Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27628

234 (2021) 222–226
September

The distribution and toxicity evaluation of polycyclic aromatic hydrocarbons in the textile dyeing sludge

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Received 20 January 2021; Accepted 15 July 2021

ABSTRACT

Within this study, the focus of the investigation was on the concentration, toxicity and skin sensitization of 16 PAHs (polycyclic aromatic hydrocarbons) in six textile dyeing sludges, which were analyzed by the gas chromatogram–mass spectrometer, Ecological Structure Activity Relationships (ECOSAR) and Pred-Skin, respectively. The concentration of Σ16PAHs of the sludges fell in the range of 983.52~2,026.88 ng g^{-1}. And the majority of PAHs were low molecular weight PAHs, which was due to different raw materials and wastewater treatment processes. The acute toxicity values of 16 PAHs to fish, daphnia and algae were 0.014~9.390, 0.012~5.940, and 0.054~6.910 mg L^{-1}, respectively. The chronic toxicity values of PAHs to fish, daphnia and algae were 0.002~1.040, 0.004~0.782, and 0.037~2.300 mg L^{-1}, respectively. Toxicity evaluation found that PAHs were toxic to organisms, even deadly toxic. Sensitization probability of PAHs by Pred-Skin showed different prediction results from five prediction models, but all indicated that most of the PAHs had a sensitization effect on the human body, with a probability of over 80.0%. This article is trying to draw people's attention to the toxicity and sensitization of PAHs in the textile dyeing sludge, in order to provide theoretical guidance for the reduction and detoxification of textile dyeing sludge.

Keywords: Textile dyeing sludge; Polycyclic aromatic hydrocarbons; Toxicity; Skin sensitization; Evaluation

1. Introduction

The composition of textile dyeing sludge is complicated, containing pollutants such as heavy metals, aromatic amine and polycyclic aromatic hydrocarbons (PAHs), which have a great threat to the ecological environment [1–4]. It will bring serious secondary pollution to the environment if not handled properly. PAHs are persistent organic pollutants, which pose a great threat to human health and the ecosystem, and have received widespread attention around the world. Many of these compounds fall into the U.S. EPA priority control pollutants list. PAHs have chronic effects of biological accumulation, teratogenic, carcinogenic and mutagenesis. The lipid solubility and carcinogenicity of PAHs will be influenced by the benzene ring. The higher the amount of benzene rings, the more soluble and carcinogenic [5]. At the same time, the longer it accumulates in the environment, the more heritable and toxic it becomes, such as benzophenanthrene and benzo(a)pyrene are carcinogenic [6,7]. PAHs can also damage cells and inhibit the growth of microbiology [8,9]. Some ecotoxicological studies have suggested that PAHs may be phytotoxic [10,11]. However, to date, most of the studies have just focused on the carcinogenicity of PAHs, there are few studies on the acute toxicity, chronic toxicity and skin sensitization of PAHs.

According to the China Environment Statistical Yearbook 2016, the discharge of textile dyeing sludge amounted to about 5.05 million tons in 2016. And it is important to note that there are large amounts of PAHs in the textile dyeing sludge. The solubility of PAHs in water is low and decreases with the increase of molecular weight [5]. As for the solid phase in general, PAHs can be quickly absorbed onto the sludge particles in wastewater [12]. PAHs are eventually fixed by adsorption to organic substrates and minerals in the solid phase, making them more difficult to degrade [13]. Therefore, PAHs can accumulate continuously in the sludge, which will cause certain harms to the organisms in the environment and needs to arouse our greater attention.

In order to raise people's awareness of PAHs in textile dyeing sludge, this study, therefore, selected six typical textile dyeing sludges from Guangdong Province of China as the object of study. This study analyzed the contents of 16 PAHs and used the Ecological Structure Activity Relationships (ECOSAR) V2.0 and Pred-Skin 3.0 to evaluate the toxicity of PAHs in the textile dyeing sludges. The goal of this study was to explore the effects of PAHs toxicity on biological and human health and fill people's blind spots on PAHs, such as acute toxicity, chronic toxicity and skin sensitization, etc. It also helped to provide theoretical support for the reduction and detoxification of textile dyeing sludge in situ.

