

Optimization of the coagulation–flocculation process for the removal of natural organic matter fractions present in drinking water sources

Oswaldo Cerón Alfaro, Alejandra Martín Domínguez, Fotis Rigas, Myriam Solís-López and Rosa-María Ramírez-Zamora

ABSTRACT

We used an experimental design to determine the best coagulation–flocculation mechanism and the optimal operating conditions for the maximum removal of the natural organic matter fractions (hydrophobic acid (HPOA) and hydrophilic neutral (HPIN)), which are the main factors responsible for irreversible membrane fouling and the generation of disinfection by-products (DBPs). Charge neutralization and sweep mechanisms (SM) were studied using the jar test experiment, and synthetic waters prepared with different hydrophobic/hydrophilic (HPO/HPI) weight ratios by adding model compounds to represent the dissolved organic matter (DOM) fractions. Significant influence factors were identified for both coagulation mechanisms. The SM was the best one for DOM removal independent of the HPO/HPI weight ratio. The SM removed HPOA and HPIN fractions with efficiencies of 87.5–90.5% and 73.6–89.8%, respectively. The dissolved organic carbon (DOC) values of all met the recommendation proposed by the United States Environmental Protection Agency (2 mg total organic carbon (TOC)/L or 1.8 mg DOC/L) for DBPs (<100 µg/L). Furthermore, all effluents met the DOC and silt density index recommended values by membrane suppliers (<3 mg DOC/L and <5%/min, respectively) to minimize fouling potential and to extend the membrane life.

Key words | coagulation mechanisms, disinfection by-products precursors, enhanced coagulation, hydrophobic/hydrophilic ratio, irreversible fouling membranes

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INTRODUCTION

Natural organic matter (NOM) in soil, peat, and water is composed of a mixture of plant and animal products in various stages of decomposition, together with substances synthesized biologically and chemically (Cornel *et al.* 1986; Chow *et al.* 2009). NOM consists of suspended organic matter and dissolved organic matter (DOM). DOM is divided into two main groups: humic substances (HS) (hydrophobic (HPO) fraction) and non-HS (hydrophilic (HPI) fraction) (Thurman 1985; Sillampää 2015).

The amounts and proportions of DOM differ considerably in surface water due to its origin and seasonal variability (Bruchet *et al.* 1990; Matilainen *et al.* 2010).

However, DOM from different origins has shown similar subunits such as fulvic acid (FA), hydrocarbons/tannins, aromatic amines, carboxylic acids, polysaccharides, peptides/amino acids identified as hydrophobic acid (HPOA), hydrophobic neutral (HPON), hydrophobic base (HPOB), hydrophilic acid (HPIA), hydrophilic neutral (HPIN), and hydrophilic base (HPIB) fractions, respectively (Choudhry 1984; Imai *et al.* 2001; Guo *et al.* 2009).

DOM in raw natural water is undesirable because it is responsible for color and odor in effluents of drinking water treatment plants, complexation with heavy metals,

and growth of microorganisms in the treatment unit or distribution system. In addition, DOM is considered to be a precursor for carcinogenic disinfection by-products (DBPs) that can be generated during chlorination (Rook 1974; Rodríguez 2003; Matilainen *et al.* 2010). Owing to this, public health concerns have arisen around the presence of DOM in water resources.

The DOM fractions representing the highest DBP formation potential are the HPO fraction and the HPIN fraction (Soh *et al.* 2008; Matilainen *et al.* 2010). Regarding disinfectants and DBPs, the United States Environmental Protection Agency (US EPA) proposes a maximum total organic carbon (TOC) content of 2 mg/L in treated water and 4 mg/L in source water as a goal to ensure acceptable levels of DBPs (British Columbia 2001).

The presence of DOM in surface water can also increase the process of irreversible membrane fouling. Fouling results in higher operating and maintenance costs and a decrease in the membrane life (Zularisam *et al.* 2006). A dissolved organic carbon (DOC) value <3 mg/L in influents of membrane systems minimizes the potential for irreversible fouling (Pikkarainen *et al.* 2004; Jung *et al.* 2006; Chen *et al.* 2007). The silt density index (SDI) test (American Society for Testing and Materials (ASTM) (D4189-95 2002)) is a widely accepted parameter for the estimation of the fouling capacity of water in reverse osmosis systems. Most membranes have shown an extremely low fouling potential when the feed water has a turbidity <1 NTU and a SDI₁₅ value <5%/min.

Zularisam *et al.* (2006, 2011) have found that HS (HPOA fraction) and HPIN are the main DOM fractions causing irreversible membrane fouling. Due to the high health risks and the negative impacts on the operational efficiency of drinking water treatment associated with DOM, the optimization of the water treatment processes for removing DOM has emerged as a critical issue. Conventional coagulation-flocculation has been widely applied worldwide due to the fact that it is an efficient and economically feasible process for removing NOM and colloidal particles of inorganic origin (Sillampää 2015). However, enhanced coagulation refers to the optimization of the coagulation process to achieve the maximum NOM removal (Hussain *et al.* 2013). Thus, it can be used as a pretreatment for a membrane system.

Two coagulation mechanisms that are widely reported for removing DOM with alum as coagulant are: (1) the charge neutralization mechanism (CNM) and (2) the sweep mechanism (SM) (Semmens & Field 1980; Chow *et al.* 2009). In the CNM, soluble Al species including monomeric $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$ and polymeric $\text{Al}_6(\text{OH})_{13}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$ are predominant. These Al species interact electrostatically with anionic DOM to form insoluble charge-neutral products. Matilainen *et al.* (2010) considered that polymeric Al species are most efficient for DOM removal, because these Al species have a higher positive charge density than monomeric Al species. While in the SM, amorphous precipitate $\text{Al}(\text{OH})_3$ (am) is the predominant Al species, the adsorption of organics compounds occurs on the precipitate of metal hydroxide (Stumm & Morgan 1962; Hendricks 2006).

Enhanced coagulation, particularly using CNM operating conditions (coagulant dose and pH values ranging from 2.4 to 6.5 mg Al/L and from 5 to 5.8, respectively), has obtained a DOM removal ranging from 34 to 75% DOC (Qin *et al.* 2006; Uyak & Toroz 2007; Walsh *et al.* 2009). Other studies found efficiencies varying from 28 to 76% DOC using SM operating conditions (aluminum dose values ranging from 4 to 16 mg Al/L at pH 6) (Uyguner *et al.* 2007; Soh *et al.* 2008; Chow *et al.* 2009; Hussain *et al.* 2013). The variation in the ranges of DOM removal using enhanced coagulation could be due to the optimal values of pH and coagulant dose, depending on the raw water quality or HPO/HPI weight ratio in the study.

