



## Using fluorescence spectroscopy EEM to evaluate the efficiency of organic matter removal during coagulation–flocculation of a tropical surface water (Agbo reservoir)

Droh Lanciné Gone<sup>a,\*</sup>, Jean-Luc Seidel<sup>b,1</sup>, Christelle Batiot<sup>b,2</sup>, Kamagate Bamory<sup>a,3</sup>, Raymond Ligban<sup>a,4</sup>, Jean Biemi<sup>c,5</sup>

<sup>a</sup> Laboratoire Geosciences et Environnement, Université d'Abobo-Adjamé, 02 BP 801 Abidjan 02, Cote d'Ivoire

<sup>b</sup> HydroSciences Montpellier, UMR 5569 – UM2 – CNRS – IRD – UM1 Place Eugène Bataillon -CC MSE, 34095 Montpellier Cedex 5, France

<sup>c</sup> Centre Universitaire de Recherche et d'Application en Télédétection (CURAT), Université de Cocody, 22 BP 801 Abidjan 22, Cote d'Ivoire

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### ABSTRACT

This study evaluate the use of fluorophores A, C and T fluorescence intensities to access the coagulation efficiency for removing dissolved organic carbon (DOC) in the raw water from Agbo reservoir in Ivory Coast. A coagulation–flocculation was conducted with aluminium sulphate as coagulant and DOC residual and fluorescence intensities were acquired. The consistency of fluorescence data was evaluated to ensure that no inner-effect, quenching or enhanced intensities affect the data. Fluorescence-inferred DOC removal was then calculated in percentage terms from the decrease in organic matter fluorescence intensity for each peak between raw and clarified water and correlated with measured DOC removal. The results indicate a high significant correlation between measured DOC removal and fluorescence-inferred DOC removal calculated for peak A ( $R^2 = 0.91$ ), peak C ( $R^2 = 0.89$ ), peak T ( $R^2 = 0.92$ ) indicating a strong linear relationship between DOC removal and fluorescence intensities. Furthermore, tryptophan-like (peak T) was found to be the least eliminated and thus, may be considered as an indicator of DOC residual after coagulation–flocculation process. This result shows that fluorescence spectroscopy offers a robust analytical technique to be used to evaluate DOM removal efficiency in water treatment.

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### 1. Introduction

In the aquatic environment, the dissolved organic matter (DOM) is a mixture of compounds with different structures and a wide range of molecular weight [1].

DOM has become increasingly important with regard to water supplies, because it reacts with chlorine during the disinfection process in drinking water treatment and produces disinfection by-products (DBPs) such as trihalomethanes (THMs). The formation of THMs is of much concern because of their perceived carcinogenic effects on humans [2,3]. Aquatic humic substances,

comprising fulvic and humic acids are the most common precursors of THMs. Organic matter in natural water can also cause poor odour, taste, colour, and bacterial regrowth problems [4] in water distribution systems. Effective removal of DOM by enhanced coagulation–flocculation is one of the challenges in modern drinking water treatment. Enhanced coagulation regards maximized DOM removal as its unique objective, which is comparable with optimized coagulation (maximize turbidity, DOM and DBPs removals, and minimize residual coagulant and operating costs) in drinking water treatment practice [5,6]. Two main ways are possible to achieve this goal: increase the dosage of the coagulant and adjust pH.

Aluminium sulphate (alum) is one of the most commonly used coagulants, easy to handle and apply and is low cost [7].

To evaluate the efficiency of the coagulation process, turbidity, dissolved organic carbon (DOC), UV<sub>254</sub> and aluminium residual are generally analysed. However, the determination of DOC does not give enough information about the nature of the DOM because DOM is a mixture of compounds with variable functional properties and solubilities, and thus, different reactivity towards coagulants. Some organic matter, being lower molecular weight and more hydrophilic is more difficult to be removed during water

\* Corresponding author. Tel.: +225 05 04 33 37; fax: +225 20 30 43 00.

E-mail addresses: [dialou25.9@yahoo.fr](mailto:dialou25.9@yahoo.fr) (D.L. Gone), [seidel@msem.univ-montp2.fr](mailto:seidel@msem.univ-montp2.fr) (J.-L. Seidel), [batiot@msem.univ-montp2.fr](mailto:batiot@msem.univ-montp2.fr) (C. Batiot), [kambamory2@yahoo.fr](mailto:kambamory2@yahoo.fr) (K. Bamory), [ligban12676@yahoo.fr](mailto:ligban12676@yahoo.fr) (R. Ligban), [jbiemi@yahoo.fr](mailto:jbiemi@yahoo.fr) (J. Biemi).

