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Residual micro organic pollutants and their biotoxicity of the effluent from the typical textile wastewater treatment plants at Pearl River Delta

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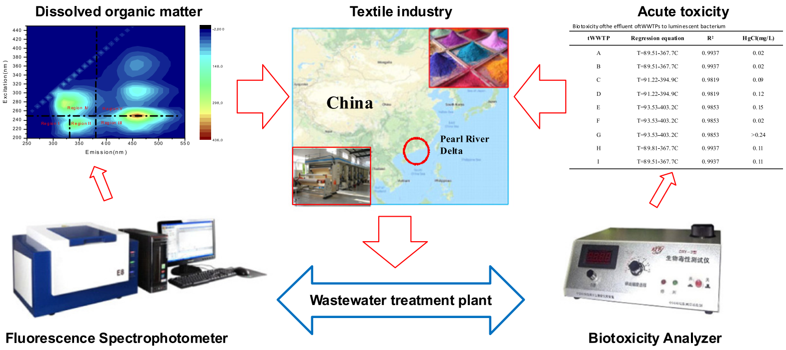
HIGHLIGHTS

- Residual DOMs are measured in the textile effluents and exhibited biotoxicity.
- Benzene-derived products and aromatic amines are the toxicity-causing substances.
- Membrane filtration is more suitable for the detoxification of textile effluents.

GRAPHICAL ABSTRACT



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ABSTRACT

This work investigated the biotoxicity and the residual dissolved organic matter (DOM) of the effluents from nine typical full-scale textile plants located at Pearl River Delta (PRD) in Guangdong province, China. The fluorescence regional integration (FRI) analysis showed that the tryptophan-like (II), soluble microbial product-like (IV) and fulvic acid-like substances (III) were the dominant compounds in the DOM. The acute toxicity test showed toxic effects still remained in most textile effluents, which might attribute to the undegraded dyes or aromatic compounds. Combining with the results from multiple methods, it indicated that the selected nine textile wastewater treatment plants (tWWTPs) all contained some residual micro organic pollutants in their effluents, and the residual benzene-derived products or aromatic amines were probably the toxicity-causing substances. Both ozonization and membrane filtration were capable of further decreasing the content of residual DOM, but by comprehensively considering the effects of removing DOM and biotoxicity, membrane filtration was better than ozonization.

1. Introduction

Textile products are necessities for the daily life of human society. However, textile wastewater, characterized by high color, high organics and high toxicity (Khandegar and Saroha, 2013; Tomei et al., 2016), can cause serious negative impacts on the surrounding environment as well as human health (Bilińska et al., 2016; Fan et al., 2014). For solving these issues, the combined physico-chemical methods and bio-degradation are commonly used in most textile wastewater treatment plants (tWWTPs) (Frijters et al., 2006; Holkar et al., 2016; Li et al., 2015). The biological process, termed as the secondary wastewater treatment process, is verified as an efficient way for removing most organic pollutants,

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which finally makes the textile effluent to meet the discharge standards. Recent years, the realistic demands to cope with the water environment crisis, especially for resolving the issues of residual micro-pollutants, or even trace amount of toxics, have promoted the technique development in textile wastewater treatment. So far, a so-called tertiary treatment process, including the advanced oxidation process (AOP) (Jin et al., 2016; Jin et al., 2013; Lotito et al., 2012) and membrane filtration (Michael et al., 2013; Sun et al., 2016), was developed and used in some practical engineering projects, especially for further removing micro-pollutants over secondary treatments. The former used some oxidizers (ozone, Fenton reagent or other super oxidizers) to decompose the residual organic pollutants. And the latter used selective filtration membranes to separate pollutants from wastewater, and finally improved the quality of effluents.

Dissolved organic matter (DOM) is a ubiquitous substance in natural aqueous environment and soil, while, it is also found in kinds of effluents even after being well biologically treated (Filloux et al., 2012; Liu et al., 2011). In previous researches and review papers, it was reported that the physico-chemical behavior of DOM in the aquatic environment actually led a potential harm to the ecosystem. For example, the formation of disinfection by-products (DBPs) (Krasner et al., 2009; Li et al., 2016) or a complexing agent for metals or organic micro-contaminants (Aiken et al., 2011; Ma and Yates, 2018; Pernet-Coudrier et al., 2008; Yoo et al., 2016). However, it is rather difficult to identify effluent DOM in the textile industries because of the contained heterogeneous and complex mixtures (non-biodegradable dyes, amines or microbial products). Recently, three-dimensional excitation-emission matrix (EEM) has been proven to be a useful technique for characterizing DOM (Borisover et al., 2011; Carstea et al., 2016; Henderson et al., 2009; Peleato et al., 2017; Sgroi et al., 2017). The rapidity, sensitivity and no using of chemical reagents are the main advantages, which are very helpful for identifying the position, intensity of fluorescence peaks and regional proportion of DOM in a variety of water systems. However, there were nearly no detailed investigations about the effluent DOM information of actual textile industries reported except for Huang et al. (2017) and Li et al. (2015), who observed different DOM composition by the method of EEM at different areas. In terms of the variation of DOM after tertiary treatment, still few relevant investigations were reported (Audenaert et al., 2013; Ayache et al., 2013; Yin et al., 2017).

