flocculant agent. (d) Treatment with aluminum-based coagulant and ADIC 828 AF as flocculant.

Table 3
Jar test experiments performed with iron-based coagulants

Coagulant	Coagulant dose(mg Fe/L)	Flocculant	Flocculant dose (mg/L)
Iron based	1.17	–	–
Iron based	1.17	ADIC GR101	2
Iron based	1.17	ADIC GR102	2
Iron based	1.17	ADIC 828 AF	2

On the other hand, when ADIC 828AF (non-natural currently marketed product) was used as a flocculant agent in the suspension (Fig. 3(D)), FI increased dramatically. When flocs reached a certain size, FI measurements became erratic and showed oscillations around a mean value. For both natural polymers used as flocculant agents—ADIC GR101 (Fig. 3(B)) and ADIC GR102 (Fig. 3(C))—intermediate results were obtained. On the one hand, ADIC GR101 led to a slight increase of the FI above the baseline comparable with the results obtained when aluminum-based coagulant was the only additive dosed. On the other hand, when combining aluminum-based coagulant with ADIC GR102 as a flocculant agent, FI increased considerably. Further studies on ADIC GR102 load need to be done to get FI values comparable with the

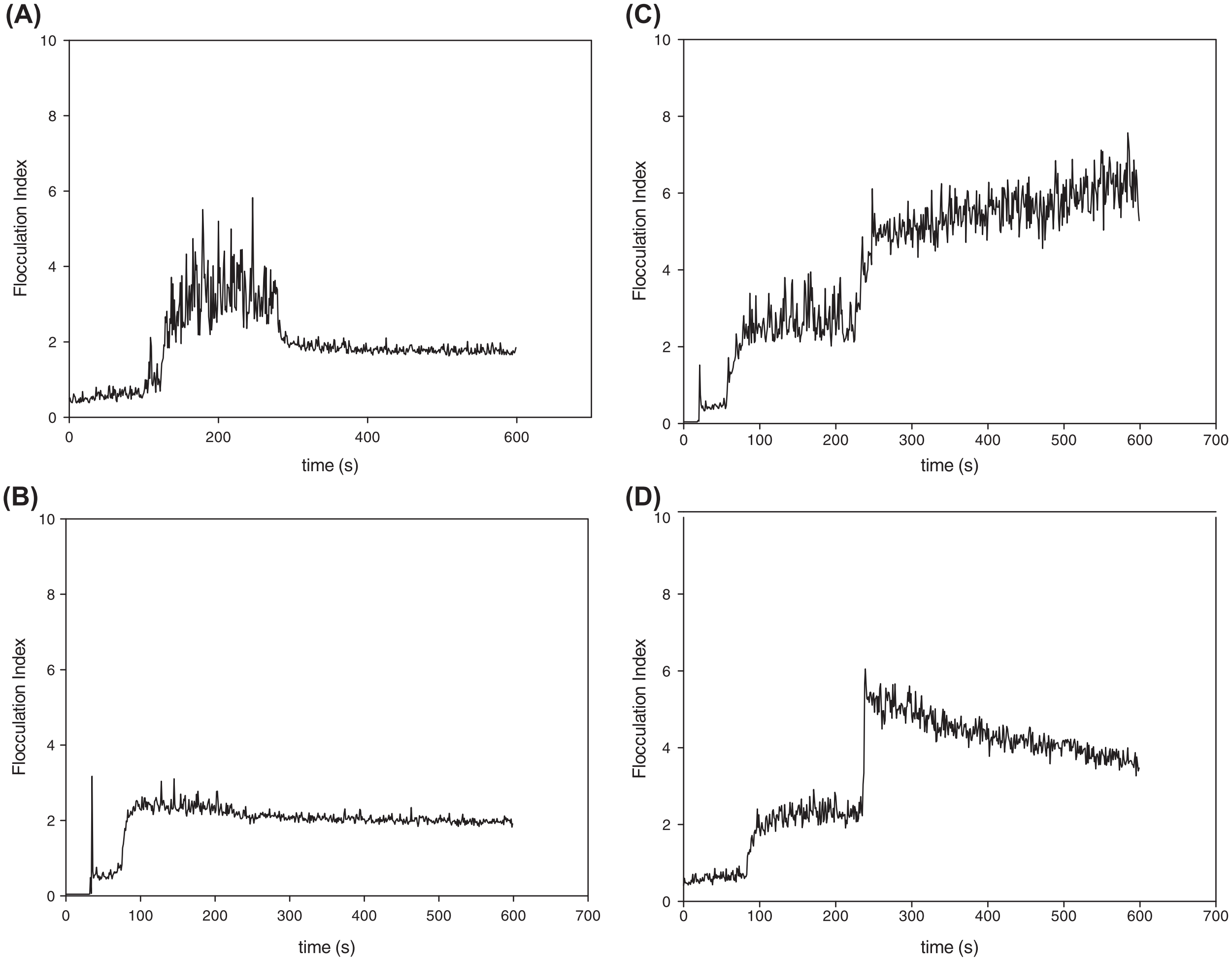

Fig. 4. FI monitoring. (A) Treatment with iron-based coagulant. (B) Treatment with iron-based coagulant and ADIC GR101 as flocculant agent. (C) Treatment with iron-based coagulant and ADIC GR102 as flocculant agent. (D) Treatment with iron-based coagulant and ADIC 828 AF as flocculant.

values obtained when using ADIC 828AF, but preliminary results point ADIC GR102 as a promising future alternative to the use of synthetic flocculants.

When analyzing residual aluminum in the treated water, concentrations below 0.06 mg Al/L were detected in all the experiments performed, which reveals that accurate coagulant addition was done. This is relevant not only from the standpoint of legislation in drinking water but also because low levels of aluminum are required on subsequent stages of drinking water treatment to avoid scaling phenomena on reverse osmosis unit operations.

