Removal of Selected Pharmaceuticals and Personal Care Products using Greater Duckweed Constructed Wetland Followed by GAC Sandwich Slow Sand Filter

By

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I, Jianan Li confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

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ABSTRACT

Removal of four emerging pharmaceuticals and personal care products (PPCPs) compounds from water (i.e. diethyltoluamide, paracetamol, caffeine and triclosan) were investigated and optimized using a novel Greater duckweed (*Spirodela polyrhiza*) based laboratory-scale free water constructed wetland (CW) followed by GAC (granular activated carbon) sandwich slow sand filtration (SSF) system. The extraction and detection methods were simplified and optimized without conditioning and equilibration for solid phase extraction (SPE), and without derivatization for gas chromatography-mass spectrometry (GC-MS). Effects of light intensity, aeration, *E.coli* abundance and plant biomass on the removal of target compounds at batch scale with the aid of experiment design were investigated. Continuous flow tests were conducted using optimized four factor levels, with and without post-treatment, using a stabilization tank (ST). The CW-ST system showed better performance than the CW alone and both showed good stability of removal after stopping aeration. However, poor removal of diethyltoluamide indicated the importance of further effluent treatment. Thus, GAC sandwich SSFs using coarse sand with different GAC layer depths at different filtration rates were further evaluated to remove target PPCP compounds. Filter of 10 cm sand/20 cm GAC/20 cm sand achieved the overall optimal average target PPCP removal (98.2 %) at 10 cm/h filtration rate. Both adsorption and biodegradation contributed to the removal during the filtration process. Type 1 pseudo-second-order model fitted best the adsorption kinetics of target PPCP compounds onto GAC and the adsorption isotherms were described by the Freundlich model. Finally, the optimized CW-ST and SSF systems were connected in series to verify removal of target PPCPs from both synthetic wastewater and natural water. Average removal of above 95 % was achieved for all compounds in the combined system and the system performance presented good stability, suggesting application of the CW-SSF system for removal of PPCPs from water.

IMPACT STATEMENT

Impacts of this thesis fall into the following areas:

Inside academia:

- A simplified PPCP extraction and detection method were developed without conditioning and equilibration for SPE and without the need for derivatization for GC-MS. Avoidance of these two steps not only shortens the overall process time and reduces cost, but also lessens the potential risk of toxicity to humans resulting from organic solvents.
- Greater duckweed was proven to have the potential ability to remove target PPCPs in CWs.
- Orthogonal design was successfully employed in the batch scale CW test. This methodology was proven to be useful in designing CWs with multiple parameters, which economizes manpower and the use of material resources.
- Light, oxygen, microbes and plants can all contribute to PPCP removal via Greater duckweed-based CW system. *E.coli* (ATCC 11775) demonstrated the ability to eliminate organic pollutants.
- A simple sterilization method for live plants was developed in this study, which provides an efficient means to sterilize plants in the laboratory.
- The GAC sandwich SSF was shown to be effective in removing PPCPs and could thus replace the conventional system consisting of sand filtration followed by a GAC contactor. This would reduce both capital and operational costs.
- Investigation of the adsorption kinetics and the isotherms of PPCPs onto GAC gave a deeper insight into the adsorption mechanisms, which can benefit removal techniques via surface and molecular chemistry.

Outside academia:

- Real CWs generally use large rooted plants (e.g. *Phragmites australis*) which grow more slowly than small-leaf plants. Greater duckweed is a common floating plant in tropical and subtropical regions and its good treatment performance at laboratory-scale indicates its potential effectiveness for large-scale CW. This result may be of interest to CW engineers and practitioners seeking an alternative to traditional CW plants.
- Conventional SSF employs fine sand only, which is not effective in removing PPCPs and causes increased headloss, reducing filter lifetime. In addition, GAC contactors are usually constructed in capsule-shaped tank with complex structures. Integration of sand and GAC in a single unit can combine their individual advantages and compensate for the drawbacks of the two separate systems, increasing treatment efficiency. This can reduce the capital and operational costs of treatment.
- CW and SSF processes are eco- and cost-friendly tertiary treatment techniques compared to other high-cost technologies such as reverse osmosis and ultrafiltration. They may also be applied to meet the water treatment requirements of small communities without the addition of other processes, especially in low-income countries. The novel CW-SSF mode represents a good option for water/wastewater treatment engineers and practitioners.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
AOPs	Advanced oxidation processes
ARGs	Antibiotic resistance genes
AT	Additional test
BNR	Biological nutrient removal
BOD_5	5 day biochemical oxygen demand
CAF	Caffeine
CAS	Conventional activated sludge
CFU	Colony-forming units
COD	Chemical oxygen demand
CWs	Constructed wetlands
CW-SSF	Constructed wetland-slow sand filtration
CW-ST	Constructed wetland-stabilization tank
DEET	Diethyltoluamide
DO	Dissolved oxygen
EC_{50}	Half-maximal effective concentration
E.coli	*Escherichia coli*
EI	Electron ionization
EMB	Eosin methylene blue
ESI	Electrospray ionization
GAC	Granular activated carbon
GAR	Graphene adsorption reactor
GC-MS/MS^2	Gas chromatography-(tandem) mass spectrometry
HLR	Hydraulic loading rate
HRT	Hydraulic retention time
HSSF-CWs	Horizontal subsurface flow constructed wetlands
IC	Ion chromatography

LC-MS/MS^2	Liquid chromatography-(tandem) mass spectrometry
LC-UV	Liquid chromatography-ultraviolet
LLE	Liquid-liquid extraction
LODs	Limits of detection
LogKow	Logarithm octanol/water partition coefficient
LOQs	Limits of quantification
MBR	Membrane bioreactor
NTU	Nephelometric turbidity units
O/M	Operation and maintenance
PAR	Paracetamol
PNEC	Predicted no-effect concentration
PPCPs	Pharmaceuticals and personal care products
R^2	Correlation coefficient
RP	Redox potential
RSD	Relative standard deviation
SF-CWs	Surface free water constructed wetlands
SPE	Solid phase extraction
SPME	Solid phase microextraction
SSF	Slow sand filtration
ST	Stabilization tank
TCS	Triclosan
TOC	Total organic carbon
TSS	Total suspended solids
UV	Ultraviolet
VSSF-CWs	Vertical subsurface flow constructed wetland
WWTPs	Wastewater treatment plants

CHAPTER 1 INTRODUCTION

1.1 Motivation behind the research

PPCPs (pharmaceuticals and personal care products), which was first described by Daughton and Ternes (1999) [1], are emerging environmental contaminants that have increased the concerns of both researchers and the public over the last three decades [2]. They have been widely detected in water sources (wastewater, drinking water, river water, hospital waste water) in the United Kingdom, China, Spain, Sweden, Romania and other countries [3–8]. Concentrations of PPCPs vary in different water sources and their fate usually depends on their physico-chemical properties, environmental temperature, rainfall, sunlight and treatment technique employed [9–12]. Although their concentrations may be low (in the range of ng/L-μg/L), their persistence, toxicity and corresponding problems (such as antibiotic resistance) may cause potential risk to human health in the long term [4,13,14]. Generally, effluents from wastewater treatment plants (WWTPs) are considered as important sources of PPCPs in the environment [15]. Conventional WWTP processes are generally designed to remove organic matter, nitrogen and phosphate but not PPCPs, and a number of PPCPs have been detected in WWTP effluents around the world [2,15–17].

Different treatment technologies (e.g. chemical, biological, physico-chemical) have been investigated in the context of PPCP removal. However, the effectiveness of their removal varies greatly with the technology used and the PPCP load [18–23], with some treatment processes also being quite expensive [24,25] or not stable in removal [26]. Today, eco- and cost- friendly techniques that consume fewer chemicals and less electricity are becoming hot topics in the water treatment area. In the last few decades,

constructed wetlands (CWs) and slow sand filters (SSFs) have become popular and have been regarded as promising tertiary treatment processes for wastewater [27,28]. And in recent years, some studies have been conducted on the removal of PPCPs using CWs and SSF [29–33]. Although efficiency varies, these two techniques have the potential to further treat emerging contaminants which are not removed well by conventional WWTP processes [34–36].

CW and SSF systems are usually used separately in the tertiary treatment process of WWTPs [37]. A SSF system followed by a CW unit has only been reported by Gunes and Tuncsiper (2009) [38] for small community wastewater treatment. However, a SSF-CW can only receive influent which has a certain quality [39] and the service life may be not satisfying due to headloss development [40]. In contrast, CW followed by SSF system has never previously been used for the treatment of PPCPs. Adsorption of PPCPs onto soil, sediment and the substrate by CWs of subsurface flow were also reported but these do not constitute a real CW-SSF system [10,41]. Hence, whether this combination is capable of effectively removing PPCP compounds is worth investigating and the optimization of the corresponding parameters is worthy of exploration. In addition, usually CW systems or hybrid CWs have complex structures catering for macrophytes vegetation. As a natural floating aquatic plant, Greater duckweed (*Spirodela polyrhiza*) has promising properties as a vegetation for use in a low-cost CW [42–44] but this plant has not been investigated in terms of its role in PPCP removal. In addition, studies have shown that a SSF system does not always perform satisfactorily in the removal of PPCPs [31,36,45]. Sand and GAC tanks in series [46] and dual-layer media (GAC-sand) filtration [47] have also been investigated but these suffer from a number of limitations such as high capital and operational costs [48]. A GAC sandwich SSF system with fine sand combining the advantages of GAC and SSF has been attempted [48], but not

employed using coarse sand to treat PPCPs before, since fine sand can cause the problem of clogging [49].

Hence, in this research work, a laboratory-scale Greater duckweed (*Spirodela polyrhiza*) based CW system followed by GAC sandwich SSF system has been proposed to study the removal of four widely used and detected PPCPs, namely diethyltoluamide, paracetamol, caffeine and triclosan.

1.2 Aims and Objectives

The aims of this thesis were to investigate the proposed CW-SSF system for removing target PPCPs in water and optimize the effectiveness of tested systems on target PPCP removal

The specific objectives of this study were:

1. Establish simultaneous extraction and detection methods for the four PPCPs.

   Establish a simple extraction approach of target PPCPs from water using SPE by optimising cartridge, sample pH, sample loading rate and eluent type on recoveries. Develop an accurate and simplified detection method of target PPCP compounds using GC-MS.

2. Investigate the Greater duckweed-based CW.

   Test light, microbe, oxygen and plant effects on target PPCP compounds removal from synthetic wastewater at various factor levels using experimental design. Discuss photodegradation, biodegradation and plant degradation of target compounds in CW system. By using design analysis, discuss statistically the

optimal factor level combination on different target compounds. Test the target PPCP removal using continuous CW with/without the adjunction of ST tank after.

3. Study the removal of target PPCPs by a GAC sandwich SSF system using coarse sand with different GAC layer depths at different filtration rates.

   Use coarse sand building GAC sandwich filters with different GAC layer depth. Test all filters at various filtration rates to investigate the PPCP removal from synthetic wastewater. Discuss PPCP removal and filter performance at different filtration rates, and compare removal performance among all filters.

4. Evaluate the removal of target PPCPs by the combination in series of CW and SSF.

   Combine the CW and SSF units as a new serially connected CW-SSF system with the optimized factor levels and parameters achieved from former tests. Use both natural water and synthetic wastewater to conduct the tests, respectively and to study the system stability on selected PPCP removal with/without aeration.