The effluent toxicity from most tWWTPs is also a great concern. Firstly, the raw wastewater from textile industry contains lots of toxic recalcitrant organics (Fan et al., 2016; Frijters et al., 2006; Michael-Kordatou et al., 2015). Secondly, the biological process cannot remove these hazardous persistent micro-pollutants (Somensi et al., 2010; Tehrani-Bagha et al., 2010). The tertiary treatment therefore is employed by some tWWTPs to reduce toxic residual pollutants. Meanwhile, relevant toxic bioassays are developed and used to detect the toxicity of effluent, termed as "biotoxicity", in most researches. Punzi et al. (2015) once compared the biotoxicity of artificial and real textile effluents treated by biodegradation and ozone oxidation with the biological indicators of *Vibrio Fischeri* and shrimp *Artemia Salina*. Pazdzior et al. (2017) studied the acute toxicity of textile wastewater after being treated by chemical, biological and combined chemical-biological treatments. These investigations confirmed a biotoxicity test was necessary for assessing the detoxification effect of a process. Though a number of papers on textile effluent toxicity were published, the lab-scale research for textile effluent is difficult to provide actual referencing information for full-scale applications. Therefore, toxic experiments for actual textile effluent together with a reliable, fast, sensitive, inexpensive and easy-operation detecting method should be necessary (Jin et al., 2013; Zeng et al., 2015).

Pearl River Delta (PRD), locating at the central part of Guangdong Province, is the most active area in the economic and industrial development of China. In the past decades, so many industries were built and operated in this area at a surprising speed, especially the textile industry, which discharged millions of tons of textile wastewater into the surrounding aqueous environment every year. Different secondary or even tertiary treatments were commonly adopted to reduce the produced pollutants in terms of color, COD and BOD, but the biotoxicity of effluents was still not rationally evaluated. Therefore, in this study, nine typical full-scale tWWTPs in PRD were chosen as the sampling sites with the following purposes: 1) to detect the residual micro organic pollutants in the effluents of the selected tWWTPs; 2) to evaluate the biotoxicity of their effluents after treatment; 3) to compare the difference in detoxification effect between different tertiary treatment processes. It's hoped that the obtained results would provide a useful reference for better understanding the residual micro organic pollutants and biotoxicity of the effluents from the full-scale textile industries.

2. Materials and methods

2.1. Water samples

The selected nine textile plants locate at PRD, which are the main typical textile plants in this area and they produce volumes of wastewater every day. Seven of which adopted a secondary treatment process to treat the produced wastewater, and the other two employed a tertiary treatment process, whose details are shown in the Supporting information (SI). Water samples were collected from the effluents of these wastewater treatment facilities during the period from Sep. 2017 to Jul. 2018. Samples were collected in triplicate by using Amber glass bottles, the basic water quality indexes, including pH and temperature, were measured on-site. After collection, all of the other samples for measuring organics were acidified to pH of 2 using H_2SO_4 and transported to the lab and stored at 4 °C. All the water quality indexes were measured within 2 d after the samples were taken back to the lab.

2.2. Measurement of the basic water quality indexes

The pH value of all samples was measured by a pH meter (CT-6021A, Kedida, China). Specific UV absorbance at 254 nm (UV_{254}) was measured as an indicator by using a standard 1.0 cm quartz cuvette and an ultraviolet spectrophotometer (UV 2400, Shanghai Sunny Hengping Scientific Instrument, China). Dissolved organic carbon (DOC) was analyzed using a TOC-V_{CPH}/TOC-V_{CPH} Total Organic Carbon Analyzer (TOC-V_{CPH}/TOC-V_{CPH}, Shimadzu, Japan) and TOC-Control V software after samples were filtered through 0.45 μm filters prior to measurement. All the other mentioned water quality indexes were measured according to the standard methods (APHA et al., 2005).

