



Occurrence and removal of polycyclic aromatic hydrocarbons in real textile dyeing wastewater treatment process

Zaisheng Yan^{a,*}, Haichen Zhang^{a,b}, Huifang Wu^{b,*}, Mingzhong Yang^{a,b}, Shihe Wang^c

^aState Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China, Tel. +86 25 86882210; emails: zshyan@niglas.ac.cn (Z. Yan), 309962667@qq.com (H. Zhang), renzaita2006@126.com (M. Yang)

^bCollege of Environment, Nanjing University of Technology, Nanjing 211816, China, Tel. +86 25 86882210; email: whfkh1@163.com (H. Wu)

^cDepartment of Municipal Engineering, Southeast University, Nanjing 210096, China, email: 33932098@qq.com

Received 6 September 2015; Accepted 9 December 2015

ABSTRACT

In this work, the occurrence and removal of polycyclic aromatic hydrocarbons (PAHs) were investigated in a combination process of anoxic baffled reactor (ABR)-hybrid coagulation/membrane bioreactor (HCMBR) for real textile dyeing wastewater treatment. It was found that the target compounds except for the chrysene, benzo(*b*)fluoranthene, dibenzo(*a,h*)anthracene, and benzo(*g,h*)perylene occurred widely in raw textile dyeing wastewater, treated effluent and sludge samples. In the raw wastewater, two-ring naphthalene was the dominant compound, while three-ring PAHs predominated in the final effluent. The dominant compounds in the raw sludge samples were phenanthrene, while they were pyrene and indeno(1,2,3-*cd*)pyrene for final discharge sludge. The combination process achieved over 88% removal for all the PAHs. Low molecular weight (LMW) PAHs might be mainly removed by volatilization, adsorption, and sedimentation in the ABR treatment unit. High molecular weight (HMW) PAHs might be mainly removed by adsorption and sedimentation processes after coagulation and solid–liquid separation in the HCMBR treatment unit. The final discharge of treated textile dyeing wastewater and sludge was biologically safe based on the toxicity evaluation test.

Keywords: Polycyclic aromatic hydrocarbons; Textile dyeing wastewater; Anoxic-hybrid coagulation/membrane technology; Removal mechanism

1. Introduction

Textile dyeing is an important economic pillar industry in China, which uses a complicated process involving washing, scouring, bleaching, dyeing, and finishing process. These processes produced large quantities of highly toxic, low biodegradable, colored

wastewater [1,2]. This type of wastewater is difficult to treat due to the high content of contaminants, such as dyes, their breakdown products (aromatic amines, benzidine, naphthalene, etc.), surfactants, solvents, and recalcitrant compounds [3]. These contaminants are also likely to accumulate in sewage sludge. Among these pollutants, polycyclic aromatic hydrocarbons (PAHs) as priority pollutants should be paid

*Corresponding authors.

more attention due to large amounts of PAHs existing in dyes and textile dyeing sludge [4].

In recent years, the occurrence, behavior, and removal of PAHs in wastewater treatment plant (WWTP) have been paid much attention due to their high toxicities, such as carcinogenicity, mutagenicity, and allergic diseases [5,6]. The removal efficiencies and potential mechanisms of PAHs during biological treatment processes have been well investigated in previous studies [4,5,7,8]. The removal of low molecular weight (LMW) PAHs (two–three rings) was higher than high molecular weight (HMW) PAHs (four–six rings). The removal of LMW-PAHs might be due to volatilization or/and biodegradation, and HMW-PAHs mainly by adsorption [5]. However, so far, there are few investigations on the fate of PAHs in real textile dyeing wastewater treatment. Moreover, the removal of PAHs in real textile dyeing wastewater by hybrid coagulation/membrane technology has also never been reported. In a previous study [1], the high removal efficiency (92%) of colored compounds from dyeing wastewater using the combined process of anoxic baffled reactor (ABR)-biological contact oxidation was investigated. Also, the removal of organic compounds, such as halogenated alkanes, phenols, organic acid, and alcohols from real textile dyeing wastewater was determined [9,10]. To date, the occurrence and removal of PAHs have not been investigated, even though the textile dyeing wastewater has seriously polluted the nature's water environment. In addition, the toxicity and risk assessments of PAHs in the textile dyeing wastewater and sludge were very limited.

The aim of this work was to investigate the occurrence and removal of PAHs in a combination process of ABR-hybrid coagulation/membrane bioreactor (HCMBR) for real textile dyeing wastewater treatment. The concentrations of the individual PAH were determined in the raw wastewater, ABR effluent, HCMBR effluent, raw sludge, ABR sludge, and HCMBR sludge. The removal capacities of PAHs were assessed in the ABR-HCMBR combination, and the toxicity and risk assessments of PAHs in the textile dyeing wastewater and sludge were also discussed.