<sup>1</sup> Tel.: +33 04 67 14 36 61; fax: +33 04 67 14 47 74.

<sup>2</sup> Tel.: +33 04 67 14 37 03; fax: +33 04 67 14 47 74.

<sup>3</sup> Tel.: +225 66 83 59 34; fax: +225 20 30 43 00.

<sup>4</sup> Tel.: +225 05 07 50 65; fax: +225 20 30 43 00.

<sup>5</sup> Tel.: +225 05 09 92 02; fax: +225 22 44 52 70.

treatment, especially for coagulation–flocculation process. Moreover, due to cost and practicability, DOC analysis did not be used on-line in a water treatment plant. Therefore, optical equipment such as ultraviolet photometry has generally been used as detectors for organic compounds in natural and treated waters. However, various researchers have demonstrated that the removal rate of  $UV_{254}$  is greater than that of DOC in the enhanced coagulation process for surface water treatment [5,8,9] and as well as DOC,  $UV_{254}$  does not give enough information about the nature of DOM.

Characterization of DOM in raw water and coagulation/flocculation steps can provide designers and operators with additional understanding of process selection and operation, and also confirming the process performance.

Fluorescence spectroscopy has been widely used to investigate the chemical properties and source of DOM in natural waters, and especially three-dimensional excitation emission matrix (EEM) fluorescence spectroscopy has been successfully used to probe the chemical structure of DOM because they can distinguish among different classes of DOM of different origins [10,11]. EEM spectra are acquired by sequential fluorescence emission scans at successively increasing excitation wavelengths, and consist of three-dimensional spectra showing excitation and emission wavelengths and fluorescence intensity. They are presented as contour maps of the fluorescence landscape with iso-intensity levels delineating various peaks. An EEM typically covers a range of excitation and emission wavelengths from  $\sim 200$  nm (short wavelength UV) through to  $\sim 500$  nm (visible blue-green light), and may contain fluorescence centres that are attributable to both natural DOM groups such as humic and fulvic-like material, as well as fluorescent protein-like material [12,13]. Coble [12] named the humic and fulvic-like material fluorescence centres as fluorophores A and C, and protein-like material fluorescence centres as fluorophores T and B. Protein-like fluorophores were found to occur at enhanced levels in waters impacted by domestic sewage and other wastes [14]. Fluorescence spectroscopy has received attention in the water industry with respect to its potential application as a monitoring technique. Fluorescence monitoring is attractive as it is a rapid, reagentless technique that requires no sample preparation prior to analysis. It has been investigated as a monitoring tool for a range of application including water quality and pollution monitoring in rivers [15], process control in sewage treatment works [15], specific pollutants in industrial wastewater [16], oil in water [17] and disinfection by-product formation potentials in drinking water treatment [18]. Concerning the application of fluorescence spectroscopy to evaluate the water treatment efficiency, Cheng et al. [19] using a single excitation wavelength of 315 nm and emission wavelength of 417 nm, found that fluorescence analysis was an appropriate alternative in detecting the removal efficiency or DOC residue in water treatment plants. However, this approach is limited since the excitation at a single wavelength does not give access to the removal efficiency of the different fluorophores.

The objective of this study is to use EEM to provide an assessment of DOC removal during coagulation–flocculation with alum.

The study evaluates the use of the peaks (A, C and T) fluorescence intensities reduction between freshwater (raw) and clarified water as a measure of organic matter removal. The work focuses on the generation and analysis of additional data which are not available from the more routine DOC analyses undertaken by the water industry and assesses the use of fluorescence as a complementary performance indicator. To reach this goal, coagulation–flocculation by jar tests was conducted with alum as coagulant and DOM removal efficiency was evaluated by classic and fluorescence intensities analysis approaches.

## 2. Materials and methods

### 2.1. Water source

The raw water used for this study comes from the reservoir “Agbo”, located in Agboville (Ivory Coast) under tropical climate. Its maximum depth is about 4.5 m and the reservoir is colonized by aquatic plants. This reservoir is the main source of drinking water production for the population of Agboville.

### 2.2. Jar tests procedure

A standard jar test apparatus, a Phipps & Bird six-paddle stirrer with illuminated base, was operated for tests, with six 2-1 squareB-Ker<sup>2</sup> Plexiglas jars. The jars are provided with a sampling port, 10 cm below the water line, which allows for repetitive sampling with minimal impact on the test. The six flat paddles are all driven by a single variable speed motor from 0 to 300 rpm. An illuminated base helps observation of the floc formation and settling characteristics.

