RESEARCH ARTICLE

Characterization of fluorescent-dissolved organic matter and identification of specific fluorophores in textile effluents

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Abstract This study focused on the characterization of fluorescent-dissolved organic matter and identification of specific fluorophores in textile effluents. Samples from different textile wastewater treatment plants were characterized by high-performance liquid chromatography and size exclusion chromatography as well as fluorescence excitation-emission matrix spectra. Despite the highly heterogeneous textile effluents, the fluorescent components and their physicochemical properties were found relatively invariable, which is beneficial for the combination of biological and physicochemical treatment processes. The humic-like substance with triple-excitation peaks (excitation (Ex) 250, 310, 365/emission (Em) 460 nm) presented as the specific fluorescence indicator in textile effluents. It was also the major contributor to UV absorbance at 254 nm and resulted in the brown color of biologically treated textile effluents. By spectral comparison, the specific fluorophore in textile effluents could be attributed to the intermediate structure of azo dyes 1-amino-2-naphthol, which was transferred into the special humic-like substances during biological treatment.

Keywords Azo dyes · Fluorescence excitation-emission matrix · 1-Amino-2-naphthol · Soluble microbial products · Textile effluent

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Introduction

The textile industry consumes substantial water and generates huge quantities of hazardous wastewater with high color and complex chemical substances (Robinson et al. 2001; Verma et al. 2012). Improper discharge of dye wastewater into water bodies is aesthetically unpleasant and could destroy the aqueous ecosystems by light attenuation and toxic effects (Sarayu and Sandhya 2012). Thus various methods have been developed to remove synthetic dyes from textile wastewater before their discharge to the environment. However, biological treatment is still the most attractive method, because it is eco-friendly and cost-competitive (Saratale et al. 2011; van der Zee and Villaverde 2005).

In the last decades, numerous studies covering biodegradation or biotreatment of various dye compounds have been performed (Saratale et al. 2011; Sarayu and Sandhya 2012). Many of these studies were conducted with selected dyes in lab and focused on their decoloration and detoxification. However, in biologically treated textile effluents, soluble microbial products (SMPs) can be a predominant component of dissolved organic matter (DOM) besides the residual dyes and other synthetic chemicals. SMPs are defined as the pool of organic compounds mainly including polysaccharides, proteins, and humic-like substances, which are released from substrate metabolism and biomass decay (Barker and Stuckey 1999). It has been shown that the formation of SMPs increased under stressful conditions, e.g., extreme temperature change, high salinity, and presence of toxic compounds (Aquino and Stuckey 2004; Wang and Zhang 2010). With the tightening governmental legislation, the combination of biological and physicochemical treatment processes seems to be the most feasible solution (Bafana et al. 2011). Therefore, investigation of the components and properties of DOM in biologically treated textile effluents is quite necessary for the development of advanced treatment processes.

Fluorescence excitation-emission matrix (EEM) spectroscopy has been extensively used for characterization of DOM in natural and engineered systems (Ishii and Boyer 2012). Due to its rapid, selective, and sensitive performance, EEM can provide a useful tool to estimate contamination of river, ground water, and drinking water systems (Baker 2001; Dahm et al. 2013; Goldman et al. 2012; Hambly et al. 2010; Phong et al. 2014). In the past decades, a series of methods have been developed for the interpretation of EEM, such as fluorescence regional integration (Chen et al. 2003) and parallel factor analysis (PARAFAC) (Stedmon and Bro 2008). However, most of these interpretation methods are statistically based on the EEM data set itself, which could not reflect the variety of fluorescent species with similar fluorescence (Li et al. 2013, 2014). Fluorescence EEM and liquid chromatography have also been used together for the characterization of DOM or SMPs in biological treatment (Filloux et al. 2012; Wang and Zhang 2010). Recently, we demonstrated that high-performance liquid chromatography or size-exclusion chromatography (HPLC/HPSEC) with multiexcitation/emission scan could directly relate the physicochemical properties (i.e., polarity or molecular weight) of fluorescent DOM species to their fingerprints in EEM (Li et al. 2013). EEM spectra of the effluent from a wastewater treatment plant treating a mixture of dye and municipal wastewater were previously demonstrated with the triple excitation peaks at emission (Em) 460 nm (Li et al. 2013). However, the reoccurring EEM spectra of humic-like substances are generally of dual-excitation peaks, referring to the published literature (Baker 2002; Hambly et al. 2010; He et al. 2011; Ishii and Boyer 2012; Murphy et al. 2011; Westerhoff et al. 2001). Therefore, whether the special humic-like substance with triple excitation peaks is prevalent in effluents from textile industry remains very attractive to be explored. If so, the special humic-like substance can act as the specific indicator and then its critical fluorescent structure should be further explored.

