The effect of mixed oxidants and powdered activated carbon on the removal of natural organic matter

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ABSTRACT

Present paper studies the influence of electrochemically generated mixed oxidants on the physicochemical properties of natural organic matter, and especially from the disinfection by-products formation point of view. The study was carried out in a full scale water treatment plant. Results indicate that mixed oxidants favor humic to non-humic conversion of natural organic matter. Primary treatment preferentially removes the more hydrophobic fraction. This converted the non-humic fraction in an important source of disinfection by-products with a 20% contribution to the final trihalomethane formation potential ($THMFP_F$) of the finished water. Enhanced coagulation at $40\,mg\,l^{-1}$ of polyaluminium chloride with a moderate mixing intensity ($80\,rpm$) and pH of 6.0 units doubled the removal efficiency of $THMFP_F$ achieved at full scale plant. However, gel permeation chromatography data revealed that low molecular weight fractions were still hardly removed. Addition of small amounts of powdered activated carbon, $50\,mg\,l^{-1}$, allowed reduction of coagulant dose by 50% whereas removal of $THMFP_F$ was maintained or even increased. In systems where mixed oxidants are used addition of powdered activated carbon allows complementary benefits by a further reduction in the $THMFP_F$ compared to the conventional only coagulation–flocculation–settling process.

1. Introduction

Conventional drinking water production includes coagulation–flocculation–settling (CFS) followed by sand filtration and chlorine disinfection. Alternatives to chlorine, such as ozone and chlorine dioxide, have been constantly pursued due to the appearance of harsh microorganisms as well as the formation of chlorinated disinfection by-products of chlorine [1,2]. In order to avoid algae proliferation within treatment plant, pre and intermediate chlorination is usually effected. During these previous oxidation steps, water contains higher loads of organics, rich in dihydroxybenzene type structures, thus formation of chlorinated disinfection by-products (DBP) is favored [3,4].

Many researchers [5,6] focused attention to the association of DBPs, and specifically trihalomethanes, with noxious health effects in the carcinogenesis, reproductive and developmental areas. Humans are primarily exposed to trihalomethanes (THMs) through drinking water consumption and also dermal and respiratory pathways from bathing and swimming [7]. Consequently, the health risk associated to DBPs formation is forcing authorities to closely examine and optimize the disinfection procedures in water treatment plants.

Electrochemically produced mixed oxidants are generated in situ by electrolysis of brine. In this reaction chlorine, also known as nascent chlorine, is produced as primary reaction. Ozone and chlorine dioxide are produced as secondary reaction [8,9]. Ozone has a greater disinfection effectiveness than other oxidizers whereas chlorine dioxide is a powerful oxidizer and germicidal agent which does not react with ammonia. Furthermore, it remains in its molecular form in the pH range typically found in natural waters. Previous works [10,11] reported that the nascent chlorine, ozone and chlorine dioxide combination exhibits greater oxidative power (synergy) for selected microorganisms than conventional chlorine. This way it is possible, with a smaller dosage, to eradicate the pathogenic germs and avoid the presence of resistant germs. However, the exact composition of the intermediates produced from these electrochemically mixed oxidants is still not well understood [12].

Few works have examined the effect of electromechanically generated mixed oxidants on natural organic matter at full scale drinking water utilities. The present paper presents results of the use of this alternative oxidation strategy when used in conjunction with conventional treatment and also with adsorption by powdered activated carbon. The effect of this mixed oxidants system on the content, nature and reactivity to form THMs of the natural organic matter (NOM) has been analyzed.

2. Experimental

The selected water treatment plant (WTP) is a small utility that treats $1400 \, m^3$/day and uses a mixed oxidant generator manufactured by Cetolar to produce nascent chlorine as primary and secondary oxidant. The amount of each species produced depends on several factors such as the electric power supplied during electrolysis of brine. The overall disinfectant dosage is quantified in terms of free chlorine residual (FCR). Treatment includes preoxidation, coagulation–flocculation–settling, intermediate oxidation, sand filtration and disinfection. Alum is added as coagulant in a concentration range from 15 to $20 \, mg \, l^{-1}$. The dosage of oxidant is automatically regulated to ensure a free chlorine residual between 0.5 and $0.8 \, mg \, l^{-1}$ at plant outlet stream. For this study, raw, settled and filtered water from the full scale plant were analyzed.

