Novel insights into the coagulation process for pharmaceutical wastewater treatment with fluorescence EEMs-PARAFAC

Xiying Gou, Panyue Zhang, Yonghui Song, Feng Qian, Huibing Yu and Guangming Zeng

ABSTRACT

In this study, coagulation process was applied to treat the effluent of pharmaceutical wastewater using polymeric ferric sulfate as a coagulant. Three-dimensional excitation-emission matrix fluorescence spectroscopy coupled with parallel factor analysis (EEMs-PARAFAC) was applied to investigate the fluorescent characteristics of dissolved organic matter (DOM) from pharmaceutical wastewater and the reduction of contaminant and fluorescent variations in the coagulation process. It shows that coagulation was effective to remove contaminants in the effluent of pharmaceutical wastewater, and the optimum coagulate dosage was 0.5 g/L, where the removal efficiency of total organic matter (TOC), UV_{254}, turbidity and NH_4^+-N were achieved 44.2%, 43.3%, 87.0% and 10.27%, respectively. Five fluorescence components were identified by EEMs-PARAFAC, including one fulvic-like component (C1), one xenobiotic-like component (C2), two humic-like components (C3 and C5) and one protein-like component (C4); DOM of pharmaceutical wastewater was dominated by C3, C4 and C2. Under the optimum coagulation condition, the decreasing order of removal efficiencies was C5 (49.92%), C3 (40.95%), C4 (10.58%), C2 (9.68%) and C1 (5.05%). Principal component analysis (PCA) showed C3, C5 had remarkable correlations with TOC and UV_{254}, suggesting that C3 and C5 may be a good indicator for the reduction of TOC and UV_{254}. PCA indicated that the EEM-PARAFAC could be successfully applied to the evaluation of the coagulation efficiency for pharmaceutical wastewater treatment.

Key words | coagulation, DOM, EEMs-PARAFAC, PCA, pharmaceutical wastewater

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INTRODUCTION

Pharmaceutical wastewater is one of the by products of pharmaceutical production, which contains a considerable amount of hardly biodegradable pollutants, such as ketones, phenols, pyridines and sulfonamides (Kumar & Xagoraraki 2010). Many of those toxic materials were identified as carcinogenic, mutagenic and teratogenetic contaminants, which could produce significant adverse ecological and human health effects (Webb *et al.* 2003; Manciocco *et al.* 2014). Pharmaceutical wastewater after the bio-treatment may reach the standard of discharged wastewater into municipal sewage treatment plants, but it still contains a lot of hardly biodegradable recalcitrant and toxic components which may disturb the operation of the municipal sewage treatment plant (Qiu *et al.* 2013; Shi *et al.* 2014). Pharmaceuticals as one of the contaminants of emerging concern has been detected in surface waters and effluent of wastewater treatment plants (WWTP) (Joss *et al.* 2006; Matongo *et al.* 2015; K'Oreje *et al.* 2016). Therefore, it was urgent to further treat the effluent of pharmaceutical wastewater, and to effectively reduce its harm to aquatic organisms and humans.

The coagulation process was the most commonly used pre-treatment technology in wastewater treatment facilities; it could efficiently remove suspended particles, colloidal particles, dissolved organic matter (DOM) and has been

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applied to treat landfill leachate, reverse osmosis concentrate wastewater (ROC), coke wastewater, etc. (Kumar & Xagoraraki 2010; Liu *et al.* 2012; Li *et al.* 2016). Therefore, coagulation is a feasible alternative to treat industrial wastewater. Research has been found that the colloidal surface charge of wastewater influences the removal efficiency in the coagulation (Son & Hsu 1981); others indicated that the physical properties of floc influence the solid–liquid separation as well as the interparticle bonds between particles (Boller & Blaser 1998). Fewer studies focused on the correlations between water quality parameters with DOM fractions (Zhu *et al.* 2014).

DOM is a heterogeneous mixture of organic polymers which is extremely complex (Yu *et al.* 2013). As a control parameter in the water treatment process, DOM gains more and more concentration as a control parameter in the water treatment process, due to its concentration and composition affecting the water treatment efficiency. More research focuses on the characterization and removal of DOM due to the precursor of disinfection byproducts and its concentration and composition affecting the treatment processes (Yu *et al.* 2013; Yang *et al.* 2015). DOM can control coagulation efficiency, disinfection byproduct formation, membrane fouling (Ishii & Boyer 2012; Yue *et al.* 2015; Li *et al.* 2016). Engineered systems are meeting great challenges with the increasing concentration of DOM. DOM monitoring during treatment is extensively required to evaluate the treatment efficiency and may reveal the correlations of water characteristics with DOM fractions clearly in the coagulation process (Ishii & Boyer 2012).

Unlike traditional water quality parameters such as total organic matter (TOC), chemical oxygen demand (COD), turbidity, etc., which often depend on time-consuming or expensive methods, and unable to assess the water quality comprehensively (Qin *et al.* 2012). There are many approaches to obtain DOM, such as infrared spectroscopy, fluorescence spectroscopy and nuclear magnetic resonance system, which were more convenient and fast. Fluorescence spectroscopy as a widely used tool has been applied to assess wastewater quality for discharge detection in aquatic ecosystems and for process control in water treatment facilities (Osburn *et al.* 2012; Zhu *et al.* 2014; Carstea *et al.* 2016). It is highly sensitive and requires little sample preparation (Yu *et al.* 2013; Zhu *et al.* 2014).