Because of the variety of dyestuffs depending upon the production schedule, concentration, and composition of textile effluents vary from mill to mill. This study did not consider assessing the treatability of various synthetic dyes. It rather focused on the identification and characterization of fluorescent DOM and specific fluorophores in the biologically treated textile effluents. To this end, (1) effluents from different wastewater treatment plants were characterized by HPLC/HPSEC analysis as well as EEM spectra; (2) the fluorescent humic-like substance which might act as the specific indicator was isolated and its critical fluorescent structure was also explored. The results may provide a novel insight on the characteristics of fluorescent DOM in biologically treated textile effluents, which is meaningful for the frequent monitoring of textile effluents and the development of advanced treatment processes.

Material and methods

Samples and chemicals

Rather than synthetic dye wastewater in lab, it is more relevant to research on real-field textile effluents. Samples of the biologically treated textile effluents were collected from eight wastewater treatment plants (defined as the acronym of their names) situated in four cities of China. Sampling campaigns ranged from summer 2010 to spring 2014, from Eastern China to Central China. The detailed information is given in Table 1. The wastewater samples were transported back to lab in clean polyethylene bottles and filtered through 0.45 μm acetate fiber membrane. The pretreated samples were stored at 4 °C and analyzed within 3 days in each sampling campaign.

A series of dyestuffs and dye intermediates were used in this study to explore the possible origin of fluorescent structure. Such analytical reagents are as follows: Acid Green 9 (CAS 4857-81-2), Acid Yellow 23 (CAS 1934-21-0), Methylene Blue (CAS 61-73-4), Crystal Violet (CAS 548-62-9), Reactive Blue 4 (CAS 13324-20-4), CongoRed (CAS 573-58-0), Orange G (CAS 1936-15-8), 1-amino-2-naphthol-4-sulfonic acid (CAS 116-63-2), and 8-amino-1-naphthol-3, 6-disulfonic acid monosodium salt (CAS 5460-09-3).

EEM fluorescence scan

EEM fluorescence spectra were obtained with operation parameters as previously described (Li et al. 2013). The scanning field was set at excitation from 200 to 400 nm and emission from 280 to 550 nm with 5 and 1 nm sampling interval on excitation (Ex) and emission (Em) modes, respectively. Samples or chemical solutions were scanned with corrected spectra and shuttle control on, and fluorescence intensities were presented in color variations without normalization, since EEM was not used for quantitative analysis in this study.

HPLC/HPSEC-DAD-FLD analysis

HPLC equipped with Eclipse XDB-C18 column (150× 4.6 mm, 5 μm) was applied. The mobile phase was modified as the mixture of ammonium acetate solution (10 mmol/L) and acetonitrile at a flow rate of 1 mL/min, and the gradient elution progress started at 10 % acetonitrile linearly to 90 % acetonitrile in 10 min. The HPSEC (Agilent 1200 series) application as well as molecular weight calibration was according to our previously established methods and the mobile phase was ammonium acetate solution (10 mmol/L) at a flow rate of 1 mL/min (Li et al. 2013).

