Environmental Pollution 231 (2017) 115-122

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Elimination and ecotoxicity evaluation of phthalic acid esters from textile-dyeing wastewater *



POLLUTION

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A R T I C L E I N F O

Article history: Received 8 April 2017 Received in revised form 28 July 2017 Accepted 1 August 2017 Available online 8 August 2017

Keywords: Phthalic acid esters Textile-dyeing wastewater Ecotoxicity evaluation Wastewater treatment Dissolved organic matter

ABSTRACT

Phthalic acid esters (PAEs), presented in fabrics, surfactants and detergents, were discharged into the ecosystem during textile-dyeing wastewater treatment and might have adverse effects on water ecosystems. In this study, comprehensive investigations of the content and component distributions of 12 PAEs across different units of four textile-dyeing wastewater plants were carried out in Guangdong Province, China. Ecotoxicity assessments were also conducted based on risk quotients (ROs). On average, 93.54% TOC and 80.14% COD_{Cr} were removed following treatment at the four plants. The average concentration of Σ_{12} PAEs in effluent was 11.78 µg/L. PAEs with highest concentrations were dimethylphthalate (6.58 μ g/L), bis(2-ethylhexyl)phthalate (2.23 μ g/L), and dibutylphthalate (1.98 μ g/L). The concentrations of the main toxic PAEs were 2.23 µg/L (bis(2-ethylhexyl)phthalate), 0.19 µg/L (diisononylphthalate) and 0.67 μ g/L (dinoctylphthalate); corresponding RQs were 1.4, 0.55, and 0.54 for green algae, respectively. The RQs of Σ_{12} PAEs in effluent of the four plants were >0.1, indicating that Σ_{12} PAEs posed medium or higher ecological risk to fish, Daphnia and green algae. Physicochemical-biochemical system was found to be more effective than biochemical-physicochemical system for TOC and COD_{Cr} removal, because pre-physicochemical treatment helped to remove macromolecular organic substances, and reduced the competition with other pollutants during biochemical treatment. However, biochemical-physicochemical system was more effective than physicochemical-biochemical system for elimination of PAEs and for detoxification, since the biochemical treatment might produce the toxic PAEs that could helpfully be settled by post-physicochemical treatment. Moreover, ecotoxicity evaluation was recommended for current textile-dyeing wastewater treatment plants.

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1. Introduction

Approximately 1.84 billion metric tonnes of texitle-dyeing wastewater was produced in 2015 according to the China Environment Statistical Yearbook (2015). Textile-dyeing wastewater was a heterogeneous, poorly characterized and quite complex mixtures of several contaminants (Khandegar and Saroha, 2013; Prigione et al., 2008), and contains large quantities of dyes, surfactants, detergents solvents, and other recalcitrant organic matters. These organic pollutants also contributed a significant

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share to the textile-dyeing wastewater's organic load (Lotito et al., 2012; Li et al., 2012). Although textile-dyeing wastewater was purified via physical, chemical, and biological treatment processes, degradation products and metabolites from chemical oxidation and microbial degradation could be added to the organic constituent of the discharged effluent (Van der Zee and Villaverde, 2005). A large of such pollutants was detrimental to the aquatic environment. Particular attention should be paid to phthalic acid esters (PAEs) because some PAEs were endocrine-disrupting chemicals, posing potentially impact ecosystem functioning and public health (Abdel Daiem et al., 2012). PAEs presented in fabrics, surfactants and detergents, were discharged into the ecosystem during wastewater treatment of textile-dyeing plants (TDPs) (Net et al., 2015). Moreover, very limited studies have been focused on the doseecotoxicity effect relationship of the PAEs during textile-dyeing wastewater treatment.



 $^{\,^{\}star}$ This paper has been recommended for acceptance by Dr. Harmon Sarah Michele.