2. Materials and methods

2.1. Pilot plants and operating conditions

A pilot-scale experimental installation was used for this study. The system consisted of an anoxic bioreactor and aerobic membrane bioreactor (Fig. 1). The anoxic bioreactor was an ABR as a hydrolysis process pretreatment [1,10]. The aerobic membrane bioreactor

was hybrid coagulation membrane bioreactor (HCMBR) [9]. In this study, both the influent textile dyeing wastewater and seed sludge were taken from a WWTP located in the Changshu, PR China. The capacity of treatment plant was 10,000 m³ per day of highly colored textile dyeing wastewater, which was composed of 93% textile dyeing wastewater, 6% chemical fiber industrial wastewater, and 1% domestic sewage. The main component of textile dyeing wastewater was from the production process of dyeing, printing, and terylene fiber printing and dyeing.

The effective volume of ABR and HCMBR were the same. Each one was about 1.67 m³. The hydraulic retention times of combination process was 16 h in steady treatment phase. Polyvinylidene fluoride (PVDF) membrane (Tianjin Motian Membrane Engineering and Technology Co., Ltd, Tianjin, PR China) was set up and submerged in the HCMBR system. A nominal pore size was 0.2 μm and an effective filtration area was 25 m². During the experiment, the suitable dosage and dosing interval were once per day at the dosage of 40 mg Al per L of amount of mixed liquor into the HCMBR system according to an early study [9].

2.2. Sample collection and analytical procedure

Water and sludge samples (W1, W2, W3, S1, S2, S3) were collected from the effluent of each unit of the combination treatment process, as signed in Fig. 1. After back to the laboratory, all samples were centrifuged for the separation of the water phase and solid phase. Wastewater samples were filtered through glass microfiber filters (Waterman GF/F 47-mm diameter, 0.7-μm pore size) and extracted within 2 d for PAH analysis. The sludge samples were dried in a vacuum freeze dryer (FD-1B-50, Boyikang, Beijing, China) and stored at -20 °C until analysis.

2.3. Extraction and determination of PAHs in samples

PAHs in water and sludge samples were extracted according to the procedure described in the previous studies [11–15]. A brief description of the method was listed below. To extract PAHs in water samples, aliquots of the samples (100 mL) was sonicated with 100 mL dichloromethane in an ultrasonic bath for 60 min. The extraction mixture was allowed to stand still for 30 min to completely separate the dichloromethane and water. Organic phases were dehydrated by percolation through Na₂SO₄ anhydride, concentrated by rotary evaporation, and solvent-exchanged into acetonitrile (1 mL). The supernatant liquid was

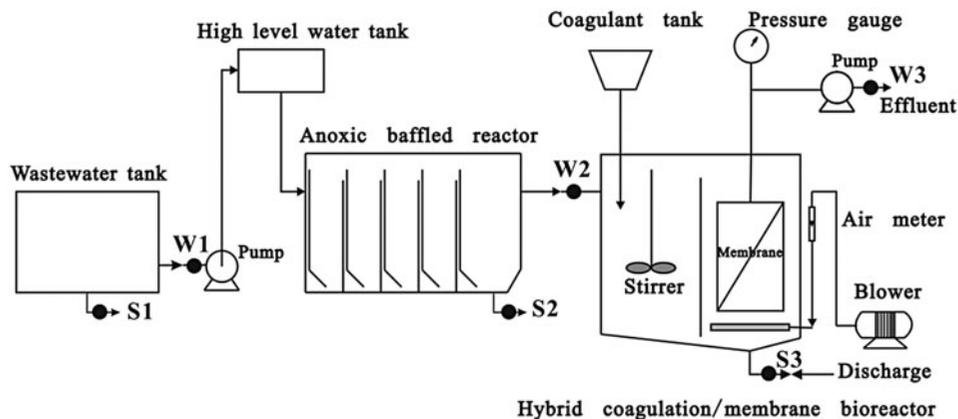


Fig. 1. The textile dyeing wastewater treatment progress with sampling sites. W1: raw wastewater; W2: effluent of ABR; W3: effluent of HCMBR; S1: primary sludge, sludge from the wastewater tank; S2: sludge from ABR; S3: Sludge from HCMBR.

filtered through 0.22- μm filter units and analysis. PAHs in sludge samples were extracted with accelerated solvent extraction (ASE, Dionex ASE 300) with acetone/dichloromethane solvent (1:1, v/v). The extracts were cleaned up via silica gel/alumina column, and PAHs fraction was obtained by elution with 70 mL of a mixture of hexane/dichloromethane (7:3, v/v). The samples were then analyzed with a high-performance liquid chromatography (HPLC) (Agilent 1,200, USA) fitted with a 4.6 \times 150-mm reverse phase C_{18} column using 8:2 acetonitrile:water (v:v) as the mobile phase at a flow rate of 1 mL min^{-1} at 30°C. The HPLC analysis was conducted with UV detection and fluorescence detector. The detection wavelength was 254 nm for UV detector, while the excitation and emission wavelengths were changed according to a time program for fluorescence detector. The excitation wavelength was 260 and 290 nm. The emission wavelength was 380 and 410 nm. All data were subject to strict quality control procedures. Quantification was performed using a calibration curve established using hexane-based internal standard for each individual PAH. Calibration plots had satisfactory linear regression coefficients with R^2 values greater than 0.99. The PAH recoveries were determined by adding the known concentration of standards solutions containing 16 priority PAH compounds. Recovery ranged from 62.3 \pm 5.6% to 102.6 \pm 6.2% for the 16 PAHs. The recoveries obtained in the study correspond to data observed in other studies for complex organic matrixes [16,17]. The detection limits were 0.1–5.0 $\mu\text{g kg}^{-1}$ for sludge samples and 0.5–3.0 ng L^{-1} for water samples.