The four THMs species were determined by Gas Chromatography (GC)/Electron Capture Detector (ECD) (HP 5890 Series II). Analysis conditions: injection on-column, volume $0.5 \, \mu l$; oven temperature $50 \, °C$ for 5 min, $50–105 \, °C$ at $6 \, °C$/min; carrier gas N_2 at $6 \, ml \, min^{-1}$, make-up gas N_2 at $60 \, ml \, min^{-1}$; detector temperature $300 \, °C$; column HP-1 methyl siloxane $30.0 \, m \times 530 \, mm \times 2.65 \, mm$. Detection and quantification levels (defined as peak height to noise ratio of 3:1 and 10:1, respectively) correspond to 0.15 and $0.50 \, \mu g \, l^{-1}$, respectively. pH measurements were carried out with a Crison (GLP-22) pH-meter. DOC was measured as Non-Purgable Organic Carbon in a TOC analyzer with non-Dispersive Infrared detector (Shimadzu TOC 5050A). UV absorbance was measured at 254 nm in a Helios-γ (TermoSpectronic) spectrophotometer with 1 cm optical path lengths. Fractionation and quantification of NOM was done by two different procedures: (i) by using two non-ionic macroporous resins in series; amberlite DAX-8 and supelite XAD-4 [13] and (ii) by using a weak ionic exchange resin (DEAE) [14,15]. NOM characterization procedure involves the separation of NOM into hydrophobic acid (HPOA-DAX8), transphilic acid (TPHI), hydrophilic acid (HPIA-XAD) using XAD resins [16]. DEAE resin was used to obtain the so-called HPOA-DEAE and HPIA-DEAE fractions. Both procedures were applied in parallel to fractionate NOM in water samples. Precursor concentration in this study was quantified as UV absorbance, dissolved organic carbon and by standardized chlorination tests. Chorination tests, namely THM formation potential tests, were done according to Standard Methods [14]. $THMFP_F$ denotes final or maximum THMs that can be formed. Chlorination conditions were $22 \, °C$, initial chlorine concentration $78 \, mg \, l^{-1}$, contact time 7 days, pH 7.0 units. SPTHMFP refers to simulated plant formation potential. Chlorination occurs at similar conditions to those set at WTP. Chlorination conditions were $10 \, °C$, initial chlorine concentration $15 \, mg \, l^{-1}$, contact time 15 h, pH 8.0 units. THMs were determined by Gas Chromatography (GC)/Electron Capture Detector.

Jar-test experiments were performed using a laboratory jar-test device (flocumatic). A commercial coagulant was used, polyaluminium chloride (PACl) (ref. PA/18.B, Al_2O_3 17.5%, 40% basicity). An anionic polyacrylamide based flocculant (Flocosul-AP/1) was used in all experiments. Jar-test mixing conditions were as follows: water samples (0.5 l) and coagulant were flash mixed (80 rpm) for 2 min. Anionic flocculant was added ($10 \, mg \, l^{-1}$) just before flash mixing terminates followed by slow mixing (20 rpm) for 30 min. Flocs were allowed to settle for 1 h. Water samples from each jar were vacuum filtered through $0.45 \, \mu m$ PTFE filter. pH was adjusted with sulphuric acid (0.1 M). When needed PAC was added and rapid mixing at 100 rpm was maintained for 5 min. Then, coagulant was added and the previously described procedure was followed (2 min 80 rpm, flocculant addition, 30 min 20 rpm, $0.45 \, \mu m$ PTFE). 15% of jar-test experiments (randomly selected) were duplicated in order to check for reproducibility. The measured average standard deviation was below 10%.