1.3 Thesis outline

Chapter 2 (*Literature Review*) reviews in three sections: PPCPs, CW and SSF, respectively. Section 2.1 reviews the potential risks of PPCPs in aquatic environment, current PPCP pollution in water, PPCP detection and removal techniques and information of four target PPCP compounds. Section 2.2 reviews types of CW system, parameters affecting PPCPs in CWs and give information of Greater duckweed. Section 2.3 reviews general SSF system, PPCP removal mechanisms in SSF, SSF with GAC for PPCP

removal and GAC sandwich SSF system. Combination of CW and SSF system is reviewed in the last.

Chapter 3 (*General Methodology*) describes the details of the chemicals, materials and equipment used in this study. General methods are also described in the chapter, i.e. extraction and detection methods of target PPCPs, preliminary treatment of Greater duckweed and filtration media.

Chapter 4 (*Simplified Extraction and Quantification Method of Selected PPCPs*) establishes a simplified PPCP extraction and detection method without conditioning and equilibration for SPE process and without derivatization for GC-MS process. Method validation was also carried out.

Chapter 5 (*Removal of Selected PPCPs using Greater Duckweed-based CW*) applies an experimental design to investigate four factors at different levels on PPCP removal in batch-scale CW system. Based on the analysis results, batch verification test and continuous flow CW tests were experimented. CW with adjunction of stabilization tank (ST) were also studied.

Chapter 6 (*Removal of Selected PPCPs using GAC Sandwich Slow Sand Filtration*) examines the removal of target PPCPs using GAC sandwich SSF system, with different GAC proportion and filtration rates, as well as the kinetics and isotherms of target compounds onto GAC.

Chapter 7 (*Removal of Selected PPCPs by Greater duckweed CW Followed with GAC sandwich SSF*) presents the results of the investigation on the removal of target PPCPs by serially connected CW-SSF system from both synthetic wastewater and natural

water. Comparisons of removal effectiveness among different tested systems were conducted.

Chapter 8 (*Conclusions and Future Work*) draws the main conclusion of the thesis and suggests future work

1.4 Publications

Li, Jianan, Qizhi Zhou, and Luiza C. Campos. "Removal of selected emerging PPCP compounds using greater duckweed (*Spirodela polyrhiza*) based lab-scale free water constructed wetland." *Water Research* 126 (2017): 252-261. (Appendix 8)

Li, Jianan, Qizhi Zhou, and Luiza C. Campos. "The Application of GAC sandwich slow sand filtration to remove pharmaceutical and personal care products." *Science of the Total Environment* 635 (2018): 1182-1190. (Appendix 8)

CHAPTER 2 LITERATURE REVIEW

2.1 Pharmaceuticals and Personal Care Products (PPCPs)

2.1.1 Introduction to PPCPs

The first study of PPCPs was the review "Pharmaceuticals and Personal Care Products in the Environmental: Agents of Subtle Change?" by Daughton and Ternes (1999) [1]. Also, in 1999, the United States government carried out a project detecting 24 pharmaceuticals, including ibuprofen, erythrocin and carbaryl in surface water [50]. Since then, PPCPs have been regarded as new, emerging pollutants.

PPCPs are comprised of a large and diverse group of organic compounds. Pharmaceuticals include antibiotics, steroids, depressants, eikonogen, painkillers, stimulant drugs, anti-epileptics, hypotensor, anti-inflammatories, hypnotics, acyeterion and so on. Personal care products usually refer to antimicrobial agents, synthetic musk, insect repellents, preservatives, and sunscreen UV (ultraviolet) filters in shampoos, soaps, toothpastes, cosmetics, opacifier, tint and other commodities [1,51].

2.1.2 Potential risks of PPCPs in the aquatic environment

2.1.2.1 Microbes

Many PPCP compounds are synthetic chemicals, which do not exist in the environment naturally. Some PPCPs are toxic to organisms and reaction to PPCPs can occur for some environment creatures, especially microbes. Tamura et al. (2017) [52] found that the contribution of triclosan to the algal toxicity of urban river water was estimated to be at most 69 % and the contribution of linear alkylbenzene sulfonate for

cladocera could be substantial. Ribeiro et al. (2018) [53] also observed an ecotoxicity effect of veterinary antibiotics on green algae and cladocera and Halling-Sorensen et al. (1998) [54] observed that tetracycline antibiotics inhibited protein synthesis in *Microcystis aeruginosa* and *Selenastrum capricornutum*. The EC_{50} (half-maximal effective concentration) values of diclofenac, ibuprofen and naproxen to *Desmodesmus subspicatus* at 71.9, 342.2 and 625.5 mg/L were found [55].

2.1.2.2 Plants

Contamination of agricultural soils by PPCPs resulting from the application of reclaimed or treated wastewater also constitutes a potential risk for plants. Cleuvers (2004) [55] found that 300~900 mg/L sulfadimethoxine affected the development of *Hordeum distichum* plants. A mixture of 17 PPCPs were tested using cucumber seedlings, and at the level of 5~50 μg/L, the mature leaves exhibited burnt edges as well as a reduction in photosynthesis pigments, with all PPCPs detected at higher concentrations in the roots than the leaves [56]. An et al. (2009) [57] exposed paracetamol in wheat (*Triticum aestivum L.*), observing that wheat shoots and root elongation decreased significantly ($p<0.05$) with increasing paracetamol concentration and that the inhibition of root elongation of EC_{50} was 668.8 mg/L.

2.1.2.3 Animals

Some PPCP compounds can also affect the growth and development of organisms. Nassef et al. (2010) [58] investigated the effects of carbamazepine (6.15 mg/L), diclofenac (1.0 mg/L) and triclosan (0.17 mg/L) on Japanese medaka fish. It was found that feeding behaviour was affected by carbamazepine and diclofenac, while swimming speed was altered by carbamazepine and triclosan. Gürcü et al. (2016) [59] observed that

the use of metronidazole caused toxic effects in fish tissues as well as matrix protein alteration (e.g. laminin and collagen IV). In addition, ecotoxicological effects of endocrine compounds have also been found for vertebrates, invertebrates and ecosystem [60–62].

2.1.2.4 Antibiotic resistance genes

Apart from the direct effect of PPCPs on the environment and organisms, corresponding problems have also occurred, with the topic of greatest concern being antibiotic resistance genes (ARGs). The excessive use of antibiotics has been regarded as an important cause of ARGs in the environment with Peak et al. (2007) [63] and Smith et al. (2004) [64] respectively investigating the concentration of tetracyclines and the abundance of tetracycline ARGs, finding a significant relationship (p<0.05) between them. Li et al. (2015) [3] studied the concentrations of 8 antibiotics (3 tetracyclines, 4 sulfonamides and 1 trimethoprim) and the abundance of 12 ARGs in the effluent of residential areas, hospitals and WWTP systems. Various relationships were identified between antibiotics and ARGs (p<0.05), among which the ARGs tet (A) and tet (B) displayed noticeable relationships. Research studying ARGs in drinking water treatment process and the water distribution system showed that 6 transposase genes were detected in tap water samples, and the transposase gene TnpA-04 was enriched up to 124.9-fold compared to effluent [65]. The wide detection of various ARGs in environmental samples indicates the potential risks to human health.

2.1.3 PPCP pollution in the aquatic environment

2.1.3.1 Pathways of PPCPs in the aquatic environment

In recent years, various PPCPs have been detected in different aquatic environments, including rivers, lakes, reservoirs, sea water and wastewater. Figure 2-1 summarizes the sources and pathways of PPCP compounds in the aquatic environment [66]. Generally, PPCP compounds in water appear through the following pathways:

- Wastewater treatment system: domestic wastewater, hospital wastewater and recreational and leisure site wastewater in populated areas enter the WWTP system. PPCPs are not removed thoroughly and consequently enter the aquatic environment (e.g. surface water, ground water) via WWTP effluents.
- Non-point-source pollution: in rural areas of some developing countries, domestic wastewater is discharged directly into the environment. Animal husbandry and aquaculture industries also use large quantities of pharmaceuticals, such as antibiotics and antibacterial agents. Untreated domestic/agricultural wastewater with PPCPs enter the aquatic environment with the help of rainwater and/or surface infiltration.
- Pharmaceutical and chemical industries: specific PPCPs of high concentration and corresponding chemicals always exist in the wastewater of sites related to the pharmaceutical and chemical industries. This wastewater could also contaminate the nearby aquatic environment directly and/or indirectly if not effectively treated.

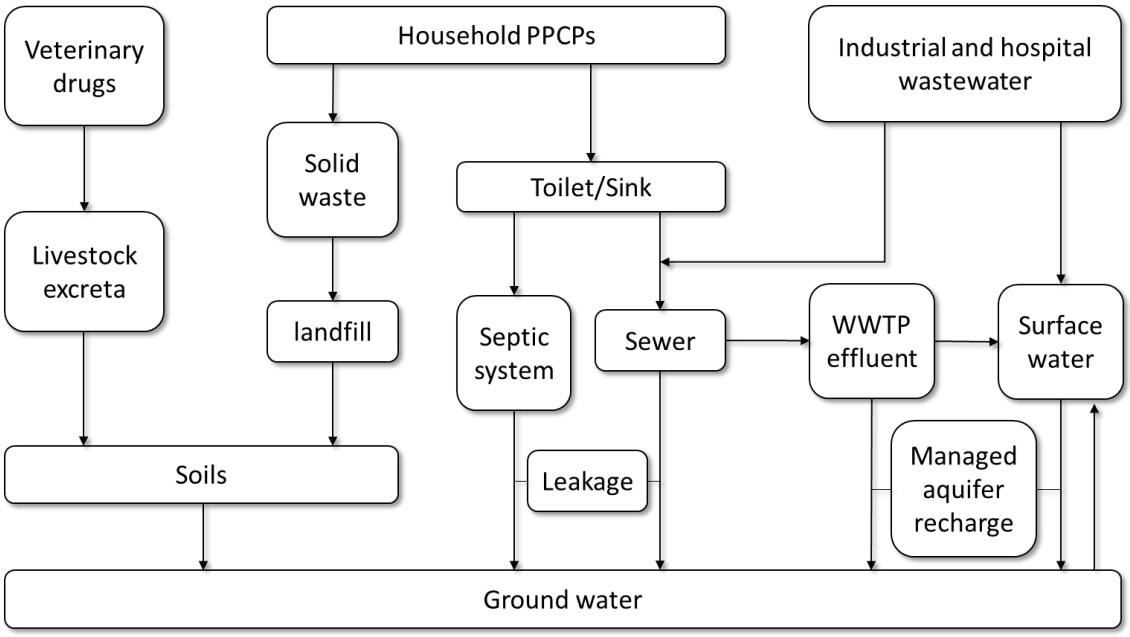

Figure 2-1 Sources and pathways of PPCP compounds in aquatic environment, adapted from Sui et al. (2015) [66]

2.1.3.2 Municipal wastewater

Municipal wastewater is usually considered the main source of PPCP discharge [15]. Kosma et al. (2010) [67] investigated the concentrations of 11 PPCPs in wastewater from one hospital in Greece and found that their concentrations ranged from 0.6~70.1 μg/L. Brown et al. (2006) [68] conducted a research on wastewater from five hospitals in United States and found that the concentrations of sulfamethoxazole, trimethoprim, ofloxacin and penicillin G could be as high as 2,100 ng/L, 5,000 ng/L, 35,500 ng/L and 5,200 ng/L, respectively. In a study investigating antibiotics in the wastewater of urban residential areas, hospitals and WWTP, the highest concentrations of a total of 7 antibiotics reached 3,700.8 ng/L in hospitals, 2,152.1 ng/L in residential areas and 3,323.8 ng/L in WWTP influent [3]. Archer et al. (2017) [69] found that three parental illicit drug compounds in the influent of a WWTP, with concentrations ranging between 27.6 and 147.0 ng/L for

cocaine, 35.6 and 120.6 ng/L for mephedrone and 270.9 and 450.2 ng/L for methamphetamine. Ben et al. (2018) [70] investigated 42 PPCPs in 14 WWTPs, finding ofloxacin, roxithromycin and azithromycin with median concentrations of 479.7, 405.4 and 351.4 ng/L in their influents and median concentrations of 253.3, 108.4 and 105.4 ng/L in their effluents, respectively. For personal care products, concentrations of galaxolide and tonalide at the range of 2,100~3,400 and 900~1,700 ng/L, respectively, were found [19]. In a study of triclocarbon in the WWTPs of Gauteng Province, South Africa, triclocarbon concentrations were found to be 0.0860–2.84 μg/L in the influent and up to 1.89 μg/L in the effluent [71]. Evidence of high concentrations of PPCPs in WWTP effluents indicate that effective and efficient treatment needs to be applied.

