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Capability of shallow open-water unit for emerging contaminants attenuation and ecological safety improvement in a treated effluent polishing process

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A B S T R A C T

Nature-based solutions of polishing treated effluent are drawing increased attention because of their potential to mitigate ecological risks, and the shallow open water unit (SOWU) process is one of the most promising options. In this study, a pilot experiment was conducted to assess the efficiency of SOWU for effluent quality polishing in a municipal wastewater treatment plant targeting 33 residual emerging contaminants (ECs) that were categorized into six groups, namely pharmaceuticals, sunscreens, bactericides, pesticides, flame retardants and phenols. In the 14-day monitoring period, each of the ECs decayed following a first order reaction, and about 61 % total ECs removal was achieved, indicating the remarkable photolysis effect of the SOWU under natural conditions. The significant removal of ECs, especially the very high removals of pharmaceuticals (76 %) and sunscreens (77 %), was associated with the attenuation of both the acute luminescent bacterial toxicity and genotoxicity. From the linear relationship between the acute toxicity and chromophoric dissolved organic matter and that between genotoxicity and UV absorbance at 254 nm, it was likely that the attenuation of biotoxicities resulted from the decay of chromophoric and aromatic compounds. By analyzing several reactive species, the excellent photo-reactivity of the SOWU was further identified.

1. Introduction

Wastewater treatment plant (WWTP) effluents still contain a multitude of dissolved organic matter, comprising recalcitrant natural organic matter, soluble microbial products, trace concentrations of synthetic organic compounds, transformation products and others [1]. After WWTP effluents discharge into receiving water bodies, the chemical mixtures they contain could pose a hazard to aquatic organisms [2]. With the development of innovative analytical techniques, the occurrence of emerging contaminants (ECs) in the treated effluents have been

revealed worldwide [3,4], including pharmaceuticals, sunscreens, hormones, fungicides, and organophosphate flame retardants (OPFRs) [5–7]. Studies of those micropollutants have focused on their potential risks to aquatic environments (e.g., estrogenic effects) and human health (e.g., carcinogenicity) [8,9]. Several regulated guidelines have been published to control the emission of ECs to the aquatic environment. For instance, the Decision 2018/840/EU proposed a total of 15 priority chemicals to be monitored [10] and 349 chemicals with guideline values were listed in the Australian Guidelines for Water Recycling (AGWR) [11].

Abbreviations: ACT, acetamidrid; Azobin, azoxystrobin; BEQ, bioanalytical equivalent concentration; BP1, benzophenone-1; BP3, oxybenzone; CBM, carbendazim; CBZ, carbamazepine; CDOM, chromophoric dissolved organic matter; CLR, clarithromycin; DDVP, dichlorvos; DFZ, difenoconazole; DMM, dimethomorph; DPH, diphenhydramine hydrochloride; EBT, effect-based trigger value; EHMC, octyl 4-methoxycinnamat; ERY, erythromycin; HC5, hazardous concentration for 5 % of aquatic organisms; IBU, ibuprofen; IMP, imidacloprid; KPF, ketoprofen; MEF, mefenamic; NPX, naproxen; OC, octocrylene; OPFRs, organophosphate flame retardants; PCL, prochloraz; ROX, roxithromycin; SMX, sulfamethoxazole; SOWU, shallow open-water unit; TBP, tributyl phosphate; TCEP, tris(2-Chloroethyl) phosphate; Thixam, thiamethoxam; TMM, trimethoprim; TPhP, triphenyl phosphate; TPPO, triphenylphosphine oxide; 2,4,6-TCP, 2,4,6-trichlorophenol.

WWTP effluents with numerous known and unknown mixtures can lead to various detrimental biological effects, including non-specific, reactive, and specific modes of action [8,12]. It has been demonstrated that most specific receptor-mediated effects (e.g., estrogenic effects and photosynthesis inhibition) can be explained by known chemicals. However, for non-specific biological effects such as cytotoxicity and oxidative stress response, even the most thorough chemical analysis can explain only a small fraction (<3 % of the observed biological effects [13,14]). This means that considering the removal of only certain ECs still might not ensure the ecological safety of the effluent. Hence, both residual ECs and biotoxicities detected in WWTP effluents should be carefully monitored and require effective mitigation prior to wastewater discharge or reuse [8,15].

To further improve the quality of treated effluents, additional and alternative strategies could be incorporated into WWTPs. A promising strategy is using natural treatment systems such as constructed wetlands (CWs [16,17] and open-water polishing ponds [18–21]). The open-water polishing ponds comprise shallow engineered basins, which stabilize and treat wastewater via natural processes driven by sunlight and photosynthetic microbial biomats [19,22,23]. The open-water polishing ponds can create a self-contained system or engage with other natural treatment systems, which are characterized as cost-effective and eco-friendly, especially in economically constrained countries and regions. Several studies have employed polishing ponds for the post treatment of treated effluents, such as upflow anaerobic sludge blanket reactors followed by polishing pond [24], activated sludge treatment followed by polishing pond [25], and constructed wetland (CW followed by polishing pond [26]. With the dominant photodegradation and biodegradation processes, the polishing pond could remove ECs [20]. More than 80 % removal of KPF, IBU, BP3, diclofenac and terbutin can be achieved in this unit [25,27]. To maximize the use of natural sunlight and enhance the photodegradation of micropollutants, a polishing pond with shallow water depth (≤ 50 cm) was recommended [19,28]. However, only limited studies on the photodegradation of ECs in polishing ponds have been published under field conditions with sunlight and in real wastewater effluents [20]. Most studies focused mainly on removal efficiency of small part of ECs, by comparing their concentrations in influent and effluent of polishing ponds [29]. There is a significant knowledge gap in the treatability of various ECs and associated removal kinetics under environmentally realistic concentrations in shallow polishing ponds [18,20,29]. Moreover, few studies have considered the performance of polishing ponds in the reduction of biotoxicity, let alone aquatic ecological safety.

In the present study, an outdoor shallow open-water unit (SOWU) that functioned as the post treatment for WWTP effluent polishing was constructed. The treatability and removal kinetics of residual ECs were studied under environmentally realistic concentrations, including pharmaceuticals, sunscreens, bactericides, pesticides, OPFRs and phenols. The SOWU performance in the reduction of biotoxicity from the effluent (including luminescent bacterial toxicity and reactive genotoxicity) was investigated synchronously. From the perspective of aquatic ecological safety, the biotoxicity reduction effectiveness in the SOWU was evaluated based on the threshold of biological effect.