Table 1 Information of the investigated textile wastewater treatment plants

Name	Influent Sources	Treatment Capacity	Treatment Process	Location
TQ	Wastewater of TQ Dyeing & Weaving Co., Ltd	~4,000 m³/day	Anaerobic-Aerobic-Coagulation	Changzhou, China
LS	Wastewater of LS Dyeing & Weaving Co., Ltd	~10,000 m³/day	Anaerobic-Aerobic-Coagulation	Changzhou, China
QY	Mixture of industrial and municipal wastewater in the industrial park including five Dyeing & Weaving Co., Ltd.	~10,000 m³/day	Anaerobic-Aerobic-Coagulation	Changzhou, China
FZY	Mainly wastewater from the industrial park of dyeing and weaving	~20,000 m³/day	Coagulation-Anaerobic-Aerobic-Coagulation	Zhengzhou, China
XB	Mixture of industrial and municipal wastewater in an industrial park with certain dyeing corporations included.	~20,000 m³/day	Anaerobic-Aerobic-Coagulation	Wuxi, China
JB	Mixture of industrial and municipal wastewater in an industrial park with dyeing corporations included.	~100,000 m³/day	Anaerobic-Aerobic-Coagulation	Changzhou, China
LF	Wastewater of dyeing & weaving Co., Ltd	~20,000 m³/day	Anaerobic-Aerobic-Coagulation	Nantong, China
RG	Mixture of industrial and municipal wastewater in a textile industry park with certain dyeing corporations included.	~20,000 m³/day	Anaerobic-Aerobic-Coagulation	Nantong, China

Both HPLC and HPSEC systems were equipped with diode array detector (DAD) and fluorescence detector (FLD) in this study. DAD with multiabsorption scan was conducted from 200 to 300 nm. In tandem with DAD, FLD was conducted with multiexcitation scan or multiemission scan for the same sample. According to results of EEM, HPLC with multiexcitation scan was set up at Em=340/Ex=220~300 nm for protein-like components and Em=460/Ex=230~400 nm for humic-like components. Additionally, humic fractions collected from HPLC were lyophilized, redissolved and then analyzed by EEM. HPLC/HPSEC multiemission scan was set up as Ex=240/Em=300~500 nm. Because the HPLC/HPSEC multiexcitation/emission scan was established during the sampling campaigns, only the samples on the date July 6, 2012 have been analyzed by HPLC/HPSEC.

Results and discussion

EEM fluorescence spectra

As well known, EEM spectra of DOM are overlapped spectra of heterogeneous species with different fluorescence efficiency. And the fluorescence intensity could also be influenced by the inner-filtration effect. Therefore, the analysis of EEM spectra in this study focused on the qualitative analysis (i.e., peaks' locations) rather than the quantitative analysis (i.e., peaks' intensities). The typical EEM spectra are shown in Fig. 1, and EEM spectra of other samples could be found in Supplementary Material Fig. A.1. Generally, fluorescence peaks with Em <380 nm represent protein-like fluorescence, and fluorescence peaks with Em >380 nm represent humic-like fluorescence (Chen et al. 2003). It is highly attractive that all the available EEM spectra exhibited five fluorescence peaks with similar locations, in which two protein-like peaks are roughly at Ex230/Em340 and Ex280/Em325 nm, and the other three humic-like peaks are roughly at Ex250/Em460, Ex310/Em460, and Ex365/Em460 nm. The different peaks at the similar emission wavelength have been previously verified as the results of fluorophores' multiexcitation (Li et al. 2013). The HPLC Excitation-Time-Maps further verified this conclusion (Supplementary Material Figs. A.2 and A.3). The phenomena of multiexcitation peaks can be elucidated by the fluorescence process that electrons can be excited to different electronic and vibrational levels while emission occurs predominantly from the lowest singlet state because of rapid relaxation (Lakowicz 2006).