Nowadays, due to the heterogeneous properties of textiledyeing wastewater, regulations related to this wastewater mainly focus on elimination of integral organic matter by measuring organic sum-parameters, e.g., the chemical oxygen demand (COD) and the total organic carbon (TOC). Comparatively, there was less frequent evaluation of the reduction in and ecotoxicity of specific pollutants resulting from different wastewater treatment (Supowit et al., 2016; Köhler et al., 2006). Many studies have investigated the relationship between mixture toxicity and chemical evaluation of priority pollutants in the discharged effluents (Stalter et al., 2010; Giannis et al., 2007; Punzi et al., 2015a, 2015b; Justino et al., 2009; Woo et al., 2009), but there have been limited analytical and toxicological investigations throughout the different industrial wastewater treatment processes. Köhler et al. (2006) investigated elimination of a fluorescent whitening agent and its degradation products during the wastewater treatment. The results indicated that TOC and the single contaminants could be slightly eliminated by adsorption to activated carbon, while 40% toxicity of the wastewater could be decreased. However, up to 80% TOC could be removed by biological treatment but whole effluent toxicity even increased. Supowit et al. (2016) investigated the fate of the pesticide fipronil and its major degradation products during wastewater treatment. The results indicated that 12-31 ng/L fipronil presented in each processing stage, suggesting that conventional wastewater treatment was unfit for reducing overall toxicity because of the generation of harmful fipronil degradation products. However, the reduction of the toxic pollutants was always neglected due to their contents were very low but actually they might pose high toxicity. Thus, it is very necessary to trace the organic pollutants during the wastewater treatment. Moreover, different wastewater treatment technologies were seldom compared, although such comparisons would allow a better and more comprehensive evaluation of the efficiency of pollutant elimination during textile-dyeing wastewater treatment processes. Such information was also particularly meritorious when textile-dyeing wastewater treatments were altered due to process optimization or introduction of novel advanced treatment.

Some previous research have been done on the toxicity of different units of wastewater. Zhang et al. (2013) reported that ecotoxicity of municipal wastewater treatment plant was not significantly reduced, but rather increased after anoxic-oxic processes. Zhang et al. (2012) also found that the genotoxicity and acute toxicity in anaerobic tanks increased, and that the genotoxicity of effluent of textile-dyeing plants had no obvious change of that from influent. Al-Saleh et al. (2017) also found that treated wastewater was generally genotoxic using comet and micronuclei assays. However, these authors did not make clear the toxicity degree caused by one kind of pollutants due to the complex mixture of wastewater. Therefore, this study sought to evaluate the ecotoxicity of Σ_{12} PAEs in textile-dyeing wastewater, ignoring the complex mixture. Risk quotients (RQs) maybe one of the best options to evaluate the toxicity of each PAEs in textile-dyeing wastewater. There was no previous research that reported the toxicity of PAEs in wastewater using the RQs. However, some research have reported RQs of antibiotics. Park and Choi. (2008) found that RQs of chlortetracycline, amoxicillin, oxytetracycline, sulfamethoxazole, and sulfathiazole > 1, indicating they posed potential ecological risk. Isidori et al. (2005) also reported that RQs of clarithromycin, lincomycin and erythromycin were 10, 3.6 and 1, respectively, suggesting that this kind of pollutant was environmentally harmful. González-Pleiter et al. (2013) observed that RQs of erythromycin and tetracycline were >1, which suggested that they posed a significant risk to aquatic ecosystems. Therefore, it was feasible to use RQs to evaluate the ecotoxicity of PAEs in textiledyeing wastewater.

This study aimed to compare different textile-dyeing wastewater treatment systems by chemical analyses and ecotoxicity evaluation. Organic sum-parameters (e.g., TOC and COD) were firstly detected across textile-dyeing wastewater samples from different units of four TDPs. Further, content and component distributions of PAEs were analyzed to examine whether these indicators were sufficient for process control. An ecotoxicity evaluation of PAEs by RQs was also carried out. As far as we know, this was the first effort to comprehensively evaluate the ecological risk posed by PAEs across different textile-dyeing wastewater treatment processes in China.

2. Materials and methods

2.1. Chemicals and materials

Twelve target PAEs, namely dimethylphthalate (DMP), dinprolphthalate (DPRP), diethylphthalateeach (DEP), dimethylphthalate (DIBP), benzylbutylphthalate (BBP), dibutylphthalate (DBP), dinamylphthalate (DAP), dinhexylphthalate (DHP), bis(2ethylhexyl)phthalate (DEHP), dinonylphthalate (DNP), diisononylphthalate (DINP), and dinoctylphthalate (DNOP) were used in this study at the concentration of 1000 mg/L with a purity > 99.5%, which were obtained from O₂si Smart Solutions (Charleston, SC, USA). Dichloromethane, methanol and n-hexane were highperformance liquid chromatography (HPLC)-grade and purchased from Fisher Scientific (USA). Deionized water (18.25 M Ω cm) was obtained via a Millipore Milli-Q water purification system. Other chemicals were of analytical grade or better and used without further purifying.