The removal efficiency (RE %) of PAHs in wastewater and sludge during the treatment process was determined by the next Eq. (1):

$$\text{RE \%} = (C_{\text{in}} - C_{\text{out}}) / C_{\text{in}} \times 100 \quad (1)$$

where C_{in} is the concentration in the influent, C_{out} is the concentration in the effluent of an individual treatment or the whole treatment process.

2.4. Toxicity assessment of wastewater and sludge

The toxicity test of dyeing wastewater was performed by Microtox[®] bioassay (Model toxicity analyzer DXY-2, Institute of soil science, Chinese Academy of Sciences, Nanjing, China) following the basic protocol [18,19]. The toxic effects were measured as a percent inhibition of the bioluminescent bacterium *Photobacterium phosphoreum* T3. The luminescence inhibition after 15-min exposure was taken as endpoint. In the Microtox[®] test, the inhibition of the light emission for each sample dilution was measured in relative units of luminescence. The obtained value was used to determine the EC_{50} , which was the median sample concentration that caused a 50% reduction in bacteria bioluminescence. The relative units of bacteria bioluminescence was 50% when the control concentration of toxic HgCl_2 was 0.10 mg L^{-1} .

The wastewater samples from raw wastewater (W1), effluent of ABR (W2), and effluent of HCMBR (W3) were determined by performing the toxicity test. Every sample was measured in triplicate.

Table 1
Concentration and total mass flow of PAHs in textile dyeing wastewater and sludges

Compounds	Ring number	W1 (ng L ⁻¹)	W2 (ng L ⁻¹)	W3 (ng L ⁻¹)	S1 (μg kg ⁻¹)	S2 (μg kg ⁻¹)	S3 (μg kg ⁻¹)
Naphthalene	2	420.1 ± 20.3	65.3 ± 9.2	0.6 ± 0.1	18.4 ± 2.6	10.6 ± 8.4	2.3 ± 0.6
Acenaphthene	2	12.8 ± 2.6	24.1 ± 5.3	0.6 ± 0.1	3.1 ± 0.3	6.5 ± 0.2	13.2 ± 2.2
Fluorene	2	51.4 ± 3.6	6.2 ± 0.9	ND ^a	10.2 ± 3.2	9.3 ± 1.2	26.3 ± 10.2
Acenaphthylene	2	6.3 ± 0.8	1.2 ± 0.3	ND	0.6 ± 0.1	6.2 ± 0.7	29.3 ± 6.4
Phenanthrene	3	172.0 ± 14.3	80.9 ± 20.4	9.3 ± 0.5	83.2 ± 12.4	203.1 ± 21.4	402.3 ± 29.4
Anthracene	3	ND	20.6 ± 3.1	6.5 ± 1.9	4.2 ± 0.5	79.3 ± 1.8	112.1 ± 32.1
Fluoranthene	3	26.1 ± 9.5	5.8 ± 0.1	ND	ND	96.2 ± 32.1	20.6 ± 6.5
Pyrene	4	31.9 ± 10.3	35.3 ± 3.9	1.0 ± 0.0	10.3 ± 2.6	107.8 ± 31.6	304.2 ± 23.6
Chrysene	4	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	4	11.4 ± 2.9	10.5 ± 3.6	ND	ND	ND	67.3 ± 13.1
Benzo(b)fluoranthene	4	ND	ND	ND	ND	ND	ND
Benzo(k)fluoranthene	4	21.5 ± 9.7	15.2 ± 2.9	2.5 ± 0.0	ND	20.5 ± 3.2	106.5 ± 54.3
Benzo(a)pyrene	5	0.8 ± 0.6	0.8 ± 0.2	ND	ND	ND	57.3 ± 13.2
Dibenzo(a,h)anthracene	5	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	5	1.4 ± 0.1	1.1 ± 0.1	ND	ND	4.3 ± 0.9	183.4 ± 43.2
Benzo(g,h,i)perylene	6	ND	ND	ND	ND	ND	ND
ΣPAHs		755.7	266.9	20.6	130.0	543.8	1,324.8
Total mass flow of PAHs (mg d ⁻¹)		1.9	0.7	0.1	4.6	1.2	4.3

Note: Data are means ± standard deviation.

^aND: not detected, below the detection limit. W1: Raw wastewater; W2: Effluent of ABR; W3: Effluent of HCMBR; S1: Primary sludge, sludge from the wastewater tank; S2: Sludge from ABR; S3: Sludge from HCMBR.