It is noteworthy that the triple-excitation peaks at Em 460 nm are very special, because most of humic substances reoccur with dual-excitation peaks at Em 400~500 nm (http://
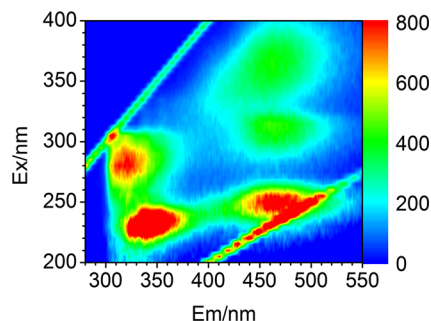

Fig. 1 Typical EEM spectra of effluents from textile wastewater treatment plants

www.humicsubstances.org/spectra.html). As shown in Table 1, the investigated wastewater treatment plants were highly diverse in treatment capacity, but the common characteristic was that all the influents consisted of dye wastewater from textile industry. The sampling campaigns were conducted on a large scale of time and space. Since the triple-excitation peaks at Em 460 nm were extensively observed in textile effluents, such fluorescence fingerprint can be proposed as a potential source-specific indicator for textile industry. Compared with previous EEM applications (Baker 2001; Dahm et al. 2013), no further quantitative analysis is needed because of its significant fluorescence characteristics, but it is necessary to identify the special fluorophores in textile effluents.

HPLC/HPSEC fingerprints

Identification of fluorescent DOM

Because of the multiexcitation phenomena of fluorophores, the Emission-Time-Maps scanned at the fixed excitation wavelength (Ex 240 nm) can provide abundant information to reflect the diversity and specificity of fluorescent DOM (Li et al. 2013). The HPLC and HPSEC Emission-Time-Maps of TQ and QY effluents are shown in Figs. 2 and 3, in which the Em-axis denotes the emission wavelength, the time-axis represents the elution time and fluorescence intensities are presented in color variations. Similarly, the fluorescence peaks with higher emission wavelength (e.g., Em >380 nm) represent the humic-like substances while the fluorescence peaks with lower emission wavelength (e.g., Em <380 nm) represent the protein-like substances.

For humic-like substances, there were two fluorescence components with different emission spectra. Herein, it can be scrutinized in HPLC Emission-Time Maps (Fig. 2a, b) together with related Excitation-Time Maps (Supplementary Material Fig. A.3), peak A was the humic-like component
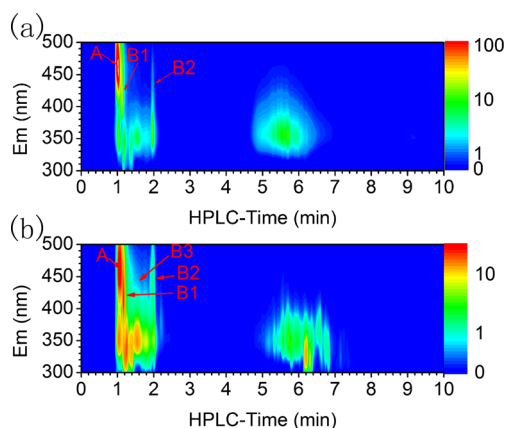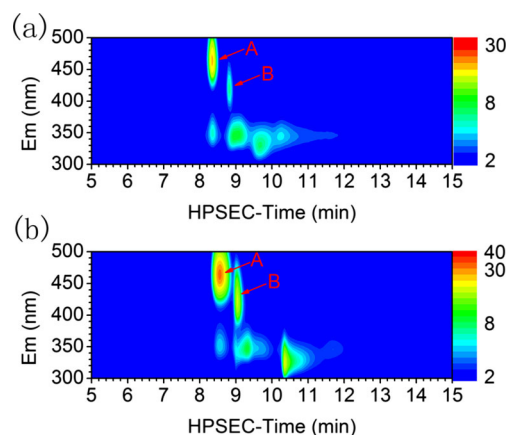

Fig. 3 HPSEC fluorescence Emission-Time-Maps at Ex 240 nm: **a** TQ and **b** QY

with triple-excitation peaks at Em 460 nm (HS-Em460-Ex3), while peaks B1, B2 and B3 were another humic-like component with dual-excitation peaks at Em ~430 nm (HS-Em430-Ex2). Inferred from the emission wavelength, peak A and peak B in HPSEC Emission-Time Maps (Fig. 3a, b) corresponded to humic-like components HS-Em460-Ex3 and HS-Em430-Ex2, respectively. That is to say that the humic-like component HS-Em430-Ex2 consisted of different species with similar molecular size but different polarity. It is conceivable that the fluorescence of HS-Em430-Ex2 was overwhelmed by that of HS-Em460-Ex3 in EEM spectra.