Physical and chemical properties of PAC are presented in Table 1. A porosimeter system (ASAP 2010, Micromeritics) was used to determine the textural properties. The total pore volume was calculated from the adsorbed volume of gas near the saturation point ($P/P_o = 0.98$). The S_{micr}, S_{mes} and dp were determined using density functional theory (DFT) by assuming the graphite model with slit shape geometry. Surface area was calculated from the BET method. The determination of the pH_{pzc} was done by the bottle-point method. The pH within each flask (20 ml) was adjusted to a value between 2 and 12 by adding HNO_3 0.1 M or NaOH 0.1 M. Then 0.1 g of carbon was added to each flask, and the final pH was measured after 24 h under agitation at room temperature. The amount of acidic and basic functional groups on carbon surface was measured from titration techniques [17]. 65 ml vials were filled with 0.1 g of carbon and 20 ml of 0.05 N NaOH or 0.05 N of HCl. Vials without carbon and containing either acid or base were prepared as blanks. Samples and blanks were shaken at 200 rpm for 48 h at room temperature. Finally, samples were filtered ($0.45 \, \mu m$) and 15 ml of the solution was titrated with 0.05 N of either NaOH or HCl solution.

Molecular weight distribution of NOM was determined by HPLC-UVA/RI. Calibration standards were polyethylene glycol and polyethylene oxide. Analytical conditions were as follows: column TSK α-3000, column temp. $40 \, °C$, injection volume $150 \, \mu l$, mobile phase phosphate buffer 0.004 M (pH 6.8), Na_2SO_4 0.0025 M, ionic strength 0.1 M, flow rate $1.0 \, ml \, min^{-1}$. Experimental set-up consists of a HPLC system with a RI and UV detectors in series. Retention time of standard solutions was determined using refractive index detector (detector temp. $40 \, °C$) whereas NOM in samples was quantified using UV absorbance detector (254 nm).

3. Results and discussion

THMs precursor content of raw water that supplied WTP, measured as $THMFP_F$ was $113 \, \mu g \, l^{-1}$, which exceeds maximum contaminant level of $100 \, \mu g \, l^{-1}$ established by European Directive [18]. SUVA value ($2.4 \, l \, mg^{-1} \, m^{-1}$) denotes low to moderate aromaticity of NOM in sample. The variation in distribution of hydrophobic and hydrophilic fractions in NOM throughout the plant is shown in Fig. 1. Based on $THMFP_F$ measurements DEAE absorbed 92% of raw water values whereas the sum of DAX8 and XAD4 extracts accounted for 57% of raw water. When UV absorbance was used for quantification these fractions accounted for 72% and 77% or

Table 1
Physical and chemical properties of powdered activated carbon.

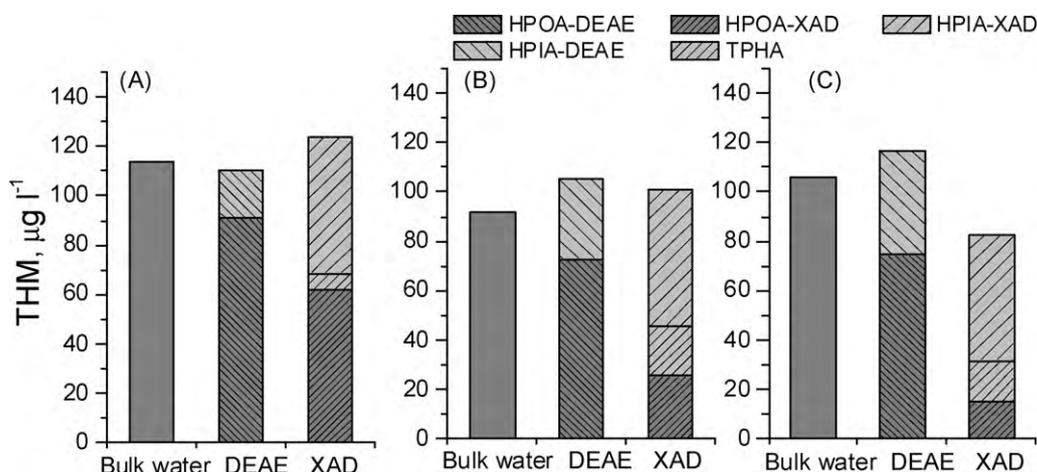|	Origin	ρ (g cm^{-3})	V_T (cm^3 g^{-1})	S_{BET} (m^2 g^{-1})	S_{micr} (m^2 g^{-1})	S_{mes} (m^2 g^{-1})	dp (Å)	pH_{PZC}	Surface acidity (meq g^{-1})	Surface basicity (meq g^{-1})
F-400	Coal	0.425	0.483	852	639	43	10.1	10.5	0.10	0.29

Fig. 1. Contribution of NOM fractions to THMFP$_F$ along full scale WTP. (A) Raw water, (B) settled water and (C) filtered water.