2.3. FTIR characterization

Fourier transform infrared spectroscopy (FTIR) was employed to characterize the special functional groups of the textile effluent by a spectrometer (Nicolet 6700, Thermo fisher, USA) in the range of 4000–400 cm^{-1}. Before measurement, each sample was dried to solid at 65 °C and grinded into powder with KBr pellets.

2.4. EEM fluorescence spectra

EEM fluorescence spectra were obtained by referencing the report of Borisover et al. (2011) with a fluorescence spectrophotometer (Hitachi F-7000, Hitachi Inc., Japan). Each EEM analysis was conducted at a scan rate of 12,000 nm/min, with the sampling interval on excitation (Ex) and emission (Em) modes both setting at 10 nm. The slit bandwidth of Ex and Em was 2.5 nm and 1 nm, respectively, whereas the emission scanning field was set from 250 nm to 550 nm and excitation from 200 nm to 450 nm. The peak Ex/Em pairs were picked with the Hitachi FL Solutions software. In order to obtain more accurate fluorescence information of EEM spectra, the Raman scatter was removed by subtracting EEM of high-purity water as a blank sample from the EEM of textile effluent samples (Peleato et al., 2017), and those fluorescence intensities were converted to zero for removing light scattering interference according to a reported method (Sgroi et al., 2017).

Peak-picking was used as a qualitative method to analyze each fluorescence peak of five regions or the representative peaks (Chen et al., 2003). And fluorescence regional integration (FRI) divided EEM spectra into five regions defined by different excitation/emission boundaries, then calculated to obtain the proportion of five compounds. In this study, peak-picking method combining FRI was used as the analytical method to estimate the residual DOM in the textile effluents.

The regional fluorescence intensity ($\Phi_{i,\ n}$) and total regional fluorescence intensity ($\Phi_{T,\ n}$) could be obtained by using the following equations.

$$\Phi_i = \sum_{ex}\sum_{em} I(\lambda_{ex}\lambda_{em})\Delta\lambda_{ex}\lambda_{em} \tag{1}$$

$$\Phi_{i,n} = MF_i\Phi_i \tag{2}$$

$$\Phi_{T,n} = \sum_{i=1}^{5}\Phi_{i,n} \tag{3}$$

where Φ_i is the fluorescence volume of each fluorescence region i; $I(\lambda_{ex}\lambda_{em})$ is the fluorescence intensity at each excitation-emission wavelength; $\Delta\lambda_{ex}$ and $\Delta\lambda_{em}$ is the 10 nm scanning interval of excitation wavelength and emission wavelength, respectively. $\Phi_{i,\ n}$ is the standardized fluorescence volume of each region i; MF_i is the multiplication factor. $\Phi_{T,\ n}$ is the total fluorescence volume.

2.5. Biotoxicity test

A microtox toxicity analyzer (DXY-3) and luminescent bacteria (*Photobacterium phosphoreum* T_3 spp.), provided by the Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China, were used for the biotoxicity analysis. Specific experimental operation of the luminescence inhibition test was described in the national standard method of China (Water quality – Determination of the acute toxicity – Luminescent bacteria test. GB/T15441-1995). Prior to the acute toxicity assay, 1 mL of cold 2.5% NaCl solution was injected into a vial contained 0.5 g of *P. phosphoreum* sp. T_3 stored at 2–5 °C, then shook to ensure them thoroughly mixing. After 2 min, *Photobacterium phosphoreum* T_3 was revived, then 10 μL of bacterial liquid was inoculated into the tube containing 2 mL of textile effluent solution or a 3% NaCl solution as the blank sample. The toxic values were determined by a microtox toxicity analyzer when the bacteria were exposed for 15 min at 25 °C. The equivalent concentration of Mercuric chloride (mg/L) was used to describe the acute toxicity of textile effluent. The relative luminosity (T) was calculated according to Eq. (4).

$$T = \left(\frac{L_{sample}}{L_{blank}}\right) \times 100\% \tag{4}$$

where, L is the luminosity.

3. Results and discussion

3.1. General evaluation of the performance of the selected tWWTPs

The water quality indexes of the effluent from the selected tWWTPs, such as pH, temperature, COD, TOC and UV_{254}, were measured according to the methods described in Section 2, and the results are shown in Table 1.

From the results in Table 1, the values of COD, TOC and UV_{254} of the textile effluents did not show any obvious difference in summer or winter, which indicated the tWWTPs performed well and stably. The results indicated that the COD values ranged from 21.3 to 117.34 mg/L, and the higher COD values were found at D and G in summer, and A, B, D, E, G in winter. The TOC values ranged from 5.31 to 46.24 mg/L, and the higher TOC values were also found at B in summer, G in summer and winter. As for UV_{254} value, representing the relative content of aromatic DOM composition (Ayache et al., 2013; Jin et al., 2016), it ranged from 0.081 to 2.054 m^{-1}, and higher UV_{254} values were found in F in summer, E in winter, and G in summer and winter.