Three-dimensional fluorescence excitation-emission matrix (EEMs) is known as the most commonly-used technique to record fluorescence spectra. It has been used successfully to characterize DOM in natural and engineered systems (Ishii & Boyer 2012). Fluorescent fractions are excited at a range of wavelengths and emission recorded across a range of wavelengths which makes EEMs contain a large amount of information (Carstea *et al.* 2016). In order to interpret EEMs, multivariate data analysis techniques have been applied (Zhang *et al.* 2016). Among these methods, Parallel Factor Analysis (PARAFAC) was the increasingly used technique. PARAFAC can decompose EEMs of DOM into independent fluorescent components, and facilitate the identification and quantification of these components (Carstea *et al.* 2016). EEMs coupled with PARAFAC have been used for a range of applications including water quality, pollution monitoring in fresh water and seawater, specific pollutants in industrial wastewater, process control in WWTP and disinfection by product formation potentials in drinking water treatment (Osburn *et al.* 2012; Zhu *et al.* 2014; Yue *et al.* 2015; Zhang *et al.* 2016).

In this study, EEMs coupled with PARAFAC were applied to characterize DOM fluorescence properties of the effluent of pharmaceutical wastewater in the coagulation process. The objectives were: (1) to compare the removal efficiency in TOC, turbidity, UV absorbance at 254 nm (UV_{254}), and fluorescence components of coagulation process under different coagulant dosages, and, finally, optimized the most advantageous coagulation conditions; and (2) characterize and identify fluorescent components of pharmaceutical wastewater for obtaining a better understanding of the coagulation process.

MATERIALS AND METHODS

Materials and sampling

Polymeric ferric sulfate (PFS, industrial grade) used in this study was purchased from Sinopharm Chemical Reagent Co., Ltd (China). The effluent of pharmaceutical wastewater was collected from a pharmaceutical WWTP in Liaoning, China. The effluent quality of the pharmaceutical wastewater is given in Table 1. As we can see, the wastewater has high COD value and low B/C value, indicating that it contains a considerable amount of hardly biodegradable pollutants, and turbidity was relatively high. Hence, a post-treatment was needed.

Coagulation process

The coagulation experiments were carried out in beakers using conventional Jar-test apparatus using 500 mL samples at room temperature ($22 \pm 0.2\,^{\circ}C$), with PFS was applied as a

Table 1 | Characteristics of raw pharmaceutical wastewater

Parameter	Value
pH	6.5–7.2
TOC (mg/L)	60–80
COD (mg/L)	200–240
NH_4^+-N (mg/L)	13–15
UV_{254} (/cm)	0.96–1.02
Turbidity (NTU)	45–51
BOD_5 (mg/L)	20–25
Conductivity (mS/cm)	14.95–15.57

coagulant. A range of coagulant dosage (0.1–0.6 g/L) was investigated for the pharmaceutical wastewater to find the best dosage. The samples were rapidly mixed at an agitation speed of 250 rpm for 2 min followed by slow mixing at 50 rpm for 10 min, and then a 1 h setting time. The supernatant water was extracted from the beaker for sample analysis.

Sample analysis

TOC was determined using a Shimadzu TOC-VCPH analyzer. Turbidity was measured with a turbidity meter (WGZ-1, XinRui, China). UV absorption scan in the range of 200–600 nm was measured with a UV-visible spectrophotometer (UV-6100, METASH, China). UV_{254} was determined on the spectrophotometer at 254 nm. Ammonia nitrogen (NH_4^+-N) was analyzed using standard method (HJ 535–2009). Soluble residual iron was measured by the standard method with a PE Optima ICP-OES. All samples were filtered through 0.45 μm membrane glass fiber filters except for the measurement of turbidity.

Samples were diluted until absorbance was below 2.0 in a 1 cm cell to make sure absorbance-based correction could be used (Ohno 2002). EEMs were obtained using an F-7000 fluorescence spectrophotometer (Hitachi, Japan) in a 1 cm quartz cuvette at room temperature. The PMT voltage was set at 700 V and the scanning speed at 2,400 nm·min^{-1}. EEMs were measured with an emission wavelength of 260–580 nm in a 5 nm intervals and an excitation wavelength of 200–450 nm in 5 intervals. The slit bandwidths were 5 nm for both emission and excitation.

Rhodamine B and a ground quartz diffuser were used to correct the instrument biases (Stedmon *et al.* 2003). Accounting for the adsorption of both emission and excitation light by the sample, absorbance correction approach was applied to eliminate the inner filter effects (Ohno 2002). The Raman scatter peaks were removed by subtracting the Milli-Q water spectrum from the sample spectrum while the Rayleigh effect was eliminated using Delaunay triangulation interpolation. The fluorescence intensity of samples was normalized to Raman scatter intensity units of Milli-Q water setting excitation wavelength at 275 nm (Murphy *et al.* 2013).