Table 2
WTP performance in terms of UV absorbance, DOC, THMs and THMFP$_F$ concentration at different treatment levels.

	Raw	Settled	Filtered
DOC (mg l^{-1})	1.9	1.3	1.2
UV$_{254}$ (cm^{-1})	0.060	0.014	0.015
THM (μg l^{-1})	49.7	36.6	30.2
THMFP$_F$ (μg l^{-1})	113.1	98.2	105.2

raw water, respectively. It is noteworthy the high contribution of non-humic material to THMFP$_F$ measured by XAD resins fractionation. Its contribution strongly varies depending on the source of NOM. Wietlik et al. [19] based on DOC quantification reported a contribution below 15% whereas others [2] revealed considerably higher percentages of hydrophilic components in total NOM. In this work, DEAE humic extract accounted for most of the THMFP$_F$ and SPTHMFP what suggests that it is a more adequate method for quantification of DBP precursors compared to DAX resins.

It can be observed that for both extraction procedures the hydrophilic fractions (HPIA-DEAE and HPIA-XAD) showed a similar behavior. HPIA-DEAE contribution significantly increased along WTP from 8% in raw water to 20% in finished water. Fractionation by XAD resins revealed the conversion of hydrophobic substances into transphilic as deduced from HPOA-DAX decline, from 50% in raw water to 18.5% in finished water, and increase of TPHI fraction. Similar results (not shown) were obtained when simulated plant (SPTHMFP) chlorination tests were applied. THM formation coming from hydrophilic fractions was not effectively removed. The formation of ozone in electrochemically generated oxidants could be the responsible of such trend. Ozone application is known to destroy NOM aromaticity [20,21]. Ozone is effective in destroying hydrophobic substances while hydrophilic and neutral fractions are usually unaltered by this oxidant [2,22]. This fact gains special relevance on view of the high THMs formation capability showed by hydrophilic fraction.

Table 2 summarizes results obtained from the screening through the full scale plant. WTP removed up to 70% of UV absorbance of water, reflecting a high reduction in aromatic structures. DOC progressively decreased throughout treatment; 1.9, 1.3 and 1.2 mg l^{-1} for raw, settled and filtered water, respectively. However, surprisingly precursors reduction, measured as THMFP$_F$, was minimal. Its value slightly descended from 113 μg THM l^{-1} in raw water to 105 μg THM l^{-1} at outlet stream.

Sand filtration in WTP was not effective in removing THM precursors. Even more, filtration step generates a slight increase in UV and THMFP$_F$. CFS was the most effective step in removing overall DBP precursors. However, as shown before, hydrophilic fractions of NOM were not removed. Furthermore, it increased after preoxidation with mixed oxidants. Uyguner et al. [23] studied the adsorption and coagulation characteristics of humic acid samples subsequent to ozonation, photocatalysis and sequential oxidation systems. They concluded that preoxidation increased adsorption onto activated carbon while efficiency of coagulation was slightly reduced. This behavior was attributed to changes in the molecular sizes, functional groups, hydrophobicity and charge densities. Based on these results the incorporation of powdered activated carbon in order to enhance removal of precursors of THM was evaluated.

3.1. Combined treatment by mixed oxidants and powdered activated carbon

Preliminary jar-test experiments were carried out to establish the enhanced coagulation conditions for CFS process. Then, the effect of the addition of powdered activated carbon (PAC) on the process efficiency was compared. Jar-test studies revealed that coagulation with 40 mg l^{-1} polyaluminium chloride (PACl) at pH 6 were the most effective conditions for this natural water. The effectiveness of enhanced coagulation for this natural water was discussed in detail in a previous work [24]. Under these conditions process performance, in terms of DOC, THMFP$_F$ and UV absorbance

Table 3
Summary of the removal efficiencies (percent value, %) under optimum CFS conditions. EC, enhanced coagulation; RD, reduced dose.