The coagulant solution ( $10\text{ g L}^{-1}$  aluminium sulphate)  $[\text{Al}_2(\text{SO}_4)_3, 18\text{ H}_2\text{O}]$  was prepared before each experiment. Each jar was filled with 2 L of raw water measured with a graduated cylinder. The coagulant dose added to each jar was carefully measured with a burette. Addition of coagulant was followed by 1 min of rapid mixing at 150 rpm, flocculation for 15 min at 20 rpm and 30 min of settling. Water was then filtered through Whatman glass fiber filters membranes ( $0.45\ \mu\text{m}$ ) previously grilled at  $500\ ^\circ\text{C}$  overnight and filtered waters submitted to analysis to evaluate the water treatment efficiency. Wide ranges of alum dosage and pH were explored to achieve optimum removal of DOC.

### 2.3. Dissolved organic carbon analysis

A total carbon analyser Shimadzu TOC-VCSH was used to analyse organic carbon in raw and treated waters by catalytically aided platinum  $680\ ^\circ\text{C}$  combustion technique, with auto-sampler TOC-ASIV. The non-purgeable organic carbon (NPOC) determination method was employed, samples were sparged with 2 M HCl to remove all inorganic carbon prior to combustion. Samples to measure organic carbon concentration were collected using amber glass bottles previously rinsed with nitric acid solution (20%) and copious amounts of analytical grade water (Milli-Q) from a laboratory system (Millipore Milli-Q academic) and then grilled ( $500\ ^\circ\text{C}$  overnight). Each sample was determined three times, the average value was considered as the DOC data. The standard deviation of the analysis was less than 2%.

### 2.4. EEM data measurements

All samples (raw and treated waters) were at room temperature (approximately  $20\ ^\circ\text{C}$ ), to minimize temperature influence. Furthermore, they were filtered through a micro-filtration membrane ( $0.45\ \mu\text{m}$ ) prior to analysis, for removing all the insoluble organic particles.

A spectrofluorometer RF – 5301 PC Shimadzu equipped with a 150 W xenon lamp was used. Excitation (Ex) wavelength was set from 220 to 500 nm, and emission (Em) wavelength from 250 to 600 nm. Ex and Em increment were respectively 10 and 1 nm with a slit of 10 mm for both Ex and Em. EEMs were measured using 1-cm path length quartz cells. In order to confirm the consistency of measurement conditions, scans of quartz cell containing analytical grade water (Milli-Q) were run systematically and intensity of the Raman line of water at 348 nm excitation wavelength recorded. The mean Raman value during the study period was  $10.5 \pm 0.6$  intensity units (required value =  $10 \pm 2$ ). All the fluorescence intensities were corrected to a Raman peak intensity of 10 units. DOC value from raw

**Table 1**  
Characteristics of raw water from reservoir Agbo.

	Raw water
COT (mg C/L)	20.85
COD (mg C/L)	20.32 (97.46% TOC)
POM (mg/L)	0.53 (2.54% TOC)
pH	6.64
Turbidity (NTU)	15.1

water (20.85 mg/L) and clarified water (6–14.3 mg/L) were such that an inner-filter correction was applied. Simple sample dilution to a concentration at which the inner-filter effects are negligible was used following Baker et al. [20]. The dilution factor was varied from 1 to 10.

### 2.5. Residual aluminium

Soluble residual aluminium has been measured by Hach colorimetric method with a spectrophotometer Hach 2010. Soluble aluminium has been measured instead of total aluminium since soluble aluminium is more concerned with Human Health (Alzheimer's disease) than total aluminium residual [21].

## 3. Results and discussion

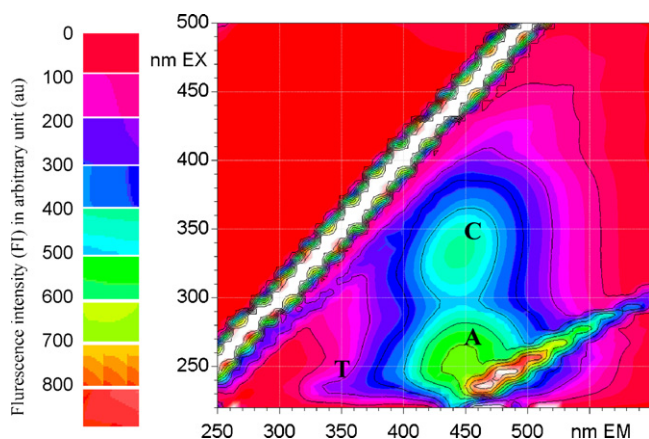
### 3.1. Characterization of the Agbo reservoir DOM

The chemical characteristics of the reservoir Agbo water are summarized in Table 1. The percentage of particulate matter accounting for TOC is less than 3%, which appears to be consistent with results published in the literature, less than 10% [1].