Table 2

Concentrations of PAHs in the influent and effluent of other wastewater treatment plants (WWTPs)

Sampling date/site	Country	PAH (ng L ⁻¹) concentrations		Refs.
		Influent	Effluent	
Five municipal WWTPs	Italian	320–1,540	<50–<195	[7]
November, Catalonia WWTP	Spain	1,990, 2,510	NA ^a	[30]
Oct. 2005–Sept. 2006, Hiroshima	Japan	219 ± 210	43.5 ± 42.5	[31]
May, Tai'an City WWTP	China	1,147.5	129.2	[6]
November, Tai'an City WWTP		1,156.9	261.1	
Summer, Beijing WWTP	China	372 ± 56.5	182 ± 9.35	[5]
Winter, Beijing WWTP		749 ± 69.9	241 ± 44.8	
Shaoguan coking WWTP	China	5,470,000	4,700	[32]
October, Shaoguan coking WWTP	China	862,000	21,300	[20]
Coking WWTP by ultrafiltration technique	Poland	44,800–53,500	8,900–19,300	[21]
Summer, Changshu textile dyeing WWTP	China	755.7	20.6	This study

^aNA: not available.

3. Results and discussion

3.1. Concentrations of PAHs in dyeing wastewater and sludge

The contents of the 16 PAHs monitored in the dyeing wastewater and sludge samples are shown in Table 1. As shown in Table 1, the total concentration of PAHs input to the system was 755.7 ng L⁻¹, which was equal to the influent of WWTPs in other cities of the world except coking wastewater (Table 2). The influent of total PAHs concentration of textile dyeing WWTP were markedly lower than the influent of coking WWTP due to containing significant amounts of PAHs [20,21]. The most abundant PAHs in the raw wastewater were the two-ring naphthalene and three-ring phenanthrene with concentrations of 420.1 and 172 ng L⁻¹, respectively. After ABR treatment, the contents of individual PAH except acenaphthene, anthracene, and pyrene in W2 decreased. As shown in Table 1, the concentration of total PAHs in W2 was 266.9 ng L⁻¹, and the dominant compounds were also naphthalene and phenanthrene. The effluent concentrations of total PAHs in W3 achieved a low level with concentrations of 20.6 ng L⁻¹, and the dominant compounds were phenanthrene and anthracene, which could be attributed to phenanthrene and anthracene as components of synthetic dyes being the most dominant components in the wastewater of textile dyeing plants [4]. Furthermore, Table 1 showed a continuous decreasing trend in PAH concentrations of dyeing wastewater from 755.7 ng L⁻¹ in the primary effluent to 20.6 ng L⁻¹ in the final effluent. In addition, the contribution of two-ring PAHs decreased, while three-ring PAHs increased after the

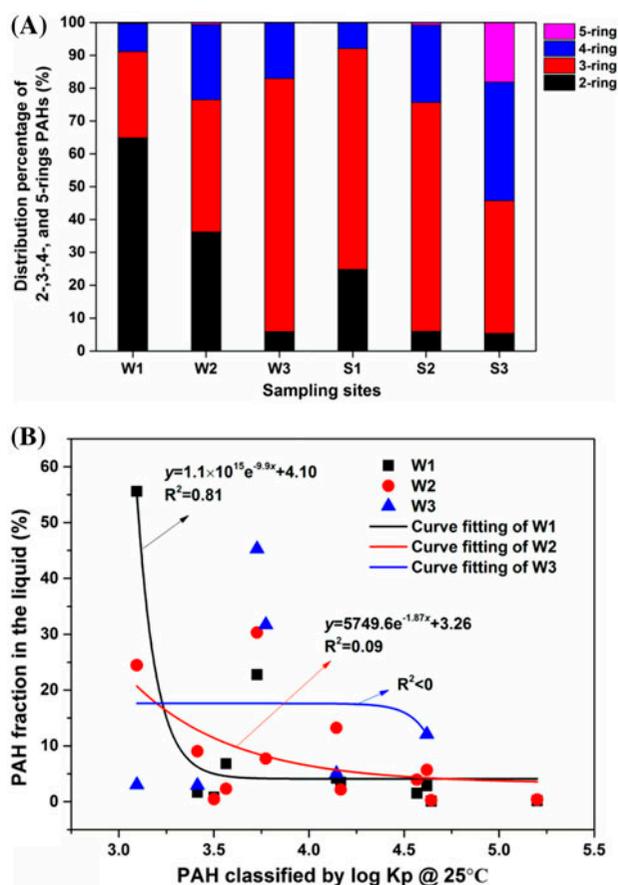


Fig. 2. (A) Distribution percentage of 2-,3-,4-, and 5-rings PAHs (%) in each sample; and (B) PAHs liquid–solid partitioning over the treatment stages in the dyeing wastewater.