The above results indicated that the effluents from the selected tWWTPs all met the requirement of the national discharge standard exclusive of G. However, the detected organic content in terms of COD, TOC and UV_{254} also implied the effluents in these tWWTPs still contained some residual DOM, especially for G. Additionally, obviously lower values in the concentration of residual COD, TOC and UV_{254} were found at D and F, which verified that the used tertiary treatments by D and F were effective. It should be noted that residual DOM was still detected in the effluents even after the secondary or tertiary treatment process. Other similar literature once reported the complicated occurrence of incomplete-biodegraded dyes or intermediate microbial products was likely the reasonable explanation (Khan and Malik, 2018). Therefore, a further and detailed approach should be adopted for better understanding the residual micro organic pollutants in the effluents to evaluate their eco-security.

3.2. FTIR analysis

FTIR is widely used to identify the functional groups, then interpret the potential organics for solid or water samples. This tool is helpful to analyze the information of residual matters of textile effluents. Thus, in the presented investigation, the water samples were measured with FTIR, and the spectra are shown in Fig. 1.

According to the results (Li et al., 2012; Liu et al., 2018), the characteristic band at 3450 cm^{-1} was attributed to the stretching vibration of —OH groups. The band at 1630 cm^{-1} was corresponded to the double bond vibration of C═C or N═N, which indicated that the residual alcohol, ether or ketone still contained in all the effluents, especially for that at B. The band at 1450 cm^{-1} was assigned to be a benzene ring, which also showed that the benzene-derived products also contained. The benzene-derived products at B and D, F, H and I were more than that in other samples. Additionally, the peak at 1130 cm^{-1} represented the residual amines, and the peaks at 1380 cm^{-1} and ranging in 618–1000 cm^{-1} involved the out-of-plane bending vibration of C—H, indicating a high aromatic content in the effluents (Cui et al., 2017), which was consistent with the results of UV_{254} analysis. In summary, the benzene-derived products and aromatic amines should be the major residual organic pollutants contained in the effluents.

3.3. EEM fluorescence spectra of DOM

The residual micro organic pollutants in the effluents of the selected tWWTPs include the undegraded dyes and microbial products, and are very complex. For the reason, it's rather difficult to give an accurate description of residual organics. Thus, in the present section, EEM spectra were used to identify the organic component in the textile effluents, including seven secondary effluents of A, B, C, E, G, H, I, and two tertiary effluents of D, F. All the results (Dec. 2017–Jan. 2018) are shown in Fig. 2.

As shown in Fig. 2, five main peaks (Peak A, B, C, D, E), exhibiting peak location at Ex/Em 230–240/340–360 nm, 280/320–340 nm, 240–250/450–460 nm, 300–310/450–460 nm, 360/440–460 nm, were observed in the effluent of A, C, D, E, H, I and F, and two obvious fluorescence peaks (Peak A, B) located at Ex/Em 230–240/340–360 nm and 280/320–340 nm (B, G) were also observed. According to the reported results (Chen et al., 2003; Sgroi et al., 2017), the peak at Ex/Em 230–240/340–360 nm and 280/320–340 nm corresponded to the aromatic tyrosine-like (Peak A) and aromatic tryptophan-like (Peak B) substances. Additionally, the peak at Ex/Em 240–250/450–460 nm, 300–310/450–460 nm, 360/440–460 nm were assigned to be the

Table 1
Information of water quality parameters of tWWTPs.

		A	B	C	D	E	F	G	H	I
Samples (Sep. 2017–Oct. 2017)	pH	7.3	7.1	7.6	8.1	ND	7.2	7.1	ND[a]	ND
	T (°C)	32	29.7	30.3	32.7	ND	30.2	33.4	ND	ND
	COD (mg/L)	26.67	45.34	53.34	64	ND	42.67	112	ND	ND
	TOC (mg/L)	21.61	45.41	21.82	36.53	ND	29.33	46.24	ND	ND
	UV_{254} (abs)	0.754	0.825	0.762	0.366	ND	1.217	1.617	ND	ND
Samples (Dec. 2017–Jan. 2018)	pH	7.0	6.9	7.4	7.8	8.4	7.2	7.3	7.7	8.2
	T (°C)	30.6	28.1	26.5	30.9	25.6	22.8	33.3	30	29.2
	COD (mg/L)	58.67	53.3	21.3	53.4	53.34	26.67	53.34	26.67	32
	TOC (mg/L)	20.54	24.14	16.67	21.98	33.33	16.44	41.62	14.38	21.56
	UV_{254} (abs)	0.648	0.452	0.463	0.597	1.072	0.741	1.440	0.653	0.764
Samples (Jun. 2018–Jul. 2018)	pH	ND	ND	7.1	8.2.	ND	7.1	7.7	ND	7.8
	T (°C)	ND	ND	32.8	36.3	ND	32.3	38.4	ND	38.7
	COD (mg/L)	ND	ND	26.67	64	ND	34.67	117.34	ND	37.33
	TOC (mg/L)	ND	ND	5.31	12.8	ND	13.97	41.79	ND	9.243
	UV_{254} (abs)	ND	ND	0.081	0.784	ND	1.062	2.054	ND	0.493