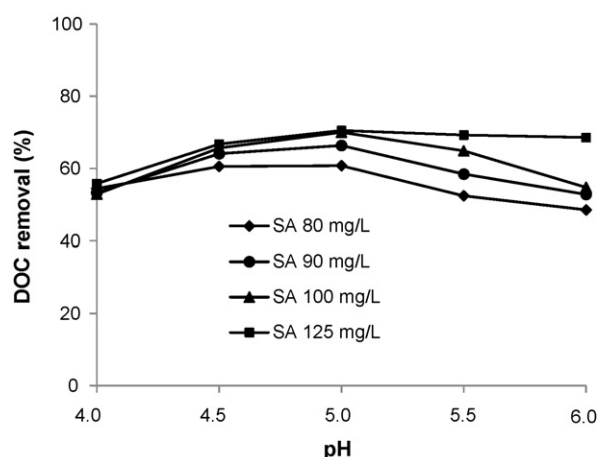
The EEM spectrum (Fig. 1) qualitatively indicates the DOM composition. Three peaks have been detected. A peak (peak T) is present at  $\lambda_{ex} = 230\text{--}240$  and emission  $\lambda_{em} = 350\text{--}400$ . A second peak (peak A) is observed at  $\lambda_{ex} = 240\text{--}250$  and emission  $\lambda_{em} = 440\text{--}450$ . A third fluorescence centre (peak C) is observed at  $\lambda_{ex} = 330\text{--}340$  and emission at  $\lambda_{em} = 440\text{--}450$ . These peaks have been widely identified in previous studies [12,22].

Peak T is identified as tryptophan-like. Tryptophan-like fluorescence may be exhibited by natural waters where tryptophan is present as 'free' molecules or bound in proteins, peptides or humic structures. It is related to microbial activity and may be transported into the system (allochthonous) or be created by microbial activity within the system (autochthonous).

Peaks A and C are related to humic-like (mainly humic and fulvic acids) derived from the breakdown of plant material. These two



**Fig. 1.** Fluorescence EEM of Agbo reservoir raw water (sample 10-fold diluted).



**Fig. 2.** pH effect on percent DOC removal for different doses of alum using standard jar test with 150 rpm rapid mixing for 1 min, low mixing for 15 min at 20 rpm and 30 min settling time.

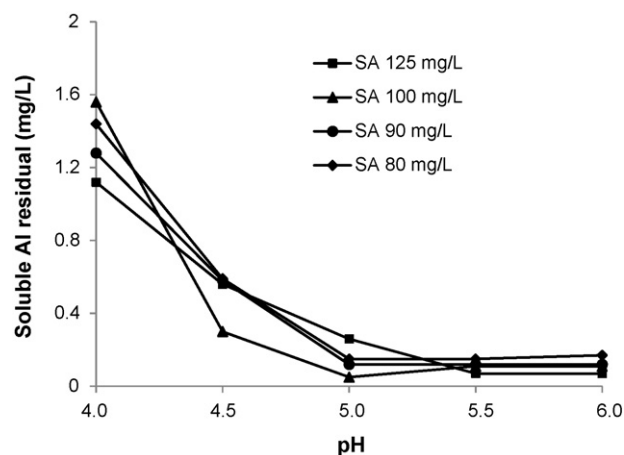
components are the most common fluorophores in natural surface waters.

### 3.2. Removal of NOMs during the coagulation–flocculation process

#### 3.2.1. Effect of pH and alum dose

To improve the coagulation–flocculation process, pH effect was studied. Different doses of alum were added at different pH to determine the optimal flocculation pH and alum dose. It is supposed that improvement of flocculation pH may reduce the alum dose necessary for the process optimization. The experiment was then carried out for alum doses ranging from 80 to 125 mg/L and a pH 4–6 range. To evaluate the process efficiency, DOC and residual aluminium were analysed.