2. Material and methods

2.1. Wastewater effluent

Wastewater effluent studied in this experiment was collected from a local WWTP. The plant is located in a semi-arid northwest city, Xi'an, China (34°14'03"N, 109°04'09"E), with an average domestic wastewater treatment capacity of 2000 m³/day [30]. An anaerobic-anoxic-oxic unit combined with a membrane separation process (A²O-MBR) was employed in the WWTP to treat the wastewater. The conventional water quality parameters of the effluent complied with the Discharge Standard of Pollutants for Municipal Wastewater

Treatment Plant (GB, 18918-2002). During the experimental period, the samples were collected from the WWTP effluent once every 2 weeks for residual ECs analysis and bioassays.

2.2. Experimental-setup and operation

Outdoor SOWU was constructed in the open-air space of the local WWTP. Two identical SOWUs were conducted in parallel, each of which comprised a cascade containing four shallow rectangular channels. The channel was made of fiberglass with dimensions and was 2.4 m in long and 0.45 m in wide. In this study, effluents from the WWTP were pumped into the SOWUs and the depth of pond water was set at 0.45 m with a working volume of 1944 L (Fig. 1). After addition of the WWTP effluents into SOWU, the effluents were treated for 2 weeks without inflow or outflow. During this time, the wastewater was automatically recirculated in the system using peristaltic pumps to promote the mixing of pond liquid and the penetration of sunlight. For practical sampling, the nominal hydraulic retention time (HRT) for the batch experiments and subsequent tests were maximally set at 14 days [31]. During this period, water sampling was performed (days 0, 2, 4, 6, 10 and 14) for each SOWU between 10:00–11:00 am. In each sampling campaign, approximately 5 L wastewater from the SOWU was collected into an amber glass bottle for subsequent EC analyses and bioassays.

On the experimental site, the average open-air temperature was 24.2 °C (with values ranging between 16 °C and 31 °C within a single day). The average sunlight intensity was 74125 lx (equal to 692 w/m² [32]), which was determined by lux meter, and the average water temperature was 23.0 °C. The evaporation loss was recorded weekly. Specifically, the water depth of SOWU was manually recorded on days 7 and 14, so the height of the water level depression could be obtained, after which the daily evaporation was calculated while considering the amount of water lost by sampling. No rainfall occurred throughout the whole sampling period.

2.3. Photoreactivity of the effluent

To characterize the photoreactivity of the WWTP effluent in this study, photolysis experiments were conducted to quantify the photochemical reactive intermediates (PRIs) generated by the sunlight excitation of photosensitizers. Five 5 L beakers were initially filled with 3000 mL filtered effluents and placed near the SOWU. The steady-state

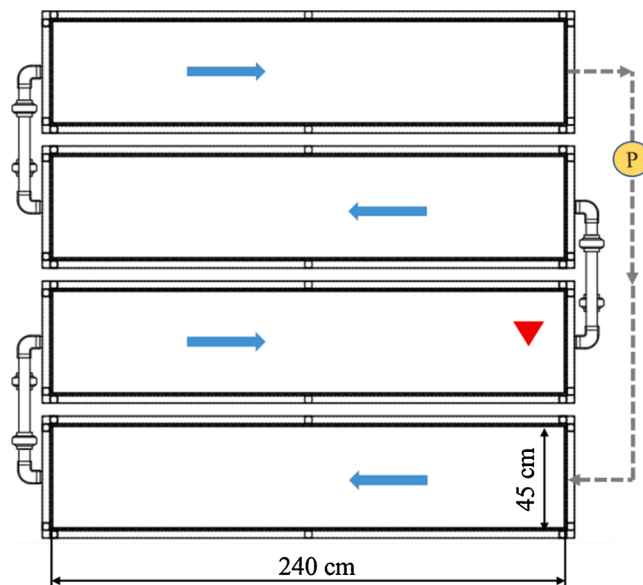


Fig. 1. Planform of the pilot-scale experimental setup. The red triangle represents the sampling site. P indicates the pump.

concentrations of singlet oxygen ($^1\text{O}_2$) and triplet-state dissolved organic matter ($^3\text{DOM}^*$) in the irradiated solutions were indirectly measured by monitoring the attenuation of furfuryl alcohol (FFA and 2,4,6-trimethylphenol (TMP, respectively [33]. For detection of steady state concentrations of hydroxyl radical ($\text{HO}\bullet$) terephthalic acid (TA) was used to trap $\text{HO}\bullet$ and 2-hydroxy-terephthalic acid (2HTA) was generated [34]. The photolysis experiments were conducted on a sunny day and started at 8:00 a.m. The irradiated solutions were sampled at 0, 2.5, 4, 7, and 11 h, respectively, and kept in the dark for subsequent analysis.

2.4. Sample pretreatment

Acquired water samples from the two SOWUs were taken to the nearby laboratory immediately, and then separately filtered through a 0.7 μm glass microfiber filter ($\Phi 150$ mm; Whatman™). In order to extract a wide range of contaminants from the water samples for chemical analysis and bioassays, the solid phase extraction (SPE) protocol was conducted following previous studies with some modifications [9,13]. Briefly, filtered samples were acidified to pH 2.5 with 2 M H_2SO_4 and added up to 5 % methanol before extraction. The cartridges were preconditioned with 10 mL dichloromethane: hexane mixture (1:1, v:v, 10 mL methanol, 10 mL milli-Q water in sequence.

For EC analysis, 2 L water samples were extracted with Waters Oasis® HLB cartridges (500 mg, 6 mL) using an extraction vacuum chamber (SUPELCO VISIPREP). After extraction, the cartridges were dried under vacuum for 20 min to remove the residual water and then sealed individually and kept at -20°C until elution. The cartridges were defrosted and dried completely under vacuum. They were eluted with 10 mL of methanol and 10 mL of dichloromethane: hexane mixture, and were evaporated to 1 mL under purified nitrogen gas (99.999 % pure). Finally, 1 mL extracts was divided equally. One part was mixed with methanol to 1 mL for Ultra Performance Liquid Chromatography/tandem Mass Spectrometry (UPLC-MS/MS) analysis. The other part was evaporated to nearly dry under purified nitrogen gas and the solvent was exchanged to acetone: hexane mixture (1:9, v:v) to achieve a final volume of 1 mL for Gas Chromatography-Mass Spectrometer (GC/MS) analysis. For bioassays, 1 L water samples were extracted with Waters Oasis® HLB cartridges (200 mg, 6 mL). After the same elution steps with chemical analysis, eluates were evaporated to dryness. The residues were then dissolved in 2 mL 1 % dimethyl sulfoxide solution (DMSO).