2.1.3.3 Surface water

PPCP compounds have also been detected frequently in surface waters and usually come from WWTP effluents [72]. Kasprzyk-Hordern et al. (2008) [8] investigated 56 PPCPs in two rivers in south Wales, United Kingdom and found that the majority of the target PPCPs could be detected at concentrations reaching μg/L level. In addition, treated wastewater effluent was found to be the main cause of water contamination with PPCPs. 139 rivers in the United States were studied and about 80 % were found to be contaminated with antibiotics [73]. In the Pearl River, China, concentrations of ofloxacin and norfloxacin were 16 and 13 ng/L in the dry season, while in wet season they were 108 and 251 ng/L [74], respectively. Yang et al. (2017) [75] detected 93 PPCPs and 5 artificial sweeteners, among which 52 were found in median concentrations ranging from 0.06~504 ng/L. Zhu et al. (2013) [76] investigated 12 PPCPs in the Qingshan basin (two rivers and one lake), China, finding that caffeine showed the highest concentration (23.8~344.7 ng/L) throughout the year. It has been determined that, sulfamethoxazole and

triclocarban could pose the highest eco-risk based on risk evaluation. Based on the study of Bendz et al. (2005) [77], carbamazepine, atenolol, metoprolol, sulfamethoxazole, gemfibrozil and propranolol were detected at concentrations ranging from 0.16 to 1.18 μg/L and demonstrated a high degree of persistence in the Hoje River in Sweden. In a study of 37 rivers in Japan, concentrations of the total target antibiotics were up to 626 ng/L, with a median of 7.3 ng/L. Downstream of rivers, human antibiotics had higher concentrations than animal antibiotics, although there were farms alongside the rivers, indicating that WWTPs might not be the main source [78]. The occurrence and distribution of PPCPs with concentrations of ng/L to μg/L in lakes and rivers worldwide has demonstrated their ubiquity in surface water.

2.1.4 PPCP determination techniques

2.1.4.1 PPCP detection

In recent years, LC-UV (liquid chromatography-ultraviolet), LC-MS/MS^2 (liquid chromatography-(tandem) mass spectrometry) and GC-MS/MS^2 (gas chromatography-(tandem) mass spectrometry) have been the most commonly used PPCP determination techniques.

2.1.4.1.1 Liquid chromatography-ultraviolet

Liquid chromatography-ultraviolet is a basic chromatography technique for PPCP determination. As most organic compounds have UV and/or visible light absorption groups, this technique has a good instrumental sensitivity and broad application range. However, for some compounds, such as unsaturated hydrocarbons, the sensitivity of the technique is low [79]. Babić et al. (2006) [80] developed a method for detecting 7 PPCPs in wastewater with a Limit of Detection (LODs) ranging from 0.1 to 40 μg/L. Since the

concentrations of PPCPs in the aquatic environment are usually at the ng/L level, matrix effects can limit the application of this method, with overlapping response peaks of similarly structured compounds and the method's long running time further limiting this technique for complex samples.

Compared to UV determination via absorption groups, qualitative and quantitative analyses with diagnostic (m/z) ions by mass spectrometry is more reliable and accurate.

2.1.4.1.2 Liquid chromatography-(tandem) mass spectrometry

The method of LC-MS/(MS^2) has gained great popularity since the late 1980s due to its compatibility with polar, non-volatile and thermally labile PPCP compounds [81]. For this technique, LC is used for the separation of the target compounds and MS confirms the target analytes, resulting in lower LODs compared with LC-UV. For different target compounds in different matrices, instrument parameters should always be optimized, including a mobile phase pH, a combination of different mobile phases and flow rate. Pompei et al. (2016) [32] used LC-MS to detect 6 PPCP compounds in intermittently operated slow sand filters for household water purification the LODs of which compounds varied from 0.2 to 0.7 μg/L. Zhu et al. (2013) [82] developed a method of detecting 18 PPCP compounds from surface water using LC-MS/MS with LODs that ranged from 0.02~10.00 ng/L. Li et al. (2015) [3] used LC-MS/MS to detect 8 antibiotics from wastewater with LODs of between 0.12 and 2.40 ng/L, where all compounds were separated within five minutes. When applying LC-MS/(MS^2), large quantities of consumables (e.g. organic solvents and liquid nitrogen) and electricity are used, with matrix effects yielding another major drawback of LC-MS/(MS^2), especially when working in the electrospray ionization mode (ESI) [83]. Matrix effects may result in the

suppression or enhancement of analyte signals, sometimes leading to erroneous results [84,85].

2.1.4.1.3 Gas chromatography-(tandem) mass spectrometry

Compared with the use of LC-MS and LC-MS/MS, GC- MS/(MS^2) is more cost effective as significantly fewer solvents are needed, and it is also easier to operate and suitable for routine analysis [81]. As high temperatures (>100 ℃) are applied in the instrument, the target compounds should be thermally stable. Compared to electrospray ionization (ESI)-based LC- MS/(MS^2), there are fewer matrix effects in the detection of GC-MS [86]. These advantages make GC-MS a promising method for laboratories with a very high demand for sample analysis. Gomez et al. (2007) [87] detected 10 PPCP compounds in wastewater by GC-MS/MS and obtained LODs of 0.2~120 ng/L. In a study of triclosan and carbamazepine in Indian rivers, LODs of 3.0 and 1.6 ng/L were obtained using GC-MS [88]; however, one major drawback of GC-MS is that some compounds need derivatization before injection to achieve good instrument responses. Derivatization usually increases compound stability at high temperature as well as the instrumental response of target compounds. This however also means that the technique is laborious and time consuming, giving the possibility for analyte degradation, reduction of analytical column lifetimes and possible additional cost [87]. In addition, some derivatization agents are toxic, carcinogenic and explosive [89]. Therefore, GC-MS methods without derivatization steps are more attractive [67]. In recent years, researchers also applied GC-MS detection without derivatization and achieved good results, in both water and plasma samples, usually by increasing the injection volume [67,89,90]. The successful application of GC-MS without derivatization not only shortens the sample pre-treatment

time and saves costs, but may also lessen the potential toxic risks to health and the possible formation of unwanted products [91].

2.1.4.2 PPCP extraction from water

There are several extraction techniques for PPCPs from aquatic matrices, including LLE (liquid-liquid extraction), SPME (solid phase microextraction) and SPE (solid phase extraction), among which SPE and SPME are the two most commonly used techniques [81,92].

2.1.4.2.1 Solid phase microextraction

Solid phase microextraction is an extraction technique that uses a fused-silica fibre that is coated with a stationary phase. The technique is based on the partitioning of the analyte between the stationary phase and the matrix [93] and its advantages include a short operation time and the small sample and solvent volumes required. Wen et al. (2005) [94] developed a SPME method to extract 5 sulphonamide compounds in milk, with recoveries of between 10 and 100 %. Balakrishnan et al. (2006) [93] compared the recovery performance of SPME and SPE, extracting 13 sulphonamide compounds in wastewater, and showed that better recoveries of 29.0~229 % could be obtained for SPME compared to n.a. to 115 % for SPE. However, there are also drawbacks of SPME. SPME fibres are expensive and have a limited lifetime, tending to degrade with increased usage [95]. Fibre breakage and mechanical damage of the coating during operation and handling can also occur. The most limiting disadvantage is the limited sample capacity [96]. As the concentrations of some PPCPs in the aquatic environment are very low (< ng/L), a large volume of sample (several litres) is usually needed to obtain sample concentrations

that meet the LODs although, SPME is generally only suitable for small volume sample (e.g. plasms, urine) and is not capable of dealing with samples of large volume.

2.1.4.2.2 Solid phase extraction

Solid phase extraction has become a widely used technique for PPCP purification of water samples with a large sample volume due to the advantage of simultaneous target extraction and clean-up [81]. Different commercial products (e.g. Oasis HLB, Strata X, Oasis MCX) with special sorbents have been used, such as C-18, ion-exchange and polymeric materials [97,98]. Li et al. (2017) [99] tested 4 PPCP compounds using Oasis HLB cartridges in a constructed wetland system and with recoveries within the range of 85~105 %. Gros et al. (2006) [83] developed a method of using SPE determining 29 PPCP compounds in surface and wastewaters. Oasis HLB, Isolute ENV+, Isolute C_{18} and Oasis MCX cartridges were compared, with the Oasis HLB cartridge achieving the overall best recoveries. In a study investigating 18 PPCP compounds from Zhu et al. (2013) [82], 53.9~112 % and 45.1~156.6 % recoveries were achieved using Oasis HLB cartridges in pure water and surface water, respectively. Usually the SPE process consists of conditioning (including equilibrium), sample loading, washing and elution steps. In general, factors affecting SPE performance include sorbent type, the pH of the samples, sample loading rate, eluent type and other factors [100]. Compared with SPME, samples with a large volume can be used so that PPCPs with trace concentrations can be extracted and purified. However, the main disadvantage of SPE is its long processing time [101]. A proper sample loading rate should be chosen, since target compounds may not be adsorbed under a fast loading rate if the time for adsorption or exchange to occur is not sufficient [82]. Thus, in practice, the sample loading rate needs to be optimized.

2.1.5 PPCP removal techniques

As wastewater is considered to be a major source of PPCP pollution, wastewater treatment in WWTP is important for PPCP elimination and studies on PPCP removal techniques have been carried out in recent years.

2.1.5.1 Primary treatment processes

Primary treatment processes are usually ineffective in removing most PPCP compounds [102] which are primarily removed by sorption of sludge [9]. Behera et al. (2011) [103] investigated the occurrence and removal efficiencies of 20 PPCPs in five WWTPs at Ulsan, Korea. Only up to 28 % removal for diclofenac and estriol was found by primary processes (grit removal and clarifier). In the research described in Stasinakis et al. (2013) [18], 36 PPCP compounds were studied in a WWTP treatment process, with removal of 13 % and 43 % for nonylphenol monoethoxylate and bisphenol A, respectively, observed with primary sedimentation tank treatment. Generally, during the primary treatment process, compounds with high partition coefficients between the liquid and solid phases were thought to be better eliminated [19].