Table 3

Removal efficiencies of PAHs in the wastewater in the ABR, HCMBR, and total treatment processes

Compounds	$\log K_{ow}^a$ [33]	ABR (%)	HCMBR (%)	Total (%)
Naphthalene	3.37	84.5	99.1	99.9
Acenaphthene	3.92	NA ^b	97.5	95.3
Fluorene	4.18	87.9	100.0	100.0
Acenaphthylene	4.07	81.0	100.0	100.0
Phenanthrene	4.46	53.0	88.5	94.6
Anthracene	4.54	NA	68.3	NA
Fluoranthene	5.22	77.8	100.0	100.0
Pyrene	5.18	NA	97.1	96.8
Benzo(a)anthracene	5.91	7.9	100.0	100.0
Benzo(k)fluoranthene	6	29.3	83.7	88.5
Benzo(a)pyrene	6.04	7.3	100.0	100.0
Indeno(1,2,3-cd)pyrene	7	21.5	100.0	100.0

^aRef. [33].^bNA: not available.

combination system treatment. The results indicated the composition of PAHs showed change to some degree during the treatment process. In this study, over 88% removal of PAHs was achieved by the ABR-HCMBR combination.

As strong hydrophobicity, PAHs are poorly water-soluble and tend to be adsorbed onto the activated sludge produced in this system. Thus, sludge would have a higher content of these compounds. The concentrations of total PAHs in the sewage sludge (S1) were $130 \mu\text{g kg}^{-1}$, and the dominant compounds were naphthalene fraction accounting for 14.2% of total PAHs and phenanthrene fraction accounting for 64%. Compared with the S1, the concentrations of total PAHs in the sludge (S2) and the sludge (S3) increased by 4 and 10 times, respectively (Table 1). In the sludge (S2) and the sludge (S3), the dominant compounds were phenanthrene and pyrene. The concentrations of HMW-PAHs such as four-ring pyrene in the final discharge sludge (S3) increased significantly ($p < 0.05$) than in the S1 and S2. These results demonstrated that four-ring PAHs tend to enrich in the final discharge sludge (Fig. 2(A)). However, the chrysene, benzo(b)fluoranthene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene were not detected in the textile dyeing wastewater and sludge during the experiment.

The total mass flows of PAHs along the biological treatment process were calculated (Table 1) to understand the removal mechanisms of the target compounds in each treatment unit. The final mass fraction of the effluent (W3) to the total initial loadings (100%) was 0.8%, and the final mass fraction of excess sludge (S2 and S3) to the total initial loadings was 84.9%. Residual fraction of PAHs was mainly from volatile

organic compounds loss and high-level water tank (Fig. 1) detained loss.

3.2. Removal of PAHs during the dyeing wastewater treatment process

The PAHs removal efficiencies of ABR, HCMBR, and total treatment processes were shown in Table 3. The removal efficiencies of individual PAH showed significant differences, which might be associated with their physical and chemical properties [6,7]. As hydrophobic compounds with a $\log K_{ow}$ of 3.37–7.0 (Table 3), PAHs tend to be adsorbed onto the solids present in the treatment system. As Fig. 2(B) shows, the K_p value of the PAH is expressed as a functional of the compound octanol-water partitioning coefficient K_{ow} ($\log K_p = 0.58 \log K_{ow} + 1.14$) [7] for sorption to solids in wastewater. The higher the K_p value of the PAH indicated the higher the solid bound fraction in the raw wastewater (W1) as shown in Fig. 2(B). However, the effluent of ABR (W2) and final effluent of HCMBR (W3) did not follow this distribution law, which suggested that the partitioning between aqueous and solid phases was affected by operational factors such as multiple mixed flows in ABR, velocity of flow, stirring, air stripping, and temperature [20]. Lower temperature might enhance the adsorption resulting in a higher removal of HMW-PAHs [5]. In addition, the content of organic matter in the activated sludge may also influence the adsorption of PAHs.

The removal of two-ring (except for volatile PAHs) and three-ring PAHs observed in the wastewater were mainly in the ABR treatment process. The fractions of LMW-PAHs losses observed in the ABR were

53.0–87.9%, suggesting that the phase-split anoxic condition in the ABR [1] favored the LMW-PAHs metabolism and gravitational sedimentation. These results agree with those of other studies [8,20], in which adsorption to sludge and transformation was the main pathway for the removal of these PAHs. PAHs are adsorbed to sludge that are already well separated by the conventional gravitational sedimentation, in which PAH removal ranged from 28 to 67% by sedimentation [22–24]. Nevertheless, naphthalene was mainly volatilized in the ABR due to the amount of water turbulence. However, the removal of HMW-PAHs depended on coagulation and solid–liquid separation mechanisms in HCMBR. The elimination of PAHs in the coagulation stage was attributed to the addition of the coagulants such as poly-aluminum chloride [23,25], the complex formation by polymer flocculants and the enhanced removal of PAHs by the particles. Coagulation method was proved to be an effective approach to flocculate the PAHs complex into large flocs, which tended to be removed from the aqueous solution [26,27]. Additionally, this modification of sludge properties due to coagulation, shear stress, and membrane retention might modify particulate and colloidal matters, and then could modify transport and partitioning phenomena [8]. In the HCMBR, the filtration step may have played a significant role in HMW-PAHs removal. The decrease in compounds concentration may be related to the decrease in effluent chemical oxygen demand (COD) as a result of membrane filtration as previous studies reported [9,10]. Individual PAH show a decrease of more than 68% through the HCMBR. The high removal for the most volatile compounds in HCMBR could be explained by the aeration of the membrane module

playing a significant role in this HCMBR. For the most hydrophobic molecules with the least volatile, the removal in the HCMBR units was probable that PAHs sorption on dissolved or colloidal matter, as well as organic deposit on the membrane and form a fouling layer [28]. PAHs removal from the final effluent would be enhanced by advanced solid–liquid separation mechanisms in the HCMBR. HMW-PAHs were more difficult removals than the LMW-PAHs from the biological treatment system due to the different removal mechanisms that the HMW-PAHs were prone to absorbed on the sludge [5]. These results confirm that volatilization, coagulation, and sorption play a significant role in PAHs removal in the HCMBR.