2.5. Analytical methods

UV-vis absorbance spectra were measured using UV-vis spectrophotometer (UV-1800, Shimadzu, Japan). Absorption spectra from 200 to 600 nm were scanned at 1 nm intervals. Total chromophoric dissolved organic matter (CDOM) was then quantified and calculated through the integrated absorption from 250 to 450 nm [35]. A Shimadzu LC-2010A system with ultraviolet detector and fluorescence detector equipped with an analytical reversed-phase C18 column (Shim-pack VP-ODS, 4.6 mm \times 25 cm \times 5 μm , Shimadzu, Japan) was employed for quantification of the FFA, TMP and 2HTA. Details of the instrumental analysis procedures are presented in Table 1.

For ECs analysis, a total of 33 ECs was selected on the basis of their frequent detection and concentration in previously published study [9, 30]. Instrumental analysis method of these ECs consisted of solid phase extraction (SPE), concentration and quantification using UPLC-MS/MS (ACQUITY UPLC - Xevo TQ MS, Waters, USA) and GC/MS (TSQ Quantum XLS, Thermo, USA). Details of the instrumental analysis procedures could be found in our previous study [36]. The concentration of targeted chemicals was calculated using a 6-point calibration curve (0.5, 2, 5, 20, 50 and 200 $\mu\text{g/L}$). If the reported concentration of the chemical was below the limit of quantitation (LOQ), its removal efficiency was calculated using the LOQ as the concentration of the detected ECs.

Table 1

Instrumental analysis procedures for photochemical reactive intermediates in this study.

Reactive Species	Probe Molecule	Initial Concentration	HPLC method
$^1\text{O}_2$	Furfuryl alcohol	1mM	85 % ACN:15 % PO4 buffer (2 mM, pH 3.0); flow rate = 1.0 mL/min; $\lambda = 277$ nm
$^3\text{DOM}^*$	2,4,6-Trimethylphenol	1mM	90 % ACN:10 % water; flow rate = 1.0 mL/min; $\lambda = 220$ nm
$\text{HO}\bullet$	2-Hydroxyl terephthalic acid	20 μM (Terephthalic acid)	45 % ACN: 55 % water; flow rate = 0.7 mL/min; $\lambda_{\text{ex}}=315$ nm, $\lambda_{\text{em}} = 425$ nm

2.6. Bioassays

Two bioassays were selected to detect the biotoxicities of the wastewater. Acute luminescent bacterial toxicity was detected by bioluminescence inhibition assay using *Aliivibrio fischeri* according to modified ISO 11348 [37]. The umuC test without metabolic activation was selected to detect the reactive genotoxicity using *Salmonella typhimurium* TA1535/pSK1002 according to ISO 13829 [38]. The EC_{50} (effective concentration causing 50 % inhibition) and IR (induction ratio) were used to quantify the acute toxicity and genotoxicity, respectively. If the IR value is above 1.5, the result is considered to be positive. The bioanalytical equivalent concentration (BEQ) was calculated through the EC_{50} or $\text{IR}_{1.5}$ of reference compound divided by the EC_{50} or $\text{IR}_{1.5}$ of wastewater sample (as Eq. (1) shown). The biotoxicities of different samples were comparable by using BEQ.

$$\text{BEQ} = \frac{\text{EC}_{50} \text{ or } \text{IR}_{1.5} \text{ of reference compound}}{\text{EC}_{50} \text{ or } \text{IR}_{1.5} \text{ of wastewater sample}} \quad (1)$$

2.7. Environmental safety evaluation

The effect-based trigger (EBT) values for bioassays was applied to define the thresholds of acceptable biological effects, which are numerical values that indicate an acceptable risk to the environment [36, 39]. The EBT is primarily derived from existing environmental quality standards or from the HC5 (hazardous concentration for 5 % of aquatic organisms) based on species sensitivity distributions (SSD) [36,39,40]. In the present study, the acceptable levels of biological effects (HC5-EBT) were used to determine whether the biotoxicity of WWTP effluent is acceptable for ecological safety after the SOWU treatment.

To construct SSD curves, single-species acute toxicity data (EC_{50}) were collected from the US EPA ECOTOX database (<http://www.epa.gov/ecotox>). The HC5 values and their 95 % confidence intervals were estimated using the SSD Generator software (<https://www.epa.gov/caddis>). In total, 491 toxicity values were collected for phenols, which were tested with 85 aquatic species belonging to five taxonomic groups (fish, mollusca, vermes, insects/spiders, and crustaceans). The extrapolated median HC5-EBT of phenol (the positive control of the bioluminescence inhibition assay) from the SSD curve was 6.04 mg/L (4.10–9.00 mg/L at 95 % confidence interval). Because of the lack of toxicity data, the HC5-EBT of 4-nitroquinoline 1-oxide (4-NQO) (the positive control of the umuC test) could not be derived using the SSD curve. Therefore, the HC5-EBT of 4-NQO used in the present study, which was 0.64 $\mu\text{g/L}$, was obtained from a previous study [36].

2.8. Data analysis

2.8.1. Removal efficiency of ECs

Removal efficiency of targeted ECs was corrected with water loss due to evapotranspiration and calculated following Eq. (2).

$$Removal(\%) = \left(C_0 - C_t \left(1 - \frac{t \cdot EVR}{V} \right) \right) / C_0 \quad (2)$$

where C_0 is the initial concentration of the WWTP effluent, C_t is the concentration on each sampling campaign. The average evaporation rates (EVRs) are 27.5 L/d for the SOWU during sampling period. V is 1944 L of the total wastewater volume based on used water depth. The overall removal efficiencies of individual EC are roughly categorized as highly removed (>80 % removal), easily removed (60 %–80 % removal), moderately removed (40 %–60 % removal), and recalcitrant (<40 % removal).

2.8.2. Steady-state concentrations of the PRIs

The steady-state concentrations for the PRIs generated in the irradiated effluent can be calculated as Eq. (3).

$$[PRIs]_{SS} = k_{obs,P} / k_{PRIs,P} \quad (3)$$

where $[PRIs]_{SS}$ (M) is the steady-state concentrations of 1O_2 or $^3DOM^*$, $k_{obs,P}$ (s^{-1}) is the pseudo first order degradation rate constant for probe loss (FFA or TMP). $k_{PRIs,P}$ ($M^{-1} s^{-1}$) is the second order rate constant between probe and PRIs. The reaction rate constant of 1O_2 with FFA was $1.2 \times 10^8 M^{-1} s^{-1}$, and the reaction rate constant of $^3DOM^*$ with TMP was $3 \times 10^9 M^{-1} s^{-1}$ [41].