2.2. Wastewater sampling

To account for the heterogeneity of textile-dyeing wastewater plants in Guangdong Province, four typical textile-dyeing wastewater plants located in three cities (Zhongshan, Dongguan and Guangzhou) were chosen for studying. The basic information, process design parameters and operating parameters of the four TDPs was given in Table 1. Two wastewater treatment systems (Fig. 1) for processing textile-dyeing wastewater were examined. Some photos of the experimental unit about the four typical textiledyeing wastewater plants were shown in Fig. S1. The first system (TDPs 1 and 2) includes sedimentation basin to anaerobic digester and aeration basin with subsequent other treatment (sand-filtration or sedimentation basin to biological aerated-filtration), representing a classical physicochemical-biochemical system. The second system (TDPs 3 and 4) includes anaerobic digester and aeration basin to physicochemical process (membrane-filtration or sedimentation basin to sand-filtration), representing a classical biochemical-physicochemical system. As sampling campaign was performed on January 11th, 2017. To eliminate the variability of the influent and effluent, the samplers were programmed to sample a certain amount of wastewater each 2 h when the plants ran normally. The composite was replaced with empty bottles of 5 L capacity, which were filled with textile-dyeing wastewater to avoid any headspace. After sampling, the bottles were sealed and delivered to the laboratory under 4 °C refrigerator and analyzed as soon as possible.

2.3. Analytical procedures

The dichromate method was used for COD measurement. A TOC-VCPH analyzer (Shimadzu, Japan) was used to determine TOC in sample filtrate. Solid phase extraction (SPE) was used to extract the water samples. Firstly, each 500 mL wastewater sample was

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Parameter	TDP 1	TDP 2	TDP 3	TDP 4
Main dyes	Disperse dyes	Ionic dye, disperse dyes	Basic dyes	Ionic dye,
Textile material	Cotton	Cotton	Cotton	Chemical fiber
Design capacity (m ³ /d)	13,000	14,000	13,000	11,000
Operating capacity (m ³ /d)	13,000	10,000	13,000	11,000
Total hydraulic retention (hours)	12.0	10.0	12.0	11.0
Filling and aeration time (h)	1.5	1.2	1.2	1.0
Settling time (h)	1.2	1.0	1.2	1.0

filtered using glass fiber filters. An SPE cartridge (CNWBOND, HC-C18, 6 mL, 500 mg) was conditioned using 6 mL of dichloromethane, 6 mL of methanol, followed by 6 mL of nanopure water. Then, the filtered wastewater samples were then passed through the pre-conditioned SPE cartridges at an approximate rate of 5–10 mL/min. After passing through the air, 10 mL methanol/water (2:8) was used to elute PAEs from the cartridges. Anhydrous sodium sulfate was used to dehydration. Extracts were dried under a gentle flow of nitrogen stream and were redissolved in 1 mL of n-hexane. Final extracts were kept at -18 °C until analysis.

An Agilent 7890A gas chromatograph-5975C mass spectrometer (GC-MS, Agilent, USA) was used to determine PAEs. Chromatographic separation was achieved using a HP-5MS column $(30 \text{ m} \times 0.25 \text{ mm}, 0.25 \text{ }\mu\text{m}$ film thickness, Agilent, USA) with a constant flow rate of 1.2 mL/min. The column temperature for GC was as follows: oven temperature program began at 100 °C (held for 1 min), ramped to 180 °C at 30 °C/min (held for 1 min) and further ramped to 300 °C at 15 °C/min (held for 10 min). An injection volume of 1 µL was carried out in a splitless mode. Three minutes was set as the time for solvent delay. The mass spectrometer was used under the following conditions: electron impact ionization mode, 70 eV; transfer line temperature, 250 °C; ion source temperature, 230 °C. The mass spectrometer was operated in full scan mode (130-450 amu) for identification purposes. The base peak ion was chosen and three additional qualifiers ions were monitored for quantification (SIM mode).