PARAFAC model

PARAFAC decompose fluorescence EEMs (sample × excitation wavelength × emission wavelength) into the underlying fluorescence components. The data signal finally decomposed into a set of trilinear terms and a residual array:

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + \varepsilon_{ijk}, \ (i = 1, 2, 3 \ldots I; \ j = 1, 2, 3 \ldots J; k = 1, 2, 3 \ldots K) \quad (1)$$

In the equation, the number x_{ijk} presents the fluorescence intensity of sample i measured at emission wavelength j and excitation wavelength k. ε_{ijk} is the residual, representing the variability not accounted for by the model. The outcome parameters a, b, and c represent the concentration, emission spectra, and excitation spectra, respectively. A detailed description of the PARAFAC model was given by Murphy *et al.* (2013). Matlab R2014a was applied for PARAFAC modeling with 'N-way' toolbox. Notably, the outcome was the relative intensities of components (score) by PARAFAC. In this study, the variations of the fluorescence components were examined with the maximum intensity of each component (Fmax) in samples (Zhu *et al.* 2014). The total relative fluorescence intensity for a sample was calculated as the sum of the maximum intensity of each component in the sample:

$$TF_{\max} = \sum_{1}^{n} F_{\max} \quad (2)$$

The ratio of the nth component relative fluorescence intensity to total relative fluorescence intensity presents the percentage contribution of the nth component into total fluorescence intensity (Kowalczuk *et al.* 2010).

Statistical analyses

Principal component analysis (PCA) was applied to analyze the correlations between physico-chemical characteristics

and fluorescence component characteristics. All statistical analyses were conducted using SSPS 16.0 and OriginPro 8.0 for Windows.

RESULTS AND DISCUSSION

Reduction of organic matter during the coagulation process

To improve the coagulation process, the effect of coagulant dosage on the reduction of TOC, turbidity, NH_4^+-N and UV_{254} was studied. The TOC and turbidity were commonly used as indicators in the process of coagulation, UV_{254} represents the aromatic constituents in DOM and has been widely accepted as an index of aromatic structure (Lv *et al.* 2014). NH_4^+-N was another normal parameter to evaluate treatment efficiency. In this study, pH of raw water ranged from 6.5 to 7.2, and the optimum coagulation pH ranged from 6.0 to 9.0 (Wen & Chi 2002), therefore, considering the application of coagulation in the engineering system, pH was maintained, and a range of coagulant dosage (0.1–0.6 g/L) was investigated for the pharmaceutical wastewater to find the best dosage. The results are shown in Figure 1.

Research has found that the mechanisms of PFS by coagulation process are charge neutralization, adsorption-bridging, and sweep flocculation, and was usually affected by the pH value of the solution (Shu *et al.* 2016).

As shown in Figure 1, the reduction of TOC and turbidity increased with the increase of coagulant dosage, the maximum removal efficiency were 44.2%, 86.7% at coagulation dosage of 0.5 g/L, respectively. Research revealed that the coagulant mechanisms of PFS were charge neutralization and adsorption-bridging at pH 7.0, hence, more coagulant dosage means more positive iron will be produced, and the removal efficiency could be increased (Wen & Chi 2002). Further increasing the coagulant dosage resulted in a decrease. The main reason for the decrease would be the overdose of coagulant, too much coagulant dosage would form a phenomenon of colloidal particles which would decrease the reduction of contaminates (Zhu *et al.* 2014). In terms of UV_{254} and NH_4^+-N, as the coagulant dosage increased, the apparent removal efficiency of UV_{254} increased with the maximum removal efficiency up to 48% at coagulant dosage of 0.6 g/L, while the removal of NH_4^+-N was not obvious, the highest removal was just 12.66% at a coagulant dosage of 0.4 g/L. It is worth noting that with the coagulation dosage higher than 0.5 g/L, the reduction of organic matter increased gently, or even resulted in a decrease. Considering the cost of engineering application, PFS dosage of 0.5 g/L was selected for further experiment and engineering application. Overall, the increase of PFS dosage could result in the decrease of contaminants in the pharmaceutical wastewater in the investigated range and the optimum coagulation dosage was 0.5 g/L.

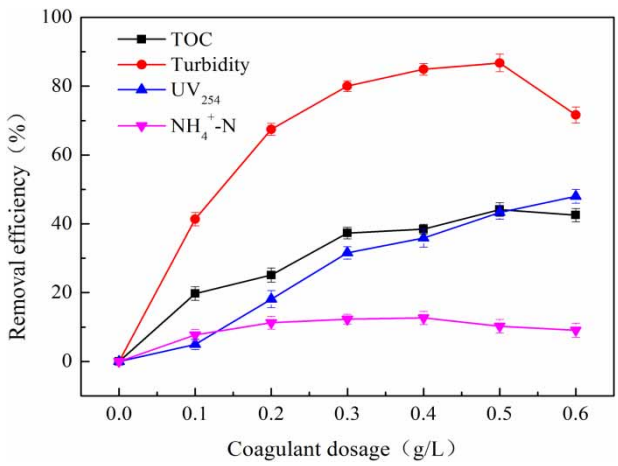

Figure 1 | Effect of coagulant dosage on the removal of TOC, turbidity, UV_{254} and NH_4^+-N.

EEM spectral characteristic

The EEM spectra of DOM of raw wastewater and the EEM spectra after coagulation at seven coagulant dosages are shown in Figure 2. Five key fluorescence peaks were identified in the EEM spectrum based on the traditional peak-picking method (Carstea *et al.* 2016).

T1 and T2 had peaks at Ex/Em = 230–240/340–350 nm and 280–290/340–350 nm, respectively. These two peaks have been observed in all studies and were identified as a tryptophan-like material which may derive from anthropogenic activity and microbial activity (Bridgeman *et al.* 2013; Yu *et al.* 2014). Peak M was located at Ex/Em = 315–325/445–455 nm which was assigned to the microbial humic-like material (Ishii & Boyer 2012). Peak A at the Ex/Em of 255–265/470–480 nm was categorized as fulvic-like substance. Peak C had a peak at Ex/Em = 355–365/465–475 nm and was associated with humic-like material (Lee & Jin 2016).