The steady-state concentrations for the $HO\bullet$ ($[HO\bullet]_{SS}$) generated in the irradiated effluent can be calculated as Eq. (4).

$$[HO\bullet]_{SS} = k_{obs,2HTA} / (\eta k_{HO,TA} [TA]) \quad (4)$$

where $k_{obs,2HTA}$ ($7 \times 10^{-10} M \cdot s^{-1}$) is the generation rate for 2HTA, deriving from the photolysis experiments (chapter 2.3). The parameters of η and $k_{HO,TA}$ were from the reference [34], which were 28 % and $4.4 \times 10^9 M^{-1} s^{-1}$, respectively, $[TA]$ is the probe concentration.

2.8.3. k-C* model

The modified first-order k-C* model has been used to describe the performance of batch-loaded system for pollutants removal (e.g. BOD, COD, and ECs) in natural treatment systems [42,43]. In the present study, k-C* model was first tried to describe the biotoxicity (BEQ) attenuation in the SOWU. The modified first-order k-C* model is given by Eq. (5).

$$C_t = C^* + (C_0 - C^*) \times e^{-k_v t} \quad (5)$$

Where C_t is the biotoxicity of the SOWU water on each sampling campaign; C^* is the irreducible background value; C_0 represents the initial biotoxicity detected in the WWTP effluent; k_v is first-order volumetric rate constant (d^{-1}); t is the retention time (d). For biotoxicity, C_t and C^* were standardized to BEQ (mg/L or $\mu g/L$).

3. Results and discussion

3.1. Residual ECs and biotoxicity in WWTP effluent

All 33 ECs were identified in the WWTP effluents at ng/L level, including 11 pharmaceuticals, 4 sunscreens, 5 bactericides, 6 pesticides, 4 OPFRs and 3 phenols (Table 2). Of the 33 targeted ECs, 26 chemicals were always detected (FOD = 100 %), while 3 chemicals (KPF, NPX and SMX) were only detected at 25 % frequency. The mean concentration of individual ECs varied from 0.2 ng/L to 967.6 ng/L, and CBZ, BP3 and CBM were present at the highest concentrations (>100 ng/L, on average), which was in line with previous reports [4,9]. The groups of pharmaceuticals, sunscreens and bactericides accounted for most of the total ECs, and had total concentrations of 528.8, 1076.5 and 239.5 ng/L, respectively. The other three groups including pesticides, OPFRs and phenols were detected at low concentrations (63.2, 68.2 and 126.4 ng/L, respectively).

Table 2

Frequency of detection (FOD), mean concentration (Conc.) and standard deviations of target ECs in the studied effluent samples (n = 4).

Group	Chemical	Abbreviation	FOD (%)	Conc. (ng/L)	MDL in EU list (ng/L)	AGWR guideline value ($\mu g/L$)
Pharmaceuticals	Erythromycin	ERY	100 %	60.4 ± 20.6	19	17.5
	Diphenhydramine	DPH	100 %	42.4 ± 50.3	–	–
	Roxithromycin	ROX	100 %	41.6 ± 44.4	–	150
	Ibuprofen	IBU	100 %	90.4 ± 38.6	–	400
	Ketoprofen	KPF	25 %	2.2 ± 3.9	–	3.5
	Clarithromycin	CLR	100 %	27 ± 7.4	19	250
	Carbamazepine	CBZ	100 %	166.1 ± 53.1	–	100
	Trimethoprim	TMM	50 %	31 ± 31.2	–	70
	Naproxen	NPX	25 %	9.7 ± 16.7	–	220
	Mefenamic acid	MEF	75 %	52.8 ± 37.2	–	–
	Sulfamethoxazole	SMX	25 %	5.2 ± 9	–	35
Sunscreens	Benzophenone-1	BP1	100 %	47.9 ± 65.1	–	–
	Octyl 4-methoxycinnamat	EHMC	100 %	39.5 ± 24	–	–
	Octocrilene	OC	100 %	21.5 ± 31.7	–	–
	Oxybenzone	BP3	100 %	967.6 ± 674.7	–	–
	Azoxystrobin	Azobin	100 %	25.5 ± 18.8	–	–
Pesticides	Dimethomorph	DMM	100 %	27.1 ± 15.4	–	–
	Prochloraz	PCL	100 %	6.6 ± 1.6	–	–
	Difenoconazole	DFZ	100 %	7.8 ± 1.9	–	–
	Carbendazim	CBM	100 %	172.5 ± 174.3	–	100
	Imidacloprid	IMP	100 %	21.2 ± 21.6	8.3	–
	Thiamethoxam	Thixam	100 %	17.5 ± 2.2	8.3	–
Bactericides	Ametryn	Ametryn	50 %	0.2 ± 0.2	–	–
	Dichlorvos	DDVP	100 %	3 ± 1.1	–	1
	Atrazine	Atrazine	100 %	1.7 ± 0.1	–	40
	Acetamiprid	ACT	100 %	19.7 ± 4.3	8.3	–
	Tributyl phosphate	TBP	75 %	7 ± 3.8	–	0.5
OPFRs	Triphenylphosphine oxide	TPPO	100 %	10.3 ± 1.3	–	–
	Triphenylphosphate	TPhP	100 %	4.8 ± 3.1	–	1
	Tris(2-chloroethyl) phosphate	TCEP	100 %	46 ± 8.1	–	1
	2,4,6-trichlorophenol	2,4,6-TCP	100 %	46.1 ± 31.5	–	20
Phenols	Phenol	Phenol	100 %	66.3 ± 39.6	–	150
	p-cresol	p-Cresol	100 %	14 ± 10	–	600

Note: EU list chemicals were in bold and AGWR list chemicals were in italic.

Among the 33 residual ECs, 5 chemicals belonged to the EU watch list (Decision 2018/840, while 18 chemicals were in the AGWR list (Table 2). The concentrations of the 18 chemicals (ERY, ROX, IBU, KPF, CLR, CBZ, TMM, NPX, SMX, CBM, DDVP, Atrazine, TBP, TPhP, TCEP, 2,4,6-TCP, phenol and p-cresol) were all below the AGWR guideline values; however, the concentrations of the five chemicals (ERY, CLR, IMP, Thixam and ACT) all exceeded the maximum acceptable limits of detection (MDL) in the EU watch list. Barbosa et al. [44] also reported the occurrence of ERY, CLR and IMP in wastewater effluents with concentrations of 16–148 ng/L, 54–1809 ng/L and 2–34 ng/L, respectively. The results indicate that the potential detrimental effects to aquatic organisms posed by these ECs in WWTP effluents might still be present.