The detection spectrum analysis of 12 PAEs was shown in Fig. 2. Textile-dyeing wastewater sample from Zhongshan (TDP 3) was

collected to calculate PAE recovery. Using external calibration method to determine PAEs in wastewater, the recoveries of PAEs in textile-dyeing wastewater were shown in Table S2. The mean recoveries of PAEs ranged from 74% to 108%. The relative standard deviations (n = 3) were <15%. The limit of quantification ranged from 0.01 µg/L to 0.04 µg/L, which was set as three times the ratio of signal to noise. The obtained result was similar to Gani and Kazmi, (2016). Quality assurance/quality control (QA/QC) practices were followed from sampling to analysis. Procedural, solvent, and spiked blanks, and quality control samples were included in analysis and extraction process.

2.4. Risk quotients of PAEs

Due to the complex mixture of wastewater, it seem impossible to evaluate the toxicity caused by PAEs using the real wastewater. Therefore, the ecotoxicity risks of PAEs from different units of four TDPs were evaluated using RQs, which were often used to evaluate actual underlying ecological risk of contaminants. These quotients were calculated by measuring the ratio of environmental concentrations (MEC) and predicted no effect concentrations (PNEC) (Von der Ohe et al., 2011; Sanderson et al., 2003). In this study, RQs were estimated by calculating the ratio of MEC to PNEC for single PAE, as the following equation (Von der Ohe et al., 2011; Sanderson et al., 2003):

$$RQ = \frac{MEC}{PNEC}$$
(1)



Fig. 1. Textile-dyeing wastewater treatment systems.



Fig. 2. Chromatograms of 12 PAEs in the standard solution (1000 μ g/L).

Three different trophic levels of aquatic organisms including fish, Daphnia, and green algae were considered to evaluate the ecological risk. PNEC was based on the LC₅₀ (the concentration of contaminant that result in the death of 50% of Daphnia and fish after 48 h and 96 h of exposure, respectively) and EC_{50} (the concentration of contaminant that inhibits green algae growth of 50% after 96 h) by an assessment factor of 1000. These values were based on the ECOSAR program. The structure-activity relationships (SARs) presented in this program were used to predict the aquatic toxicity of chemicals based on their similarity of structure to chemicals for which the aquatic toxicity had been previously measured. Most SAR calculations in the ECOSAR Program were based upon the octanol/water partition coefficient (K_{ow}) and the average length of carbon chains or the number of ethoxylate units. According to the European Commission, in general, RQs <0.1 suggested that they might pose a low ecological risk; RQs >0.1 but <1 indicated medium ecological risk; and RQs >1 indicated high ecological risk.

3. Results and discussion

3.1. TOC and COD_{Cr} elimination

The contents of TOC in different unit were shown in Table S1 and TOC elimination rates were shown in Fig. 3a. The TOC contents of four influent samples were 209 mg/L, 315 mg/L, 242 mg/L, and 132 mg/L, respectively. In the first system, 47.75% and 13.04% TOC were removed in the sedimentation basins of TDPs 1 and 2. Generally, hydrophobic pollutants with $\log K_{OW} > 4$ and dissolved organic matter could be simultaneously eliminated during the complexation-flocculation treatment (Zhang and Wang, 2009). Therefore, the sedimentation basin was very important for TOC elimination. Removal of TOC increased to 69.97% and 55.80% in TDPs 1 and 2 after anaerobic digester and aeration basin, which were responsible for biodegradation. The removal of TOC further increased from 70% to 92.60% in sand-filtration of TDP 1. Sandfiltration used a bed of sand with diameter of 0.15-0.4 mm that was helpful for removing trace organic compounds (D'Alessio et al., 2015) from tertiary treated wastewater. In TDP 2, TOC removal from the sedimentation basin to biological aerated-filtration increased from 45.80% to 97.73%, which was higher than TDP 1. Kim et al. (2014) indicated that generally high TOC removal rates were achieved in biological aerated-filtration, but different biofilm microbial communities in biological aerated-filtration may result in different treatment efficiencies. Thus, sedimentation basin and biological aerated-filtration were more effective for TOC removal than sand-filtration.

In the second system, 30.29% and 54.25% TOC were removed via the anaerobic digester and aeration basin of TDPs 3 and 4. Membrane-filtration showed excellent TOC removal in TDP 3, which increased from 30.29% to 92.11%. However, residual organic pollutants in textile-dyeing wastewater could easily cause membrane fouling and clogging (Amar et al., 2009; Kang and Cao, 2012). The elimination of TOC from the sedimentation basin to sandfiltration in TDP 4 increased from 54.25% to 91.72%. Therefore, the order of the TOC removal was thus TDP 2 > TDP 1 > TDP 3 > TDP 4, indicating that the physicochemical-biochemical treatments were more effective in eliminating TOC than the biochemicalphysicochemical treatments when different characteristics of influent from different TDPs were ignored, because prephysicochemical treatments were more effective at removing macromolecular organic substances and reducing competition with other pollutants in biochemical treatment.