[a] ND = no detected.

humic-like structure (Peak C, Peak D, Peak E). It was noteworthy that three humic-like peaks almost located at the similar emission wavelength (Li et al., 2013), which might attribute to the result of fluorophores' multi-excitation. Meanwhile, Li et al. (2015) indicated that five similar locations including two protein-like peaks and three humic-like peaks were observed in effluents. However, Huang et al. (2017) indicated that only four peaks including two protein-like peaks and two humic-like peaks were found. The significant differences among these investigations were probably caused by different dyes in the raw textile wastewater discharging from different textile plants. As described in the report (Li et al., 2015), 1-amino-2-naphthol moieties, as a common intermediate of azo dyes, were easily converted into humic-like substances. And in the other investigation of Huang et al. (2017), the incompletely-degraded disperse dyes and aromatic matters produced by cationic dyes during the biodegradation process were the origin of protein-like peaks.

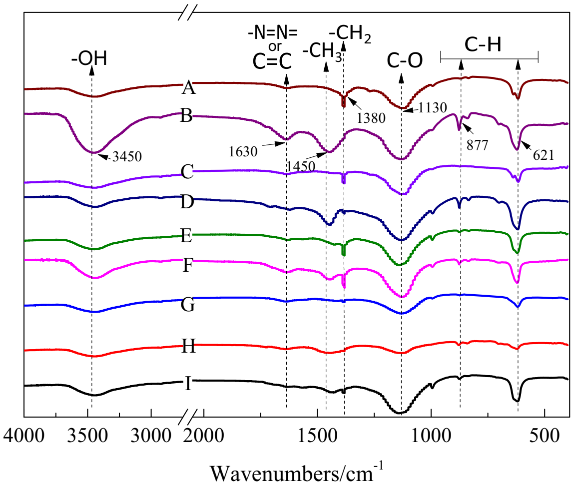

Fig. 1. FTIR spectra of the pollutants contained in the effluents.

For better understanding the distribution of the effluent DOM of each tWWTP and comparing their similarities and differences, FRI method was used. By referencing the report of Chen et al. (2003), DOM included aromatic tyrosine-like (I), aromatic tryptophan-like (II), fulvic acid-like (III), soluble microbial product-like (IV) and humic acid-like substances (V). The results are shown in Fig. 3.

In Fig. 3(a), the higher total fluorescence intensities of effluent were always found in the secondary effluents of A, C, E, H, and I. However, the total fluorescence intensities of DOM were not in accordance with the variation tendency of COD, TOC and UV_{254} measurement. Besides the effluents of B and G, the fluorescence intensities of D and F were also significantly lower than that in other textile effluents, which might attribute to the tertiary process used by D and F. And from Fig. 3(b), DOM of the nine tWWTPs was mainly composed of aromatic tryptophan-like (II) and soluble microbial product-like substances (IV), and accounted for approximately 16–36% and 19–43%, respectively. Furthermore, the fulvic acid-like substances (III) occupied a higher ratio at B, C, D, E, and F. The aromatic tyrosine-like (I) and humic acid-like substances (V) occupied a lower proportion at the nine tWWTPs and accounted for approximately 10–17% and 4–10%. According to the previous investigation (Huang et al., 2017; Li et al., 2015), it could be speculated that different organic dyes or other chemical auxiliaries in the textile wastewater might be the most likely reason to explain the difference. The incomplete treatment process and unsuitable operational parameters also might be another reason. In summary, the DOM in effluent should be paid more attention due to its occurrence in most of the secondary and tertiary effluent. Meanwhile, the tryptophan-like (II), fulvic acid-like (III) and soluble microbial product-like substances (IV) are proposed as a potential indicator to evaluate the treatment efficiency of a newly developed process due to their frequent observation and larger proportion in the textile effluents.