On the other hand, little research has been performed for removing the different DOM fractions by enhanced coagulation. Chow *et al.* (2004) and Soh *et al.* (2008) studied fractionated DOM removal (expressed as a very high acid (HPOA fraction) of 72–79, HPI charged of 38–68, and HPIN of 8–16% DOC) applying SM operating conditions (coagulant dose ranging from 8.2 to 9.8 mg/L of Al and at pH 6). Studies about enhanced coagulation using CNM operating conditions were not identified in the literature. Therefore, the present research focused on optimizing the coagulation mechanisms to obtain the maximum DOM removal independently of the HPO/HPI weight ratio by the response surface methodology. In addition, the identification of the best coagulation mechanism was made to establish the maximum removal of the

HPOA and HPIN fractions in order to reduce the irreversible membrane fouling and health problems associated with DBPs.

MATERIALS AND METHODS

Raw water

Laboratory coagulation–flocculation experiments were carried out using solutions prepared by dissolving DOM model compounds in distilled water with different HPO/HPI weight ratios expressed as DOC (%) (Table 1). Bentonite and sodium bicarbonate were added to solutions to obtain different values of turbidity and a constant alkalinity of 750 mg/L as CaCO₃ to control the pH after the coagulation–flocculation process (CFP). The pH was adjusted using H₂SO₄ and NaOH (ACS grade from Sigma-Aldrich & J. T. Baker).

Model compounds of the DOM

FA and humic acid (HA) (HPOA fraction), gallic acid (GA) (HPON fraction), aniline (AN) (HPOB fraction), citric acid (CA) (HPIA fraction), polysucrose (PS) (HPIN fraction) and glutathione (GL) (HPIB fraction) were used as DOM model compounds, as reported in the literature (Guo et al. 2009). All of these compounds were of analytical grade from Sigma-Aldrich, Mallinckrodt Chemicals, and J. T. Baker.

Coagulation–flocculation reagents and experimental system

Aluminum sulfate Al₂(SO₄)₃ × 18H₂O, provided by J. T. Baker, was used as coagulant. An alum stock solution was prepared in distilled water at a concentration of 10 g Al/L. The CFP was performed in a jar test apparatus (Jar Tester PB 700 Phipps & Bird) equipped with a variable mixing system, using the operating conditions as specified in the ‘Coagulation Flocculation Jar Test of Water’ procedure (ASTM D2035-80 2003).

Experimental designs

Two experimental stages were used due to the high number of selected factors studied in this research (n ≥ 6). In the first stage, a fractional factorial design (FFD) (2^{k-2} = 1/4 2^k, k: factors number equals 6) was used to determine the significant influence factors (SIFs) for DOM removal by the CFP. Table 2 shows the coded and natural values for the design factors selected for the FFD. All values were chosen according to information reported in the literature (Camp 1955; de Vargas 2004).

We established that the HPO/HPI average weight ratio is 50/50 for surface water worldwide, in accordance with Imai et al. (2001), Kimura et al. (2004), and Chen et al. (2007).

The values of coagulation time (CT) and flocculation time (FT) were constant in the CNM experiments, and coagulation gradient (CG) and FT were constant in the SM trials because these factors do not have significant

Table 1 | Initial concentrations of the model compounds for different HPO/HPI weight ratios

| DOM fraction | Raw water (HPO/HPI weight ratio (DOC (%))) | | | | | | | | | | | | | |
|------------------------|--|------------------|-------|------------------|-------|------------------|-------|------------------|-------|------------------|-------|------------------|-------|------------------|
| | 100/0 | | 84/16 | | 80/20 | | 50/50 | | 20/80 | | 16/84 | | 0/100 | |
| | [M] | DOC ^a | [M] | DOC ^a | [M] | DOC ^a | [M] | DOC ^a | [M] | DOC ^a | [M] | DOC ^a | [M] | DOC ^a |
| HPOA (HS) ⁺ | 13.91 | 4.46 | 11.67 | 3.74 | 11.13 | 3.57 | 6.96 | 2.23 | 2.77 | 0.89 | 2.22 | 0.71 | – | – |
| HPOB (AN) | 0.36 | 0.19 | 0.3 | 0.16 | 0.29 | 0.15 | 0.18 | 0.09 | 0.08 | 0.04 | 0.06 | 0.03 | – | – |
| HPON (GA) | 1.2 | 0.35 | 1.03 | 0.3 | 0.96 | 0.28 | 0.6 | 0.18 | 0.25 | 0.07 | 0.2 | 0.06 | – | – |
| HPIA (CA) | – | – | 1.23 | 0.27 | 1.54 | 0.35 | 3.81 | 0.86 | 6.09 | 1.37 | 6.39 | 1.44 | 7.62 | 1.72 |
| HPIB (GL) | – | – | 0.21 | 0.05 | 0.26 | 0.06 | 0.63 | 0.16 | 1.02 | 0.25 | 1.07 | 0.27 | 1.26 | 0.32 |
| HPIN (PS) | – | – | 0.8 | 0.48 | 1 | 0.59 | 2.25 | 1.48 | 3.49 | 2.38 | 3.63 | 2.49 | 4.92 | 2.96 |
| DOM total | 15.47 | 5 | 15.24 | 5 | 15.18 | 5 | 14.43 | 5 | 13.7 | 5 | 13.57 | 5 | 13.8 | 5 |

⁺HS (HPOA): HA + FA (30/70% as DOC); [M]: mass concentration as mg/L.

^aDOC contributed for each DOM fraction as mg DOC/L.