4.2.2. Iron-based coagulant

Parallel experiments were performed using iron-based coagulants (Table 3) and same flocculant agents as in Section 4.2.1.

After proceeding as described in Sections 3.2.2 and 3.2.3, NOM removal percentage was measured. All experiments yielded 95–97% of NOM removal, even without using a flocculant agent.

When analyzing flocs' state of aggregation by coupling Jar test experiments with PDA device (Fig. 4(A)–(D)), the following observations could be made:

- When no flocculant was added in the suspension, that is, when the only chemical added was iron-based coagulant, the observed FI was higher than the obtained when water was treated only with aluminum-based coagulant. Same trend was observed when ADIC GR101 was used as flocculant agent.
- When using ADIC GR102 and non-natural flocculant agent ADIC 828AF, opposite trends were observed. After adding the flocculant agent, an increase in the FI was detected for both experiments. However, time evolution for both revealed different behaviors. On the one hand, when using non-natural flocculant agent (Fig. 4(D)), a progressive decrease on FI was detected during the time after flocculant addition. This could be consistent with a possible floc breakage due to poor resistance to shear stress. On the other hand, when using ADIC GR102 as a flocculant agent, FI kept on increasing throughout the monitoring time of the experiment, showing better performance to shear stress.

As for the residual iron values, levels below 0.05 mg/L were detected for all the experiments, on the supernatant after water treatment, that is, acceptable from the standpoint of legislation.

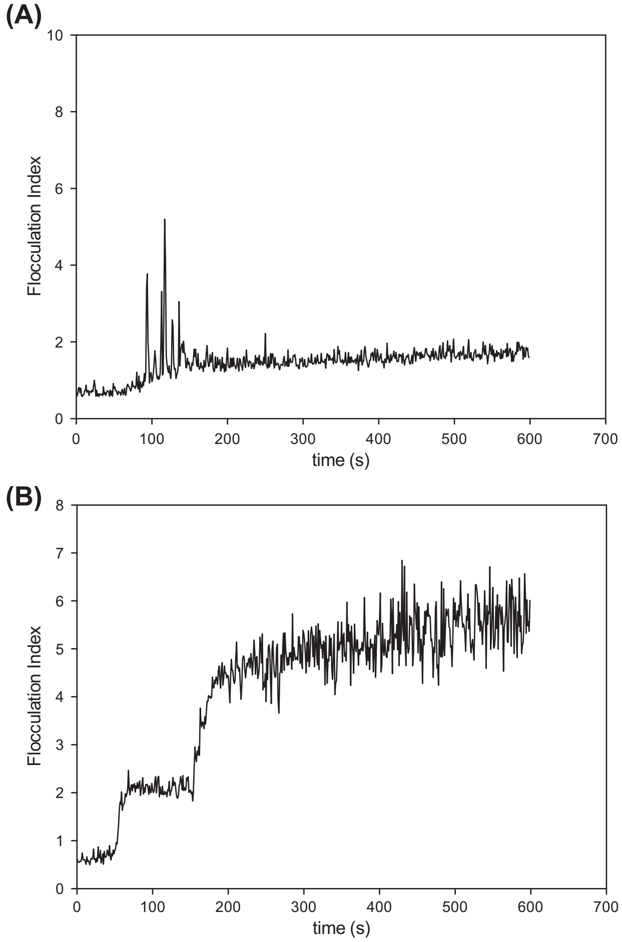

Fig. 5. FI monitoring. (A) Treatment with aluminum-based coagulant (80% of required amount for charge neutralization) and ADIC GR102 as flocculant agent. (B) Treatment with iron-based coagulant (80% of required amount for charge neutralization) and ADIC GR102 as flocculant agent.

4.3. HMS savings

As pointed in Section 1.3, two assays were carried out to elucidate whether 20% savings on HMS addition (compared with required load for surface charge neutralization) could be possible without compromising the key parameters of the process, that is, NOM removal yield, FI (Fig. 5(A) and (B)), and metal residual value after treatment.

Regarding NOM removal, values above 95% were achieved for both assays. However, when looking at the metal residual values after treatment, these were somewhat higher (0.07 mg Al/L, 0.089 mg Fe/L) than the obtained when working at full coagulant load. This is consistent with the fact that lower levels of metal hydroxide supersaturation were achieved, remaining then in solution.

As for FI (Fig. 5), when coagulation was carried out by using aluminum-based compounds, values achieved were lower than those obtained when working at full coagulant load. Lower amounts of aluminum hydroxide precipitate could delay or even cancel nucleation phenomena where flocs could have started growing from. On the other hand, when working at 80% of required iron-based coagulant, FI also showed a slight decrease compared with results obtained at full coagulant load. However, results were considerably good. Further research needs to be done in flocculant dosage in order to balance the decrease of coagulation contribution in the global NOM removal process.

5. Conclusions

Streaming current measurements (zeta potential) has been adopted as a tool to assess the optimal required coagulant load to increase pollutants' aggregation kinetics in a specific type of water to be fed into a reverse osmosis unit. On the studied case, the iron-based coagulant requirements were lower than those of aluminum-based compounds. Results obtained were satisfactory not only because of NOM removal yields achieved (>95%) but also because low metal residual levels remain in water after treatment.

In parallel, the use of a PDA allows to compare the performance of several flocculant agents as a second stage for NOM removal. In this sense, ADIC GR102 may be a promising future alternative since it provides FI comparable to those obtained with currently marketed synthetic products at similar dose. Moreover, some assays reveal that ADIC GR102 gives flocs better properties against shear stress and breakage.

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