2.1.5.2 Biological treatment techniques

The biological treatment technique is an important secondary treatment process in the traditional wastewater treatment system and is designed to remove organic matter, nitrogen and phosphate, but not PPCPs [2]. In secondary treatment, PPCPs can be subjected to a variety of processes, including biodegradation, dispersion, dilution, partition and abiotic transformation [9]. Carballa et al. (2004) [19] investigated the removal of 13 PPCP compounds in a sewage treatment plant. Except for estrone and

iopromide, all of the other 11 PPCPs could be removed at the level of 30~75 % in secondary biological treatment. Removal of 16 PPCPs under aerobic and anaerobic conditions was studied by Suarez et al. (2010) [20]; more than 75 % of synthetic musk compounds could be removed in aerobic tank and about 65 % in anaerobic tank. Naproxen, roxithromycin and erythrocin could only be eliminated under aerobic conditions (above 80 %). Other compounds, including carbamazepine, sulfamethoxazole and trimethoprim, were resistant to biological treatment. Sui et al. (2011) [26] compared conventional activated sludge treatment (CAS), the biological nutrient removal process (BNR) and a membrane bioreactor (MBR) on the removal of 12 PPCPs in two WWTPs. MBR showed better performance. Diclofenac, trimethoprim, trimethoprim and gemfibrozil could be removed in moderation in MBR but no removal was found in CAS and BNR. Recalcitrant PPCPs such as carbamazepine showed no elimination regardless of the season or treatment process. Nevertheless, using modelling, Xia et al. (2005) [104] determined that the majority of PPCPs could not be removed thoroughly in the WWTP process and would thus enter surface water with the effluents. Moreover, as biodegradation is a complex process and various mechanisms occur based on the compounds' properties and treatment conditions, even compounds that are in the same therapeutical group can show great differences in their biodegradability [9].

2.1.5.3 Advanced oxidation processes

In recent years, advanced oxidation processes (AOPs), such as photocatalysis, ultraviolet (UV) and ozonation, have been applied after the traditional treatment process as the tertiary treatment. By using a visible-light-driven magnetic N-TiO_2@SiO_2@Fe_3O_4 nanophotocatalyst, 93 % of benzophenone-3 within 5 h and 71 % of carbamazepine within 9 h were degraded under the visible light of compact fluorescent lamps [105]. Kim

and Tanaka (2009) [22] investigated the removal of 30 PPCP compounds using UV, finding that by using UV light for 10 min at 230 mJ/cm^2, only 5 PPCPs could be eliminated by more than 90 %. However, on combining UV with hydrogen peroxide [106], after 30 min at a dose of 691 mJ/cm^2, the majority of PPCPs could be eliminated (more than 90 %). Zheng et al. (2010) [107] studied the elimination of oxytetracycline by ozonation and found that for a dose of 657 mg/L, 96 % of oxytetracycline was removed after 120 min. In addition, using a low ozone dosage of 3 mg/L, sulfamethoxypyridazine was effectively removed under a pH of 8 in wastewater, and it could be almost removed within 7 hours under a pH of 6 using UV/TiO_2 [23]. As AOPs are typically advanced techniques, small WWTPs, for example in rural areas, usually do not use such processes. Chemicals and electricity are required for AOPs and consequently their running costs are generally high, making their large-scale application cost prohibitive [24,25]. Besides, if not properly operated, AOPs can also result in the formation of mostly unknown and sometimes toxic oxidation intermediates [46].

2.1.5.4 Eco- and cost-friendly techniques

In recent years, techniques such as CW and SSF have become popular. Simplicity and the little to no chemical and electricity requirements make these techniques eco- and cost-friendly. As water treatment processes, unlike AOP techniques, CW and SSF can be used both in a WWTP as a tertiary processes and alone at small community/rural sites [108,109]. Removal of conventional pollutants by household-scale SSF has been successfully applied and studied [109–111]. Research on small-scale CWs for conventional pollutants and PPCP removal in small communities have also been investigated [28,112,113]. WWTPs are designed for conventional pollutant removal but not the removal of PPCPs. Since PPCPs are generally not removed thoroughly during the

conventional treatment process, PPCP compounds in effluents of WWTPs may pose potential risks to the environment and humans, and hence further treatment is necessary. The flexibility and eco-friendliness of the application of CW and SSF make them good treatment options for tertiary wastewater treatment. More details regarding CW and SSF are shown in the following Sections 2.2 and 2.3.

2.1.6 Target PPCP compounds of this study

In the current study, four widely used and detected PPCPs, namely diethyltoluamide (DEET), paracetamol (PAR), caffeine (CAF) and triclosan (TCS), were selected as target compounds. Their chemical properties are summarized in the Methodology section (Chapter 3).

2.1.6.1 Diethyltoluamide

Diethyltoluamide (N,N-deethyl-m-toluamide, Figure 2-2) is an oily liquid synthetic compound and classified as an insect repellent by the United States EPA, especially aimed at mosquitos, and 1.8 million kilograms were estimated to be used during 1990 in the United States [114]. Predicted no-effect concentration (PNEC) of DEET in water is 71.3 μg/L [115].

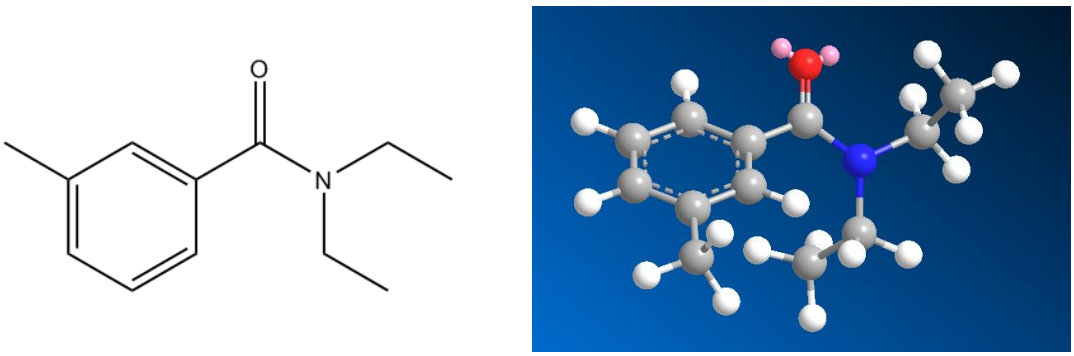

Figure 2-2 2D and 3D structures of diethyltoluamide (drawn by the author using ChemOffice 2016)

DEET as a mosquito repellent is usually applied directly onto skin/clothing and thus enters the environment directly. It has been found in various aquatic environments. Zhu and Chen (2014) [2] detected 12 PPCPs in one WWTP and found that the DEET concentration was up to 266 ng/L in wastewater and can be as high as 40 μg/kg in excess sludge. According to the previous studies [116–118], DEET concentrations have been found at up to 3,000 ng/L in aqueous samples from around the world, 1,500 ng/L in coastal waterways in Australia and 3,700 ng/L in United States stream waters. Even in drinking water, 66 ng/L of DEET were detected in two streams suppling water to drinking water treatment plants [119]. According to a survey [116], DEET detection frequencies in German and Australian wastewater and surface water were above 97 %. DEET is usually regarded as a recalcitrant compound [7]. Sui et al. (2010) [120] investigated 15 PPCP compounds in four WWTPs in China and found that 69 ± 21 % of DEET could be removed by secondary biological treatment. Tran et al. (2013) [121] used fungal laccase to remove DEET and a poor removal efficiency of DEET was noted by laccase alone, while 50 % of DEET was removed by laccase-mediated systems. However, only less than 5 % of DEET was found to be removed by membrane bioreactors (MBRs). Good removal of DEET was observed when using advanced physical and chemical techniques (e.g. reverse osmosis, photocatalytic degradation, nanofiltration) but these have disadvantages that include energy consumption, high cost, toxic residue formation, and therefore cheaper methods should be sought [106,121–123]. In recent years, toxicological studies have shown that DEET has potential cardiovascular and carcinogenic influences to humans and may pose toxic risks to the environment [124–126].

2.1.6.2 Paracetamol

Paracetamol (N-acetyl-p-aminophenol, Figure 2-3) is an anti-inflammatory pharmaceutical and common analgesic/antipyretic drug, which has been heavily used and prescribed all over the world [127,128]. A total of 3.2×10^9 tablets were consumed in the United Kingdom alone in 1998, while more than 400 tons PAR were prescribed in 2000, which means that it ranks as one of top three drugs prescribed in England [128–130]. PNEC of PAR is 1 μg/L [131].

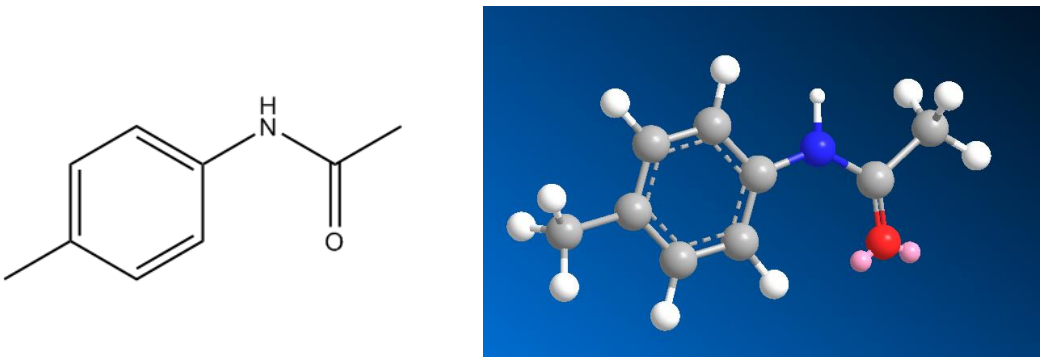

Figure 2-3 2D and 3D structures of paracetamol (drawn by the author using ChemOffice 2016)

Due to its very high level of consumption, high concentrations of PAR have been found in different waters. Roberts and Thomas (2006) [132] detected paracetamol in wastewater at the high concentration of 69,570 ng/L. In Spain, the concentration of PAR in the wastewater of a hospital with only 75 beds was found to be around 16,000 ng/L [133]. Even higher concentrations, of up to 325,000 ng/L, was once reported in hospital wastewater from Norway [134]. As for natural waters, 65,000 ng/L of PAR in the Tyne River (United Kingdom) and up to 10,000 ng/L in the United States natural waters were also reported [73,132]. Compared with DEET, PAR is more easily removed from

wastewater. Various treatment techniques (e.g. CWs, photocatalysis, biofiltration and activated sludge) for PAR removal have been investigated and more than 80 % removal was observed [128,135–137]. Due to its physico-chemical properties, PAR is considered to be not very persistent in the environment, but its huge consumption with the properties of good solubility and hydrophilicity[1], and consequent high concentration and detection frequency in natural waters because of its continuous input, has caused increasing concern about its potential risks to the ecosystem and human health [138,139]. In the study by Henschel et al. (1997) [127], PAR was found to have potential negative effects on cell cultures, ciliates, algae, fish in the environment and side effects on the human liver (half-life at 1~3 hours within the human body). Besides, in the study of Khan et al. (2006) [140], 4-aminophenol, one of the PAR hydrolytic products, was found to have significant nephrotoxicity and teratogenic effects on humans.

2.1.6.3 Caffeine

Caffeine (1,3,7-trimethylpurine-2,6-dione, Figure 2-4), aimed at coughs, headaches and the enhancing of athletes performance in modern societies is one of the most widely used stimulants and pharmaceuticals around the world [141,142]. PNEC of CAF is 151 μg/L [115].