COD_{Cr} contents in the effluent of four TDPs were 353 mg/L, 894 mg/L, 825 mg/L, and 645 mg/L, respectively (Table S1) and their elimination rates were shown in Fig. 3b. After the treatment of anaerobic digester and aeration basin, COD_{Cr} removal rates in the four TDPs were 70.22%, 54.89%, 57.10% and 51.28%, respectively. Activated sludge of biological treatment offered high removal of COD_{Cr}, however, COD_{Cr} could not be completely eliminated. In the first system, sedimentation basin to biological aerated-filtration showed better efficiency than sand-filtration, achieving 83.33% COD_{Cr} removal. González-Martínez et al. (2007) also found that 81% and 84% of total and dissolved COD_{Cr} were removed in municipal wastewater after biological aerated filtration treatment. Furthermore, COD_{Cr} removal in membrane-filtration in TDP 3 (increase to 81.84%) was slightly better than in the sedimentation basin to sandfiltration (increase to 76.92%) in TDP 4. However, the COD_{Cr} values in effluents of TDP 1-4 were still 115 mg/L, 149 mg/L, 149 mg/L and 147 mg/L, respectively. According to the Chinese emission standard for textile-dyeing wastewater (GB4287-2012), the permissible limit values of COD_{Cr} were 100 mg/L for direct emission and 200 mg/L for indirect emission. Therefore, these four textile-dyeing wastewaters did not meet the direct discharge standard.



Fig. 3. The removal of TOC and COD_{Cr} through different units from textile-dyeing wastewater treatments at four TDPs (a): TOC; (b): COD_{Cr} (PC: primary clarifier; AD: aeration digester; AB: aeration basin; SF: sand-filtration; BSB: biochemical sedimentation basin; ESB: end sedimentation; BAF: biological aerated-filtration; MF: membrane filtration; SB: sedimentation basin).

Overall, COD_{Cr} removal was in the order: TDP 2 > TDP 3 > TDP 1 > TDP 4. When comparing TDP 1 with TDP 4, COD_{Cr} removal efficiencies in the physicochemical-biochemical system were better than that in the biochemical-physicochemical system. The four different textile-dyeing wastewater treatment achieved good TOC and COD_{Cr} removal. On average, 93.54% TOC and 80.14% COD_{Cr} were removed in currently-used textile-dyeing wastewater treatment systems. However, it does not mean that the toxic organic pollutants being recalcitrant, persistent and poisonous.

3.2. The elimination of PAE

Fig. 4 describes the contents of Σ_{12} PAEs in different units of four TDPs. The content of Σ_{12} PAEs in influent of TDP 1 was 202.93 µg/L 74.23% Σ_{12} PAEs were removed in the sedimentation basin. Only 0.48% were removed in the anaerobic digester. However, Σ_{12} PAEs in



Fig. 4. Content of Σ 12PAEs following different units from textile-dyeing wastewater treatment of four TDPs (Unit: μ g/L, PC: primary clarifier; AD: aeration digester; AB: aeration basin; SF: sand-filtration; BSB: biochemical sedimentation basin; ESB: end sedimentation; BAF: biological aerated-filtration; MF: membrane filtration; SB: sedimentation basin).