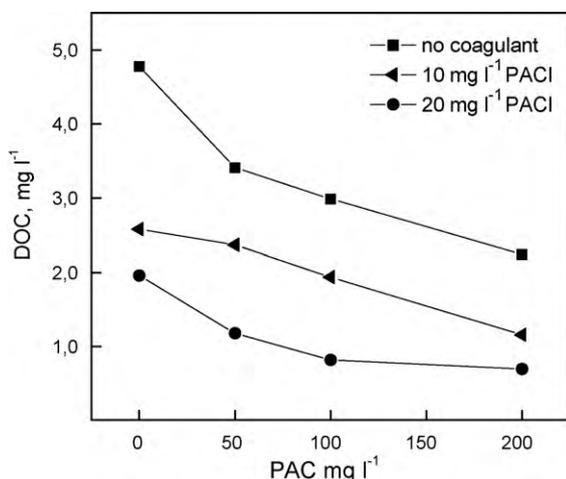| Treatment conditions	CFS conditions				Attained removal efficiencies			
	PAC	rpm	Dose	pH	SPTHMFP	THMFP$_F$	UV$_{254}$	DOC
CFS(EC)	–	80	40	6.0	72.7	64.2	59.7	30.9
CFS(WTP)	–	80	20	8.0	50.9	43.0	42.2	30.4
CFS(WTP)+PAC	50	80	20	8.0	68.3	66.1	56.3	32.4
CFS(RD)+PAC	50	80	10	8.0	50.4	49.6	40.9	28.0
WTP	–	–	20	7.9	32.4	27.5	55.0	28.8

Fig. 2. Residual concentration of DOC as a function of PAC addition and at different coagulant dosages (PACl).

removal, doubled compared to that achieved in WTP (Table 3). Fig. 2 shows the removal of NOM in the raw water preoxidized with mixed oxidants as a function of PAC added and at different coagulant (PACl) dosages. It is observed how removal efficiency increased with increasing PAC dose. It is remarkable that at the same coagulant dose applied at WTP, $20\,mg\,l^{-1}$, removal of DOC saturates at PAC dose of $100\,mg\,l^{-1}$ while at lower coagulant doses a steadily increasing removal efficiency was observed. The amount of coagulant and the need of acidification increases the operational costs during water treatment. However, a means of reducing coagulant dose and pH modifier requirements is the use of powdered activated carbon as coadjuvant of CFS process.

GPC chromatograms for different treatment levels are shown in Figs. 3A and 4A. One main band with three small peaks are identified. The last corresponding to small molecules of few hundreds of Dalton. For the main peak two shoulders can be detected. By using a peak separation and analysis software (PeakFit 4.12) six different fractions of NOM were differentiated. This heterogeneity can be attributed to the cracking effect of the mixed oxidants on NOM molecules. It is known that ozonation alters the chemical structure and characteristics of NOM [25]. Chiang et al. [26] reported that pre-ozonation influences UV absorbance reduction more than DOC removal.

In Figs. 3B and 4B the height of bar represents the removal efficiency for fractions of NOM of different MW. Average molec-

ular weight of NOM treated by mixed oxidants plus PAC slightly increased as deduced from the displacement observed in the main band (Fig. 3B). Average pore size of PAC was about 1 nm and therefore access of NOM molecules to the pores would be expected to be limited. This would explain that removal efficiency of each fraction significantly increased, up to complete removal, as MW decreased. However, when only PAC was used, the lowest dose of $50\,mg\,l^{-1}$, removed large fractions (fractions 1–3) of NOM in the range of 22–60% what is comparable to values obtained by CFS, from 25% to 63% (Fig. 4B). Since the working pH is lower than the pH_{pzc} of the PAC, electrostatic interactions would favor adsorption of the deprotonated NOM molecules onto the positively charged surface of PAC. This suggests that adsorption onto PAC is strongly affected by surface chemistry to the point that it can overcome "a priori" non-adequate physical properties of the PAC. On the contrary CFS alone (Fig. 4B) removes preferably large molecules of NOM and showed two to three times less effectiveness than PAC in the removal of small fractions, MW < 660 Da, of NOM. As a result, average MW of bulk water was reduced as deduced from the displacement of the main band in the GPC chromatogram (Fig. 4A). CFS performance was especially low at coagulant dose of $10\,mg\,l^{-1}$ which seems to be insufficient for an adequate neutralization and coagulation of the preoxidized NOM.