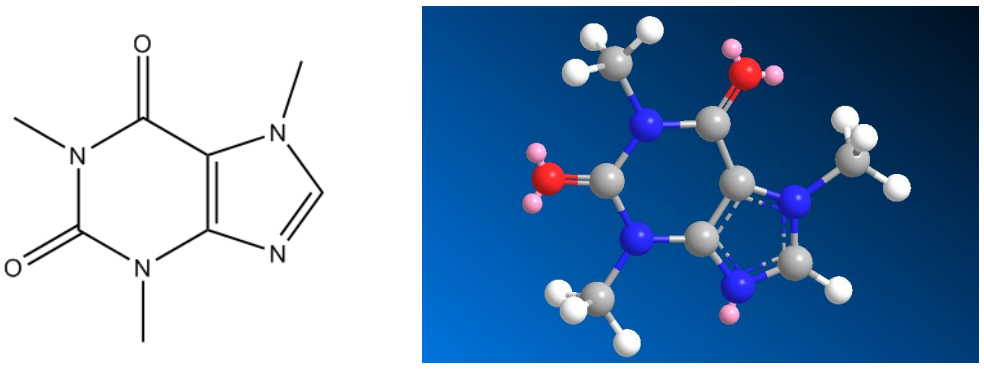

Figure 2-4 2D and 3D structures of caffeine (drawn by the author using ChemOffice 2016)

[1] Hydrophilic compounds are attracted to water molecules and tend to be dissolved by water.

Because of its huge use by humans, CAF has been regarded as a wastewater chemical marker [141,143]. In a WWTP located in a Mediterranean coastal city, CAF concentrations of 52,000~192,000 ng/L were found in influents and 1,400~44,000 ng/L in effluents [90]. In China, CAF concentrations in the range of 3,400~6,600 ng/L in domestic wastewater of Beijing were reported [120]. In one city in eastern China, about 5,000 ng/L caffeine was found in wastewater and the highest caffeine concentration in its downstream water could be up to 629.5 ng/L, varying seasonally [2,76]. By activated sludge and disinfection treatment, around 75 % of CAF removal was investigated in a WWTP in Greece, with influent concentrations of 17.1~113.2 μg/L [67]. Using the anaerobic MBR technique, 87.5 ± 5.3 % removal of CAF was found by Chen et al. (2018) [144]. From a 1-year long research of the wastewaters from four WWTPs (primary settling treatment-activated sludge) in Seville, removal of CAF was 44~75 % [145]. As CAF is also a natural substance in plants (e.g. tea leaves), WWTP treatment cannot thoroughly deal with its environmental pollution and more eco-associated treatments should be studied [76]. As for the toxicity, the effects of CAF on freshwater organisms are not well understood, although it was thought that it may have lethal and sublethal effects on freshwater species such as *Ceriodaphnia dubia* and *Pimephales promelas* [146].

2.1.6.4 Triclosan

Triclosan (2,4,4'-trichloro-2'-hydroxydipheyl ether, Figure 2-5), which has been used for more than forty years throughout the world as an ingredient in disinfectants, toothpastes, soap, mouthwash, detergent, deodorants, shampoos and plastic additives, is a broad spectrum antimicrobial synthetic compound [147]. PNEC of TCS is 121 μg/L [76].

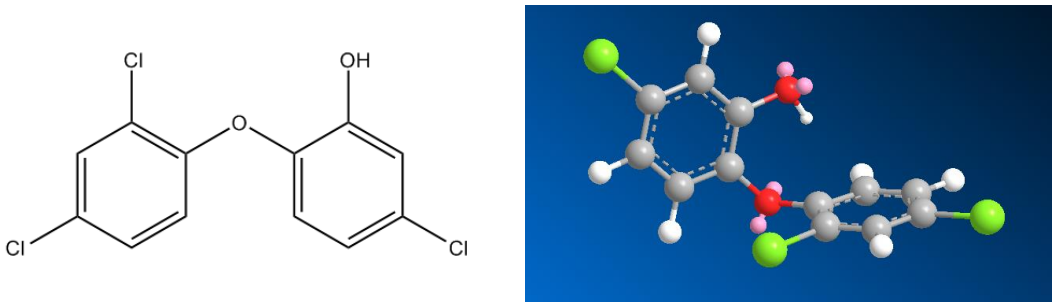

Figure 2-5 2D and 3D structures of triclosan (drawn by the author using ChemOffice 2016)

In the research from Zhang et al. (2015) [148], in all household and personal care products, 100 ton/year of TCS were estimated to be used in China in 2014. The annual usage of TCS in the United States is estimated to be about 300 ton/year. However, 5,200~18,824 kg/year TCS, of which about 50~56 % came from WWTP effluents, were thought to be directly entering the United States surface waters [149]. In the EU, its yield was estimated to be within the range of 10~1,000 ton/year [150]. Today, TCS is considered to be a ubiquitous contaminant and can be found in all types of natural waters (lakes, rivers, estuarine and coastal waters), WWTPs effluents, domestic and drinking waters, soils, sediments and biosolids [151]. In wastewater, TCS at concentrations of 7,500~21,900 ng/L in influent and 340~1,100 ng/L in effluent were found in the United Kingdom [152]. Kumar et al. (2010) [153] also found concentrations of TCS of 13,700~86,200 ng/L in influents and 180~5,370 ng/L in effluents of WWTPs. By using CAS treatment, 69 % of TCS was found to be removed in a WWTP [154]. Photolytic degradation of TCS in freshwater and seawater has also been found [155]. As for its toxicity, it is observed that, by amplification of the food chain, TCS can be bio-accumulated and persist in the environment [156]. In rainbow trout exposed to wastewater effluent, high levels of TCS (0.24~4.4 mg/kg) were reported in the bile, while TCS was also found in the plasma of wild Atlantic bottlenose dolphins [157,158]. Although TCS

is an antimicrobial compound, concerns have also been raised regarding its toxicity to other aquatic communities [159]. For example, algae was thought to be more sensitive to TCS than bacteria [112,160]. In addition, Lawrence et al. (2009) [161] found that a 10 μg/L concentration of TCS had a negative influence on river biofilms.

2.2 Constructed wetlands

2.2.1 Overview of constructed wetlands

Constructed wetlands are treatment systems that use natural processes involving wetland vegetation, soils and their associated microbial assemblages to improve water quality (United States Environmental Protection Agency). In the past few decades, CWs have been demonstrated to be efficient and effective in treating conventional pollutants in domestic wastewater, agricultural wastewater, industrial effluents, contaminated ground water and urban runoff [28,162–164].

Constructed wetlands have been regarded as promising tertiary treatment techniques in WWTPs or in treatment processes in rural areas [10,113]. In comparison with conventional WWTP processes, CWs have low-energy consumption, low cost and are eco-friendly [2,165]. Although using CW to treat traditional pollutants is not new, its application to treat emerging pollutants is quite recent [28]. As the CW is a system involving plants to improve water quality, different aquatic plants have been employed using emergent plants, submerged plants, floating leaved plants and free-floating plants [164]. Table 2-1 shows the most commonly used vegetation.

Table 2-1 Plants commonly used in constructed wetlands [166]

Plant type	Plant name
Emergent species	*Phragmites* spp. (Poaceae), *Typha* spp. (Typhaceae), *Scirpus* spp. (Cyperaceae), *Iris* spp. (Iridaceae), *Juncus* spp. (Juncaceae), *Eleocharis* spp. (Spikerush)
Submerged species	*Hydrilla verticillata, Ceratophyllum demersum, Vallisneria natans, Myriophyllum verticillatum , Potamogeton crispus*
Floating leaved species	*Nymphaea tetragona, Nymphoides peltata, Trapa bispinosa, Marsilea quadrifolia*
Free-floating species	*Eichhornia crassipes, Salvinia natans, Hydrocharis dubia, Lemna minor* (duckweed)

2.2.2 Greater duckweed

In practice, vegetation selection is based on the local climate, treated water type, CW design, cost and work management. In this study, *Spirodela polyrhiza* (Greater duckweed) is selected as the plant for the CW experiments and the reasons for this choice are described as follows. Some studies have reported the removal of PPCP compounds using different aquatic plants (examples in Section 2.2.4.2), but to the author's knowledge, Greater duckweed has not yet been tested for the removal of the aforementioned 4 PPCP contaminants.

Spirodela polyrhiza, widely-found in tropical and subtropical areas, belongs to Genus of *Spirodela*, Family of *Lemnaceae*, Order of Alismatales and Class of Liliopsida.

This floating aquatic plant consists of a single thallus which is 3~9 mm long and 2.5~7 mm wide. The thallus is oval, broadly obovate or orbicular in shape and its outer margin is smooth. The texture of the thallus is slightly succulent and it is filled with minute pockets of air, enabling it to float. The upper thallus surface is light to medium green, while the lower thallus surface is usually purplish red (rarely light green). Both surfaces are glabrous and nearly flat. Toward one side of the upper surface of each thallus there is a single node that is often red. About 5~12 veins originate at this node, curving inward (Illinois Wildflowers-Great duckweed, https://www.illinoiswildflowers.info/). Figure 2-6 shows pictures of Greater duckweed.

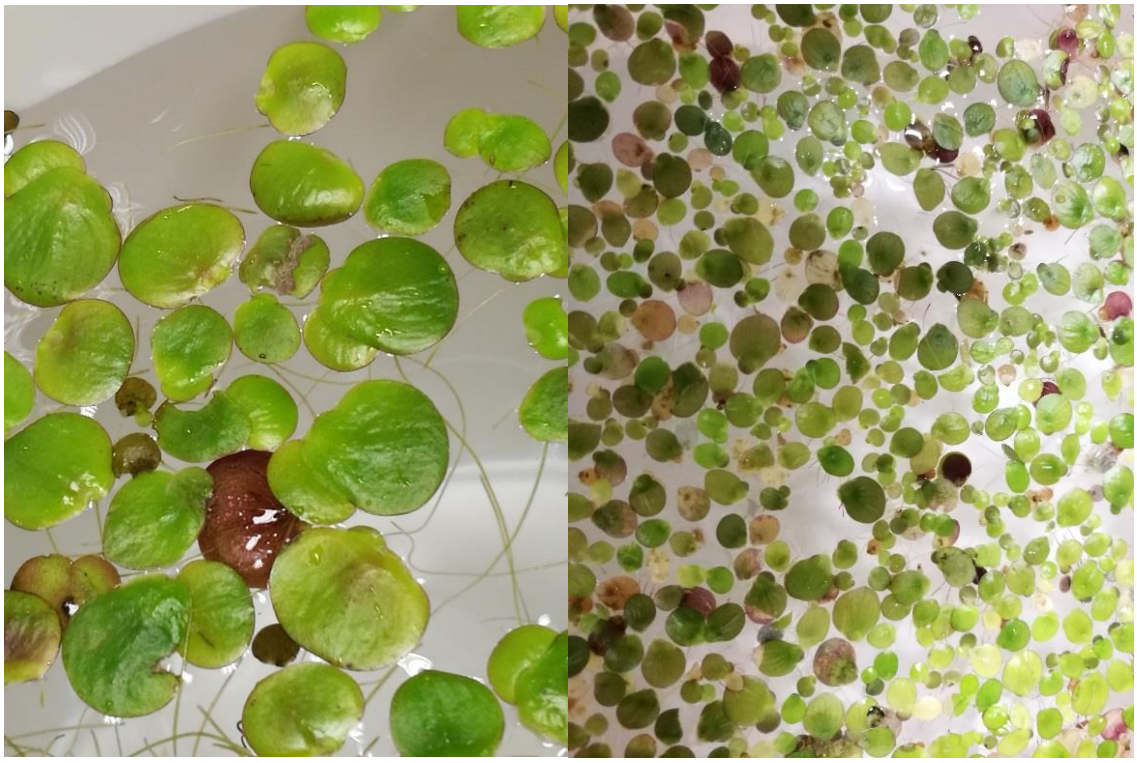

Figure 2-6 Pictures of Greater duckweed (photos taken by the author)