3.4. Biotoxicity test of the textile effluents

Biotoxicity effects have a direct influence on the aquatic ecosystem. Table 2 gives the acute toxicity results of the nine textile effluents by using the Regression equation, Correlation coefficient (R^2) and Equivalent concentration of $HgCl_2$.

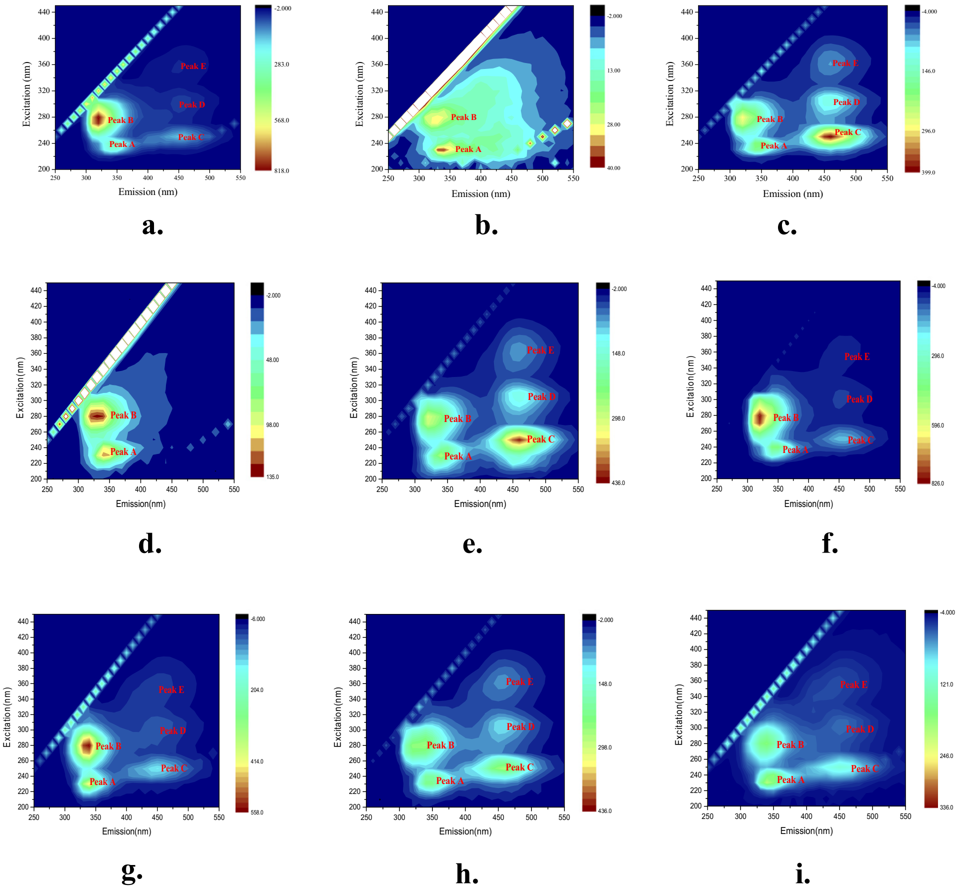

Fig. 2. EEM spectra of the selected nine textile effluents: a. A; b. B; c. C; d. G; e. E; f. H; g. I; h. D; i. F.

The results indicated the toxic values of the final effluents from the nine plants ranged from 0.02 mg/L to 0.24 mg/L. The highest toxic value was found at G (0.24 mg/L) followed by D, E, H and I, only the effluents of A, B and F were nontoxic. According to the report (Khan and Malik, 2018), the incompletely-degraded residual dyes in raw textile wastewater or the aromatic amines produced through biological processes might attribute to the toxicity of textile effluent. Combining the above results and FTIR spectra, it confirmed that the residual benzene-derived products or aromatic amines are probably the toxicity-causing substances. It should be noted that almost all the values of Hg^{2+} (an indicator of biotoxicity) were much higher than the specified value of the World Health Organization ($Hg^{2+} < 0.001$ mg/L) (WHO, 2011), therefore, a suitable tertiary treatment is necessary for reusing textile effluents.