Table 2 | Coded and natural values for the design factors selected for the FFD

| Factor | ID letter | Coagulation mechanism | | | | | | |
|--|----------------|-----------------------|-----------|----------------|----------------|----------------|-------|-------|
| | | Charge neutralization | | | Sweep | | | |
| | | Coded values | | | Coded values | | | |
| | | - 1 | 0 | + 1 | ID letter | - 1 | 0 | + 1 |
| Natural values | Natural values | Natural values | ID letter | Natural values | Natural values | Natural values | | |
| pH | A | 4.5 | 5 | 5.5 | A | 6 | 7.25 | 8.5 |
| Coagulant dose (mg Al ₂ (SO ₄) ₃ /L) | B | 3.6 | 63.2 | 122.7 | B | 44.2 | 104.9 | 165.6 |
| CG (s ⁻¹) | C | 3000 | 4000 | 5000 | - | 600 | 600 | 600 |
| CT (s) | - | 1 | 1 | 1 | C | 1 | 4 | 7 |
| FG (s ⁻¹) | D | 20 | 60 | 100 | D | 20 | 60 | 100 |
| FT (min) | - | 20 | 20 | 20 | - | 20 | 20 | 20 |
| HPO/HPI weight ratio (DOC (%)) | E | 100/0 | 50/50 | 0/100 | E | 100/0 | 50/50 | 0/100 |
| Turbidity (NTU) | F | 5 | 127.5 | 250 | F | 5 | 127.5 | 250 |

effects on DOM removal for these coagulation mechanisms (Camp 1955; de Vargas 2004).

The concentration of organic matter in natural surface waters varies worldwide, with a calculated average concentration of 5–6 mg TOC/L (Rodríguez 2003). Therefore, in these experiments the total initial concentration of DOM was 5–5.5 mg DOC/L independently of the HPO/HPI weight ratio. Twenty-one experiments, including five replicates at the center point, were run in a random manner to minimize the effect of uncontrolled variables on the responses. The response parameter selected for these experimental tests was DOM removal, expressed as mg DOC/L.

After SIFs were identified, jar tests were conducted using a central composite design (CCD) ($2^k + 2k + n_c$; k = number of factors, n_c = replicates in the central point) in the second experimental stage. The SIFs, determined for both coagulation mechanisms, were evaluated to optimize the operating conditions and to determine the best coagulation mechanism for the maximum removal of the fractionated DOM (HPOA and HPIN), representing problems of water quality. Similar to FFD, the response parameter was DOM removal expressed as mg DOC/L.

Analytical methods

Different analytical methods based on solid-phase extraction and followed by high performance liquid chromatographic

(HPLC) separation with diode-array detection or spectrophotometry were developed or improved for the measurement of all DOM model compounds after CFP. HS, AN, GA, and PS were concentrated using Oasis HLB cartridges (3.9 × 150 mm), and CA and GL were retained using Hypersep retain AX cartridges (3.9 × 150 mm). Quantification of HS and PS was carried out using a Thermo Scientific GENESYS 10S UV-Vis spectrophotometer at wavelengths of 254 nm and 490 nm, respectively. Measurements of AN, GA, CA, and GL were carried out with a HPLC Agilent 1100 chromatograph.

DOC was determined with a Shimadzu TOC analyzer (model TOC-L CSH/CSN) (APHA method 5310). Measurement of pH and turbidity was carried out using a Thermo Orion 3 Star Series pH meter (APHA 4500H + B) and a Turbiquant 1100 IR turbidimeter (APHA 2130B), respectively (APHA/AWWA/WEF 1999).

SDI tests were carried out for raw waters and clarified effluents produced for different HPO/HPI weight ratios, using the standard test method ASTM (D4189-95 2002). Membrane suppliers recommended SDI values <5%/min for raw water treatment with membrane systems in order to minimize the fouling potential and extend the membrane life. Table 3 shows some recommendations for the fouling potential of raw and treated water according to SDI value (Baker 2012).

Table 3 | SDI₁₅ values and recommendations for membranes

| SDI ₁₅ values (%/min) | Recommendations for membranes |
|----------------------------------|---|
| <1 | Several years without colloidal fouling |
| <3 | Several months between cleaning |
| 3–5 | Particular fouling likely, frequent cleaning needed |
| >5 | Unacceptable, additional pre-treatment is needed |

RESULTS AND DISCUSSION

Coagulation–flocculation tests based on an FFD: identification of the SIFs for the DOM removal process

Figure 1 shows the standardized Pareto charts, which indicate the SIFs for DOM removal for both coagulation mechanisms. According to Figure 1(a), coagulant dose (B), HPO/HPI weight ratio (E), pH (A), and the AC + BE interaction were SIFs for the DOM removal using CNM. Figure 1(b) shows that HPO/HPI weight ratio (E), coagulant dose (B), CT (C), pH (A), and interactions AF + DE, AC + BE, BF + CD and BD + CF were SIFs for SM. All of these factors were statistically significant at a 95% confidence level.

Effect of coagulant dose on DOM removal

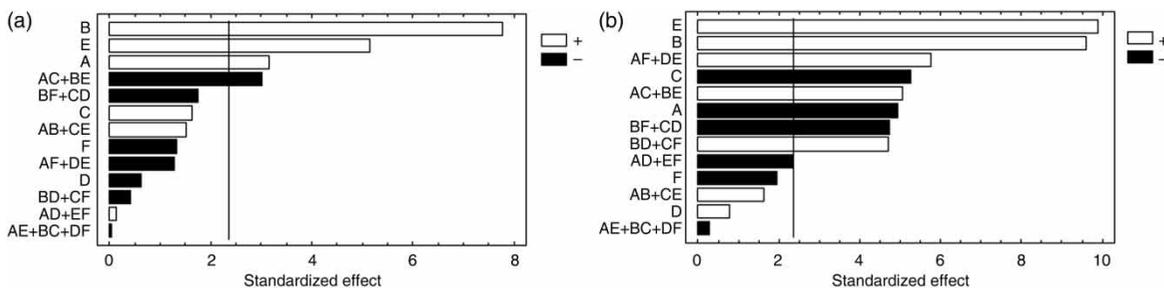
A positive effect of the coagulant dose on DOM removal was observed for both coagulation mechanisms, i.e., the higher the coagulant dose, the higher was the DOM removal. This is because the more coagulant reactive is added to the system, the more the destabilization of the negative charge of DOM is favored. This result was observed

in studies by Walsh *et al.* (2009) for CNM and Chow *et al.* (2004) and Soh *et al.* (2008) for SM. Moreover, as shown in the Pareto charts, the standardized effect value for SM was greater than the one for CNM. This is because the coagulant dose required to form the aluminum hydroxide precipitate in SM (1×10^{-4} – 5.9×10^{-4} moles/L of Al) is higher than the quantity required to form the monomeric and polymeric aluminum species in CNM (5×10^{-6} – 3.9×10^{-4} moles/L of Al) (Rodríguez 2003; Hendricks 2006).