Fig. 5 compares the removal of NOM for different combinations of coagulant and PAC doses. Compared to CFS alone, combination of CFS and adsorption allows a significant reduction on coagulant dose. For example, at a reduced coagulant dose of $10\,mg\,l^{-1}$ the removal of small molecules (fraction 6) is above 80% for all the PAC dose range. Note that only CFS removed 25–31%. The addition of PAC as coadjuvant of the coagulant seems to have an stabilization effect on the flocs formed. The fact is that simultaneous addition of coagulant and PAC slightly reduced removal of low MW molecules compared to only PAC treatment. This behavior has been also reported by others where high dosages of coagulant have proved to reduce adsorption efficiency [27,28]. The size of the flocs increases with coagulant what favors the incorporation of PAC particles into these larger flocs leading to a reduction in the efficiency of mixing. The comparison of Figs. 4A and 5A reveals that large fractions of NOM are equally removed, about 60% removal, by conventional CFS (coagulant $20\,mg\,l^{-1}$) and combined treatment with a reduced dose of coagulant and PAC, 10 and $50\,mg\,l^{-1}$, respectively. Under these conditions coagulant did not hinder PAC performance and as occurred in PAC alone conditions removal of small fractions of NOM was maintained very high. As a result, NOM in preoxidized raw water was uniformly removed in all the MW range as
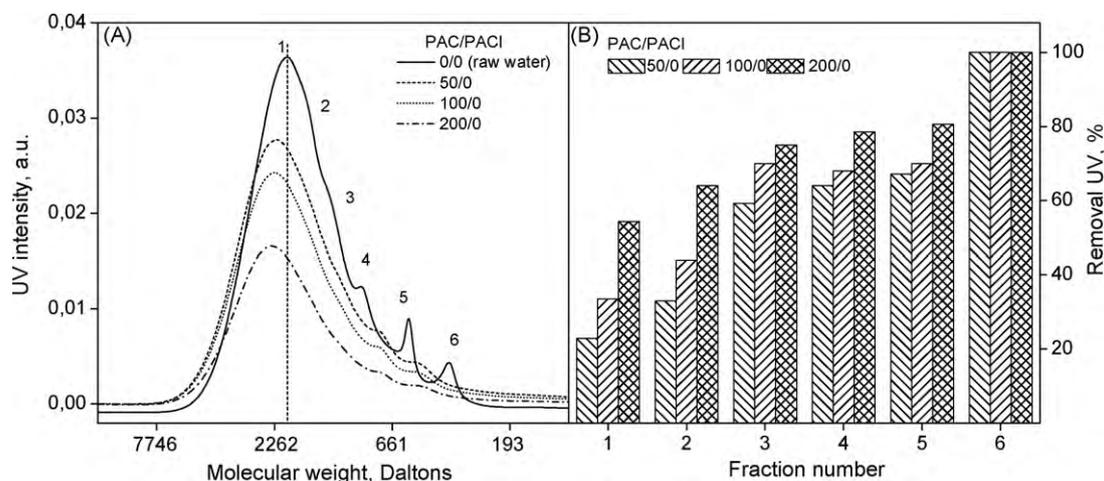