As a member of the *Lemnaceae* plant family, Greater duckweed has advantages such as the ability to survive in dry conditions, low temperature endurance and ammonia preference uptake [42–44]; however, it does not propagate as quickly as other *Lemnaceae*

species such as *Lemna minor*, which form thick mats on water surface, making it easier and cheaper to handle during practical operation and maintenance [167,168] and a potential choice for CW vegetation. Unlike complex CWs with macrophytes, its property of being as small in form as other *Lemnaceae* family plants also makes it ideal for laboratory-scale research. Ran et al. (2004) [169] used Fat duckweed (*Lemna gibba* L.) to treat domestic wastewater in Israel and found removal of COD, BOD_5, nitrogen and turbidity of 67.5±78.2 %, 70.6±79.5 %, 10~20 % and > 50 %, respectively. Reinhold et al. (2010) [170] studied the removal of 8 PPCPs using common duckweed (*L. minor*), finding negligible removal of atrazine, DEET, picloram and clofibric acid and good removal for fluoxetine, ibuprofen, 2,4-dichlorophenoxyacetic acid and TCS (exact removal of TCS not specified). As a member of the duckweed family, Greater duckweed may also have the ability to treat pollutants. Hence, whether this floating plant is capable of removing target PPCP compounds while also serving as a CW plant is worth investigation.

2.2.3 Types of Constructed wetlands

Generally basic CWs can be classified into surface free water CWs (SF-CWs), horizontal subsurface flow CWs (HSSF-CWs) and vertical subsurface flow CWs (VSSF-CWs) (Figure 2-7). In large-scale water treatment and ecological remediation processes, the combinations of serial CWs are sometimes used, which is called hybrid CWs. As a tertiary treatment stage, SF-CWs and SF hybrid CWs are the most popular [28].

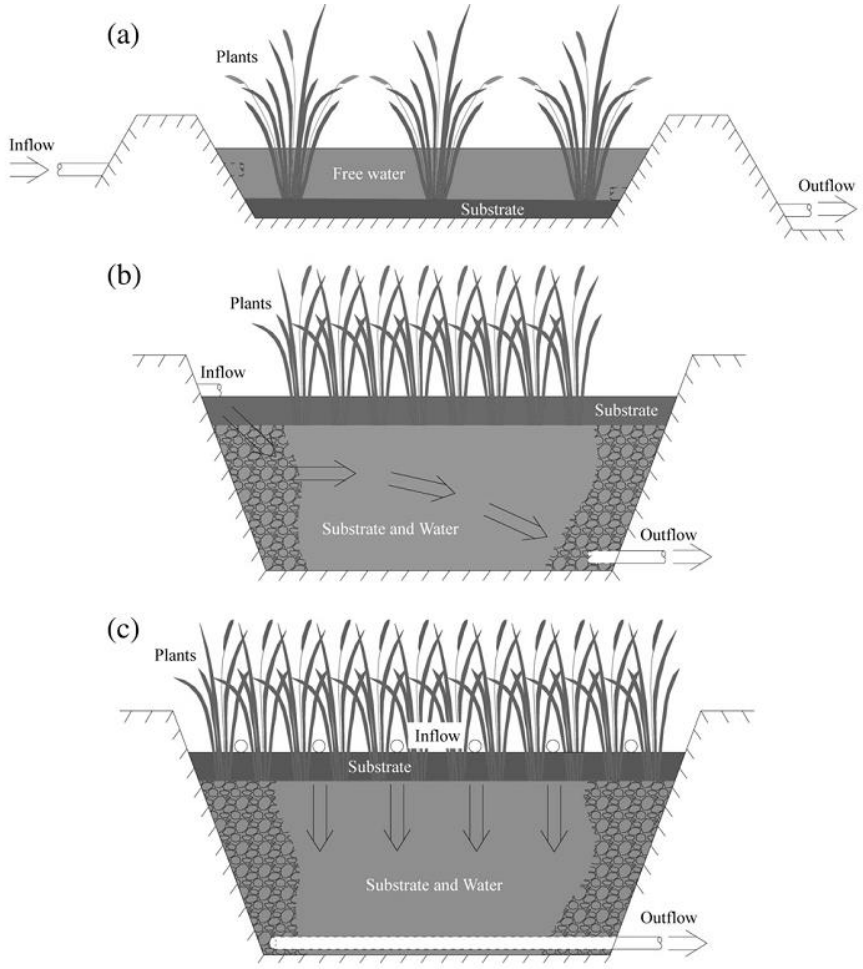

Figure 2-7 Structures of basic CWs, (a) SF-CW; (b) HSSF-CW; c (VSSF-CW) [28]

2.2.3.1 Surface free water constructed wetlands

Surface free water constructed wetlands (SF-CW) systems are shallow basins in which free wastewater flows at relatively shallow depth over the impermeable bottom liner or the packed substrate layer [28]. Pollutant removal occurs in the water as well as during the interactions between the plants and relevant biofilms [171,172]. SF-CWs is thought to be effective in removing suspended solids and organics (above 70 %) via microbial degradation, filtration and sedimentation [113,173]. In addition to phytoremediation and biodegradation, photodegradation also plays a significant role in the removal of contaminants (especially for light sensitive compounds such as diclofenac)

because of the exposure of the water to direct sunlight [174]. Usually more than 70 % of TSS (total suspended solids), COD, BOD and pathogens can be removed by SF-CWs, while nitrogen and phosphorus removal range between 40 and 50 % [171,175]. SF-CW systems typically have water depths of less than 0.4 m and hydraulic loading rates (HLR) of between 0.7 and 5.0 cm/day [113]. Hussain et al. (2012) [176] investigated the removal of monensin, salinomycin and narasin in SF-CWs, which were vegetated with alternate bands of *Phalaris arundinaceae* and *Typha latifolia* with provided removal ranging from 21 to 47 %. Kumar et al. (2011) [177] evaluated the natural degradation of 17α-ethinylestradiol and estradiol by a microcosm of SF-CWs containing floating, submerged and emergent aquatic plants. Both compounds had removal of higher than 90 %. Due to oxygen consumption in the water, the surface water of a SF-CW system can be aerobic while the deeper parts may display anaerobic properties [113]. Because SF-CWs are easy to run and clean, they are currently becoming popular as a tertiary treatment process in WWTPs [178,179].

2.2.3.2 Horizontal subsurface flow constructed wetlands

In horizontal subsurface flow constructed wetlands (HSSF-CWs), wastewater flows horizontally through a granular medium planted with vegetation [180]. Water is fed into the CW at the inlet zone and effluent is collected at the outlet zone after the treatment (Figure 2-7). Wastewater then enters aerobic, anoxic and anaerobic zones. The aerobic zones occur around plant roots and rhizomes that introduce oxygen into the substrate [113]. Based on Zhang et al. (2014) [113], HSSF-CW exhibits removal of 79.93 % for TSS, 75.1 % for BOD_5, 66.02 % for COD, 51.97 % for nitrogen and 65.96 % for phosphorus. The bed depth for HSSF-CW is generally less than 0.6 m. In the studies conducted at Spain, a shallow system of 0.27 m deep, with a less negative redox potential,

was found to be more efficient than a deeper one (0.5 m) at removing biodegradable compounds such as ibuprofen, naproxen and methyl dihydrojasmonate, indicating that a shallower depth performs better in HSSF-CW [181,182]. Ávila et al. (2010) [183] conducted an injection study using pilot-scale HSSF-CWs planted with *Phragmites australis* to remove ibuprofen, naproxen, diclofenac, tonalide and bisphenol A, achieving removal ranging from 85 to 99 %. A 700-h injection experiment was conducted in two HSSF-CWs planted with *Phragmites australis* in synthetic wastewater to remove carbamazepine and ibuprofen. Around 50 % of ibuprofen and 5 % of carbamazepine was removed [184]. The typical HLR ranges from 2~20 cm/day [113]. Wastewater enters the HSSF-CW continuously and the water flows slowly under a gravel wetland bed which is planted with macrophytes in which a generally anaerobic environment prevails [174]. The advantage of HSSF-CW is that it provides good conditions for denitrification (anaerobic condition) although it is not effective in nitrifying ammonia [113,185].

2.2.3.3 Vertical subsurface flow constructed wetlands

Vertical subsurface flow constructed wetlands (VSSF-CWs) are systems in which wastewater enters the whole surface area evenly via a distribution system and passes through the wetland vertically. Effluents are collected in the outflow (Figure 2-7). Compared with HSSF-CWs, VSSF-CWs are intermittently fed from the surface of the wetland, with feeding and resting periods [113]. Oxygen enters the wetland with water, consequently, there is greater oxygen transfer into the medium, demonstrating that a predominantly aerobic environment exists [171]. VSSF-CW performance depends highly on the loading strategy, especially the frequency of the influent dosing and volume of the pulse [186]. VSSF-CWs exhibit removal of TSS at 85.25 %, BOD_5 at 89.29 %, COD at 66.14 %, nitrogen at 50.55 % and phosphorus at 59.61 % [113]. Generally, HSSF-CWs

can provide good conditions for denitrification but denitrification is acknowledged to hardly occur in VSSF-CWs [175]. Similar to HSSF-CWs, the bed depth for VSSF-CWs is also generally less than 0.6 m, the hydraulic retention time (HRT) is usually 1~2 days [28]. Compared with HSSF-CWs, there are fewer studies of VSSF-CWs [41]. Song et al. (2009) [187] evaluated the removal of estrogens using different sand layer depths in VSSF-CWs, finding the highest removal was achieved in the shallowest wetland (i.e. 68±28 %, 84±15 % and 75±18 % for estrone, 17β-estradiol and 17α-ethynylestradiol, respectively), due to stronger aerobic conditions and high root density. Matamoros et al. (2007) [188] studied the removal of 13 PPCP compounds by VSSF-CWs. All evaluated compounds had removal of higher than 70 %, except for carbamazepine (at <30 %). A new type of CW, called a vertical up-flow constructed wetland, was investigated to remove antibiotics from swine wastewater and 69.0~99.9 % removal were obtained for tetracyclines [29].

2.2.3.4 Hybrid constructed wetlands

The hybrid CW systems are the combination of two or more wetlands or the combination of wetlands with other treatment systems such as lagoons in parallel or in series [28]. Table 2-2 shows common hybrid CW types.