Effect of HPO/HPI weight ratio on DOM removal

In the first stage, three HPO/HPI weight ratios were used: 100/0 (totally HPO), 50/50, and 0/100 (totally HPI). The results obtained in this study showed a greater DOM removal, in terms of DOC, of raw water completely HPI than with respect to a totally HPO one. However, Matilainen *et al.* (2010) established that the HPO fraction of DOM is generally removed in coagulation more efficiently than the HPI fraction. The HPO fraction exhibits high levels of negative charge due to the presence of ionized groups, such as carboxylic and phenolic groups, which allow it to be more amenable to removal.

The main reasons explaining these results are: (1) the functional groups representative of the model compounds of the DOM HPI are found to be almost totally ionized at pH >4, whereas the higher the pH value (from 4 to 8.5), the higher is the level of negative charge of the HPO fraction (Ritchie & Purdue 2003; ChemAxon 2015); (2) HS represent 89.2% of the HPO fraction, while the CA (HPIA fraction) and PS (HPIN fraction) represent 93.7% of the HPI fraction (Table 1). HS can act as ligands and form complexes with aluminum named aluminum fulvates or humates

**Figure 1** | Pareto charts for determining the SIFs for DOM removal: (a) CNM and (b) SM.

(Hendricks 2006). The CA forms complexes with aluminum (Ringbom 1979), and the hydrolysis reactions of PS break the glycosidic bond, converting it into glucose and fructose. These monosaccharides have carbonyl functional groups (C=O), which can act as reducing agents with Fe^{3+} and Al^{3+} (Lehninger *et al.* 1993), resulting in charge destabilization and enhancing their removal by CFP.

Effect of pH on DOM removal

The pH value determines the dissociation degree as the predominant aluminum species in the coagulation process. A positive effect was obtained for CNM, i.e., the higher the pH value, the higher was the DOM removal. This is because the dissociation degree of the DOM was higher at pH 5.5 than at pH 4.5 (Ritchie & Purdue 2003; ChemAxon 2015). In addition, the aluminum polymeric species predominant at pH 5.5 have a level of positive charge higher than the aluminum monomeric species predominant at pH 4.5; thus, the DOM removal can be favored. A similar result was also observed in the study performed by Trinh & Kang (2011).

On the contrary, a negative effect was obtained for SM, i.e., the lower the pH value, the higher was the DOM removal. The dissociation degree of the model compounds of DOM was almost similar independently of the pH value (6–8.5) for SM (Ritchie & Purdue 2003; ChemAxon 2015). Nevertheless, the literature established that at $\text{pH} > 8$ the aluminum hydroxide precipitate has negative charge but it is strongly positive at $\text{pH} < 7$ (Hendricks 2006); as a consequence of this the DOM removal is favored at pH 6.

Effect of CT on DOM removal

CT was a SIF only for SM. Several seconds (1–7s) are required for producing the aluminum hydroxide precipitate. However, the results obtained in this study showed that the lower the CT, the higher was the DOM removal. This can be due to the rupture of flocs generated by an intense or prolonged stirring and consequently DOM restabilization (de Vargas 2004).

Effect of interactions on DOM removal

When effects with similar hierarchy are combined, it must be decided which interaction the observed effect is

attributed to based on knowledge of the process, or the main significant individual effects that are more likely to be active in their interactions must be identified (Gutiérrez & de la Vara 2008). For example, the interaction AC + BE for CNM is an ‘alias’ of A, B, and E; i.e., pH, coagulant dose, and HPO/HPI weight ratio, since they are factors that have significant influence on the process, but not the factor C (CG). To interpret an alias effect it is necessary to assume that at least one of them is responsible for the observed effect and other effects will be null.

The individual factors that did not have a significant influence were CG (C), flocculation gradient (FG) (D), and turbidity (F) for CNM (Figure 1(a)) and FG (D) and turbidity (F) for SM (Figure 1(b)). Therefore, coagulant dose, HPO/HPI weight ratio, pH, and CT were used as experimental factors in the second experimental stage or optimization of these coagulation–flocculation mechanisms.

Coagulation–flocculation tests based on a CCD: identification and optimization of the best coagulation mechanism for DOM removal

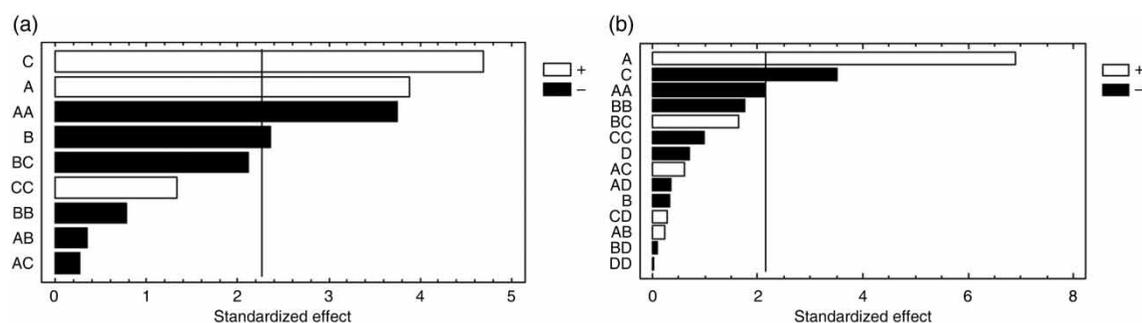
Table 4 shows the SIFs for both mechanisms and their operating intervals, which were evaluated to optimize the DOM removal by CCD. The values of non-significant factors in the FFD were kept constant in the CCD experiments. There were two CCDs, containing 19 and 29 experiments (including five replicates at the center point) for CNM and SM, respectively.

Figure 2 shows the standardized Pareto charts, which indicate the SIFs for each coagulation mechanism. According to the Pareto charts, DOM removal mainly depends on the coagulant dose (A), HPO/HPI weight ratio (B), and pH (C) for CNM (Figure 2(a)), and coagulant dose (A) and pH (C) for SM (Figure 2(b)).

Table 5 shows the statistical models (StM) and the coefficient of determination (R^2) values estimated by the Statgraphics statistical software for the optimization of DOM removal for each coagulation mechanism. The R^2 indicates how well data are fitted to a statistical model. It determines the percentage variation of the dependent variable taking into consideration the factors number included in the model.