Fig. 3. Removal of different fractions of NOM at different PAC dosages. (A) GPC chromatogram and (B) percent removal for different MW fractions.
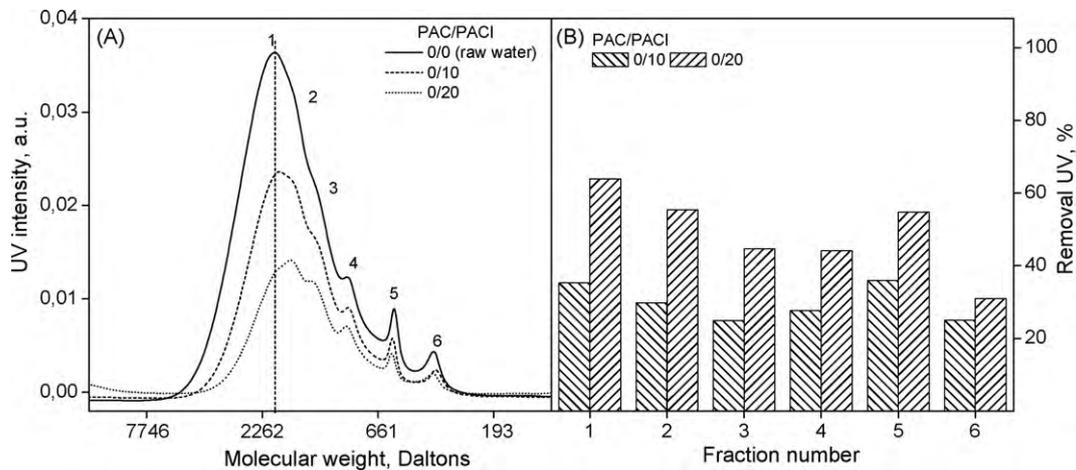
Fig. 4. Removal of different fractions of NOM at different coagulant (PACl) dosages. (A) GPC chromatogram and (B) percent removal for different MW fractions.
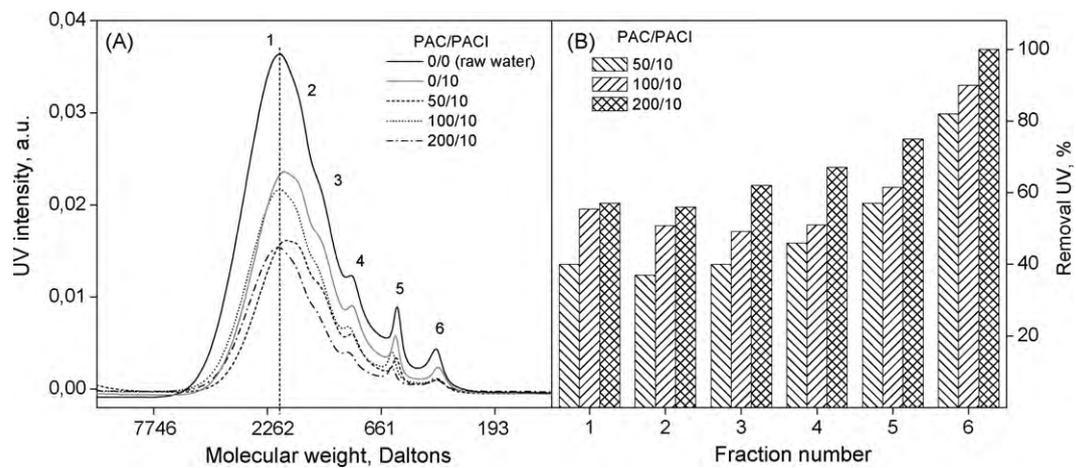

Fig. 5. Removal of different fractions of NOM for the combined application of PAC and PACl. (A) GPC chromatogram and (B) percent removal for different MW fractions.

deduced from the lack of displacement in the main band in the GPC chromatogram shown in Fig. 5A.