DOC removal (Fig. 2) is pH dependant. The optimal pH value for DOC removal (70%) is pH 5. Removal of DOC increases with increasing of pH values until pH 5. High values of pH beyond pH 5 exhibit an inefficiency of DOC removal. As shown by Exall and vanLoon [6] and Canizares et al. [23], in acidic conditions, numerous monomeric and many possible polynuclear forms positively charged of sulphate aluminium hydrolysis products are formed around pH 5. The hydrolysis products include  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}_3(\text{OH})_4^{5+}$  and  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ . It is found that these compounds



**Fig. 3.** pH effect on soluble aluminium (Al) residual for different doses of alum using standard jar test with 150 rpm rapid mixing for 1 min, low mixing for 15 min at 20 rpm and 30 min settling time.

are responsible of the removal of turbidity and humic substances by binding to anionic sites, thus neutralising their charge and giving a reduced solubility. Indeed, DOM and particularly humic substances can be regarded as natural anionic polyelectrolytes, of rather indeterminate structure. They have various functional groups, including carboxylic and phenolic, and a framework of randomly condensed aromatic rings. Because of the ionisation of carboxylic groups, humic substances will have anionic charge at pH values higher than 4 and are generally soluble under these conditions [24]. Hence, these negative charges can be neutralized by aluminium sulphate hydrolysis products positively charged at pH below pH 6 [25]. As a result, charge neutralisation may be the dominant mechanism involved in the removal of NOM, since NOM removal occurs in oper-

ational pH region where aluminium hydroxide precipitation is not theoretically maximal [26]. Aluminium hydroxide precipitation is known to occur at pH 6–7.

### 3.2.2. Soluble residual aluminium

Measurement of soluble residual aluminium content in clarified water after coagulation–flocculation process is one way to ascertain the process efficiency. Fig. 3 presents the concentrations of aluminium residual as a function of pH. Aluminium concentration decreases with increasing pH values. A coagulation–flocculation  $\text{pH} \geq 5$  is required to ensure relatively low soluble aluminium concentration. The minimum of residual aluminium (0.05 mg Al/L) is however, obtained at pH 5 for a 100 mg/L alum dose.