Table 4 | SIFs in CFP and their operating intervals evaluated by CCD

| Coagulation mechanism | SIFs in CFP | Coded values | | | | | Constant factors in CCD |
|-----------------------|---|--------------|-------|-------|-------|------------|---|
| | | $-1-\alpha$ | -1 | 0 | 1 | $1+\alpha$ | |
| CNM | A: Coagulant dose (mg $\text{Al}_2(\text{SO}_4)_3/\text{L}$) | 3.6 | 22.7 | 63.2 | 103.7 | 122.7 | CG: 5000 s^{-1} ; CT: 1 s; FG: 20 s^{-1} ; FT: 20 min; T: 5 NTU |
| | B: HPO/HPI weight ratio (DOC (%)) | 100/0 | 84/16 | 50/50 | 16/84 | 0/100 | |
| | C: pH | 4.5 | 4.66 | 5 | 5.34 | 5.5 | |
| SM | A: Coagulant dose (mg $\text{Al}_2(\text{SO}_4)_3/\text{L}$) | 44.2 | 68.5 | 104.9 | 141.3 | 165.6 | CG: 600 s^{-1} ; FG: 100 s^{-1} ; FT: 20 min; T: 5 NTU |
| | B: HPO/HPI weight ratio (DOC (%)) | 100/0 | 80/20 | 50/50 | 20/80 | 0/100 | |
| | C: pH | 6 | 6.4 | 7.25 | 8.1 | 8.5 | |
| | D: CT (s) | 1 | 2.2 | 4 | 5.8 | 7 | |

**Figure 2** | Pareto charts of the CCD results for the optimization of the DOM removal process using (a) CNM and (b) SM.**Table 5** | Fitted models for the optimization of the DOM removal process by two coagulation mechanisms

| Coagulation mechanism | Fitted model | R ² (%) |
|-----------------------|--|--------------------|
| CNM | DOC removal (mg/L) = $2.35 + 0.24A - 0.15B + 0.29C - 0.27A^2 - 0.03AB - 0.02AC - 0.05B^2 - 0.16BC + 0.09C^2$ | 87.6 |
| SM | DOC removal (mg/L) = $3.2 + 0.67A - 0.03B - 0.34C - 0.07D - 0.24A^2 + 0.03AB + 0.07AC - 0.04AD - 0.2B^2 + 0.18BC - 0.01BD - 0.11C^2 + 0.03CD - 0.004D^2$ | 83.8 |

Since the R² values might seem quite low, the *lack-of-fit test* was performed for determining whether the selected models were adequate to describe the observed data. A model is considered adequate (significant) at a 95% confidence level if the *p*-value of the *lack-of-fit test* is greater than 0.05 (Rigas et al. 2007). The *p*-values obtained using the Kolmogorov–Smirnov test, for CNM and SM, were 0.77 and 0.38, respectively. Therefore, the selected models

for both coagulation mechanisms are adequate to describe the DOM removal.

These statistical models were used to estimate the maximum DOM removal for the different HPO/HPI weight ratios evaluated in this work. Tables 6 and 7 show, for CNM and SM respectively, the optimal operating conditions (OOC), the predicted responses by the statistical models, the experimental results obtained in the laboratory, and the maximum removal of the DOM fractions (HPOA and HPIN) for each HPO/HPI weight ratio.

Table 6 shows that, independently of the initial value of the HPO/HPI weight ratio, the optimal values of pH = 5.5 and coagulant dose = 80.9 mg $\text{Al}_2(\text{SO}_4)_3/\text{L}$ (6.69 mg Al/L) were the same for the CNM. The coagulant dose was the same in all tested HPO/HPI weight ratios because the initial values of turbidity (5 NTU) and DOM content (5–5.5 mg DOC/L) were also the same in all cases.

At the OOC, the predicted and experimental responses generally show that an increase in DOM removal occurs as the HPO/HPI weight ratio tends toward hydrophobicity

Table 6 | Predicted and experimental responses obtained at OOC of the CNM for maximum DOM removal for different HPO/HPI weight ratios in water, n = 5

| | Raw water (HPO/HPI weight ratio (DOC (%))) | | | | |
|--|--|-------------|-------------|-------------|-------------|
| | 100/0 | 84/16 | 50/50 | 16/84 | 0/100 |
| pH | 5.5 | 5.5 | 5.5 | 5.5 | 5.5 |
| Coagulant dose (mg Al ₂ (SO ₄) ₃ /L) | 80.9 | 80.9 | 80.9 | 80.9 | 80.9 |
| Predicted response by StM (mg DOC/L) | 3.49 | 3.36 | 3.02 | 2.58 | 2.33 |
| Experimental results (mg DOC/L ± σ) | 2.42 ± 0.07 | 3.1 ± 0.1 | 3.04 ± 0.09 | 2.77 ± 0.1 | 2.21 ± 0.1 |
| HPOA fraction removal (mg/L ± σ) | 11.82 ± 0.05 | 9.72 ± 0.1 | 5.77 ± 0.1 | 1.84 ± 0.02 | – |
| HPIN fraction removal (mg/L ± σ) | – | 0.54 ± 0.03 | 1.62 ± 0.02 | 2.92 ± 0.06 | 3.88 ± 0.05 |

Table 7 | Predicted and experimental responses obtained at OOC of the SM for the maximum DOM removal for different HPO/HPI weight ratios in water, n = 5

| | Raw water (HPO/HPI weight ratio (DOC (%))) | | | | |
|--|--|-------------|-------------|-------------|-------------|
| | 100/0 | 80/20 | 50/50 | 20/80 | 0/100 |
| pH | 6 | 6 | 6 | 6 | 6 |
| Coagulant dose (mg Al ₂ (SO ₄) ₃ /L) | 149.3 | 149.3 | 149.3 | 149.3 | 149.3 |
| Predicted response by StM (mg DOC/L) | 3.97 | 4.13 | 4.04 | 3.55 | 3 |
| Experimental results (mg DOC/L ± σ) | 2.95 ± 0.06 | 3.53 ± 0.12 | 3.6 ± 0.1 | 3.82 ± 0.06 | 3.69 ± 0.06 |
| HPOA fraction removal (mg/L ± σ) | 12.45 ± 0.07 | 9.99 ± 0.1 | 6.05 ± 0.05 | 2.51 ± 0.04 | – |
| HPIN fraction removal (mg/L ± σ) | – | 0.74 ± 0.07 | 1.95 ± 0.04 | 3.08 ± 0.08 | 4.42 ± 0.08 |

(from 0/100 to 100/0). This result is in agreement with that published by Matilainen *et al.* (2010). At pH 5.5, it was determined that the negative charge density of the HS (HPOA fraction) was 16 meq/g C (Ritchie & Purdue 2003), which is 2.5 times greater than the value reported (Galván 2012) for poly(diallyldimethyl ammonium chloride) (PDADMAC), an organic polymer that is highly charged and is used in coagulation.