3.3. Toxicity assessment of wastewater and sludge

The toxicity of the textile dyeing wastewater in different treatment units was shown in Fig. 3. According to toxicity assessment methods in previous studies [18,19], the toxicity of raw wastewater (W1) was in heavy level (EC_{50} 0.62 mg l^{-1}) due to the textile dyeing wastewater containing lots of toxic compounds [9] and strong carcinogenic potency of HMW-PAHs, such as benzo(a)pyrene. After hydrolysis process of ABR, the decolorization and mineralization of dye in wastewater [10] resulted in an increased toxicity (EC_{50} 0.06 mg l^{-1}). The treated final effluent after HCMBR treatment showed slight toxicity toward the bioluminescent bacterium *P. phosphoreum* T3 (EC_{50} 0.056 mg l^{-1}). Although most of organic pollutants including lots of toxic pollutants were removed from the wastewater after the HCMBR treatment processes, there were still a certain number of toxic pollutants

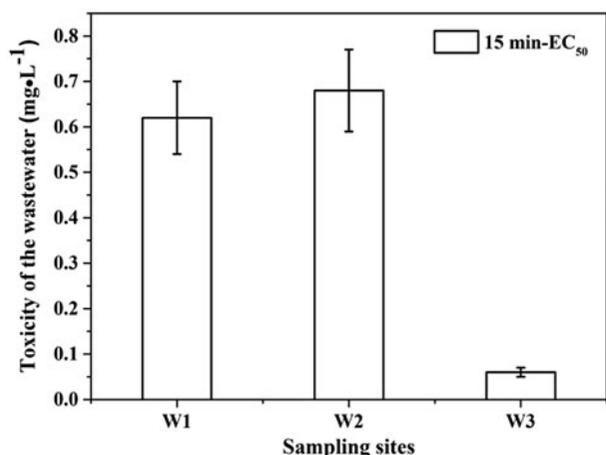


Fig. 3. The toxicity of the textile dyeing wastewater in different sampling sites.

Table 4

Comparison of PAHs concentrations in the textile dyeing sludge with ERL and ERM guideline values ($\mu\text{g kg}^{-1}$)

Compounds	This study			ERL ^a	ERM ^b
	S1	S2	S3		
Naphthalene	18.4	10.6	2.3	160	2,100
Phenanthrene	83.2	203.1	402.3	240	1,500
Pyrene	10.3	107.8	304.2	665	2,600
Benzo(a)pyrene	ND ^c	ND	57.3	430	1,600
LMW-PAHs	119.7	411.2	606.1	552	3,160
HMW-PAHs	10.3	24.8	414.5	1,700	9,600
Σ PAHs	130.0	543.8	1,324.8	4,022	44,792

^aERL: effects range-low.

^bERM: effects range-median; data cited in Ref. [29].

^cND: not detected, below the detection limit. S1: primary sludge, sludge from the wastewater tank; S2: sludge from ABR; S3: sludge from HCMBR.

present in the final effluent (Table 1) after HCMBR treatment.

Two effects-based guideline values, i.e. the effects range-low (ERL) and the effects range-median (ERM), are widely used to assess the ecological risk caused by PAHs in aquatic environment [4,29]. PAHs concentrations less than the ERL show that an adverse biological effect is rare; PAHs concentrations exceeding the ERM indicate that adverse effect would occur frequently, while PAHs concentrations between the ERL and ERM suggest that there will be an occasional adverse effect. The determined contents of individual PAH, LMW-PAHs, HMW-PAHs, and total PAHs compounds in this study were compared with ERL and ERM values (Table 4). The relatively low PAHs concentrations were observed in the sludge S1 and sludge S2, which were below the ERL. In sludge S3, only phenanthrene and LMW-PAHs concentrations were between at the ERL values and at the ERM values where adverse biological effects might occasionally occur. Toxicity assay suggested that treated textile dyeing wastewater and sludge by the ABR-HCMBR combination technology was biologically safe for discharge in this study. In any case, monitoring of toxicity is crucial and should always be used to assess the success of a treatment strategy.