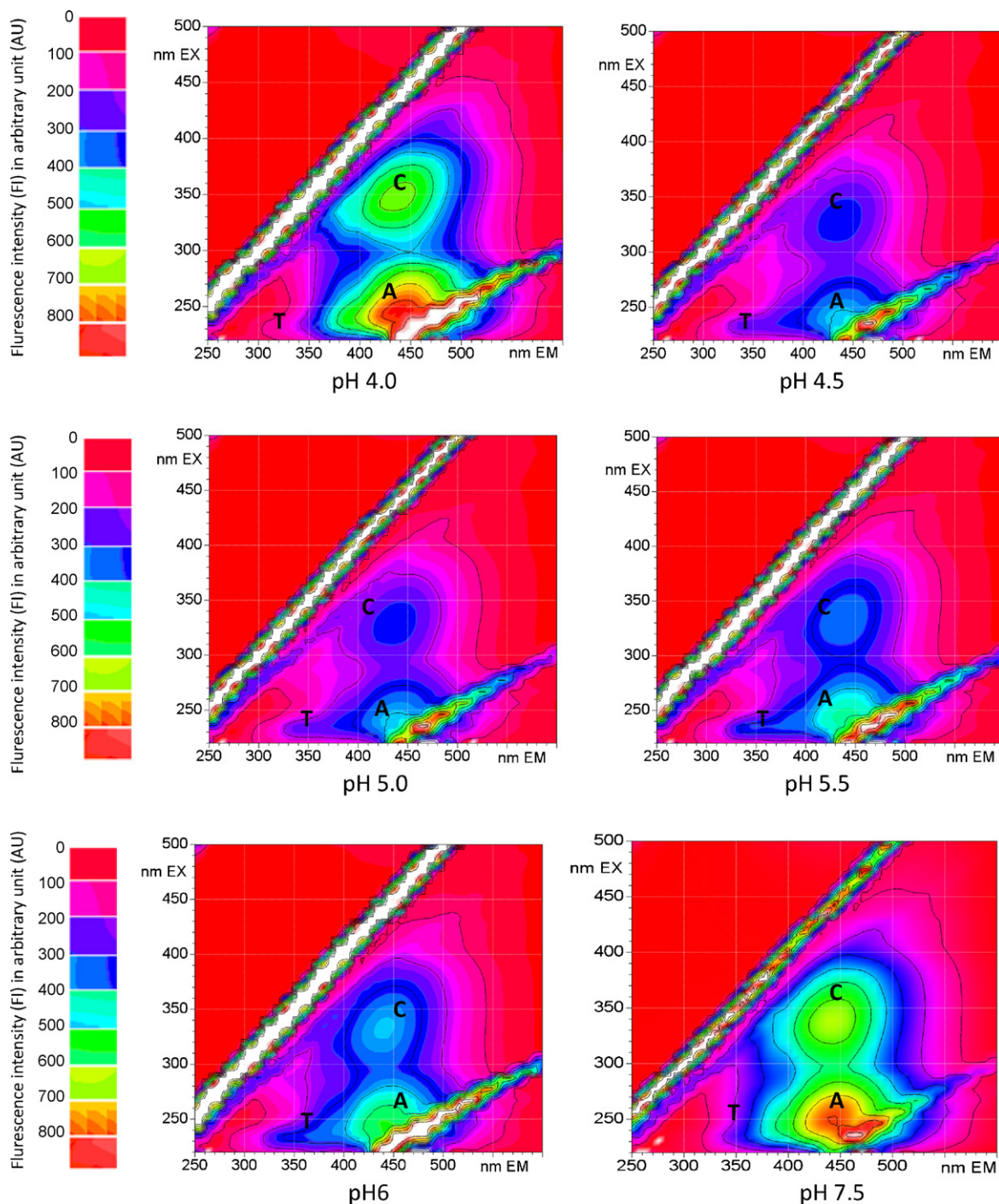


Fig. 4. Fluorescence EEMs of treated water using optimal dose of alum (100 mg/L) for different pH values (samples were 5-fold diluted).

As the result of DOC and soluble residual aluminium, 100 mg/L alum is the optimal dose of coagulant since it is the lowest dose leading to the highest DOC removal and the lowest residual aluminium. The effect of 125 mg/L alum remains practically constant above the optimal pH (pH 5) for DOC removal and leads to high concentration of residual aluminium above 0.2 mg/L (guideline value).

### 3.3. EEM characterization of treated water

Since the optimal dose of alum was determinate, an additional data from coagulation–flocculation was acquired using the optimal dose (100 mg/L alum) for different pH values from 6.5 to 7.5. The objective was to have a broad range of pH and residual aluminium for fluorescence intensities analysis. The DOC removal (in %) obtained were 46.57, 41.97, 31.41 and residual aluminium (in mg/L) were 0.35, 0.52, 1.46 respectively for pH 6.5, 7 and 7.5, indicating a decreasing of DOC removal and increasing of residual aluminium in this range of pH.

The evolution of fluorescence intensities with pH variation for 100 mg/L of alum (Fig. 4) indicates that the lowest fluorescence intensity is observed at pH 5 for both compounds T, A and C, confirming the effectiveness of alum at pH 4.5–5 for DOM removal. But previous studies demonstrated that pH variation and interaction between DOM and metal ions (such as aluminium) can affect DOM fluorescence intensity [27,28]. It has been shown that diamagnetic ions such as  $\text{Al}^{3+}$  can quench, enhanced or have little effect on fluorescence [29]. A number of studies have also shown the variable effect of pH on fluorescence intensity [30,31]. For example peak C intensity was observed to increase for pH 2–4 and stabilize between pH 4–10 [30] while peak A intensity was observed to increase with pH 2–10 then decreased slightly between pH 10–11. In order to verify the effect of pH and residual aluminium on fluorescence intensity, the fluorescence intensity of each peak (A, C and T) were plotted versus DOC for both raw and treated waters (pH 4–7.5) containing variable concentration of residual aluminium (0.05–1.46 mg/L). The results indicate a significant shift between representative water point for pH 4 and the other samples. The fluorescence intensity at pH 4 was enhanced in agreement with the results of Elkins and Nelson [29].

Consequently, this sample was not taking into consideration for the following analysis of fluorescence intensities. For the other samples, the significant correlation ( $r^2 > 0.9$ ) between the different peak intensities and DOC (Fig. 5) for different pH (4.5–7.5) and different concentration of residual aluminium, indicates a negligible pH, residual aluminium and inner-filtering effect.

Since the linear relationship has been demonstrated between DOC and the different peak intensities, these intensities were used to evaluate DOC removal efficiency. Measured DOC removal was compared to fluorescence-inferred DOC removal. Fluorescence-inferred DOC removal was calculated in percentage terms from the decrease in organic matter fluorescence intensity for each peak between raw and clarified water. Fig. 6 demonstrates a strong correlation between measured DOC removal and fluorescence-inferred DOC removal for the three peaks, indicating that the decrease in organic matter fluorescence intensity between raw and clarified water samples can be used as an accurate, yet simple predictor of DOC removal.