Fig. 6 shows the removal efficiency of precursors of THM measured as THMFP at various combinations of PAC and PACl dosages. It is observed that CFS at WTP conditions (coagulant 20 mg l^{-1}, pH 8.0) allowed 43% reduction in the THMFP$_F$. It is noteworthy to mention that this value is above the 27.5% observed at full scale plant (Table 3). Two are the possible reasons for this discrepancy (i) the more severe chemical transformation undergone by NOM at WTP due to a more prolonged contact with mixed oxidants and (ii) a non-
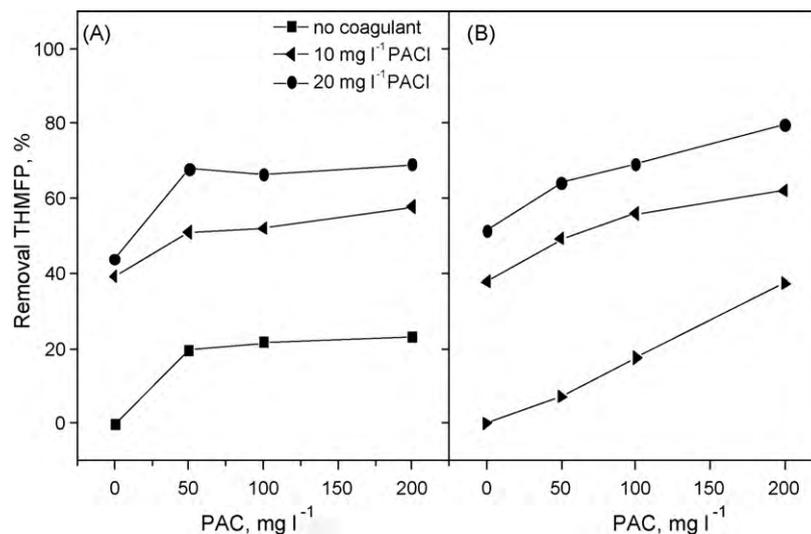

Fig. 6. Removal efficiency of THMFP as a function of various PAC and PACl dosages. (A) THMFP$_F$ and (B) SPTHMFP.

adequate mixing of chemicals at WTP coagulation chamber what reduces efficiency of the CFS process.

Results obtained by THMFP tests are in accordance with those obtained by NOM fractionation. Production of THM coming from the hydrophilic fraction of NOM can be hardly removed by CFS process. Removal of $THMFP_F$ significantly increases by addition of a small amounts of PAC. For example, addition of $50\,mg\,l^{-1}$ of PAC increased removal efficiency from 42% up to 66% (Fig. 6). However, and contrary to what could be expected from previous results, further increase in PAC does not increase removal of $THMFP_F$. Again, the lowest PAC dose used of $50\,mg\,l^{-1}$ allowed reduction of coagulant dose to the half whereas removal of precursors was still improved 10% points (from 40% to 50%). Removal of SPTHMFP steadily increased with dosage of PAC. This suggests that addition of PAC is especially effective in removing fast reacting precursors, those that react with chlorine to form THM within the first stages after chlorination. This fact gains especial relevance as far as reduction of THM concentration at WTP outlet stream is regarded.

4. Conclusions

It is known that the use of electrochemically generated oxidants has important benefits as far as inactivation of pathogens is concerned. However, the alterations produced in NOM can negatively affect the efficiency of the conventional coagulation–flocculation–settling process. Results obtained in the present work indicate that mixed oxidants promote conversion of humic matter to hydrophilic matter. HPIA-DEAE fraction accounted for 8% in raw water whereas it increased to 20% in finished water, based on $THMFP_F$ results. These results indicate that, hydrophilic fraction was an important source of THM formation in WTP effluent. Extraction and quantification of humic substances from surface waters was more effective with DEAE ionic resin. Further study should be devoted to elucidate what happens to irreversibly adsorbed fractions on DAX macroporous resin.

The addition of PAC during the coagulation of natural surface waters preoxidized with electrochemically generated oxidants can significantly improve process efficiency for the removal of low molecular weight and hydrophilic NOM fractions. Based on $THMFP_F$ and SPTHMFP results, this would allow an important reduction in THM formation during the final disinfection step. The increased cost of adding PAC can be minored by the reduction on the coagulant dose allowed by PAC addition. Addition of a small amount of PAC ($50\,mg\,l^{-1}$) allowed 50% reduction on the coagulant dose whereas removal of high MW fractions of NOM was maintained and that of small fractions was significantly increased. Chlorination tests confirmed this trend where the removal of $THMFP_F$ and SPTHMFP was improved. PAC was especially effective for the removal of fast reacting precursors as deduced from SPTHMFP results. The presence of PAC in suspension aids in the formation of the flocs. This way the minimum coagulation dose needed for coagulation can be reduced with no loss of process performance.

Parameters

ρ	apparent bulk density
dp	average pore diameter
pH_{pzc}	pH of point of zero charge
S_{BET}	BET surface area
S_{mes}	surface area in the mesopore range
S_{micr}	surface area in the micropore range
V_T	total pore volume

Acknowledgements

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