2. Materials and methods

2.1. Reagents and instruments

U.S. EPA published 16 priority PAHs mixed standard solution: naphthalene, acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), indene(1,2,3-cd)pyrene (InP), dibenzoanthracene (DBA), benzo(g,h,i)pyrene (Bp), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzene(k)fluoranthene (BkF) and benzo(a) pyrene (BaP). Five kinds of internal standard mixtures, including naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and pyrene-D12. Two kinds of recovery indicators mixtures, including fluorene-D10 and pyrene-D10 (bought from o2si). High-performance liquid chromatography grade n-hexane, acetone and dichloromethane were purchased from ANPEL Laboratory Technologies (Shanghai) Inc. The anhydrous sodium, sulfate alumina (100~200 mesh), silica gel (100~200 mesh), mercuric sulfate potassium permanganate and others were bought from Adamas Reagent, Ltd., (Shanghai, China, purity > 95%).

2.2. Contents and toxicity analysis of PAHs

The textile dyeing sludge sample (Table 1) after freeze-drying under –60°C was accurately weighed 2 g and put into a 250 mL conical flask. Ultrasonic extraction was conducted for 5 min [14]. The extraction process was repeated three times. Then the extract was concentrated to 0.5 mL by rotary evaporation, separation, purification and nitrogen blown. And the internal standard mixtures for analysis were added at last. The internal standard method and multi-point correction curve were used for quantitative analysis of PAHs.

Gas chromatogram–mass spectrometer (GC–MS, 7890A-5975C Agilent) equipped with the HP-5 MS capillary column (30 m × 0.25 mm-i.d. × 0.25 μm). GC–MS conditions: selective ion scanning mode, inlet temperature 290°C, electron energy 70 eV, carrier gas flow rate 1.00 mL min^{-1}, stigma pressure 68.9 kPa, 1 μL non-shunt injection. Program of rising temperature: initial temperature 50°C, retention for 2 min; heat up to 200°C at 20°C/min and keep it for 2 min. Then, the temperature was increased to 240°C at 5°C/min and kept for 2 min. The temperature was increased to 290°C at 3°C/min with 5 min retention. The repeat sample of PAHs analysis error was less than 5%.

Acute toxicity (LC50 or EC50), chronic toxicity (ChV) and skin sensitization analysis of PAHs in textile dying sludge were conducted by ECOSAR V2.0 and Pred-Skin 3.0 software. ECOSAR was mainly used to predict acute and chronic toxicity of aquatic organisms, such as aquatic fish, aquatic invertebrates (daphnia) and green algae. Its toxicity classification is shown in Table 2.

3. Results and discussion

3.1. Contents and distribution of PAHs

The concentration of a total of 16 PAHs (Σ16 PAHs) in six textile dyeing sludges was measured, with results shown in Fig. 1. The concentrations of PAHs in different textile dyeing sludges differed significantly. The concentrations of Σ16 PAHs were ranging from 983.52 to 2,026.88 ng g^{-1}. The average concentration was 1,765.99 ng g^{-1}. The concentrations of Σ16 PAHs of S3, S4 and S6 were twice as much as those of the other three textile dyeing sludges. Σ16 PAHs in S5 had the minimum concentration.