the aeration basin even increased to 932.8 µg/L, contributing to the increase of DIBP and DBP, which accounted for 75.20% and 9.76%, respectively (Fig. S2a). The results were attributed to the transformation of other macromolecular that increased the content of PAEs. In this case, 31.23% DEHP was removed after the aeration basin, whereas Clara et al. (2010) observed that only 14% DEHP was removed by biodegradation/biotransformation, the difference maybe attributed to the different source of wastewater. The content of Σ_{12} PAEs decreased to 16.64 µg/L after sand-filtration, which indicated that sand-filtration was helpful for removing PAEs for its absorption. The total removal of Σ_{12} PAEs in TDP 1 was 91.80%. In TDP 2, the content of Σ_{12} PAEs was 119.89 µg/L, which was gradually decreasing and suddenly increasing in the aeration basin, before they were continuing to decrease. About 93.06% Σ_{12} PAEs were removed after biological aerated-filtration, a little better than the sand-filtration. Because biofilm carrier in the aeration tank was effective for degradation of many organic pollutants including PAEs. In TDP 3, the content of Σ_{12} PAEs was 55.35 µg/L. Only 66.06% Σ_{12} PAEs were removed after membrane-filtration, possibly due to the lack of a sedimentation basin. In TDP 4, the content of Σ_{12} PAEs was only 9.91 μ g/L, and 96.26% Σ_{12} PAEs were removed after sandfiltration. Levels of Σ_{12} PAEs varied significantly in treated wastewater samples from the four TDPs, due to the characteristics of different influent and treatment technologies affecting the efficiency of PAEs removal (Melvin and Leusch, 2016). PAEs could not be completely removed by wastewater treatment but at least their levels were reduced.

The order of the removal efficiencies of Σ_{12} PAEs was TDP 4 > TDP 2 > TDP 1 > TDP 3. When comparing TDP 1 with TDP 4, it can be concluded that biochemical-physicochemical treatment was more effective than physicochemical-biochemical treatment in removing PAEs. Because the biochemical treatment might produce the toxic PAEs that could helpfully be settled by post-physicochemical treatment. Sand-filtration also exhibited advantages in removing PAEs in TDP 1 and 4. Moreover, when comparing TDP 3 with other TDPs, it could be concluded that a sedimentation basin was a necessary element of wastewater treatment systems, regardless of pre-treatment or post-treatment. Dargnat et al. (2009) explained that PAEs with long alkyl side chains could be strongly adsorb onto the suspended particulates. In such cases removal of PAEs by particle settling was more effective than

biological treatment. However, Zheng et al. (2009) reported that PAEs were not adequately removed by coagulation-flocculation, which < 30% of PAEs were removed in fresh leachate. In our research, anaerobic digesters contributed a small degree to PAEs removal in TDPs 1–3. Conversely, the aeration basin had a tendency to increase the content of Σ_{12} PAEs. This result differed from that of Gao and Wen, 2016, who found that the primary mineralization way of PAEs in wastewater was aerobic biodegradation. The different result might be due to the complex mixture of textiledyeing wastewater, in which various substances competed with each other under the same conditions. Easily degradable pollutants were more likely being removed, but the transformation of other complex pollutants or dyes might also add to total PAE content. (Pachhade et al., 2009). Moreover, the results indicated that there was no obvious relationship between TOC or COD_{Cr} and PAEs degradation during the wastewater treatment (Fig. S4). It confirmed that there was not sufficient to evaluate the quality of textile-dyeing effluent using the organic sum-parameters, because some dissolved organic matters were persistent during the wastewater treatment.

3.3. PAEs component distributions

Different component distributions of individual PAE in wastewater samples were shown in Fig. S2. In TDP 1, 60.40% DIBP, 28.82% DBP, and 6.76% DEHP were accounted in influent. As treatment progressed, there was no change in the main component except DEHP and DNOP increased to 26.07% and 6.37%, respectively, whereas DBP decreased to 14.94%. In TDP 2, PAE components in the anaerobic digester were a little complex and DMP was present in both influent and primary clarifiers. As post-treatment progressed, much DMP was removed, because DMP was a short alkyl chain PAEs that was easy to be eliminated after biological treatment (Abdel Daiem et al., 2012). However, this result differed from that of Al-Saleh et al. (2017), who found higher levels of DMP and DNOP in tertiary-treated wastewater than in secondary-treated wastewater. The authors ascribed this phenomenon to the influence of the molecular weight and polarity of the chemicals (because DMP had higher polarity and DNOP had lower solubility). In TDP 3, the main components of PAEs were DIBP, DBP, DEHP, and DNOP, which changed a little as the treatment progressed. In TDP 4, most PAEs were efficiently removed after sand-filtration. DINP was the main component, accounting for 80.3%, but it actually only comprised 0.29 µg/L.