Cheng et al. [19] also found a linear relationship ( $R^2 = 0.77$ ) between fluorescence intensity and DOC removal using a single scan at 315 nm excitation and 417 nm emission. The advantage of acquiring EEM spectra by sequential fluorescence emission scans at successively increase excitation wavelength used in this study is that, this approach allows determining the effect of treatment on each fluorophore removal and thus, provides sufficient detail for interpretation. A priori, peaks A, C or T may be used as a useful indicator of DOC removal efficiency since they all present a good linear

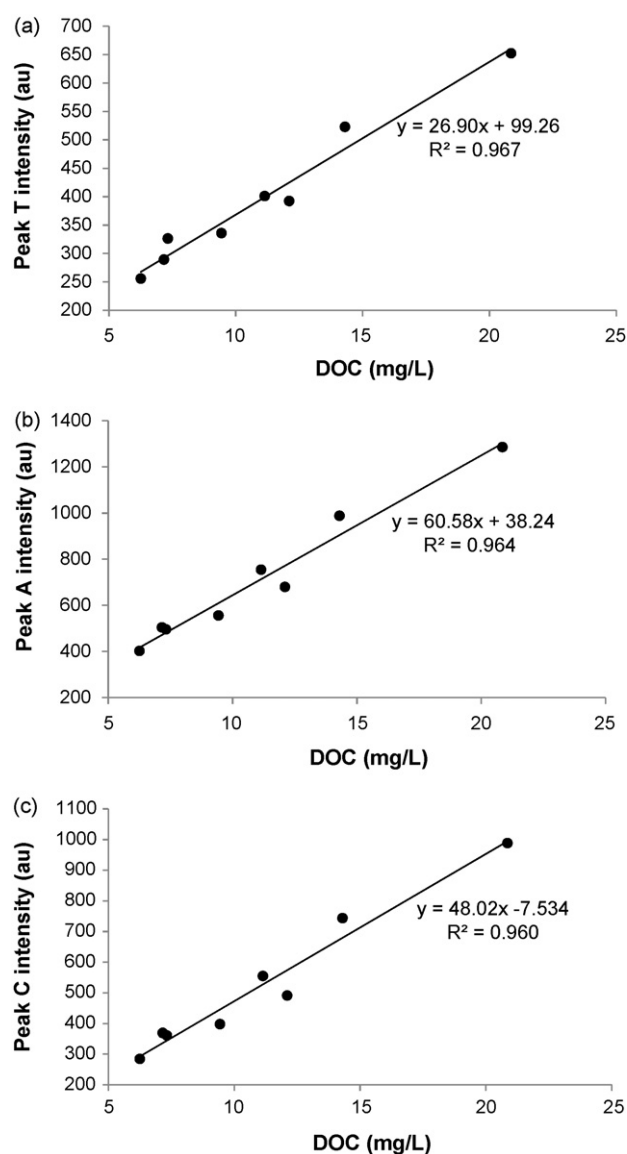
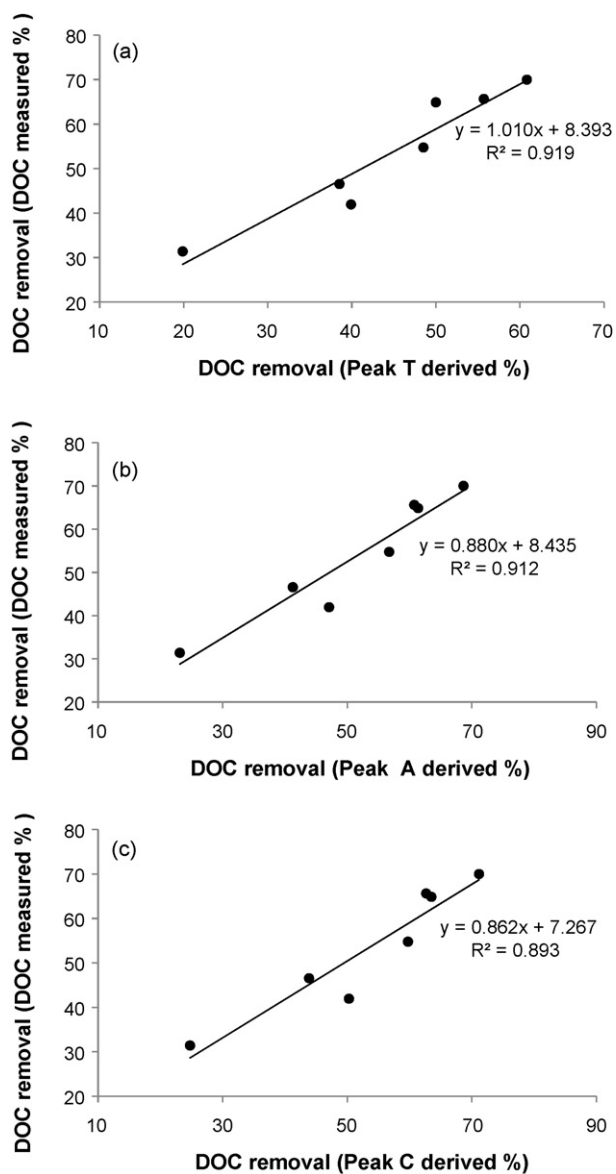