Table 2-2 Types of commonly used hybrid constructed wetlands [166]

Hybrid CWs	Types
Two stages	HSSF-VSSF, VSSF-HSSF, HSSF-SF, SF-HSSF
Multi-stages	VSSF-VSSF-HSSF, HSSF-VSSF-SF, VSSF-HSSF-VSSF …

Hybrid CWs are usually used in large-scale or full-scale treatment processes which require large areas. The concept of hybrid CW systems lies within enhancing pollutant removal since individual a CW may not be able to achieve effective results. However, a larger CW system means a longer HRT, usually 2~15 days [28]. Zhang et al. (2014) [113] reported that nutrient removal by hybrid CWs varies widely for phosphorus (14~99 %), nitrite (13~89 %) and nitrogen (31~91 %), depending on the system configuration, HLR and plant species. In a one year study of carbamazepine removal by hybrid CWs, HSSF-SF and HSSF-VSSF systems exhibited more effective performance than VSSF-HSSF, with average removal of 62 % and 59 %, respectively [189]. Reyes-Contreras et al. (2011) [190] investigated the removal of 16 PPCP compounds using an up-flow anaerobic sludge blanket reactor followed by SF-CW and HSSF-CW sequentially, finding that removal varied considerably for target chemicals due to climate change, and that the SF-CW generally exhibited the highest removal for the majority of the PPCPs analysed. A hybrid CW system (VSSF-HSSF-SF) was used to remove 16 PPCP compounds [34]. 98~99 % removal was obtained for TSS, BOD_5 and ammonium, and a removal of greater than 80 % was observed for all PPCPs in the whole treatment. Although hybrid CWs can have the advantages of various types of CWs, they have high operating and management costs, which limits their application.

2.2.4 Effect of constructed wetland parameters on PPCP removal

In a CW system, PPCP compounds undergo a series of chemical, biological and physical reactions, mainly photodegradation, biodegradation, plant degradation and adsorption. Generally, factors influencing PPCP removal are plant, microbes, operation mode, hydraulic retention time, light, temperature, oxygen and substrate.

2.2.4.1 Plant presence

The presence of plants in a CW is acknowledged to play a role in the removal of PPCPs, but the importance of plants in this process is still not fully understood [10,41]. Some studies have shown that the removal of certain PPCPs is enhanced in planted beds compared to unplanted beds [33,191,192]. Plant presence enhances PPCP removal in the following ways [30,171,192]:

- Bacteria attached to plants can help biodegrade PPCPs.
- Plant uptake.
- Exudates from plant decomposition and biofilms may help eliminate PPCP.
- Sorption which may occur due to large surface provided.

Usually aquatic plants have the ability to transfer oxygen inside the plant [193]. The main sources of oxygen in CWs are diffusion from the air into the water's surface and the transport of oxygen from plant shoots into the rhizosphere, then into the water, which increases the dissolved oxygen (DO) concentration in the water. Higher DO concentration in CW water favours microbial activity for PPCP elimination [194,195]. Additionally, generally CW plants have strong roots, which provide a large surface area for microbes to grow in water, thus stronger microbial activity can contribute to PPCP compound biodegradation [113]. Rhizosphere is the narrow region around the plant roots and is a very complex and dynamic environment. Products from this zone, such as exudates, lysates, mucilage, secretions and decaying plant material, can also be used as carbon and nutrient sources by microbes in addition to the organic carbon sources already in the water. This process can enhance the proliferation of the microbes and help eliminate PPCPs [196]. Hijosa-Valsero et al. (2011) [191] investigated 7 mesocosm-scale CWs and found rhizosphere biofilm, plant exudates and microenvironment modifications played a combination role in the removal of antibiotic tetracycline.

2.2.4.2 Plant species

The ability of plant species to treat PPCPs and which types of aquatic plant species would maximize PPCP degradation rates are not fully understood [10]. Plant species not only affect the nutrient and heavy metal uptake, but also influence the microbial communities during PPCP biodegradation [197]. Studies on different plant species for removing PPCPs have been carried out. For example, it is found that by using *Phragmites australis*, more naproxen, ibuprofen, diclofenac, caffeine and methyl dihydrojasmonate were degraded than using *Typha angustifolia* in CW [11]. Triclosan was eliminated more by *Ceratophyllum demersum* than *Lemna minor*, whereas *Lemna minor* was more effective than *Salvinia molesta* at caffeine removal, and the plants contributed to PPCP elimination through biodegradation and plant uptake [192]. In terms of plant biomass, more developed aerial and underground parts of plant species can usually yield better PPCP removal, which can be attributed to larger rhizosphere but which also depends on plant density [41]. A test was conducted using 7 mesocosm-scale CWs for 39 months and found that young systems are more efficient if vegetated, probably due to their faster uptake and metabolism [198]. However, still little generalization can be made that could help guide plant species selection for PPCP removal in CWs [199]. Since PPCP compounds differ greatly in structure and properties, their removal mechanisms by aquatic plants can be also quite different due to plant preference.

2.2.4.3 Plant uptake

Mechanisms involved in plant uptake remain poorly understood. Physico-chemical characteristics of the PPCP compounds, including logKow (logarithm octanol/water partition coefficient), water solubility and concentration are thought to be essential for plant uptake [28,163]. As there are no specific transporters in plant cells for PPCP

compounds, diffusion is the main mechanism [10]. Generally speaking, PPCP compounds with logKow at the range of 0.5~3.5 are lipophilic[1] enough to move through the lipid bilayer of plant cell membranes [163,200,201]. Compounds with logKow below 0.5 are highly hydrophilic. However, Liu et al. (2013) [202] once observed ciprofloxacin HCl, oxytetracycline HCl and sulfamethazine (logKow<0.5) were taken up by plants, probably via the transpiration water stream in the plant uptake. Further, diclofenac is a highly lipophilic compound of which logKow is above 3.5, poor plant uptake of this compound was found using *Scirpus validus* [203]. Therefore, determining whether compounds can be taken up by plants should not be based only on logKow.

Once taken up by plants, PPCPs might be degraded completely or partially via the metabolism or transformation processes. Compounds generally undergo three transformation stages in plants tissues [10,204]:

1. Chemical modification (oxidations, reductions, hydrolysis).
2. Conjugation (with glutathione, sugars, amino acids).
3. Sequestration or compartmentation (conjugants are converted to other conjugates and deposited in plant vacuoles or bound to the cell wall and lignin).

Enzymes act on PPCP molecules and mineralize them into nontoxic compounds such as carbon dioxide and water, or store them in plant tissues at more stable structures [205]. However, compared with nutrient compounds, studies on the fate of PPCPs in plant tissues and their intermediate transformation products are quite limited, which may be attributable to the complex biochemistry process and low concentrations of targets in plant tissues.

[1] Lipophilic compounds have little to no capacity to form hydrogen bonds, and are dissolvable in fats, oils, lipids and non-polar solvents.

2.2.4.4 Microbes

Biodegradation is considered an important mechanism of PPCP removal by CW. Under biodegradation, PPCP compounds may undergo [10,54,206]:

- Mineralization.
- Transformation to more hydrophobic compounds, which can be adsorbed onto the solid phase.
- Transformation to more hydrophilic compounds, which remain in the water phase.

Biodegradation of PPCPs in CWs usually involves activities of heterotrophic bacteria, autotrophic bacteria, fungi and specific protozoa in both aerobic and anaerobic conditions [28,171]. According to Li et al. (2014) [28], certain compounds can be more easily removed under aerobic conditions (such as ibuprofen and salicylic acid) or anaerobic conditions (such as naproxen).

One factor strongly influencing biodegradation is the structure and properties of PPCP compounds [207,208]. Unlike degradable compounds (such as glucose), which can be used as energy sources by microorganisms, PPCP compounds may be slowly degraded by microorganisms, possibly due to the lack of suitable degrading genes as they are not energy sources [28]. Actually, recalcitrance of PPCP biodegradation may be explained by chemical structures such as functional groups [209]. However, even for compounds from one class, the removal could differ a lot because of small chemical structure changes, such as diclofenac, ibuprofen and ketoprofen, which makes it difficult to predict PPCP biodegradation in one chemical class [10,210].

Microbial communities in CWs exposed to PPCPs may be affected. Weber et al. (2011) [211] investigated the influence of ciprofloxacin on bacterial communities in some mesocosm-scale CWs planted with *Typha angustifolia*, finding ciprofloxacin had a negative effect on bacterial activity at the beginning, at that bacterial communities then

returned to original functionality after about 1 month. In a study of the effect of triclosan on a bacterial community [159], 60 μg/L triclosan on bacterial communities in batch-loaded CWs with *Typha angustifolia*, *Hydrilla verticillata* and *Salvinia natans* were analysed. After six periods of experiment, negative effects of triclosan on bacterial community richness and diversity were observed. Similar conclusions were also drawn [32,147,212,213].

2.2.4.5 Operational mode

Operational mode can be classified into batch and continuous. In studies of conventional parameters such as BOD_5, ammonium and total phosphorous removal, batch mode performed more effectively than continuous mode [194,214]. This is because alternating the stage of by saturation and unsaturation in batch operation mode brings "entrainment of air within the micropores of the soil matrix, and thus establishes a more micro-aerobic environment, promoting microbiological activity within the bed and mineralizing organic matter" [10,215]. Zhang et al. (2012) [216] found higher removal of ibuprofen, diclofenac and naproxen in HSSF-CW planted with *Typha angustifolia* using the batch mode. This can be attributed to the higher redox status caused by saturation and unsaturation alternating cycles [41]. However, Hijosa-Valsero et al. (2011) [217] found very few differences between batch and continuous modes in the removal of 10 PPCP compounds from urban wastewater using HSSF-CWs. PPCPs removed by two modes were both reported but removal usually varied greatly [34,184,218,219]. Even though studies showed that the batch operational mode generally provides effective treatment performance not only for conventional pollutants but also for some PPCPs, in actual operation, most CWs use the continuous flow mode because of the large quantities of influents to be treated [10].

2.2.4.6 Hydraulic retention time

Hydraulic retention time (HRT) is one key parameter in CW operation and refers to the duration in which pollutants react with plants, substrate and bacteria in the CW [163]. The longer the HRT, the longer the water stays in the CW. In contrast, at a high HLR, water flows faster through CW and there is less contact time [10]. Removal efficiencies of 13 PPCPs in a VSSF-CW system at 4 different HLRs (13, 30, 70 and 160 mm/day) were investigated [33]. Ibuprofen, naproxen and salicylic acid were little affected by HLRs and were nearly completely removed at all loading rates, indicating they were removed quickly. However, carbamazepine and diclofenac were poorly removed at all loading rates. According to Zhang et al. (2014) [10], for PPCP compounds including ibuprofen, diclofenac and naproxen, significant relationships ($p<0.05$) existed between removal and HRT. Removal efficiencies for clofibric acid, carbamazepine and salicylic acid were not significantly ($p>0.05$) correlated to HRT. Generally, HRT in CW operations varies considerably from 1 to 12.9 days [220–222]. Longer HRT usually indicates a longer operation time. Thus, to balance the removal and operation duration, the HRT should be considered.

2.2.4.7 Light

Since PPCP compounds generally contain aromatic rings, heteroatoms and/or other functional groups that can either directly absorb solar radiation or react with the photogenerated transient species in water, photodegradation can be important for PPCP removal [41,223]. However, the reaction time affects the effectiveness of the removal. UV treatment as an advanced oxidation technique was proven to be effective at removing some PPCPs, as was discussed in Section 2.1.5.3. In aquatic systems, seasonal variation, light intensity and light attenuation by water depth affect the photodegradation process

[224]. However, there are no reliable rules for predicting the photodegradation behaviour of PPCPs [41]. Some unbiodegradable PPCPs can be eliminated by photodegradation. In the study of Llorens et al. (2009) [225], diclofenac and ketoprofen were efficiently removed by high HRT (one month) and sunlight exposure. Matamoros et al. (2012) [192] investigated polar PPCPs in mesocosm wetland systems planted with *Salvinia molesta*, *Lemna minor*, *Ceratophyllum demersum* and *Elodea canadensis*. Similar results for diclofenac and ketoprofen were also observed in that these compounds were mainly eliminated by sunlight. Nevertheless, light may also play a negative effect sometimes. 4-nitroso-sulfamethoxazole, a photolytic transformation metabolite of sulfamethoxazole, was observed to transformed back into the parent compound, sulfamethoxazole, demonstrating potential compound synthesis under natural conditions [226].