Based on the components extracted from the principal component analysis (Fig. S3), 12 PAEs could be divided into three principal components, which accounted for 87.91% of the total variance. Principal components 1 and 2 explained 30.71% and 31.47% of the total variance. Principal components 3 explained 26.33% of the total variance and was characterized by DMP, DPRP, DEHP, DBP and DIBP, which were the common pollutants that were recalcitrant in the wastewater treatment process. Across the 12 PAEs, the order of average content of PAEs in effluents of four TDPs were DIBP $(6.58 \ \mu g/L) > DEHP (2.23 \ \mu g/L) > DBP (1.98 \ \mu g/L) > DNOP (0.67 \ \mu g/L)$ L) > others (Table 2), which accounted for 59.66%, 20.20%, 17.96% and 5.69%, respectively. Higher DEHP and DBP concentrations were also discovered by Fromme et al. (2002), who found the level of DEHP was 1.74–182 μ g/L and the level of DBP was 0.2–10.4 μ g/L in treated sewage. Similarly, Marttinen et al. (2003) noted 6 µg/L of DEHP in treated sewage. However, directive 2008/105/EC defined a limit of DEHP was 1.3 μ g/L in surface waters (Clara et al., 2010). The World Health Organization and the United States Environmental Protection Agency had also established permissible limits for drinking water of <6.0 and 8.0 μ g/L, respectively.

3.4. Risk assessments of PAEs

Fig. 5 shows RQs of PAEs in different unit of four TDPs for fish, Daphnia, and green algae. In TDP 1, the influent posed high ecological risk to fish, Daphnia, and green algae (RQ = 2.87, 2.87, 19.95, respectively). Ecotoxicity decreased to some extent with the primary clarifier, and lower ecotoxicity was recorded following anaerobic digestion. However, according to the RO values, increased ecotoxicity was found in the aeration basin. This result maybe attributed to the increased content of PAEs or the transformation of the more toxic PAEs. The RQs of fish, Daphnia and green algae in effluent were 0.63, 0.63, and 4.14, indicating that Σ_{12} PAEs in effluent posed medium ecological risk to fish and Daphnia, and high ecological risk to green algae. In TDP 2, ecotoxicity also increased in the aeration basin because of the increase content of Σ_{12} PAEs or the generation of more toxic PAEs according to the RQs values. Ecotoxicity was also significant in anaerobic digestion and the biochemical sedimentation basin, despite a decrease in content of Σ_{12} PAEs. The result was attributed to the increase of DNOP and DIOP, which had more ecotoxicity than other PAEs. After treatment of the end sedimentation and biological aerated-filtration treatment, the RQs of Σ_{12} PAEs decreased to 0.16, 0.16, and 1.06, indicating that the effluent from TDP 2 posed medium ecological risk to fish and Daphnia, and high ecological risk to green algae. The RQs of effluent in TDPs 3 and 4 decreased with the progression of treatment, except in the aeration basin of TDP 4.

In the first treatment system, sedimentation to biological aerated-filtration was more effective than sand-filtration for detoxification. In the second system, sedimentation to sandfiltration was more effective than membrane filtration. When comparing TDP 3 to TDP 4, to some extent, a sedimentation basin was necessary for detoxification of PAEs. When comparing TDP 1 to TDP 4, it was evident that biochemical-physicochemical treatment was more effective than physicochemical-biochemical treatment for detoxification, because biochemical treatment could easily produce toxic PAEs and post-physicochemical treatment could contribute to their settling. The order of ecological risk in effluent was: TDP 1 > TDP 3 > TDP 2 > TDP 4. The RQs of fish and Daphnia in TDP 1–4 were 0.63, 0.16, 0.34, and 0.10, indicating that they might pose medium ecological risk to fish and Daphnia. The RQs of green algae in TDPs 1–3 were 4.14, 1.06, and 2.32, suggesting that they might pose high ecological risk to green algae. TDP 4 (RQ = 0.86) might pose medium ecological risk to green algae.

Among the 12 PAEs, DEHP posed a medium ecological risk to fish and Daphnia (RQ = 0.22), and high ecological risk to green algae (RQ = 1.40). DINP and DNOP posed medium ecological risk to green algae (RQ = 0.55, 0.54) (Table 2). The ecological risk of individual PAE in effluent was in following order: DEHP > DNOP > DINP > others. Therefore, an ecotoxicity assessment index was also recommended for current textile-dyeing wastewater treatment plants, apart from conventional indices (e.g., TOC, COD). Because long-term irrigation with such treated textile-dyeing wastewater could lead to accumulation of PAEs in soil, ultimately reaching the animal food chain and the human (Al-Saleh et al., 2017). A cautious use of such treated textile-dyeing wastewater for irrigation was therefore recommended to avoid severe health impacts on local people. Moreover, it is very necessary to eliminate toxic organic matter from textile-dyeing wastewater by reconstructing the existing wastewater treatment technologies or through development of novel and efficient techniques.