Table 1
Information of six textile dyeing plants

Name	Raw material	Colouring agent	Treatment capacity (m^3 d^{-1})	Treatment process	Sludge dewatering
S1	Linter	Azo dyes	600	Flocculation, A/O	Plate-frame pressure filtration
S2	Cotton, chemical fiber	Reactive dyes	25,000	Flocculation, A/O	Belt press filtration
S3	Chemical fiber	Cationic dyes	10,000	A/O, Flocculation	Belt press filtration
S4	Chemical fiber, cotton cloth	Reactive dyes, disperse dyes	50,000	A/O, Flocculation	Plate-frame pressure filtration
S5	Cotton, flax	Reactive dyes	30,000	Flocculation, A/O	Belt press filtration
S6	Cotton yarn, cloth	Reactive dyes, cationic dyes	15,000	A, Flocculation, O	Belt press filtration

Note: A – anaerobic reaction; O – aerobic reaction.

Table 2
Acute and chronic toxicity levels (units: mg L^{-1})

Classification	Acute toxicity[a]	Chronic toxicity[b]
Not harmful	LC50 > 100 or EC50 > 100	ChV > 10
Harmful	10 < LC50 < 100 or 10 < EC50 < 100	1 < ChV < 10
Toxic	1 < LC50 < 10 or 1 < EC50 < 10	0.1 < ChV < 1
Very toxic	LC50 < 1 or EC50 < 1	ChV < 0.1

[a]Criteria set by the European Union (described in Annex VI of Directive 67/548/EEC);
[b]Criteria set by the Chinese hazard evaluation guidelines for new chemical substances (HJ/T 154–2004).

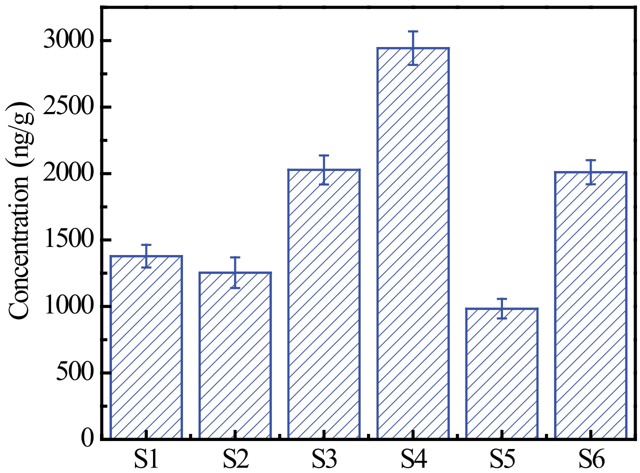

Fig. 1. Analysis of ∑16PAHs concentration.

In addition, the distribution of PAHs components in the six textile dyeing sludge samples is shown in Fig. 2. We found that the distribution of each component showed a similar pattern except for S4. The concentration of low molecular weight PAHs in textile dyeing sludge was about 570.465~1,919.965 ng g^{-1}, with 2-ring PAHs as the main component. The concentration of the high molecular weight PAHs was 344.810~1,343.295 ng g^{-1}, and the main component was 4-ring PAHs. Overall, low-ring PAHs had accounted for more than 50%, indicating that low-ring PAHs dominated in the textile dyeing sludges. According to the study of Cai et al. [15] and Pérez et al. [16], the different raw materials and wastewater treatment processes had a significant influence on the components of PAHs in the sludge residue. In the wastewater treatment process, biological treatment after coagulation precipitation is helpful to reduce the PAHs in the sludge accumulation. For example, S2, S4 and S5 have used the same fabric materials and dyes (chemical fiber cotton, reactive dyes and disperse dyes), but the Σ16 PAHs of S2 and S5 were obviously lower than that of S4. This may be due to the application of coagulation and sedimentation followed by a biological treatment process for S2 and S5, which can reduce the accumulation of PAHs in sludge. And the reason why S4 had different component