The removal efficiencies of DOM using CNM ranged from 40.2 to 57.4% (2.21 to 3.1 mg DOC/L), which are similar to data (34–67% DOC, 1.34–2.84 mg DOC/L) reported in the literature (Uyak & Toroz 2007). Nevertheless, in terms of mg DOC/L, the removal obtained in this work (2.21 to 3.1 mg/L) was better, with respect to the values reported by Uyak & Toroz (2007), which ranged from 1.34 to 2.84 mg DOC/L. This difference is significant because, despite Uyak & Toroz (2007) applying enhanced coagulation, the raw water qualities had both different initial DOM concentration (expressed as DOC) and DOM character (HPO/HPI ratio). Specifically, for an average HPO/HPI

weight ratio of 50/50, the maximum DOM removal obtained in this work was 3.04 mg DOC/L (54.3%); this value is higher than previously reported values (2.16–2.84 mg DOC/L) (Uyak & Toroz 2007) using similar coagulant doses and raw water quality. This shows that the results obtained for CNM, working with prepared waters, can be extrapolated to the treatment of natural surface waters.

The removal efficiencies of the HPOA and HPIN fractions using the CNM ranged from 1.84 to 11.82 mg/L and 0.54 to 3.88 mg/L, respectively (Table 6). These values represent removal percentages of 82.8–85% and 66.9–80.6% respectively (considering the initial concentrations indicated in Table 1). It has been concluded that the removal efficiency of the HPOA fraction did not depend on the HPO/HPI weight ratio because the difference between the lowest and highest removal efficiency values is not significant (<2.2%). These results can be attributed to the highest initial concentration of this fraction in most of the evaluated HPO/HPI weight ratios with respect to the HPIN fraction. Thus, the probability of neutralizing a

more abundant molecule is greater with respect to a less abundant one. Moreover, the low solubility in water, high molecular weight, and high negative charge density (≈ 16 meq/g C) of the SH enhance their removal by CNM.

In contrast, the HPIN removal efficiency depended on the initial HPO/HPI weight ratio due to its physicochemical properties (high solubility and low charge density) and to the relatively low abundance with respect to the HPOA fraction. The HPIN fraction (PS) is composed of very soluble compounds (2,000 g/L at 25 °C) with an aliphatic linear molecular structure, smaller molecular weight, and fewer electron-rich sites than the HPO fraction. These physicochemical properties make it difficult to remove by CFP, and removal occurs by way of other reactions mentioned in the effect of HPO/HPI weight ratio on DOM removal.

In the case of the SM, Table 7 shows that the optimal values of pH = 6 and coagulant dose = 149.3 mg $\text{Al}_2(\text{SO}_4)_3/\text{L}$ (12.17 mg Al/L) were the same for the different HPO/HPI weight ratios evaluated in these experiments. At this pH, the predominant aluminum species is $\text{Al}(\text{OH})_3$, which ensures DOM removal by SM in all cases. The coagulant dose was the same in all tested HPO/HPI weight ratios for the reasons already explained for CNM.

In contrast to the CNM data, the predicted responses obtained by using the statistical model did not show a specific pattern. In this case, for HPO/HPI weight ratios ranging from 100/0 to 50/50, the DOM removal was similar. Moreover, the DOM removal decreased for HPO/HPI weight ratios of 20/80 and 0/100. These results are explained by the lower predictive ability of the SM statistical model with respect to the CNM. Furthermore, the SM predicted results were not completely in agreement with the experimental results. These latter results showed that the DOM removal efficiency did not depend on the HPO/HPI weight ratio. This can be explained because the optimal coagulant dose (149.3 mg $\text{Al}_2(\text{SO}_4)_3/\text{L}$) is extremely high, almost twice the optimal coagulant dose of the CNM.

The average removal efficiency was calculated as approximately 3.7 mg DOC/L independent of the HPO/HPI weight ratio, except for 100/0. The experimental results obtained for the DOM removal in prepared raw waters using the SM (2.95–3.82 mg DOC/L, 54.8–69.8%) were similar to the values reported in the literature (65–76% DOC) (Hussain *et al.* 2013). The OOC values used for SM (pH 6

and coagulant dose 149.3 mg $\text{Al}_2(\text{SO}_4)_3/\text{L}$ (12.17 mg Al/L) were similar to those reported in the literature (pH 6 and coagulant dose 10–16 mg Al/L). This shows that the results obtained for SM, working with prepared waters, can be extrapolated to the treatment of natural surface waters.

The removal of HPOA and HPIN fractions using the SM ranged from 2.51 to 12.45 mg/L and 0.74 to 4.42 mg/L, respectively (Table 7). These values represent removal percentages of 87.5–90.5% and 73.7–89.8%, respectively (Table 1). These ranges are higher than those reported by Chow *et al.* (2004) and Soh *et al.* (2008) for HPOA (72–79% DOC) and HPIN (8–16% DOC) fractions.

As in the CNM, the removal efficiency of the HPOA fraction did not depend on the HPO/HPI weight ratio; the difference between the lowest and highest removal efficiency values is not significant (<3%). However, the removal efficiency of the HPI fraction depended on the initial HPO/HPI weight ratio.

In addition, the results showed that the removal efficiency of DOM using SM was higher than when using CNM. The removal efficiencies of DOM were 21.9 and 13.9% higher for SM than CNM, comparing HPO/HPI weight ratios 100/0 and 80/20 versus 84/16, respectively. Conversely, the removal efficiencies were 37.9 and 67% greater using SM than CNM when comparing HPO/HPI weight ratios 20/80 versus 16/84 and 0/100, respectively. The better removal of DOM by the SM with respect to the CNM is due to the charge density of the HS (HPOA fraction); this parameter at pH 6 was 12.5% greater than the one calculated at pH 5.5, and the optimal coagulant dose was 1.85 times higher for SM than CNM. This high coagulant dose produced a large number of flocs (coagulant species $\text{Al}(\text{OH})_3$), and, as a consequence, led to greater adsorption of DOM HPI by SM because the removal efficiency of the HPI fraction depends mainly on the coagulant dose. This result is in accordance with previous results (Matilainen *et al.* 2010).