The bioluminescence inhibition assay showed that the average acute toxicity of the effluent was 15.25 mg/L BEQ_{phenol}, while the average reactive genotoxicity was 0.30 µg/L BEQ_{4-NQO}. As an effective supplementary means of chemical analyses, bioassays with different endpoints can provide a comprehensive overview of the adverse effects induced by wastewater and indicate the presence of unknown toxic chemicals [8]. It has been demonstrated that the acute luminescent bacterial toxicity assay and the *umuC* assay for genotoxicity were most frequently highlighted in the bioassay battery for WWTP effluents [8,45]. Ma and Jia et al. [8,36] reported that the BEQ_{phenol} of WWTP effluents ranged from 5.0 to 20 mg/L, while the BEQ_{4-NQO} ranged from 0.1 to 4 mg/L, which is consistent with the results of the present study. Regarding the luminescent bacterial toxicity of the studied effluents, the BEQ_{phenol} (15.25 mg/L) was much larger than the HC5-EBT of phenol (6.04 mg/L), which indicates that the WWTP effluent might still pose substantial adverse ecological effects after direct discharge or reuse. The BEQ_{4-NQO} of the studied effluent was below the HC5-EBT of 4-NQO (0.64 µg/L), which indicates that there was no potential genotoxicity from the effluents towards aquatic organisms.

3.2. EC removal in SOWU

3.2.1. Removal efficiency

After treatment of the WWTP effluents in SOWU for 2 weeks, ERY, DPH, ROX, IBU, KPF, CLR, BP1, EHMC and IMP were highly removed (>80 %) in SOWU (Table 3). More importantly, the five chemicals belonging to the EU list (except ACT) could be easily removed in the polishing step. The mean concentrations of residual ERY, CLR, IMP and Thixam in the SOWU were 31, 16, 13 and 16 ng/L, respectively, which were all larger than the MDL in the EU watch list. As expected, the concentrations of these hazardous ECs were all below the MDL with effective elimination after the polishing treatment. The chemicals (ROX, IBU, KPF, CLR and TBP) belonging to the AGWR list were easily removed by SOWU. These results indicate that the SOWU performed well in the reduction of the regulated ECs. However, SOWU showed ineffective removal for CBM, DDVP, atrazine, ACT, TPPO, TPhP and TCEP (<40 % removal efficiency). Of which, CBM, ACT and TCEP with no change in concentrations after the polishing treatment showed strong resistance to be degraded. Matamoros et al. [27] employed a polishing pond system (depth, 1 m) as post treatment for secondary effluent from a WWTP, and the removal efficiencies of KPF, BP3 and IBU were 93 %, 80 % and 66 %, respectively, while CBZ (28 % removal), TCEP (20 % removal) and TBP (19 % removal) were refractory (HRT = 4 days). The higher removal of CBZ and TBP in this study might be because of the shallow water depth (0.45 m) and the longer retention time (14 days). In addition, Rühmland et al. [46] found that subsurface flow CW fed with effluent from a large conventional WWTP was able to effectively remove pharmaceuticals, such as ERY (>92 % and TMM (>97 %), but CBZ (<50 % and CLR (<42 % were consistently poorly removed. Matamoros et al. [47] found that horizontal flow CW fed with secondary treated wastewater was capable of removing ECs such as IBU (32 %), KPF (39 %) and BP3 (85 %) but did not remove CBZ (28 %) and TCEP (19 %). Comparatively, the SOWU fed with WWTP effluent and operated with sunlight exposure was as efficient or more efficient than CWs for residual EC removal.

Table 3

Overall removal efficiency of residual ECs, correlative observed first-order removal rate constants (k), R² values and half-life (t_{1/2}) in the SOWU fed with WWTP effluents.

Groups	Chemicals	Overall removal (%)	k (d ⁻¹)	R ²	t _{1/2}
Pharmaceuticals	ERY	99.3 ± 0	0.203 ± 0.006	0.844	3.4
	DPH	99.2 ± 0	0.104 ± 0.007	0.916	6.6
	ROX	98.0 ± 0.2	0.255 ± 0.006	0.922	2.7
	IBU	95.8 ± 0	–	–	–
	KPF	88.7 ± 0	–	–	–
	CLR	90.2 ± 4.8	0.139 ± 0.009	0.947	5.0
Sunscreens	CBZ	59.0 ± 1.4	0.069 ± 0.001	0.936	10.0
	BP1	98.6 ± 0	–	–	–
	EHMC	82.7 ± 2.5	0.146 ± 0.017	0.857	4.7
	OC	69.5 ± 5.3	0.075 ± 0.095	0.953	9.2
	BP3	74.9 ± 3.5	0.105 ± 0.011	0.947	6.6
	Azobin	65.8 ± 0.8	0.083 ± 0.002	0.941	8.3
Bactericides	DMM	50.2 ± 1.1	0.049 ± 0.001	0.939	14.3
	PCL	47.6 ± 1.1	0.050 ± 0.001	0.952	13.9
	DFZ	48.2 ± 3.9	0.057 ± 0.006	0.778	12.2
	CBM	–6.1 ± 4.2	–	–	–
Pesticides	IMP	99.0 ± 0	0.245 ± 0.004	0.974	2.8
	Thixam	72.6 ± 12.9	0.093 ± 0.038	0.983	7.4
	Ametryn	51.7 ± 0	–	–	–
	DDVP	38.4 ± 3.3	0.032 ± 0.001	0.961	21.6
	Atrazine	7.4 ± 5.6	0.015 ± 0.002	0.897	47.2
	ACT	–0.7 ± 5.9	–	–	–
OPFRs	TBP	64.0 ± 0	0.161 ± 0.002	0.766	4.3
	TPPO	34.4 ± 12.5	0.055 ± 0.004	0.952	12.6
	TPhP	3.8 ± 14.3	–	–	–
	TCEP	0.2 ± 1.7	–	–	–
Phenols	2,4,6-TCP	59.8 ± 7.9	0.069 ± 0.013	0.984	10.1
	Phenol	45.6 ± 16.9	0.043 ± 0.021	0.997	16.2
	p-Cresol	–58.7 ± 67.4	–	–	–