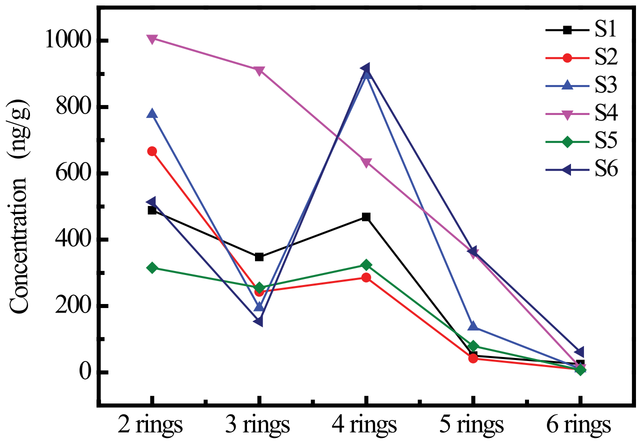

Fig. 2. Distribution of different rings PAHs.

distribution is that S4 is a wastewater centralized treatment plant, which treats wastewater with different sources of PAHs from several small dyeing nearby, therefore presenting a different distribution pattern.

3.2. Toxicity evaluation of PAHs

According to the study of Li et al. [17], ECOSAR program was used to predict the acute toxicity and chronic toxicity of PAHs. According to Fig. 3, the acute toxicity value of 16 PAHs to fish were 9.390, 2.280, 1.480, 2.110, 0.547, 1.150, 0.276, 0.042, 0.386, 0.129, 0.042, 0.042, 0.014, 0.129, 0.014 and 0.014 mg L^{-1}, respectively. And the acute toxicity values to daphnia were 5.940, 1.550, 1.030, 1.450, 0.398, 0.809, 0.208, 0.035, 0.287, 0.101, 0.035, 0.035, 0.012, 0.101, 0.012 and 0.012, respectively. The acute toxicity values to algae were 6.910, 2.420, 1.740, 2.330, 0.833, 1.470, 0.507, 0.125, 0.656, 0.290, 0.125, 0.125, 0.054, 0.290, 0.054 and 0.054. According to the European Union standards (Table 2), PAHs were classified as toxic at all three nutrient levels. Among them, Ant was highly toxic to daphnia but toxic to fish and green algae. Nap, Acy, Ace and Fl showed toxic effects on three aquatic organisms. And Phe, Flu, BaP, Pyr, BaA, BbF, BkF, DBA, Chr, Bp and InP all showed highly toxic effects.

According to Fig. 3b, the chronic toxicity values of PAHs to fish were 1.040, 0.275, 0.183, 0.257, 0.072, 0.145, 0.038, 0.007, 0.052, 0.019, 0.007, 0.007, 0.002, 0.019, 0.002 and 0.002 mg L^{-1}. And the chronic toxicity values to daphnia were 0.782, 0.248, 0.174, 0.237, 0.078, 0.144, 0.045, 0.010, 0.060, 0.024, 0.010, 0.010, 0.004, 0.024, 0.004 and 0.004, respectively. The chronic toxicity values to algae were 2.300, 0.942, 0.708, 0.922, 0.380, 0.625, 0.251, 0.076, 0.314, 0.157, 0.076, 0.076, 0.037, 0.157, 0.037 and 0.037 mg L^{-1}, respectively. According to the Chinese Guidelines for Hazard Assessment of New Chemical Substances (HJ/T 154-2004) (Table 2), PAHs were chronic toxic to fish daphnia and algae, and even highly toxic. Nap showed harmful effects on fish. Acy, Ace, Fl and Ant showed toxic effects on fish, and the others were highly toxic. Nap, Acy, Ace, Fl and Ant showed toxic effects on water fleas, while others showed highly toxic effects. Nap was harmful to the green algae. Acy, Ace, Fl, Phe, Ant, Flu, Pyr, BaA and Chr showed toxic effects to the green algae, while the other showed highly toxic effects. Therefore, PAHs were either acute or chronic toxic to organisms. And due to their hydrophobic nature, they are likely to accumulate and migrate from sludge to organisms in the aquatic environment, which may pose a greater threat to human health.