Fig. 5. The relationship between DOC and fluorescence intensities in both raw and clarified waters: (a) peak T, (b) peak A and (c) peak C.

relationship with DOC removal. However, as stated by Sharp et al. [32] and Henderson et al. [33], the least DOM fraction amenable to remove by coagulation–flocculation can be applied as the best indicator of the achievable DOC residual after coagulation–flocculation.

In order to determine DOM compounds most reacting with aluminium sulphate during the coagulation–flocculation process, ratios of fluorescence-inferred DOC removal were calculated (Table 2). These ratios indicate that humic-like compounds (peaks A and C) are most removed by coagulation–flocculation than tryptophan-like compounds (peak T). Results are consistent with previous laboratory jar tests that demonstrated that Al and Fe salts do not efficiently coagulate nitrogen compounds and proteins [34,35] such as tryptophan-like. Bieroza et al. [36] comparing DOC removal by coagulation–flocculation of waters from different sites, also found that sites with higher peak T intensities exhibited lower DOC removal. Compound T resulting from microbial activity may be low molecular weighted and more soluble than compounds A and C and therefore more refractory to coagulation process. Compound C removal is almost similar to that of A (ratio ~ 1), confirming a similar structure and properties of humic and fulvic acids even if humic acid is known to be slightly more hydrophobic and high molecular



**Fig. 6.** The relationship between DOC removal in percentage derived from direct DOC measurement and from peaks fluorescence intensities: (a) peak T, (b) peak A and (c) peak C.

weight than fulvic acid. These two hydrophobic fractions of humic substances rich in carbon double bonds are the most targeted by coagulation flocculation [37,38].

**Table 2**

Ratios of the fluorescence-inferred DOC removal for different pH values.  $R_A$ ,  $R_C$  and  $R_T$  are DOC removal percentage calculated from peaks A, C and T respectively between raw and clarified waters.

	$R_C/R_A$	$R_A/R_T$	$R_C/R_T$
pH 4.5	1.03	1.09	1.12
pH 5.0	1.04	1.13	1.17
pH 5.5	1.03	1.23	1.27
pH 6.0	1.05	1.17	1.23
pH 6.5	1.06	1.07	1.13
pH 7	1.07	1.18	1.26
pH 7.5	1.07	1.16	1.24
Mean	1.05	1.15	1.20
Standard deviation	0.02	0.05	0.06

#### 4. Conclusion

DOM removal during processes of aluminium sulphate coagulation–flocculation was conducted and three-dimensional excitation emission matrix fluorescence spectroscopy was investigated to access the DOC removal. From this study, it results that:

- Fluorescence spectroscopy has been successfully used to determine DOC removal during coagulation–flocculation with aluminium sulphate.
- A significant high correlation was observed between fluorescence-inferred DOC removal calculated for peak A ( $R^2=0.91$ ), peak C ( $R^2=0.89$ ), and peak T ( $R^2=0.92$ ) and measured DOC removal, indicating a strong linear relationship between DOC removal and fluorescence intensities.
- Ratios calculation of the different fluorescence-inferred DOC removal, indicate that humic-like (peaks A and C) compounds are most removed than tryptophan-like (peak T) as demonstrated by previous works using other approaches.
- Since tryptophan-like is the least eliminated, it may be consider as an indicator of DOC residual after coagulation–flocculation.
- The simplicity, the strong linear relationship between DOC removal and fluorescence intensities, combined with the potential for access to the removal efficiency of the different fluorophores mean that fluorescence spectroscopy offers a robust analytical technique to be used in conjunction with, or in place of the classic approach using only DOC to evaluate DOM removal efficiency in the water treatment plants.

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