For protein-like substances, there were much more species with varying emission wavelengths. It should be noted that the fluorescence of proteins is mainly based on tyrosine or tryptophan, whereas the critical fluorescent structure of tryptophan is actually the aromatic amine structure (Li et al. 2013). In the biologically treated textile effluents, aromatic amines might exist due to the degradation of azo dyes (Saratale et al. 2011; van der Zee and Villaverde 2005), which will exhibit similar fluorescence spectra to that of proteins. Hereinafter, the protein-like fluorescence might be attributed to residual aromatic amines as well as fluorescent proteins and peptides.

Polarity and molecular weight

With the reverse phase column, the relatively hydrophilic components will be eluted with shorter retention time (Wu et al. 2003). As shown in the HPLC Emission-Time-Maps (Fig. 2a, b), the protein-like substances were separated into two clusters according to their difference in polarity: relatively hydrophilic with elution time from 1 to 2 min and relatively hydrophobic with elution time from 5 to 7 min; while all the humic substances were quickly eluted, indicating they are relatively hydrophilic at the mobile phase condition (pH=7). Furthermore, the HS-Em460-Ex3 component (peak A) was a
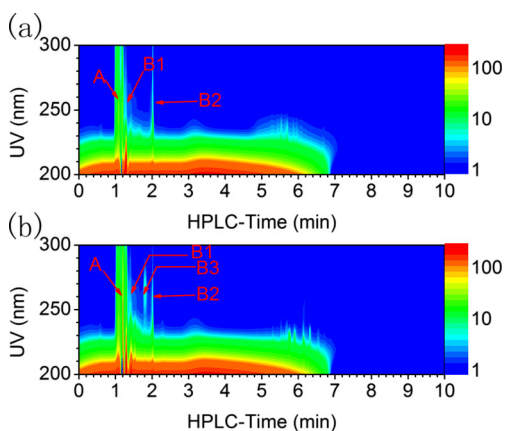

Fig. 2 HPLC fluorescence Emission-Time-Maps at Ex 240 nm: **a** TQ and **b** QY

Fig. 4 HPLC DAD spectra (UV 200 to 300 nm) of effluents: **a** TQ and **b** QY

little more hydrophilic than HS-Em430-Ex2 component (peaks B1, B2, and B3).

With the size exclusion column, DOM species with shorter retention times are of higher apparent molecular weight (MW) (Wu et al. 2003). As shown in Fig. 3a, b, the apparent MW of the HS-Em460-Ex3 component (peak A, MW approximately between 21.3 and 12.3 kDa) was larger than that of HS-Em430-Ex2 component (peak B, MW approximately between 12.3 and 7.8 kDa). In both HPLC and HPSEC, humic-like substances were generally eluted with protein-like species simultaneously. Despite the heterogeneity of their apparent MW, the protein-like substances were generally eluted into four major clusters. The apparent MWs of protein-like species eluted later than 11 min were lower than 1.5 kDa, which might be peptides, tryptophan, tyrosine, and also aromatic amines derived from dye biodegradation.

Knowledge of physicochemical properties of such fluorescent DOM in textile effluents is meaningful to understand their behavior in advanced treatment processes, such as coagulation, anion exchange, and also membrane filtration. It has to be emphasized that although the textile effluents were highly heterogeneous, the HPLC/HPSEC fingerprints of the investigated TQ and QY effluents were relatively similar, indicating the similar components and properties of fluorescent DOM. The other available chromatography fingerprints of other textile effluents provided more evidences (Supplementary Material Figs. A.4 and A.5).