4. Conclusions

This study investigated the occurrence and removal mechanisms of PAHs in real textile dyeing wastewater by the ABR-HCMBR combination treatment. PAHs compounds all existed in the textile dyeing wastewater and sludge except for the chrysene, benzo(*b*)fluoranthene, dibenzo(*a,h*)anthracene and benzo(*g,h,i*)perylene. In the raw wastewater and raw sludge, naphthalene and phenanthrene were the predominant PAHs. Although the composition of PAHs in the final effluent showed gentle change, the four-ring PAHs were significantly dominant in the final discharge sludge after the combination treatment. PAHs were efficiently eliminated from wastewater during treatment via the ABR-HCMBR combination technology (88.5–100%).

LMW-PAHs (two–three rings) might be mainly removed by volatilization, adsorption, and sedimentation in the ABR treatment unit. HMW-PAHs (four–six rings) might be mainly removed by adsorption, sedimentation processes after coagulation and solid–liquid separation in the HCMBR treatment unit. Hence, this work improves our understanding of the fate of hazardous substances PAHs in textile dyeing wastewater by the ABR-HCMBR technology treatment and provides important information for the choice of the

combination technology in industrial wastewater treatment.

Acknowledgments

This work was supported by grants from National Natural Science Foundation of China (41371456, 51109203), Major Program of Natural Science Foundation of Jiangsu Province (12KJA610001), Ministry of Housing of Science and Technology Planning Project (2014-K7-010) and State Key Laboratory of Pollution Control and Resource Reuse Foundation (PCRRF13018).

References

- [1] H.F. Wu, S.H. Wang, H.L. Kong, T.T. Liu, M.F. Xia, Performance of combined process of anoxic baffled reactor-biological contact oxidation treating printing and dyeing wastewater, *Bioresour. Technol.* 98 (2007) 1501–1504.
- [2] N.M.H. ElDefrawy, H.F. Shaalan, Integrated membrane solutions for green textile industries, *Desalination* 204 (2007) 241–254.
- [3] H.M. Pinheiro, E. Touraud, O. Thomas, Aromatic amines from azo dye reduction: Status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters, *Dyes Pigm.* 61 (2004) 121–139.
- [4] X.A. Ning, M.Q. Lin, L.Z. Shen, J.H. Zhang, J.Y. Wang, Y.J. Wang, Z.Y. Yang, J.Y. Liu, Levels, composition profiles and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in sludge from ten textile dyeing plants, *Environ. Res.* 132 (2014) 112–118.
- [5] M. Qiao, W. Qi, H. Liu, J. Qu, Occurrence, behavior and removal of typical substituted and parent polycyclic aromatic hydrocarbons in a biological wastewater treatment plant, *Water Res.* 52 (2014) 11–19.
- [6] W.J. Tian, J. Bai, K.K. Liu, H.M. Sun, Y.G. Zhao, Occurrence and removal of polycyclic aromatic hydrocarbons in the wastewater treatment process, *Ecotoxicol. Environ. Saf.* 82 (2012) 1–7.
- [7] F. Fatone, S. Di Fabio, D. Bolzonella, F. Cecchi, Fate of aromatic hydrocarbons in Italian municipal wastewater systems: An overview of wastewater treatment using conventional activated-sludge processes (CASP) and membrane bioreactors (MBRs), *Water Res.* 45 (2011) 93–104.
- [8] I. Mozo, M. Stricot, N. Lesage, M. Spérandio, Fate of hazardous aromatic substances in membrane bioreactors, *Water Res.* 45 (2011) 4551–4561.
- [9] Z.S. Yan, S.H. Wang, X.K. Kang, Y. Ma, Enhanced removal of organics and phosphorus in a hybrid coagulation/membrane bioreactor (HCMBR) for real textile dyeing wastewater treatment, *Desalin. Water Treat.* 47 (2012) 249–257.
- [10] Z.S. Yan, S.H. Wang, X.K. Kang, Y. Ma, Removal of organic compounds of real textile dyeing wastewater by pilot scale combination process of anoxic baffled reactor-hybrid membrane bioreactor, *Water Pract. Technol.* 5 (2010) 1–8.