Compared with the EEM spectra of raw wastewater, the fluorescence intensity of wastewater in the coagulation process decreased obviously. In general, with the increase of PFS dosage, the fluorescence intensity of wastewater decreased continuously. The intensities of peaks C, M and

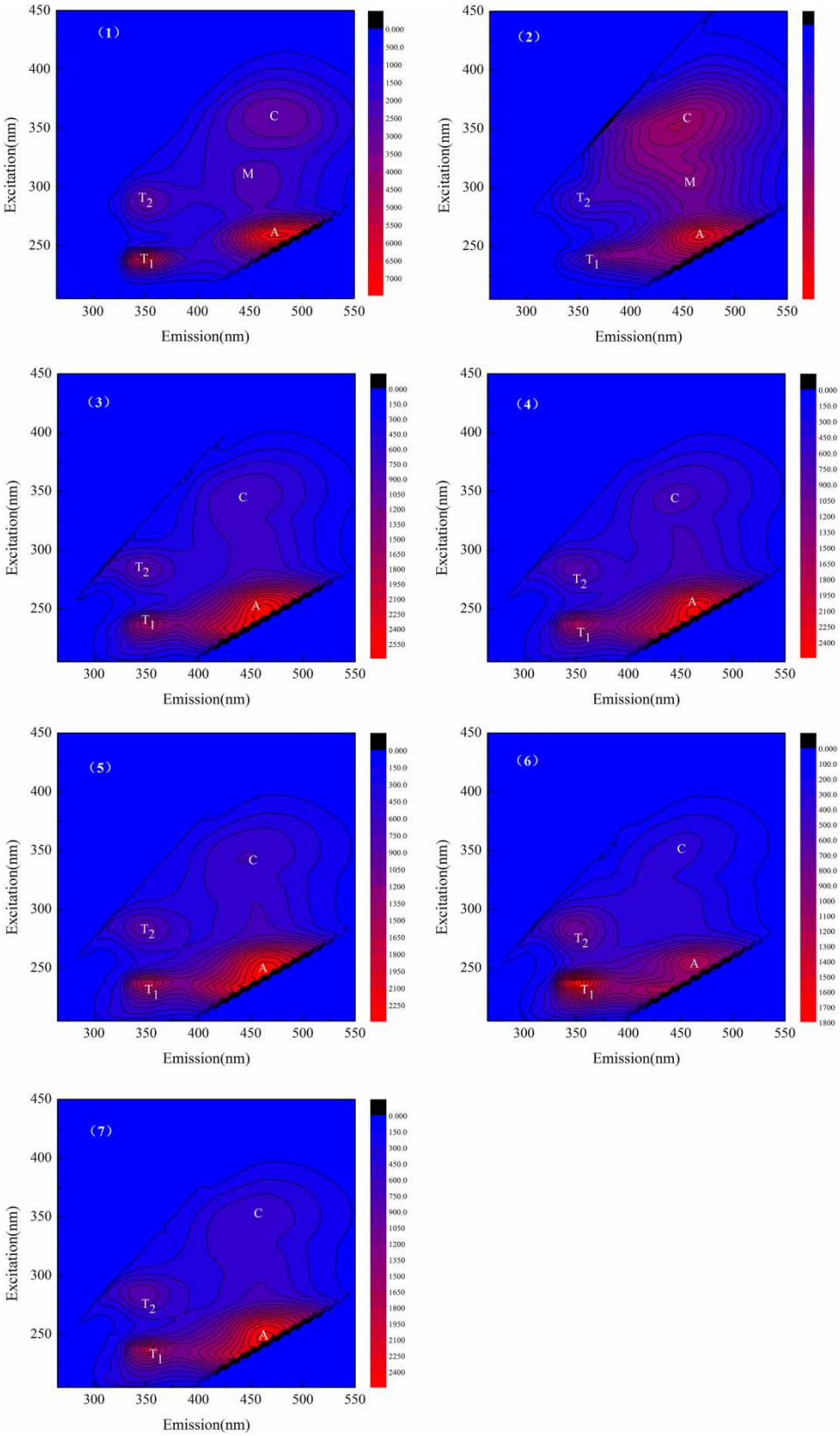

Figure 2 | The EEM spectra of DOM of raw wastewater (1) and at coagulant dosages of 0.1–0.6 g/L (2)–(7).

T_2 decreased obviously during the coagulation process compared with peak T_1 and the fulvic-like peak A. These three peaks were easier to remove by coagulation process, indicating that they were related to some components which have higher molecule size and are hydrophobic (Zhu *et al.* 2014).

EEM PARAFAC components

The traditional peak-picking method based on the maximum intensity and the excitation and emission wavelength of fluorescence peaks was commonly used. But this method may be limited because of peak shifts, overlapping of the fluorescence and interferences of peaks. In contrast, EEM-PARAFAC method could overcome these problems.

Five separate fluorescence components (C1–C5) were identified from samples using the PARAFAC model. Figure 3 shows the fluorescence components, their loadings and the proportional distribution of components. The C1 presented primary and secondary excitation peaks, occurring at 220,260 nm, respectively, with an emission peak centered at 500 nm. It indicated C1 was a combination of peak A and peak M in the traditional peak-picking method. C1 was composed of hydrophilic fractions having a smaller molecular size and was previously identified as UVC humic-like substances (Ishii & Boyer 2012). In this study, the main constituent of C1 was fulvic acid. The component exhibited a broad emission band centered around 480–530 nm suggesting that they contain more conjugated fluorescence molecules (Van Heusden *et al.* 1998).