Relationships between UV absorbance and fluorescence spectra

The UV absorbance at 254 nm (UV_{254}) is a widely used proxy to reflect the aromaticity of DOM (Dilling and Kaiser 2002), and the liquid chromatography UV absorbance spectra have also been applied to display the variation of DOM composition (Liu et al. 2010). To explore the inherent relationships between UV absorbance species and fluorescent species, the HPLC UV absorbance spectra (200~300 nm) were obtained in tandem with fluorescence scan for TQ and QY samples, shown in Fig. 4. Compared with related HPLC multiemission fluorescence spectra (Fig. 2a vs 4a; Fig. 2b vs 4b), the major contributors for UV_{254} absorbance were recognized as HS-Em460-Ex3>HS-Em430-Ex2>protein-like components. Notice that the investigated textile effluents were generally in yellowish-brown color, which should be concerned during the advanced treatment process (Supplementary Material Fig. A.6). Verified by the HPLC fractions, the specific HS-
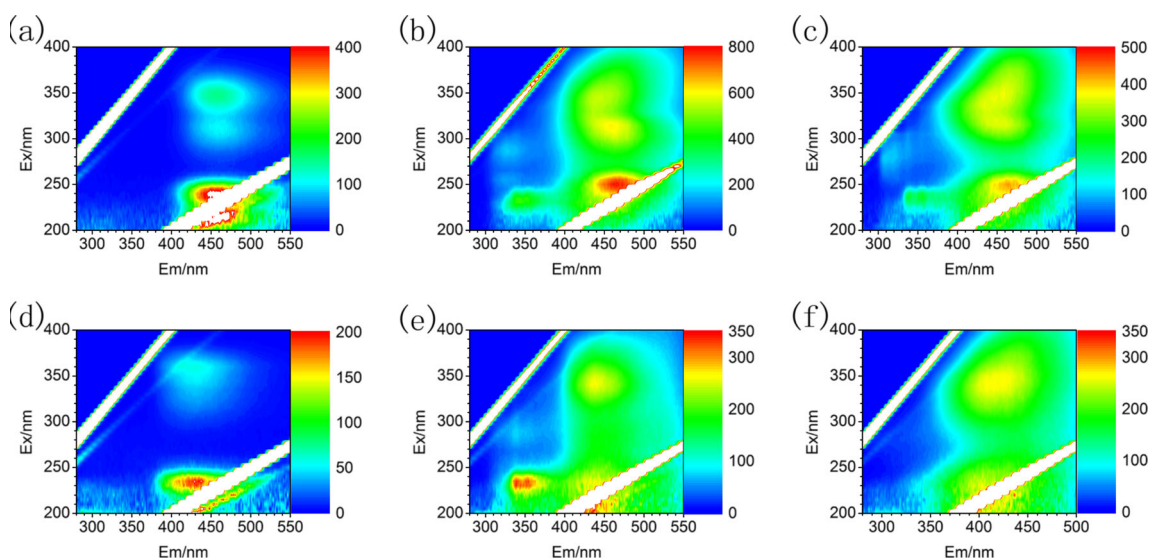

Fig. 5 EEM spectra of aminonaphthol moieties and humic substances collected from HPLC: **a** 1-amino-2-naphthol-4-sulfonic acid, **b** peak A from TQ effluent, **c** peak A from QY effluents, **d** 8-amino-1-naphthol-3,6-disulfonic acid, **e** peak B2 from TQ effluent, and **f** peak B2 from QY effluents

Em460-Ex3 component also mainly contributed to the brown color (Supplementary Material Fig. A.6).

Identification of critical fluorescence structure

Identification of the critical fluorescent structure is meaningful for frequent monitoring of textile effluents with EEM. Based on the similarities of excitation/emission properties, quinone-like moieties were proposed as the possible fluorescent structure of natural humic substances (Cory and McKnight 2005). In this study, it is also feasible to explore the critical structure by spectral comparison with possible dyestuffs.