Overall, the SOWU achieved 61 % removal of the total ECs (ΣECs) and showed high capability to remove pharmaceuticals (76 %) and sunscreens (77 %), while bactericides, pesticides, OPFRs and phenols were moderately removed or recalcitrant (Fig. 2) in this study. Considering the configuration of the SOWU, the removal mechanisms of residual ECs mainly involved direct and indirect photolysis [28,48]. Specifically, chemicals can be degraded by direct photolysis when their absorption spectra overlap with the solar irradiation spectrum. The photon energy of 472 kJ/mol at 254 nm can attack chemical bonds with low dissociation energy, like phenyl–OH (470 kJ/mol) in BP1 and phenyl–Cl (406 kJ/mol) in IMP [49]. Therefore, when the SOWU was exposed to sunlight, these residual photosensitive ECs could be eliminated via direct photolysis, such as BP1, IMP, KPF and SMX present in the studied effluents. In addition, chemicals can be degraded by indirect photolysis through the reaction with reactive intermediates formed by the sunlight excitation of photosensitizers [50,51]. These reactive intermediates might be HO•, ¹O₂, ³DOM*, peroxy radicals and hydrogen peroxide. Among the studied ECs, ERY, DPH, ROX, CLR, BP1, OC and

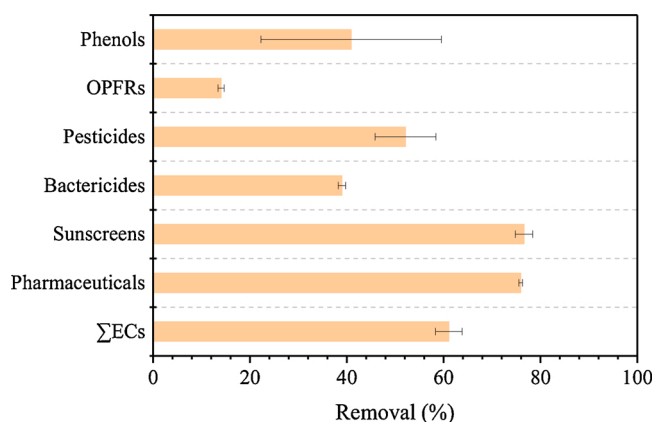


Fig. 2. Overall removal (%) of each groups of ECs by the SOWU treatment.

BP3 were all defined as direct photo-stable chemicals [52–54], but effective elimination with high removal rates (>80 %) were achieved in SOWU, which were likely ascribed to indirect photolysis.

To further confirm the indirect photolysis process in SOWU, three major reactive species generated by the irradiated effluent were identified and quantified. The production of $^1\text{O}_2$ and $^3\text{DOM}^*$ was evidenced by the decrease of probe FFA and TMP, respectively, and the production of HO^\bullet was evidenced by the generation of 2HTA. The steady state concentrations of the reactive species were calculated, and results showed that the steady state concentrations of $^1\text{O}_2$, $^3\text{DOM}^*$ and HO^\bullet were 4.9×10^{-13} , 1.7×10^{-15} and 2.4×10^{-14} M, respectively, in the WWTP effluent after irradiation. Zhou et al. [33] reported the steady state concentrations of $^1\text{O}_2$ and $^3\text{DOM}^*$ were 2.1×10^{-13} and 5.6×10^{-14} M, while Yan et al. [34] reported the steady state concentrations of $^1\text{O}_2$ and HO^\bullet were 2.2×10^{-13} and 1.4×10^{-15} M, respectively, in the irradiated wastewater effluent under laboratory conditions (Suntest XLS⁺). The results confirm that the sunlit water in SOWU can produce a range of reactive intermediates at considerable concentrations under field sunlight exposure compared with those produced in the laboratory. Among these reactive species, HO^\bullet is very reactive and important, which is the only transient reactive species to effectively degrade recalcitrant contaminants such as CBZ and some hydrocarbons [51,55]. The significant removal (59 %) of CBZ in SOWU was attributed mainly to the formation of HO^\bullet .

There are many such scenarios of sunlit water, such as rivers, landscape ponds and waste stabilization ponds, in which EC photodegradation occurred *in situ*. Although the photolysis mechanism of ECs in the actual effluents was complicated and influenced by many factors, the result reveal that SOWU as the polishing treatment for treated effluents could achieve considerable removal of residual ECs, including the chemicals contained in the regulated guidelines. When a natural treatment system is applied for polishing WWTP effluent, SOWU would be a wise supplementary unit to enhance the photolysis process for residual EC removal.

3.2.2. Removal kinetics

The kinetic parameters of ECs were calculated through contaminant decay of the along with the retention time in SOWU. The observed k was compound-dependent and ranged from 0.015 to 0.255 d^{-1} (Table 3). ROX showed the highest removal rate with a value of 0.255 d^{-1} , followed by IMP (0.245 d^{-1}) and ERY (0.203 d^{-1}). The three chemicals IBU, KPF and BP1 at environmentally relevant concentrations were quickly eliminated (below the limit of detection) without observed k values in the polishing treatment. The k values of CBZ (0.07 d^{-1}) and TBP (0.16 d^{-1}) obtained in the present study were comparable with a previously reported polishing pond system, which comprised four 1000-L tanks (80 cm wide \times 130 cm long \times 50 cm high) with a surface area of 1 m^2 for water reclamation [25]. Half-life ($t_{1/2}$) ranges of all the studied

ECs were from 2.7–47.2 days, while the half-lives of these EU listed compounds ranged from 2.8 to 7.4 days. Although sunlight could act as a driver for the removal of residual ECs, reliable data are lacking on half-lives under sunlight exposure in the polishing processes [29]. When SOWUs are constructed for the polishing of WWTP effluents, longer retention times allow more complete photolysis of micropollutants, but also allow an adaptation of floating vegetation that can prevent sunlight penetration throughout the water column. In this study, the obtained half-lives of various ECs, especially these chemicals in the EU list, would help to optimize the design of polishing treatment processes for EC removal.