3.3. Skin sensitization analysis of PAHs

Skin sensitization is an immune response to certain chemicals, characterized by skin inflammation disease. It will not threaten our life, but it has a profound effect on one's ability to work and the quality of one's life. Pred-Skin 3.0 is a tool of human body skin sensitization potential assessment, whose ability of prediction is about 89% [18]. The probability of sensitization can be obtained by Pred-Skin under different models of 16 PAHs, as shown in Table 3. In the direct peptide reactivity assay (DPRA) model, we can find that only BbF was the non-sensitizing agent, with a probability of 84.1%. And the rest of the 16 PAHs were sensitizing agents, and the probability is as high as 84.1%~92.5%. In the KeratinoSens model, we can see that Nap, Ace, Fl and Ant were identified as non-sensitizer, but the probability of Nap and Ace were low, just at about 52.6% and 69.1%, respectively. Meanwhile, the other substances were sensitizers with the probability of 82.1%~97.2%. In the h-CLAT model, the probabilities were relatively low. The Ace and BaP were non-sensitizer, with their probabilities at 58.9% and

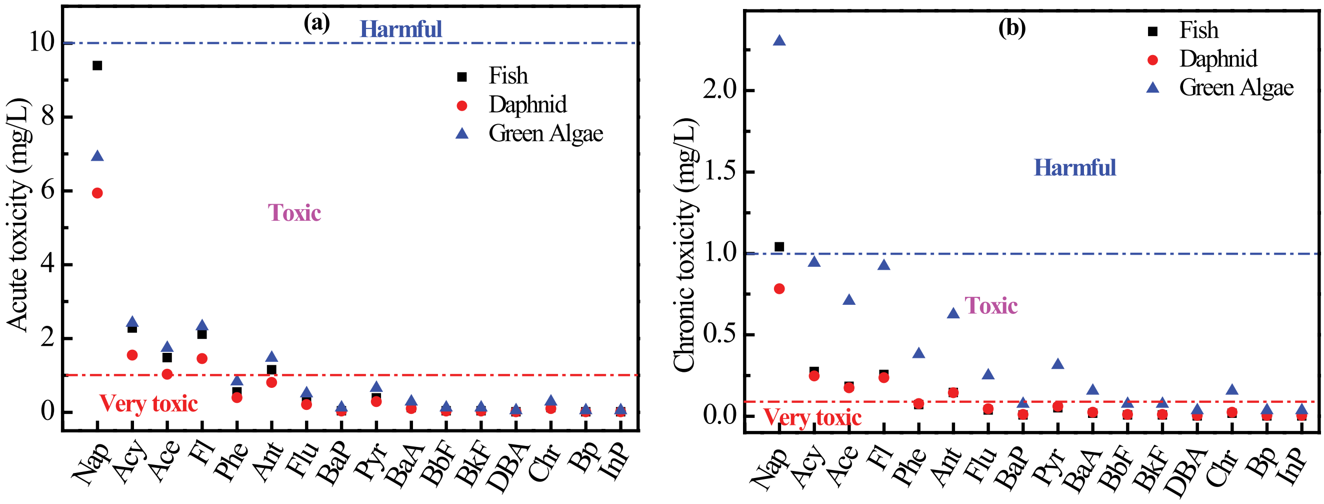

Fig. 3. The acute (a) and chronic (b) toxicities of PAHs towards fish, daphnia and green algae.

Table 3
Analysis of skin sensitization model of PAHs (%)