The C2 had a peak at Ex/Em = 235/350 nm which was identified as xenobiotic organic matter (220–230/340–370 nm). Xenobiotic organic matter like pharmaceuticals, personal care products, and phenolic compounds are kinds of chemical substances that persist in ecosystems and can bioaccumulate throughout the food chain. It was not identified in a natural water body, but has been found in the landfill leachate and sewage sample (Guo *et al.* 2010). In this study, the main resource of C2 was a pharmaceutical synthesis.

The C3 was composed of two excitation maxima at 225 and 250 nm, with an emission peak centered at 470 nm, indicating that it has a high molecular size and was hydrophobic (Lee & Jin 2016). The spectral feature of this peak was classified as UVC humic-like substance, which contains more aromatic (Schulman & Sharma).

The fluorescence maximum of C4 was located at Ex/Em of 280/330 nm. The component was similar to peaks in traditional 'peak T', hence, it was identified as protein-like substance. And it may be associated with the activities of microbial (Fellman *et al.* 2011).

C5 also has two excitation maxima at 215 and 325 nm, with an emission peak centered at 420 nm. It had a broad emission band centered around 360–540 nm and an excitation band centered around 200–350 nm, which was identified as UVC humic-like hydrophobic matter.

The maximum fluorescence intensity of fluorescent components was exported by PARAFAC model, and total relative fluorescence intensity of samples was calculated according to Equation (1). The results are shown in Figure 3. The maximum intensity of five fluorescent components (C1, C2, C3, C4, C5) in raw water were 4.9, 7.8, 11.4, 9.7, 4.87 RU, respectively. The effluent of pharmaceutical wastewater DOM was dominated by C3 (29.5%), C4 (25.0%) and C2 (20.2%). The fulvic acid component C1 accounted for 12.7% of the total fluorescence intensity and humic-like C5 accounted for 12.6%. The positions of the fluorescence maxima of the five components were compared with those previously listed in Table 2.

Removal of fluorescence components during the coagulation process

Coagulation process can be affected by many factors, including DOM, as well as coagulant type and ambient conditions (Kennedy *et al.* 2015). Therefore, the reduction of fluorescence components was investigated to clarify variation in the reduction of DOM. The fluorescence intensity of five components of raw water and of water treated after coagulation is illustrated in Figure 4. As shown in Figure 4, the fluorescence intensity of five components decreased through the coagulation process at PFS dosage of 0.6 g/L and pH 7.0. The removal efficiencies of C1, C2, C3, C4 and C5 were 5.19%, 9.24%, 44.17%, 14.93% and 56.44%, respectively. There is an urgent need to clarify the relationship of DOM and the efficiency of coagulation. For coagulant, PFS was selected because the medium polymeric species was considered the most efficient species for DOM removal (Matilainen *et al.* 2010).

The effect of coagulant dosage on the fluorescent characteristic variations was also investigated. The result is shown in Figure 5.

Coagulation was effective to remove five fluorescence components; with the increase of coagulant dosage, the removal efficiency of fluorescence components was increased, too. When the coagulant dosages were lower than 0.1 g/L, the reduction of all five components were relatively significant; the removal efficiencies were 3.52%, 6.87%, 29.28%, 5.53% and 25.35%, respectively. But the