The toxic effect of textile effluent was also confirmed by some previous papers, although the indicator organisms used by different toxicity tests were not identical. For example, Punzi et al. (2015) used *Vibrio Fischeri* and the shrimp *Artemia Salina* as indicator organisms to evaluate the biologically treated textile effluents, and confirmed the its acute toxicity and mutagenic effects. Pazdzior et al. (2017) reported that 23%–30% the residual toxic effect still remained in the effluent by using *Vibrio Fischeri* as an indicator organism. Additionally, Mathur et al. (2007) and Shehzadi et al. (2014) both indicated that the mutagenic and carcinogenic effect on secondary effluents was from the

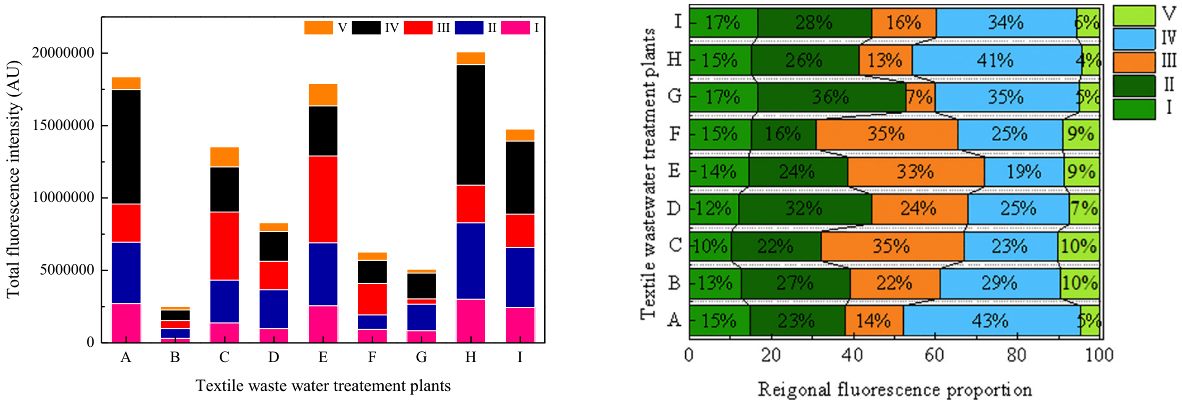

Fig. 3. Fluorescence intensity of the samples: a. Total fluorescence intensity; b. Distribution of FRI.

Table 2
Biotoxicity of the effluents.

	tWWTP	Regression equation	R^2	HgCl (mg/L)
Samples (Dec. 2017–Jan. 2018)	A	$T^{a} = 89.51–367.7C^{b}$	0.9937	0.02
	B	$T = 89.51–367.7C$	0.9937	0.02
	C	$T = 91.22–394.9C$	0.9819	0.09
	D	$T = 91.22–394.9C$	0.9819	0.12
	E	$T = 93.53–403.2C$	0.9853	0.15
	F	$T = 93.53–403.2C$	0.9853	0.02
	G	$T = 93.53–403.2C$	0.9853	>0.24
	H	$T = 89.81–367.7C$	0.9937	0.11
	I	$T = 89.51–367.7C$	0.9937	0.11
Samples (Jun.–Jul. 2018)	C	$T = 91.22–394.9C$	0.9819	0.02
	D	$T = 91.22–394.9C$	0.9819	0.12
	F	$T = 93.53–403.2C$	0.9853	0.02
	G	$T = 93.53–403.2C$	0.9853	0.24
	I	$T = 89.81–367.7C$	0.9937	0.18

[a] T = HgCl (mg/L).
[b] C = relative luminosity of *Photobacterium phosphoreum* T_3.

undegradable azo dyes and the degradation products from aromatic amines. Thus, a biotoxicity test is necessary to be developed and employed as a routine monitoring method to evaluate the eco-safety of actual tWWTPs effluents.

3.5. Effluent DOM vs acute toxicity vs treatment technologies

The frequent observation of residual DOM and toxicity in secondary effluents together with the increasing interest in water recycling, it thus is important to evaluate the weakness of current tertiary treatment. For this reason, choosing a suitable tertiary process for reducing effluent organics or toxic matters is also very urgent (Audenaert et al., 2013). In this section, the removal efficiency of DOM and toxic value was used as indicators to compare the two tertiary processes. The most recent samples (sampled during Dec. 2017–Jul. 2018) were used to make a comparison with the results shown in Table 3.