PAHs	DPRA (in chemico)	KeratinoSens (in vitro)	h-CLAT (in vitro)	LLNA (in vivo)	HRIPT/HMT (Human)
Nap	(+) 88.9	(–) 52.6	(+) 56.9	(+) 99.4	(+) 75.7
Acy	(+) 90.9	(+) 97.2	(+) 59.2	(+) 99.7	(+) 95.8
Ace	(+) 89.8	(–) 69.1	(–) 58.9	(+) 99.9	(+) 95.5
Fl	(+) 88.4	(–) 95.3	(+) 55.6	(–) 99.5	(+) 99.0
Phe	(+) 89.3	(+) 89.8	(+) 56.9	(+) 99.5	(+) 98.5
Ant	(+) 90.6	(–) 87.6	(+) 56.9	(+) 99.9	(+) 97.2
Flu	(+) 88.5	(+) 86.2	(+) 55.6	(–) 51.5	(+) 99.7
BaP	(+) 92.5	(+) 82.9	(–) 57.6	(+) 99.9	(+) 97.9
Pyr	(+) 88.8	(+) 89.5	(+) 56.9	(+) 98.7	(+) 97.6
BaA	(+) 86.8	(+) 96.7	(+) 56.9	(+) 100.0	(+) 98.9
BbF	(–) 84.1	(+) 97.2	(+) 55.6	(+) 58.5	(+) 99.8
BkF	(+) 85.4	(+) 90.3	(+) 55.6	(–) 98.0	(+) 98.7
DBA	(+) 87.0	(+) 98.5	(+) 56.9	(+) 99.9	(+) 93.4
Chr	(+) 86.3	(+) 97.9	(+) 56.9	(–) 57.8	(+) 97.1
Bp	(+) 87.1	(+) 96.9	(+) 56.9	(+) 90.6	(+) 98.4
InP	(+) 91.3	(+) 82.1	(+) 55.6	(+) 99.9	(+) 99.1

Note: (+) — Sensitizer; (–) — Non-sensitizer; DPRA — Direct peptide reactivity assay; KeratinoSens — KeratinoSens assay; h-CLAT — Human cell line activation test; LLNA — Local lymph node assay; HRIPT/HMT — Human repeat insult patch test/Human maximization test.

57.6%, respectively. And other substances were sensitization agents with their probabilities ranging from 55.6% to 59.2%. In local lymph node assay (LLNA) models, Fl, Flu, BkF and CRH were non-sensitizer with the probabilities of 51.5%~99.5%, while other compounds were sensitization agents with the probabilities of 58.5%~100.0%. In the human repeat insult patch test/human maximization test (HRIPT/HMT) model, we can find that all the 16 PAHs were identified as sensitization agents and the probabilities were from 75.7% to 99.8%. It can be seen that different models obtained different sensitization probabilities, but all indicated that PAHs had sensitization effects on the human body. It needs to arouse people's further attention to avoid causing unnecessary health damage.

4. Conclusion

Different textile dyeing production processes and wastewater treatment processes had a close relationship in terms of the content and distribution of PAHs. The concentration of Σ16 PAHs ranges from 983.52 to 2,026.88 ng g^{-1}. The concentrations of Σ16 PAHs of S3, S4 and S6 were twice as much as those of the other three textile dyeing sludges. Σ16 PAHs in S5 had the minimum concentration. The concentrations of low molecular and high molecular weight PAHs in textile dyeing sludges were about 570.465~1,919.965 and 344.810~1,343.295 ng g^{-1}, respectively. The 2-ring and 4-ring PAHs were the main components. Different raw materials and wastewater treatment processes had a significant influence on PAHs in the sludge residue. 16 PAHs in the textile dyeing sludges were toxic to organisms, even with poisonous effects in the short and long term. The acute toxicity values of 16 PAHs to fish, daphnia and algae were 0.014~9.390, 0.012~5.940, and 0.054~6.910 mg L^{-1}, respectively. And the chronic toxicity values of PAHs to fish, daphnia and algae were 0.002~ 1.040, 0.004~0.782, and 0.037~2.300 mg L^{-1}, respectively. Different sensitization models calculated by Pred-Skin showed that 16 PAHs had certain sensitization effects on the human body, with the probability of over 80.0%. Therefore, the toxicity and sensitization of textile dyeing sludge should be considered when disposing of the same to avoid its deleterious effects on the environment and human health.

Acknowledgments

The author is thankful to the School of Environment Science and Engineering, Guangdong University of Technology and the Shantou Polytechnic.

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