Regarding the fractionated DOM removal, SM was slightly better than CNM on the HPOA fraction removal (87.5% and 82.9, respectively) for a HPO/HPI weight ratio of 50/50, while the HPIN fraction removed was 14.6% higher using SM than CNM, under OOC.

Therefore, the best coagulation mechanism for DOM removal (expressed as mg DOC/L and mass percentage),

and of the HPOA and HPIN fractions (expressed as mg/L) was the SM. Nevertheless, a feasibility study must be performed considering all the technical and economic factors related to this process in order to determine the mechanism with the best cost-benefit ratio, which is beyond the scope of this study. Thus, considering only the technical aspects, we concluded in this work that the SM was the best coagulation mechanism.

The quantification of each DOM model compound was performed after treatment by the SM for HPO/HPI weight ratios of 80/20, 50/50, and 20/80 in order to determine the removal behavior of the fractionated DOM and the final HPO/HPI weight ratio in the effluents, which can be susceptible to post-treatment using the microfiltration process. Figure 3 shows the initial and final concentrations for each DOM fraction (expressed as mg/L and mass

percentage) and the initial and final concentration of DOM (expressed as mg DOC/L) for the HPO/HPI weight ratios highly HPO (80/20), 50/50 and highly HPI (20/80) (expressed as DOC (%)).

After the CFP (Figure 3), the relative most efficient removal of the HPOA fraction in the different HPO/HPI weight ratios (87.5–90.5%) produced an increase in other DOM fractions, especially of HPOB, HPIA, and HPIB. Moreover, the HPIN fraction showed similar behavior to the HPOA fraction regarding its relative abundance in the produced effluents, with the exception of the HPO/HPI weight ratio of 80/20, where a slight increase in relative abundance was observed.

Based on the fractionated DOM removal and the data presented in Table 1, it was possible to estimate the HPO/HPI weight ratio of the produced effluents. The effluent of

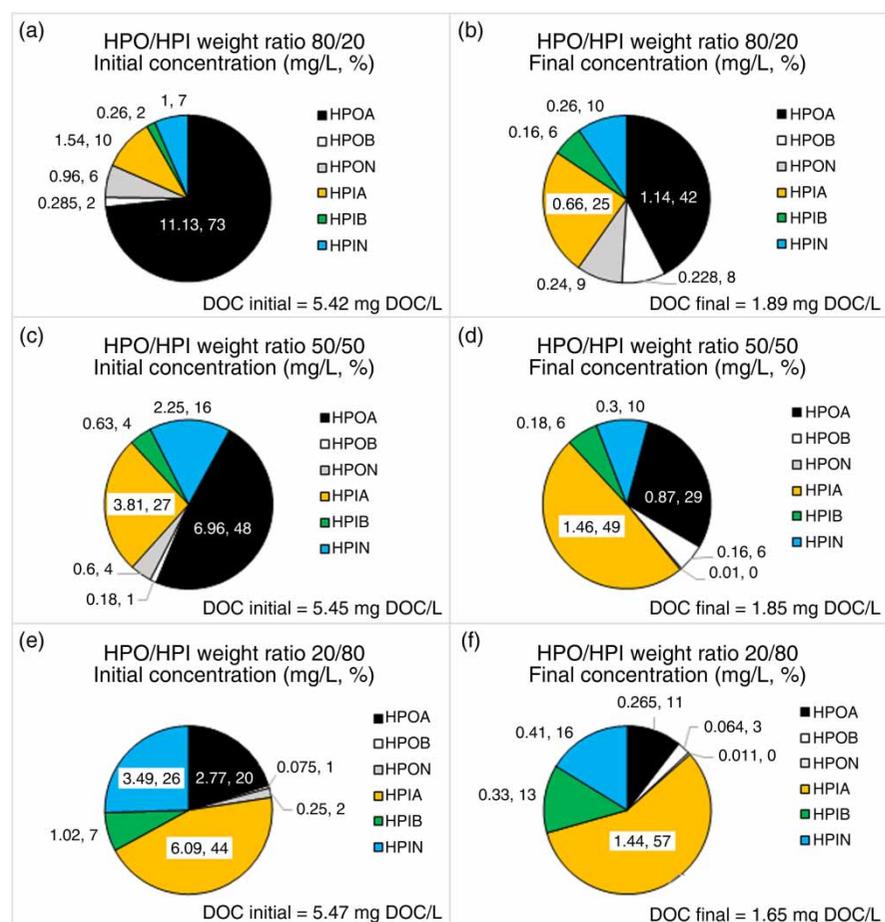


Figure 3 | Initial and final concentrations of the fractionated DOM for HPO/HPI weight ratios 80/20, 50/50, and 20/80% DOC using SM.

the HPO/HPI weight ratio 80/20 (Figure 3(b)) was slightly less HPO (62.1/37.9) than the influent. The effluent of the HPO/HPI weight ratio 50/50 (Figure 3(d)) was slightly more HPI (39/61) than the influent, despite the high removal of the HPOA and HPIN fractions. Finally, the effluent of the HPO/HPI weight ratio 20/80 (Figure 3(f)) was slightly more HPI (15/85) than the influent due to the almost complete removal of the HPO fraction.

Moreover, the DOM final concentrations in the treated waters or effluents of the HPO/HPI weight ratios 80/20, 50/50, and 20/80% DOC were less than 2 mg DOC/L (1.89, 1.85, and 1.65 mg DOC/L, respectively), starting from an average initial concentration of approximately 5.5 mg DOC/L, independent of the HPO/HPI weight ratio. SDI tests were carried out for the raw and treated waters with HPO/HPI weight ratios 80/20, 50/50, and 20/80 using the SM, to correlate the HPO/HPI weight ratios with the potential for irreversible membrane fouling.

SDI for raw and treated water with different HPO/HPI weight ratios

Table 8 shows the SDI results for raw and treated water with different HPO/HPI weight ratios using OOC for SM.