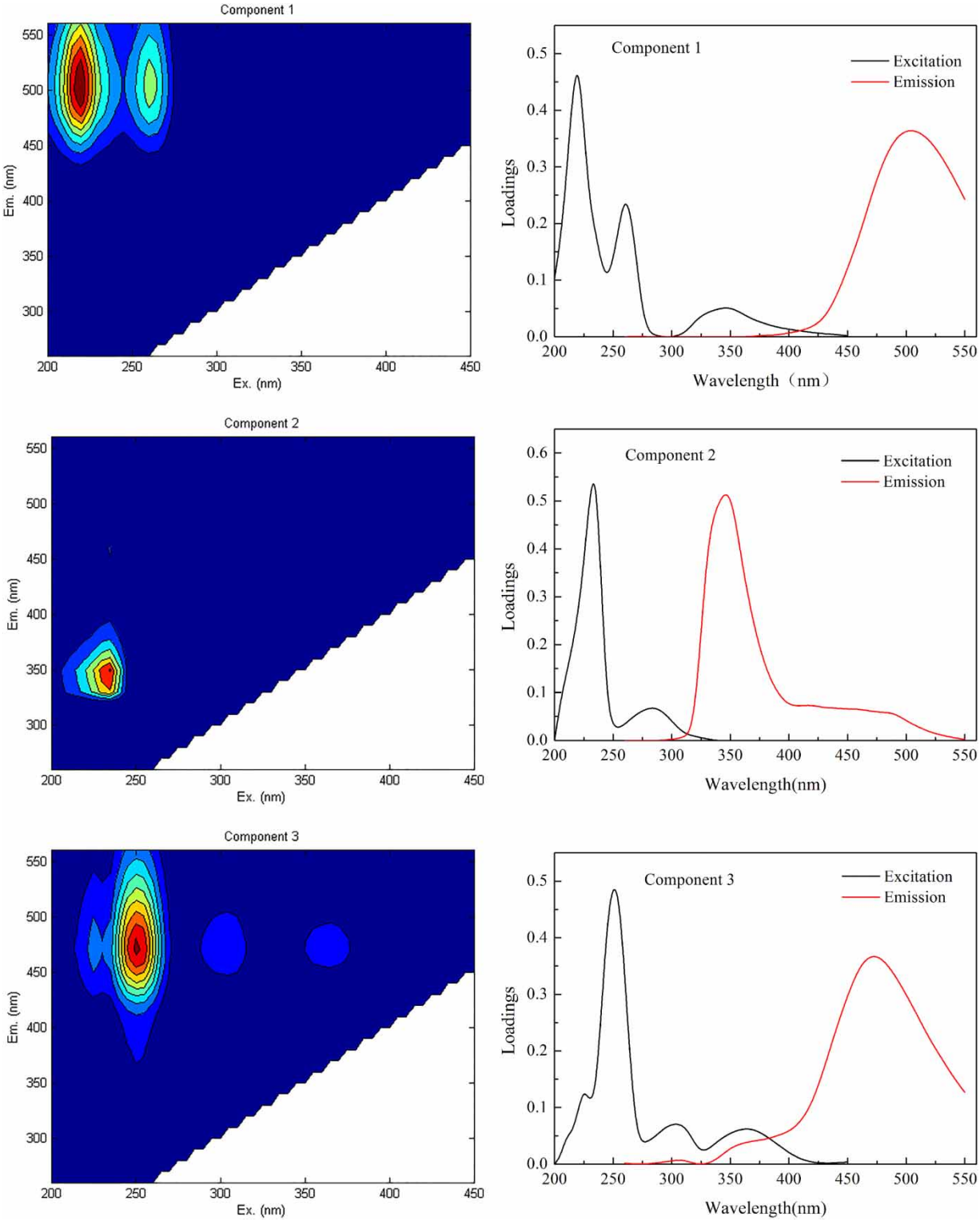

Figure 3 | Five fluorescence components EEM contours, their loadings, and proportional distribution. *(Continued.)*

further increase of coagulant dosage was less effective for removal of C1 and C2, and more effective for C3, C4 and C5. As for C1 and C2, the maximum removal efficiency of these two components was just 5.77% and 11.98% at coagulant dosage of 0.3 and 0.4 g/L, respectively. For C3, C4 and C5, the reduction of this three components were

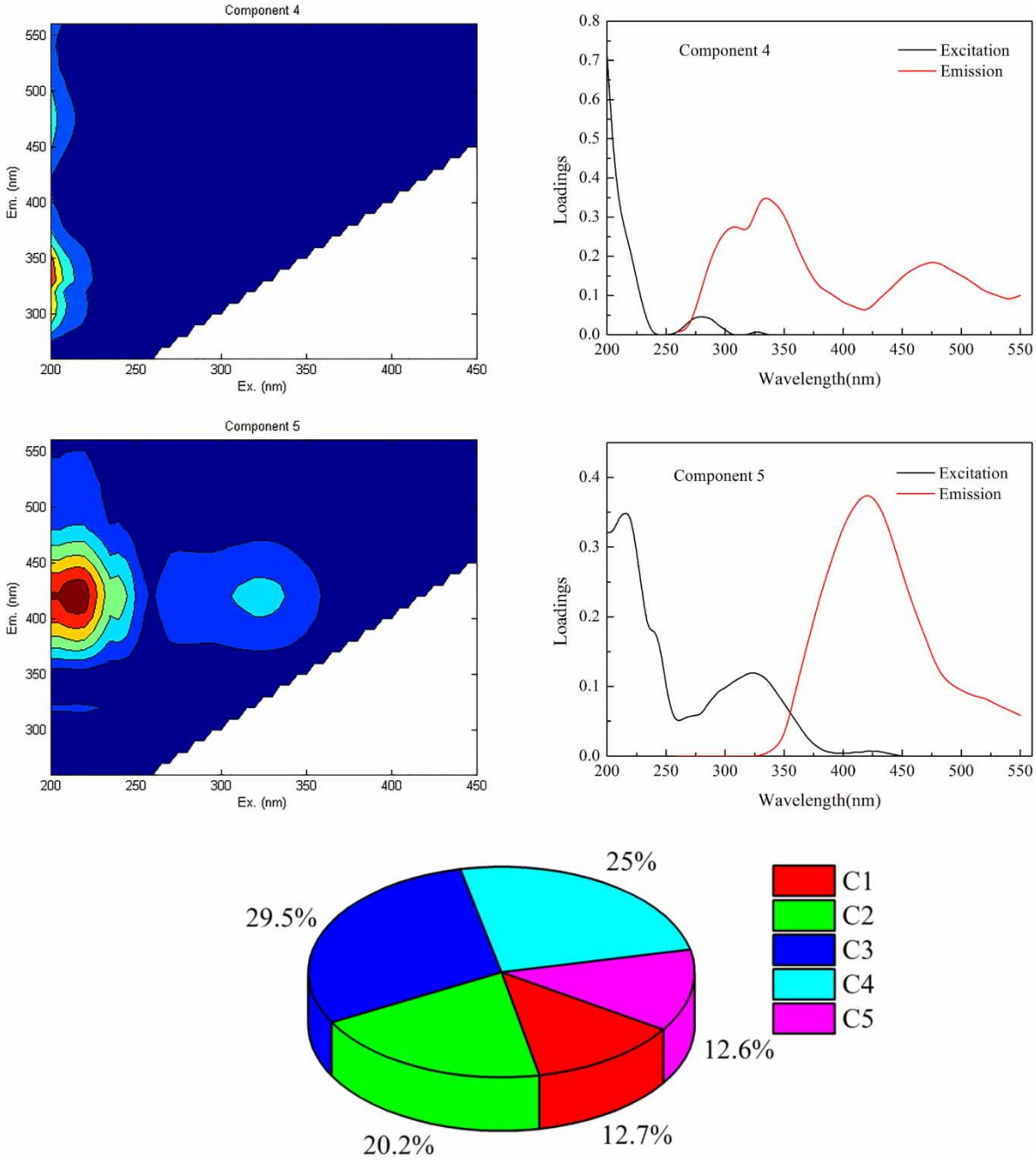

Figure 3 | Continued.

increased with increase of coagulant dosage, as the maximum removal efficiencies were 44.17%, 14.93%, 56.44%, respectively.