In Table 3, the removal of organic pollutants was obviously decreased in terms of TOC, COD and UV_{254} after ozonization and membrane filtration. The fluorescence intensity was also obviously decreased, but the major reduced substances by these two processes were quite different. It was found at D that the higher removal efficiencies of effluent DOM were fulvic acid-like substances (III) (48.16%), soluble microbial product-like substances (IV) (40.89%) and humic acid-like substances (V) (62.07%). The aromatic tyrosine-likes (I) and aromatic tryptophan-likes (II) only accounted for a very low ratio. As for F, membrane filtration had a relatively higher removal efficiency for DOM compounds, including the aromatic tryptophan-likes (II), the fulvic acid-likes (III), the soluble microbial product-likes (IV), and the humic acid-likes (V). Only the aromatic tryptophan-likes (I) accounted for a removal ratio of 24.04%. The difference might originate from the different removing mechanisms. In general, membrane process mainly relies on the physical adsorption and interception to remove pollutants from water. At a deeper level, the hydrogen-bonding characteristics of membrane material together with the nature of high molecular weight (MW) of proteins and hydrophobic of humic-like substances are indispensable conditions (Filloux et al., 2012; Pramanik et al., 2015). And ozonization process is dependent on the chemical reaction between O_3 and the residual DOM. After ozonization, higher hydrophobic compounds presenting in DOM are more readily transformed to be low MW compounds, such as humic-like and fulvic-like substances (Wu et al., 2011). Other researchers also drew a similar conclusion (Swietlik et al., 2004; Zhang et al., 2008), who thought the production of hydrophilic aromatic amino acid functional group was attributed to the breakdown of macromolecular proteinaceous substances after ozonization. It should be noted that the membrane process in winter (Dec. 2017–Jan. 2018) showed a worse performance than that in summer (Jun. 2017–Jul. 2018), which might be caused by membrane fouling. However, even during summer time, it still had a higher efficiency in removing three main compositions of DOM than that of ozonization. In this meaning, membrane filtration was a more suitable tertiary treatment than ozonization.

The results also showed the toxic effect of D (0.12 mg/L) was significantly higher than that of F (0.02 mg/L) both in winter and summer, which also confirmed that membrane filtration was a more suitable tertiary method to remove toxic matters than that of ozonization. Magdeburg et al. (2014) indicated that it might cause the formation of mutagenic compounds after ozonization, such as alkylating agents, and subsequently resulted in a mutagenic effect of textile effluent. Some papers also reported the similar conclusion that the formation of chemical by-products led to the toxic effect in the ozonized textile effluent (de Souza et al., 2010; Michael et al., 2012). On the contrary, membrane separation mainly relied on the physical adsorption and interception to remove the residual pollutants from the effluents. Thus, the physical membrane filtration can improve effluent quality and avoid the potential formation of toxic pollutants.

In summary, membrane filtration is capable of removing residual DOM and toxicity, which seems a more suitable tertiary treatment process in an actual application to decrease the potential risk to the surrounding aqueous ecosystem (Boonnorat et al., 2017). Besides, a

Table 3
Comparison of ozonization (D) and membrane filtration (F).

	tWWTP	TOC removal (%)	COD removal (%)	UV_{254} removal (%)	FRI index	Removal (%)	Toxicity (HgCl)
Samples (Dec. 2017–Jan. 2018)	D (ozonation)	59.6	69.6	28.9	Φ_1	35.8	– (before)
					Φ_2	31.8	
					Φ_3	48.16	0.12 (after)
					Φ_4	40.89	
					Φ_5	62.07	
	F (membrane filtration)	38.5	70.6	43.4	Φ_1	24.04	– (before)
					Φ_2	74.5	
					$\Phi3$	43.98	0.02 (after)
					Φ_4	56.09	
					Φ_5	61.42	
Samples (Jun.–Jul. 2018)	D (ozonation)	56.2	42.8	47.4	Φ_1	50.26	0.11 (before)
					Φ_2	0	
					Φ_3	32.11	0.12 (after)
					Φ_4	17.26	
					Φ_5	49.69	
	F (membrane filtration)	63.5	80.8	69.5	Φ_1	24.2	0.22 (before)
					Φ_2	25.4	
					Φ_3	33.8	0.02 (after)
					Φ_4	24.8	
					Φ_5	0	

comprehensive evaluation based on the treatment efficiency of pollutants and detoxicity should be considered in developing a new tertiary treatment process.

4. Conclusion

Nine typical full-scale tWWTPs at PRD were chosen to evaluate the residual micro organic pollutants contained in the effluents and their biotoxicity. By using multi-methods and comprehensive analysis, the followed conclusions were drawn:

1) Residual micro organic pollutants were commonly measured in the effluents of the selected nine tWWTPs, and the tryptophan-like (II), soluble microbial product-like (IV) and fulvic acid-like substances (III) were the dominant compounds in DOM.
2) The effluents exhibited obvious biotoxicity, in which, the residual benzene-derived products or aromatic amines were probably the toxicity-causing substances.
3) Ozonization and membrane filtration, as a tertiary treatment process, was all effective to further decrease the residual micro organic pollutants, but membrane filtration was more beneficial to decrease the toxicity of effluents in practical applications.

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Appendix A. Supplementary data

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