The standard test method for measuring the SDI value (ASTM 4189-95 2002) recommends that % P_{30} should not exceed 75% to be considered valid. If % P_{30} exceeds this value, a shorter T or filtration time (5 or 10 minutes) can be used. Due to this restriction, the SDI values of raw waters were estimated at 5 minutes. The SDI₅ values of all raw waters indicate that additional pre-treatment is needed (Table 3).

After the CFP, the SDI₁₅ value of the effluent with a HPO/HPI weight ratio 80/20 was 4.5%/min, which indicates significant fouling potential; thus, the membrane will

require frequent cleaning (Table 3). However, the final DOM concentration (1.89 mg DOC/L, Figure 3(b)) of this effluent almost met the goal proposed by the US EPA (2 mg TOC/L or 1.8 mg DOC/L considering that this value represents 90% of the TOC value (Rodríguez 2003)) for obtaining acceptable levels of DBPs (<100 µg/L) in treated waters. This final DOM concentration also met the recommended value (<3 mg DOC/L and SDI₁₅ < 5%/min) proposed by membrane suppliers for minimizing fouling and extending membrane life.

The SDI₁₅ values of effluents produced from raw water, with initial HPO/HPI weight ratios of 50/50 and 20/80, were 2.8 and 2.6%/min, respectively. These results indicate that the membrane system could operate for several months before cleaning (Table 3) if these treated waters are used in it. In addition, the final DOM concentrations (1.85 and 1.65 mg DOC/L, Figures 3(d) and 3(f), respectively) are found in the limit proposed by the US EPA, and the SDI₁₅ results of these effluents met the criteria (<3 mg DOC/L and SDI₁₅ < 5%/min) proposed by membrane suppliers for minimizing fouling and extending membrane life.

Figure 4 shows the SDI₅ and SDI₁₅ values as a function of the initial and final HPO/HPI weight ratio (%DOC) for both coagulation mechanisms. All of the correlations of SDI versus HPO/HPI weight ratio values follow a lineal trend, with R² values ranging from 0.9258 to 0.9826.

In addition, the HPO/HPI weight ratios before and after the CFP were the same for the CNM. In contrast, this parameter decreased after using SM because this mechanism was better at removing the HPO fraction.

Finally, for an HPO/HPI weight ratio 50/50, which is considered average for surface water worldwide, the SDI₁₅ value for SM (2.8%/min) represented several months of operation before cleaning the membrane, according to the Table 3. The SDI₁₅ value for CNM (3.5%/min) represented frequent cleaning of the membrane due to particular fouling. This difference could represent lower operating costs of cleaning and replacement of membranes using SM than CNM.

Table 8 | SDI values of raw water with different HPO/HPI weight ratios and the clarified effluents produced using SM

| Initial HPO/HPI weight ratio (% DOC) | Raw water SDI ₅ (%/min) | Final HPO/HPI weight ratio (% DOC) | Effluent SDI ₁₅ (%/min) |
|--------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| 80/20 | 14.1 | 62.1/37.9 | 4.5 |
| 50/50 | 12.2 | 39/61 | 2.8 |
| 20/80 | 7.6 | 15/85 | 2.6 |

CONCLUSIONS

The best coagulation mechanism for the removal of DOM was the SM, independent of the HPO/HPI weight ratio.

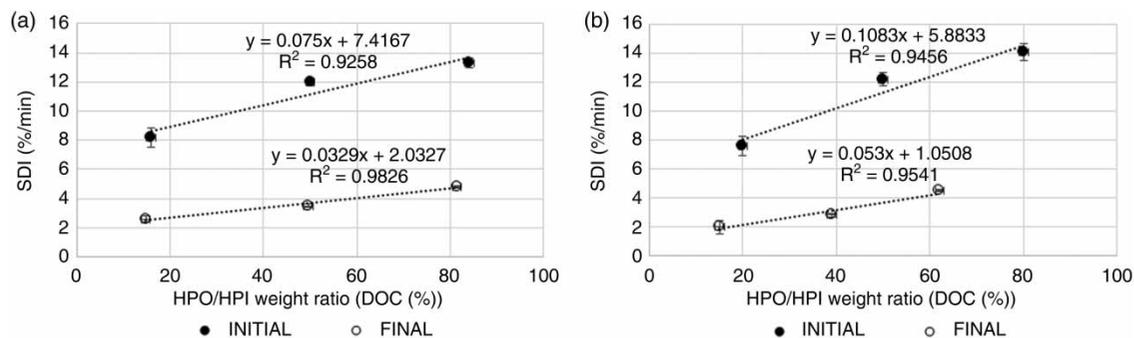


Figure 4 | SDI values as a function of the initial and final HPO/HPI weight ratios in raw and treated waters using the coagulation mechanisms: (a) CNM and (b) SM.

This mechanism showed removal efficiencies of 2.95–3.82 mg DOC/L (54.8–69.8%). The optimal operating conditions for obtaining the maximum DOM removal applying SM were as follows: coagulant dose 149.3 mg Al₂(SO₄)₃/L (12.17 mg Al/L) and pH 6.

The removal efficiency of the HPOA fraction (which is one of the main factors responsible for irreversible membrane fouling and generation of DBPs) was very similar (87.5–90.5%) using the SM for all the HPO/HPI weight ratios evaluated in this work. The removal efficiency of the HPOA fraction did not depend on the HPO/HPI weight ratio or the initial concentration of the HPOA fraction in raw water. Conversely, the removal efficiency of the HPIN fraction (another main factor responsible for irreversible membrane fouling and generation of DBPs) ranged from 73.7 to 89.8% for the HPO/HPI weight ratios evaluated in this work. The removal of these DOM fractions was affected by their physicochemical properties (solubility, charge density, and molecular weight) and their initial concentrations in raw water.

SM could reduce health risks associated with pollutants such as trihalomethanes, because the DOC residual values obtained for all the tested HPO/HPI weight ratios were found to be within the limit proposed by the US EPA for acceptable DBP levels in effluents produced in the disinfection process using chlorine and chlorine-derived products.

For an HPO/HPI weight ratio of 50/50 (the average value for surface water worldwide), the SM could significantly reduce the costs of membrane cleaning and replacement compared to CNM due to the difference in membrane fouling and SDI₁₅ value (2.8%/min versus 3.5%/min). Furthermore, the SDI₁₅ and DOC values of all effluents produced by the SM were lower than the criteria proposed by membrane suppliers

(SDI₁₅ < 5%/min and <3 mg DOC/L) to minimize fouling and to extend membrane life.

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