4. Conclusion

The four different textile-dyeing wastewater treatments investigated in this study were potentially effective for removing TOC,

Table 2
Mean concentration and RQs of $\Sigma_{12}\text{PAEs}$ in effluent of textile-dyeing wastewater plants.

Unit	(µg/L)	Fish	Daphnid	Green algae	RQs		
PAEs	Mean C	LC50	LC50	EC50	Fish	Daphnid	Green algae
DMP	0.07	40,822.0	87,973.0	39,492.0	$2.0 imes 10^{-6}$	$1.0 imes 10^{-6}$	$2.0 imes 10^{-6}$
DEP	0.02	12,471.0	24,192.0	9295.0	$2.0 imes 10^{-6}$	$1.0 imes 10^{-6}$	$2.0 imes 10^{-6}$
DPRP	0.01	3749.0	6547.0	2153.0	$2.0 imes 10^{-6}$	$1.0 imes 10^{-6}$	$3.0 imes 10^{-6}$
DIBP	6.58	1356.0	2166.0	624.0	4.9×10^{-3}	$3.0 imes 10^{-3}$	1.1×10^{-2}
DBP	1.98	1113.0	1749.0	492.0	1.8×10^{-3}	$1.1 imes 10^{-3}$	$4.0 imes 10^{-3}$
DAP	0.01	327.0	463.0	111.0	2.6×10^{-5}	$1.8 imes 10^{-5}$	$7.6 imes 10^{-5}$
DHP	N.D	95.0	121.0	25.0	$1.7 imes 10^{-5}$	$1.3 imes 10^{-5}$	$6.5 imes 10^{-5}$
BBP	0.01	911.0	1397.0	379.0	$7.0 imes 10^{-6}$	$5.0 imes 10^{-6}$	$1.8 imes 10^{-5}$
DEHP	2.23	10.0	10.0	1.6	$2.2 imes 10^{-1}$	$2.2 imes 10^{-1}$	$1.4 imes 10^0$
DNP	0.02	2.0	2.0	0.3	$1.1 imes 10^{-2}$	$1.1 imes 10^{-2}$	$7.9 imes 10^{-2}$
DINP	0.19	3.0	3.0	0.3	6.4×10^{-2}	$6.4 imes 10^{-2}$	$5.5 imes 10^{-1}$
DNOP	0.67	8.0	8.0	1.2	$8.4 imes 10^{-2}$	$8.4 imes 10^{-2}$	$5.4 imes 10^{-1}$
Σ12PAEs	11.78				$3.9 imes 10^{-1}$	$3.9 imes 10^{-1}$	$2.6 imes 10^{0}$

N.D: not detectable.

COD_{Cr}, PAEs, and for detoxification. When comparing two different wastewater treatment systems, physicochemical-biochemical system was more effective in removing TOC and COD_{Cr}, while the biochemical-physicochemical one was more focused on eliminating PAEs and detoxifying. Moreover, sedimentation basin and

tertiary treatment were necessary elements for removing substantial Σ_{12} PAEs and contributed to detoxification. Importantly, organic sum-parameters (e.g.TOC and COD) were not sufficient to evaluate the quality of textile-dyeing effluent. More focuses should be paid on the dissolved organic matter and ecotoxicity in textile-



Fig. 5. The acute toxicity of Σ_{12} PAEs through different units from textile-dyeing wastewater of four TDPs to three trophic levels of aquatic organisms (fish, Daphnia, and green algae). (PC: primary clarifier; AD: aeration digester; AB: aeration basin; SF: sand-filtration; BSB: biochemical sedimentation basin; ESB: end sedimentation; BAF: biological aerated-filtration; MF: membrane filtration; SB: sedimentation basin, the red lines represent RQs equal to 1. All RQs were higher than 0.1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

dyeing effluent.

Acknowledgments

This project was supported by the Special Applied Technology Research and Development of Guangdong Province (major project) (No. 2015B020235013), the Natural Science Foundation of China (No. 21577027), the Science and Technology Plan of Guangdong Province (No. 2015A020215032), and the Science and Technology Plan of Guangzhou (201607010330).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.08.006.

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