These phenomena were in accordance with the previous study; according to the previous study, hydrophobic fractions and high molecular mass compounds were easier to remove than hydrophilic fractions and low molecular mass compounds (Zhu *et al.* 2014). In this paper, C3 and C5 were identified as hydrophobic humic-like substances while C5 has a larger molecular size, so C5 was much easier to remove. C2 was identified as a xenobiotic organic matter that consists of aromatic organic or volatile organic compounds; these compounds are usually hydrophobic and have a larger molecular size. C1 was associated with a fulvic-like matter that has a smaller molecular size. So the order of effectiveness was: C5 (humic-like) > C3

Table 2 | Positions of the fluorescence maxima of the five components

Fluorescence components	Peak position λEx/Em(nm)	Description	Previous study λEx/Em(nm)	Reference
C1	220(260)/500	UVC fulvic-like	<230–260/400–500	Ishii & Boyer (2012)
C2	235/350	Xenobiotic-like substance	230/345	Guo *et al.* (2010)
			220–230/340–370	Baker & Curry (2004)
C3	225(250)/470	UVC humic-like	260/380–460	Stedmon *et al.* (2003)
C4	280/330	Protein-like	280/350	Zhang *et al.* (2016)
			230(280)/330	Lv *et al.* (2014)
			220(275)/339	Guo *et al.* (2010)
C5	215(325)/420	UVC humic-like	230(340)/422	Guo *et al.* (2010)
			230(325)/416	Stedmon *et al.* (2003)
			250(320)/420	Guo *et al.* (2010)

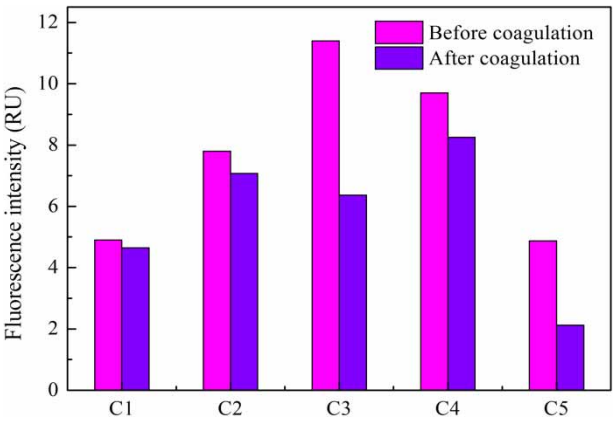

Figure 4 | The reduction of fluorescence components through the coagulation process.

(humic-like) > C4 (protein-like) > C2 (xenobiotic organic matter) > C1 (fulvic-like).

We have noticed that the changing trends in the reduction of C3 and C5 were similar to that of TOC and UV_{254} when compared with Figure 1. It indicated that there may be a correlation between DOM fractions with TOC, UV_{254}. Research has found that molecular size was associated with fluorescence pattern (Wu *et al.* 2003). So investigate the variations of fluorescence components during the coagulation process will be helpful to understand the coagulation better.

Soluble residual iron concentration

Researchers have been suggested the necessity to clarified the concentration of residual iron after coagulation process (Figure 6). On the one hand, the metal ion may have a potential risk to human health and organism (Zhu *et al.* 2014); on the other hand, it is a way to ascertain the treatment efficiency. In this study, the soluble residual iron concentration was considered not only because of these two reasons, but also because iron would enhance or quench the fluorescence intensity of DOM (McIntyre &

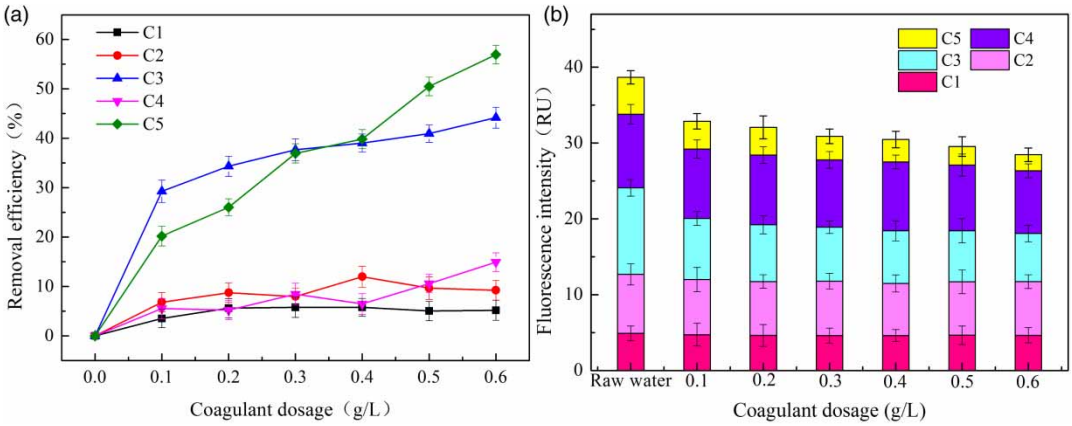

Figure 5 | Effect of coagulant dosage on the removal efficiency of fluorescence component (a) and fluorescence intensity (b).