- [11] Z.S. Yan, H.L. Jiang, X.H. Li, Y. Shi, Accelerated removal of pyrene and benzo[a]pyrene in freshwater sediments with amendment of cyanobacteria-derived organic matter, *J. Hazard. Mater.* 272 (2014) 66–74.
- [12] Z.S. Yan, N. Song, H.Y. Cai, J.H. Tay, H.L. Jiang, Enhanced degradation of phenanthrene and pyrene in freshwater sediments by combined employment of sediment microbial fuel cell and amorphous ferric hydroxide, *J. Hazard. Mater.* 199–200 (2012) 217–225.
- [13] Z.S. Yan, H.Y. Guo, T.S. Song, Y. Hu, H.L. Jiang, Tolerance and remedial function of rooted submersed macrophyte *Vallisneria spiralis* to phenanthrene in freshwater sediments, *Ecol. Eng.* 37 (2011) 123–127.
- [14] Z.S. Yan, Y. Hu, H.L. Jiang, Toxicity of phenanthrene in freshwater sediments to the rooted submersed macrophyte, *Vallisneria spiralis*, *Bull. Environ. Contam. Toxicol.* 87 (2011) 129–133.
- [15] Z.S. Yan, H.L. Jiang, H.Y. Cai, Y.L. Zhou, L.R. Krumholz, Complex interactions between the macrophyte acorus calamus and microbial fuel cells during pyrene and benzo[a]pyrene degradation in sediments, *Sci. Reports* 5 (2015) 10709, doi: [10.11038/srep10709](https://doi.org/10.11038/srep10709).
- [16] B. Macherzynski, M. Włodarczyk-Makula, A. Nowacka, Simplification of the procedure of preparing samples for Pchs and Pcbcs determination, *Arch. Environ. Prot.* 38 (2012) 23–33.
- [17] M. Włodarczyk-Makula, Preparation of wastewater samples for GC–MS analysis of PAHs, *Arch. Environ. Prot.* 34 (2008) 259–264.
- [18] C.V. Araújo, R.B. Nascimento, C.A. Oliveira, U.J. Strotmann, E.M. da Silva, The use of Microtox[®] to assess toxicity removal of industrial effluents from the industrial district of Camaçari (BA, Brazil), *Chemosphere* 58 (2005) 1277–1281.
- [19] L. Ai-ju, K. Fan-xiang, S. Xiao-li, Y. Yang, Y. Zhou, Toxicity assessment of contaminated sediments after dredging, *Bull. Environ. Contam. Toxicol.* 77 (2006) 905–911.
- [20] W. Zhang, C. Wei, G. An, Distribution, partition and removal of polycyclic aromatic hydrocarbons (PAHs) during coking wastewater treatment processes, *Environ. Sci.: Processes Impacts* 17 (2015) 975–984.
- [21] M. Smol, M. Włodarczyk-Makula, Effectiveness in the removal of polycyclic aromatic hydrocarbons from industrial wastewater by ultrafiltration technique, *Arch. Environ. Prot.* 38 (2012) 49–58.
- [22] E. Manoli, C. Samara, The removal of Polycyclic Aromatic Hydrocarbons in the wastewater treatment process: Experimental calculations and model predictions, *Environ. Pollut.* 151 (2008) 477–485.
- [23] A. Nowacka, M. Włodarczyk-Makula, Monitoring of polycyclic aromatic hydrocarbons in water during preparation processes, *Polycyclic Aromat. Compd.* 33 (2013) 430–450.
- [24] M. Włodarczyk-Makula, The loads of PAHs in wastewater and sewage sludge of municipal treatment plant, *Polycyclic Aromat. Compd.* 25 (2005) 183–194.
- [25] T.P.A. Shabeer, A. Saha, V.T. Gajbhiye, S. Gupta, K.M. Manjaiah, E. Varghese, Removal of poly aromatic hydrocarbons (PAHs) from water: Effect of nano and modified nano-clays as a flocculation aid and adsorbent in coagulation–flocculation process, *Polycyclic Aromat. Compd.* 34 (2014) 452–467.
- [26] C. Zhang, L. Wu, D. Cai, C. Zhang, N. Wang, J. Zhang, Adsorption of polycyclic aromatic hydrocarbons (fluoranthene and anthracenemethanol) by functional graphene oxide and removal by pH and temperature-sensitive coagulation, *ACS Appl. Mater. Interfaces* 5 (2013) 4783–4790.
- [27] A. Nowacka, M. Włodarczyk-Makula, B. Macherzyński, Comparison of effectiveness of coagulation with aluminum sulfate and pre-hydrolyzed aluminum coagulants, *Desalin. Water Treat.* 52 (2014) 3843–3851.
- [28] H.J. Lin, M.J. Zhang, F.Y. Wang, F.G. Meng, B.Q. Liao, H.C. Hong, J.R. Chen, W.J. Gao, A critical review of extracellular polymeric substances (EPSs) in membrane bioreactors: Characteristics, roles in membrane fouling and control strategies, *J. Membr. Sci.* 460 (2014) 110–125.
- [29] E.R. Long, D.D. Macdonald, S.L. Smith, F.D. Calder, Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments, *Environ. Manage.* 19 (1995) 81–97.
- [30] J. Sanchez-Avila, J. Bonet, G. Velasco, S. Lacorte, Determination and occurrence of phthalates, alkylphenols, bisphenol A, PBDEs, PCBs and PAHs in an industrial sewage grid discharging to a Municipal Wastewater Treatment Plant, *Sci. Total Environ.* 407 (2009) 4157–4167.
- [31] N. Ozaki, Y. Takamura, K. Kojima, T. Kindaichi, Loading and removal of PAHs in a wastewater treatment plant in a separated sewer system, *Water Res.* 80 (2015) 337–345.
- [32] W. Zhang, C. Wei, X. Chai, J. He, Y. Cai, M. Ren, B. Yan, P. Peng, J. Fu, The behaviors and fate of polycyclic aromatic hydrocarbons (PAHs) in a coking wastewater treatment plant, *Chemosphere* 88 (2012) 174–182.
- [33] J.M. Neff, S.A. Stout, D.G. Gunster, Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: Identifying sources and ecological hazard, *Integr. Environ. Assess. Manage.* 1 (2005) 22–33.