After a series of fluorescence tests (Supplementary Material Fig. A.7), only Orange-G was found with similar EEM spectra to that of HS-Em460-Ex3. However, it cannot well elucidate the prevalence of HS-Em460-Ex3 when there was actually little Orange-G in influent according to the production schedule of TQ plant. Notice that Orange-G is a kind of azo dyes, and azo dyes are the most widely used dyestuffs, making them the most common synthetic dyes released into the wastewater (Saratale et al. 2011). Removal of azo dyes is based on anaerobic treatment for the reductive cleavage of the azo linkages in combination with aerobic treatment for further degradation of the products from azo dye cleavage, which are aromatic amines (Bafana et al. 2011; Sarayu and Sandhya 2012). Inferred from the possible bond cleavage and fluorescence principle, the chemical compound 1-amino-2-naphthol-4-sulfonic acid, a common intermediate for synthesis of Orange-G and other azo dyes, was selected for fluorescence determination. As shown in Fig. 5a, its EEM spectra exhibited triple-excitation peaks Ex240/Em460, Ex310/Em460, and Ex355/Em460, coinciding well with the HS-Em460-Ex3 fractions from textile effluents (Fig. 5b, c). Both hydroxyl and amino-group are electron-donating groups, and the arrangement of such groups on the aromatic naphthalene ring might affect the fluorescence spectra. Herein, another intermediate H acid (8-amino-1-naphthol-3, 6-disulfonic acid monosodium salt) was also conducted with fluorescence determination. However, dual peaks occurred at Ex 240, 350/Em430 (Fig. 5d), which are similar to those of the HS-Em430-Ex2 fractions (Fig. 5e, f) and other humic substances in literature (Westerhoff et al. 2001). Therefore, the fluorescent structure of the specific indicator in textile effluents can be conservatively attributed to 1-amino-2-naphthol structure.

The results further indicate that a large amount of 1-amino-2-naphthol moieties could not be well biodegraded and would be transferred into the humic-like substances. In terms of the brown color and potential toxic effect, removal of the fluorescent DOM from textile effluents, especially the humic-like substances containing 1-amino-2-naphthol moieties, should be concerned in the development of advanced treatment process.

Conclusions

The HPLC and HPSEC fingerprints showed that the fluorescent DOM species and their physiochemical properties were relatively invariable across the investigated textile effluents, which is favorable for the combination of biological and physiochemical techniques. The humic-like fraction HS-Em460-Ex3 with triple-excitation peaks at (Ex 250, 310, 365/Em 460 nm) was proposed as the specific fluorescence indicator for textile effluents. By spectral comparison, its critical fluorescence structure was found to be the 1-amino-2-naphthol. The HS-Em460-Ex3 fraction also contributed to the major UV_{254} absorbance and resulted in the yellowish-brown color in biologically treated textile effluents. Thus the component HS-Em460-Ex3 should be of great concern in advanced treatment process.

References

Aquino SF, Stuckey DC (2004) Soluble microbial products formation in anaerobic chemostats in the presence of toxic compounds. Water Res 38(2):255–266

Bafana A, Devi SS, Chakrabarti T (2011) Azo dyes: past, present and the future. Environ Rev 19:350–371

Baker A (2001) Fluorescence excitation-emission matrix characterization of some sewage-impacted rivers. Environ Sci Technol 35(5):948–953

Baker A (2002) Fluorescence excitation-emission matrix characterization of river waters impacted by a tissue mill effluent. Environ Sci Technol 36(7):1377–1382

Barker DJ, Stuckey DC (1999) A review of soluble microbial products (SMP) in wastewater treatment systems. Water Res 33(14):3063–3082

Chen W, Westerhoff P, Leenheer JA, Booksh K (2003) Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. Environ Sci Technol 37(24):5701–5710

Cory RM, McKnight DM (2005) Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. Environ Sci Technol 39(21):8142–8149

Dahm KG, Van Straaten CM, Munakata-Marr J, Drewes JE (2013) Identifying well contamination through the use of 3-D fluorescence spectroscopy to classify coalbed methane produced water. Environ Sci Technol 47(1):649–656