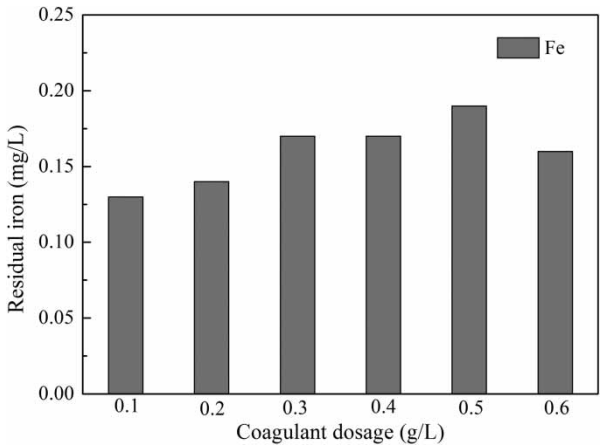

Figure 6 | Residual iron under the investigation of coagulant dosage effect.

Guéguen 2013). The results are shown in Figure 7. In general, residual iron concentration was lower than 0.20 mg/L; this value was very close to the level of natural water (Ishii & Boyer 2012). Different coagulant dosage does not affect the concentration significantly with the maximum concentrations of iron residual being 0.19 mg/L. The lower concentration indicated that the analysis of DOM and its changing trend was reliable.

Principal component analysis

In this paper, PCA produced two principal components with the total variance accounted for 95.3%. Factor 1 accounted for 83.4% and 11.9% for factor 2. The loadings of the factors are shown in Figure 7. Research has found there is a relationship between fluorescence and chemical parameters (Lv *et al.* 2014; Yu *et al.* 2015). For the factors, the absolute value of the loadings higher than 0.6 was identified as a key factor. According to Figure 7, factor 1 had strong loadings on C3, C4, C5, TOC and UV_{254} indicated that C3, C4, C5 showed remarkable correlations with TOC and UV_{254}. Fluorescence components (C1, C2) and chemical parameters (turbidity, NH_4^+-N) were clustered into a group, but the absolute value of the loadings on factor 2 was lower than 0.6 suggesting that the correlation between these factors were insignificant.

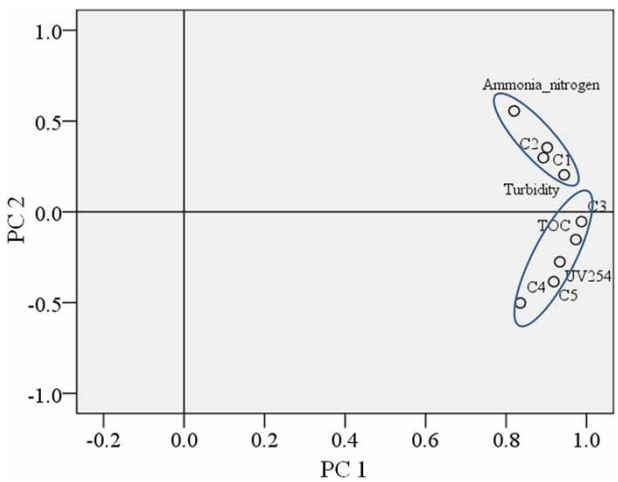

Figure 7 | Loadings plot of the factors to the reduction of fluorescence components and chemical parameters.

The correlations of fluorescence components (C3, C4, C5) and chemical parameters (TOC, UV_{254}) were studied in further study, and results showed that the reduction of TOC and UV_{254} was related to the decrease of C3, C4, C5. The R^2 of these three components were 0.875, 0.689 and 0.883, respectively, and the R^2 of C3 and C5 were higher than C4, it suggested that C3 and C5 were better indicators of TOC than C4. While in the investigation of correlations between fluorescence components (C3, C4, C5) and UV_{254}, the R^2 were 0.785, 0.723 and 0.887, respectively, and the R^2 of C5 was higher than C3 and C4, suggesting that C5 was a better indicator of UV_{254} than C3 and C4. Generally, the R^2 of C4 was lower than C3 and C5, which may be because C4 was a kind of protein-like material, which has much smaller size, and the ability of coagulation process to remove C4 was limited.

CONCLUSIONS

The coagulation process was an effective post-treatment method for the effluent of pharmaceutical wastewater with the most advantageous PFS dosage of 0.5 g/L. Five fluorescence components were identified by using EEMs-PARAFAC. C3 and C5 were identified as hydrophobic humic-like substances while C2 was identified as a xenobiotic organic matter. C1 was identified as fulvic-like matter while C4 was a kind of protein-like material. C3, C4 and C5 were easily removed by the coagulation process while C1 and C2 were difficult to remove. It was shown that the hydrophilic materials were easier to reduce than the hydrophobic matter, and the component with a larger molecule size was easier to remove than that of a smaller molecule size. PCA produced two principal components, and a significantly high correlation was observed between the removal efficiency of fluorescence components (C3, C4, C5) and the removal efficiency of TOC, UV_{254}. The results demonstrated that, in the evaluation and monitoring of pharmaceutical wastewater in the coagulation process, DOM was a feasible indicator and EEMs-PARAFAC was a reliable tool.

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