3.3. Biototoxicity reduction

Bioluminescence inhibition in *Vibrio fischeri* was conducted to evaluate the acute luminescent bacterial toxicity of samples with non-specific mode of action. The luminescent bacterial toxicity posed by the WWTP effluent decreased from 14.44 mg/L to 2.97 mg/L with increasing retention time (Fig. 3a). Regarding the reactive genotoxicity of the studied effluent, the $\text{BEQ}_{4\text{-NQO}}$ gradually declined from $0.20 \mu\text{g/L}$ to below the limit of detection, which suggest that the SOWU also showed excellent performance for genotoxicity reduction (Fig. 3b). Studies have indicated that photodegradation of CBZ can produce acridine, which is mutagenic and carcinogenic, and the photodegradation products of NPX are more toxic than the parent compound [56,57]. Although photo-transformation products may form during the SOWU process, the substantial reduction of luminescent bacterial toxicity and genotoxicity indicates that the polishing treatment is eco-friendly.

The contribution of known chemicals to the observed non-specific luminescent bacterial toxicity has been investigated by Tang et al. [13], who found that chemical mixtures ($n = 65$) explained < 10 % of the luminescent bacterial toxicity from the WWTP effluent. In addition, the reactive genotoxicity cannot be explained by known chemicals [14]. Therefore, the remarkable performance of SOWU for the reduction of two detected biotoxicities cannot be interpreted as the results of the high removal efficiency of ECs. As shown in Fig. 4a, a linear relationship ($R^2 = 0.78$) between the reduction in acute toxicity ($\text{BEQ}_{\text{phenol}}$) and CDOM was observed in SOWU. Additionally, reactive genotoxicity showed a good positive correlation with UV_{254} ($R^2 = 0.77$) which was representative of the aromatic compounds content (Fig. 4b). So, the substantial reduction in acute luminescent bacterial toxicity and genotoxicity in SOWU might be primarily related to the reduction and modification of macromolecular dissolved organic matter, which was synchronously extracted in the SPE pretreatment process. Based on Pearson correlation analysis, Chen et al. [58] also reported that aromatic compounds exhibited a high positive correlation with genotoxicity reduction during advanced wastewater treatment processes. Because WWTP effluents contain a multitude of dissolved effluent organic matters, not only the micromolecular ECs but also the macromolecular dissolved organic matter should be carefully considered during the post treatment process.

3.4. Ecological safety in SOWU

As shown in Fig. 5a, the attenuation of luminescent bacterial toxicity in SOWU was fitted well by the $k\text{-C}^*$ model ($R^2 > 0.95$), and similar results were obtained for genotoxicity ($R^2 > 0.85$) (Fig. 5b). To the best of our knowledge, this is the first time that attenuation of biotoxicity data in a natural treatment system was fitted to the $k\text{-C}^*$ model. The apparent rate coefficient k_v was 0.74 d^{-1} for the luminescent bacterial toxicity with a C^* of $2.9 \text{ mg/L BEQ}_{\text{phenol}}$, while k_v was 0.19 d^{-1} for genotoxicity with a C^* of $0.1 \mu\text{g/L BEQ}_{4\text{-NQO}}$. The results show that luminescent bacterial toxicity had a higher k_v value than that for genotoxicity, which suggests that the substances from the effluent that were responsible for the luminescent bacterial toxicity were more vulnerable to be treated than those responsible for genotoxicity.

The $\text{BEQ}_{4\text{-NQO}}$ of the initial effluent was below the HC5-EBT of 4-

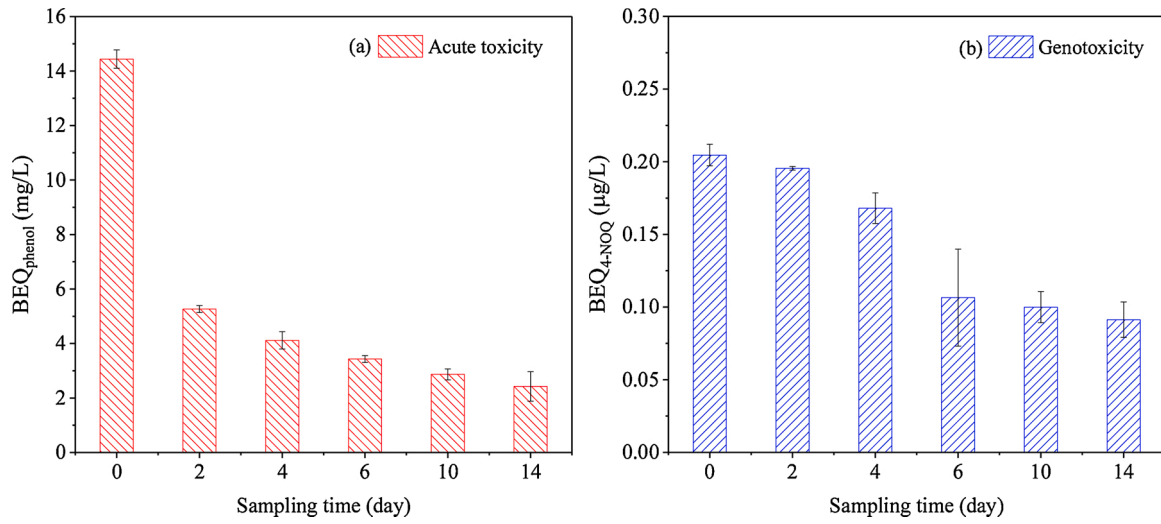


Fig. 3. Changes in luminescent bacterial toxicity (a) and genotoxicity (b) from the studied effluent polished by SOWU during the monitoring period. The LOD was <2.1 mg/L BEQ_{phenol} for the bioluminescence inhibition assay, and <0.10 $\mu\text{g/L}$ BEQ_{4-NQO} for the umuC test.