Dilling J, Kaiser K (2002) Estimation of the hydrophobic fraction of dissolved organic matter in water samples using UV photometry. Water Res 36(20):5037–5044

Filloux E, Labanowski J, Croue JP (2012) Understanding the fouling of UF/MF hollow fibres of biologically treated wastewaters using advanced EfOM characterization and statistical tools. Bioresour Technol 118:460–468

Goldman JH, Rounds SA, Needoba JA (2012) Applications of fluorescence spectroscopy for predicting percent wastewater in an urban stream. Environ Sci Technol 46(8):4374–4381

Hambly AC, Henderson RK, Storey MV, Baker A, Stuetz RM, Khan SJ (2010) Fluorescence monitoring at a recycled water treatment plant and associated dual distribution system – implications for cross-connection detection. Water Res 44(18):5323–5333

He X, Xi B, Wei Z, Guo X, Li M, An D, Liu H (2011) Spectroscopic characterization of water extractable organic matter during composting of municipal solid waste. Chemosphere 82(4):541–548

Ishii SKL, Boyer TH (2012) Behavior of reoccurring PARAFAC components in fluorescent dissolved organic matter in natural and engineered systems: a critical review. Environ Sci Technol 46(4):2006–2017

Lakowicz JR (2006) Principles of fluorescence spectroscopy. Springer Science, New York, pp 5–7

Li WT, Xu ZX, Li AM, Wu W, Zhou Q, Wang JN (2013) HPLC/HPSEC-FLD with multi-excitation/emission scan for EEM interpretation and dissolved organic matter analysis. Water Res 47(3):1246–1256

Li W-T, Chen S-Y, Xu Z-X, Li Y, Shuang C-D, Li A-M (2014) Characterization of dissolved organic matter in municipal wastewater using fluorescence PARAFAC analysis and chromatography multi-excitation/emission scan: a comparative study. Environ Sci Technol 48(5):2603–2609

Liu S, Lim M, Fabris R, Chow CWK, Drikas M, Korshin G, Amal R (2010) Multi-wavelength spectroscopic and chromatography study on the photocatalytic oxidation of natural organic matter. Water Res 44(8):2525–2532

Murphy KR, Hambly A, Singh S, Henderson RK, Baker A, Stuetz R, Khan SJ (2011) Organic matter fluorescence in municipal water recycling schemes: toward a unified PARAFAC model. Environ Sci Technol 45(7):2909–2916

Phong D, Lee Y, Shin K-H, Hur J (2014) Spatial variability in chromophoric dissolved organic matter for an artificial coastal lake (Shiwha) and the upstream catchments at two different seasons. Environ Sci Pollut Res. doi:10.1007/s11356-014-2704-3

Robinson T, McMullan G, Marchant R, Nigam P (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol 77(3):247–255

Saratale RG, Saratale GD, Chang JS, Govindwar SP (2011) Bacterial decolorization and degradation of azo dyes: a review. J Taiwan Inst Chem E 42(1):138–157

Sarayu K, Sandhya S (2012) Current technologies for biological treatment of textile wastewater—a review. Appl Biochem Biotechnol 167(3):645–661

Stedmon CA, Bro R (2008) Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. Limnol Oceanogr Methods 6:572–579

van der Zee FP, Villaverde S (2005) Combined anaerobic-aerobic treatment of azo dyes—a short review of bioreactor studies. Water Res 39(8):1425–1440

Verma AK, Dash RR, Bhunia P (2012) A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. J Environ Manag 93(1):154–168

Wang Z-P, Zhang T (2010) Characterization of soluble microbial products (SMP) under stressful conditions. Water Res 44(18):5499–5509

Westerhoff P, Chen W, Esparza M (2001) Fluorescence analysis of a standard fulvic acid and tertiary treated wastewater. J Environ Qual 30(6):2037–2046

Wu FC, Evans RD, Dillon PJ (2003) Separation and characterization of NOM by high-performance liquid chromatography and on-line three-dimensional excitation emission matrix fluorescence detection. Environ Sci Technol 37(16):3687–3693