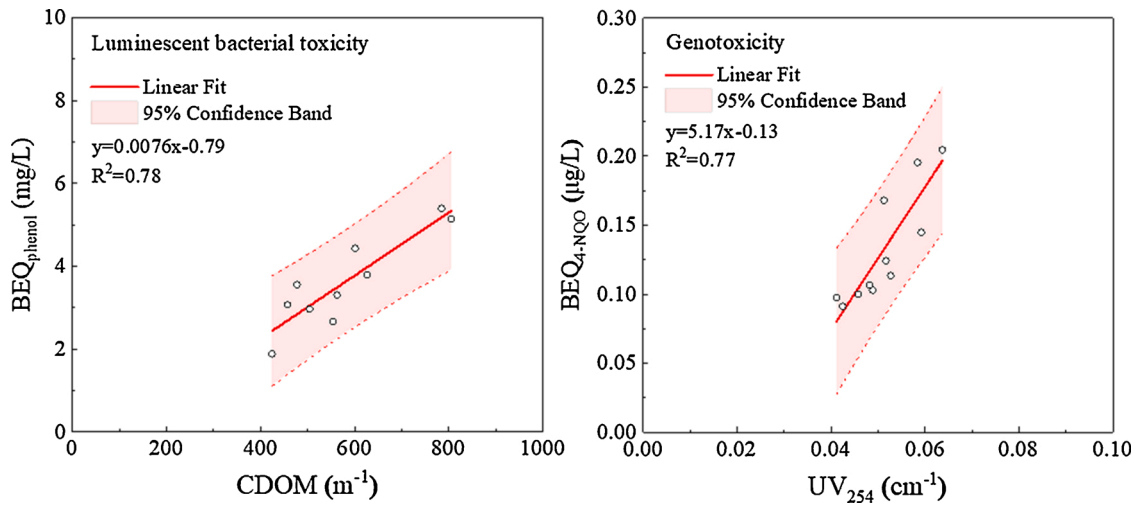


Fig. 4. Linear regression between the luminescent bacterial toxicity and CDOM (a), and genotoxicity and UV_{254} (b).

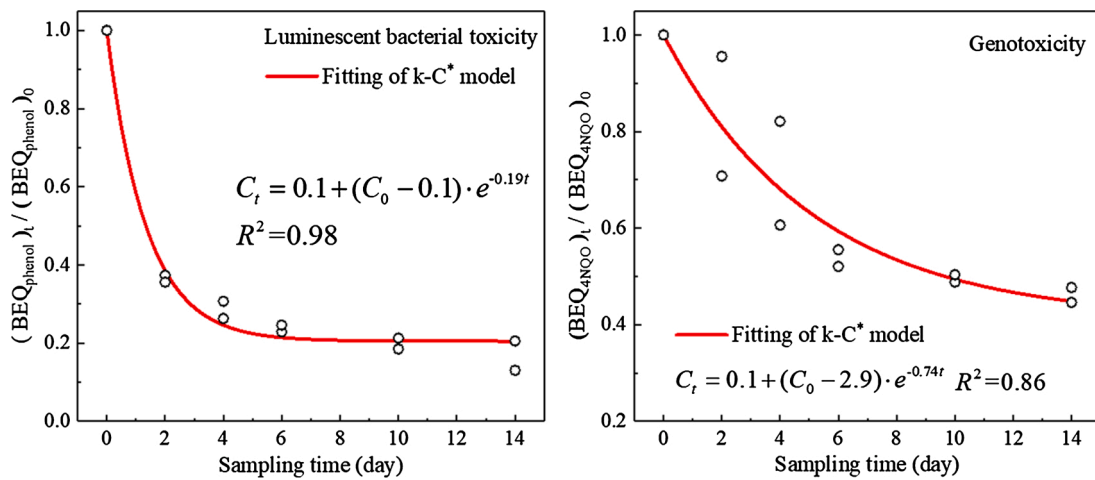


Fig. 5. Fitting of $k-C^*$ models using experimental data for luminescent bacterial toxicity (a) and genotoxicity (b).

NQO (0.20 vs. 0.64 µg/L), which indicates that there was no potential genotoxicity towards aquatic organisms. In contrast, the luminescent bacterial toxicity posed by the effluent was higher than the HC5-EBT of phenol (14.44 vs. 6.04 mg/L BEQ_{phenol}), which suggests that the effluent posed potential toxic risk to aquatic organisms. Luminescent bacterial toxicity might be the most persistent biological effect to be reduced by many advanced treatment processes [36]. To ensure that the luminescent bacterial toxicity of the WWTP effluents achieved an acceptable level (6.04 mg/L BEQ_{phenol}) after SOWU treatment, the required retention time for SOWU could be obtained from the k-C* model.

When C_t was equal to the objective BEQ_{phenol} (HC5-EBT_{phenol} = 6.04 mg/L in SOWU), the retention time (t) can be calculated using Eq. (6), which was deduced from Eq. (5).

$$t = \frac{1}{k_v} \times \ln \frac{C_t - C^*}{C_0 - C^*} \quad (6)$$

where C_0 is the BEQ_{phenol} of the SOWU influent; C^* and k_v could be obtained from the k-C* model (Fig. 5a); and C_t is the objective BEQ_{phenol}.

The calculation results show that SOWU could achieve acceptable luminescent bacterial toxicity reduction after 1.4 days polishing treatment. This result further indicates that SOWU was an effective natural treatment unit that could mitigate detrimental biological effects derived from the wastewater effluent. When the retention time was set as 1.4 days for the WWTP effluents in SOWU, a pond area of 3.5 m² (water depth, 50 cm) is required for every 1 m³/d WWTP effluent. If the water depth is set at 10 cm, a pond area of 17.6 m² is required for every 1 m³/d WWTP effluent. Comparatively, when the pond systems were constructed for removal of conventional pollutants, the required area (on average) for biochemical oxygen demand (BOD) removal was 16 m² (1 m³/d wastewater), while the required area (on average) for TN removal was 11 m² (1 m³/d wastewater) [59]. Therefore, the results of SOWU area are reasonable and practical. Photosynthetic microbial biomats would colonize in the SOWU after long-term operation in real circumstances [23], thus further study is required to calibrate the simplified results in this study. When a polishing pond with shallow water depth was applied for polishing treated wastewater, sufficient sunlight exposure was needed for efficient operation; tropical climate regions would be advantageous to the deployment of SOWU.

4. Conclusion

SOWU functioning as the post treatment for WWTP effluent polishing was operated under ambient temperature and natural sunlight exposure. The results show that the SOWU effectively removed residual 33 ECs in the WWTP effluent, especially pharmaceuticals (76 %) and sunscreens (77 %). Of the 33 ECs, ERY, DPH, ROX, IBU, KPF, CLR, BP1, EHMC and IMP were highly removed (>80 %), and the chemicals belonging to the EU or AGWR lists also showed substantial removal. Photolysis played a significant role in the SOWU treatment process, where indirect photolysis reactions involving ¹O₂, ³DOM* and HO• were identified. Additionally, SOWU could achieve significant reduction of luminescent bacterial toxicity and genotoxicity, and the attenuation of biotoxicities showed a strong linear relationship with the aromatic compounds and chromophoric compounds. To ensure that the luminescent bacterial toxicity of WWTP effluent was reduced to an acceptable level for ecological safety, the recommended retention time of SOWU for sunlight exposure was obtained. When a natural treatment system is required to deal with treated effluents, SOWU provides an effective alternative treatment unit that can achieve the dual goals of mitigating ECs and guarantee ecological safety.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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