2.2.4.8 Temperature

Higher temperature generally promotes elimination of PPCPs [41]. Higher temperature will increase enzyme activity, and subsequently increase biodegradation and plant uptake. However, as sorption may occur in some substrates, high temperature may weaken the sorption process. A total of 7 mesocosm-scale CWs of different configurations were operated for nine months to assess their ability to remove PPCPs from urban wastewaters [11]. Results showed that high temperature favoured removal of some PPCPs such as naproxen, salicylic acid, galaxolide and tonalide. Ketoprofen, carbamazepine, salicylic acid, caffeine and methyl dihydrojasmonate, tended to be more rapidly removed in summer than winter were also reported [190,198]. Similar studies also can be seen [184,227]. Overall, PPCP elimination increases with temperature.

2.2.4.9 Redox potential

High redox potential (RP) is related to aerobic conditions [10]. Anoxic (RP within −100~ +100 mV) and aerobic (RP> +100 mV) RPs can provide proper conditions for biodegradation of PPCPs through the promotion of biogeochemical reactions [41]. Hijosa-Valsero et al. (2010) [11] reported positive linear correlations between PPCP elimination and RP. RP was higher in the shallow water (−144 ~ −131 mV) compared to the deep water (−183~ −151 mV), as shallow CWs have more aerobic water areas and promote more energetically favourable biochemical reactions in bacteria, leading to higher efficiencies of PPCP removal. Although aerobic conditions promote biogeochemical reactions, some polyhalogenated compounds could be eliminated by reductive dehalogenation under anaerobic conditions, such as diclofenac [218]. However, bacteria can be alive within the RP range of −400~ +900 mV, which is out of the range of healthy CW systems [228]. CWs as treatment system should also consider microbial elimination.

2.2.4.10 Substrate

Substrate (or matrix) is another factor influencing PPCP removal, not only because it supports the growth of emergent and submerged plants, but also because it can interact directly with PPCP compounds through sorption processes, especially in HSSF-CWs [28]. A variety of materials have been used in CW systems, including natural materials (e.g. gravel, sand, calcite), industrial by-products (e.g. fly ash, slag, oil palm shell) and artificial products (e.g. compost, ceramsite), among which gravel is commonly used in CWs to remove PPCPs [166]. According to Li et al. (2014) [28], different interactions could be involved between substrate and PPCP compounds, such as hydrophobic

partitioning[1], van der Waals interaction[2] and electrostatic interaction[3]. Besides, non-polar compounds tend to be adsorbed onto the substrate materials rich in organic matter such as soil, compost and agricultural wastes via hydrophobic processes. Polar or ionic compounds are dominantly adsorbed by electrostatic interactions or ionic exchange. If various PPCP compounds are present in the CW water, competitive sorption phenomenon might occur and the sorption process may be weakened due to the competition [229].

2.2.4.11 pH

pH of water can influence the structures and behaviour of PPCPs, substrate, plant and microbe performance in CW [230]. Zhang et al. (2011) [231] used HSSF-CWs planted with *Typha angustifolia* to remove carbamazepine, diclofenac, ibuprofen and naproxen, finding that there were no significant differences for pH between CWs of planted and unplanted beds or different HRTs, indicating water pH stability in CW systems. A study from Hussain and Prasher (2011) [232] showed that soil pH has an effect on the sorption of ionophoric PPCPs. But the narrow range of pH (6.8-8.0) in the removal of ionophoric PPCPs in SF-CW makes it difficult to verify the relationships between pH and removal [176]. In addition, Hijosa-Valsero et al. (2010) [11] found that within the narrow pH range (6.48~8.34), no significant linear correlations were found between pH and 11 PPCP removal monitored in CWs (SF-CWs and HSSF-CWs). Hence, since the water in the CWs is usually around neutral, the influence of pH is not always easy to glean.

[1] Hydrophobic compounds tend to be adsorbed by lipophilic matters in substrate due to high octanol/water partition coefficients.
[2] Van der Waals interactions are distance-dependent interactions between atoms or molecules not occurring as a result of any chemical electronic bond.
[3] Electrostatic interaction is the attractive or repulsive interaction between objects having electric charges.

2.2.5 Constructed wetland with stabilization pond

2.2.5.1 Introduction to stabilization pond

Stabilization pond (tank, ST), or lagoon, is a commonly used onsite wastewater treatment technology in North America and in some European countries [233]. The ST can be used individually, or linked in a series for improved treatment. Differing by depth, there are three types of ponds (Figure 2-8), (1) anaerobic, (2) facultative and (3) aerobic (maturation) [234]. Biodegradation, photodegradation and sorption processes have been regarded effective for the removal of PPCPs in ST [235].

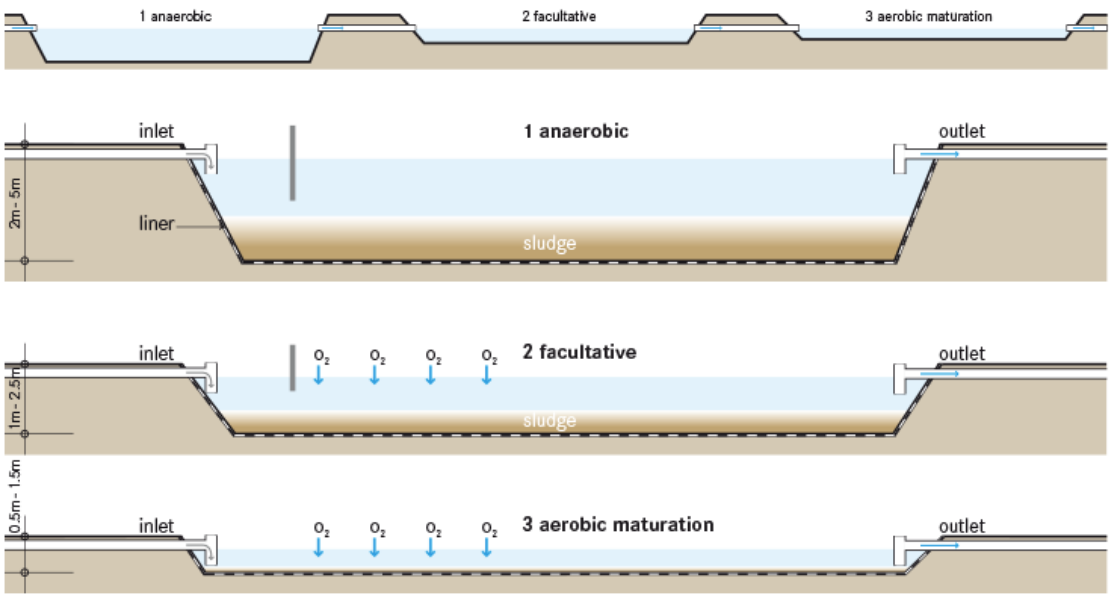

Figure 2-8 Types of stabilization ponds [234]

When combining with CW, the ST followed by the CW system was reported (Figure 2-9). In a study investigating performance of CWs (HLR at 75 mm/day and 225 mm/day, planted with *Cyperus papyrus* and *Echinochloa pyramidalis*) polishing effluent from sugar factory ST (parameters not specified) in Kenya, a positive linear relationship between mass removal rates (removal varied with temperature and location) and mass

loads of total phosphorus, NH_4^+ and TSS were found and season had a significant effect on the removal rates [236]. Belmont et al. (2004) [237] carried out a pilot-scale experiment consisting of a serially connected ST, HSSF-CW and VSSF-CW system planted with *T. angustifolia* and *Chrysanthemum cinerariaefolium*. The HRT was 2.3 days in each CW and the average volume of wastewater treated daily was 2.88 m^3/day. The average removal of COD, TSS, NH_4^+, NO_3^- and total nitrogen from domestic wastewater were 84.9 %, 58.6 %, 53.9 %, 81.7 % and 71.7 %, respectively.

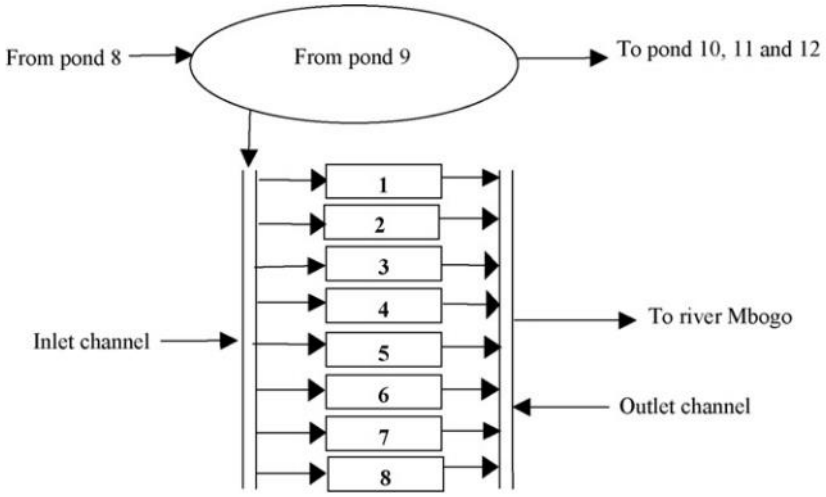

Figure 2-9 One example of ST followed by CWs system [236]. CWs 1, 3, 5 and 7 were planted with Cyperus papyrus and 2, 4, 6 and 8 were planted with *Echinochloa pyramidalis.*

2.2.5.2 Constructed wetland with stabilization pond in PPCP removal

However, studies of stabilization pond-CW system dealing with PPCP removal are very rare. The only study author found is by Conkle et al. (2008) [238], who investigated 15 PPCP removal via aeration ST (basins, HRT at 27 days) followed by a CW (HRT of 1 day, plants included *Hydrocottle spp.* and *Phragmites australis*). Only 9 compounds were above the detection limits and most of these were removed by greater than 90 %,

while carbamazepine and sotalol were only removed by 51 % and 82 %, respectively. The entire system was regarded capable of removing several kilograms per year of PPCPs from wastewater.

To author's knowledge, ST-CW system has been reported but CW-ST system has not been tried before to remove PPCP compounds. If ST is placed in front of CW unit, products from the CW, such as decaying plant material may enter the effluent, potentially deteriorating water quality. However, if the ST is located after the CW unit, ST unit can also perform as a buffer zone. Hence, whether the addition of a ST after CW system (CW-ST) can enhance the performance of CW would be meaningful to explore.

2.3 Granular activated carbon (GAC) sandwich slow sand filtration

2.3.1 Overview of slow sand filtration

The first application of filtration as a mean of water treatment dates back to 1804 when John Gibb designed and built a slow sand filter for his bleachery and sold the surplus treated water to the public [239]. Slow sand filtration (SSF) (Figure 2-10) has usually a continuous flow and for over 200 years, it has been an effective technique for treating water in both small and large community water supplies [39]. Over the last three decades, SSF has gained more attention mainly due to its simplicity, low chemical and electricity requirements and high level of water treatment [39,240]. SSFs can be applied as tertiary stage in conventional treatment processes or be used as an efficient single-stage treatment for raw waters within a certain water quality range [241,242]. Besides, usually

a high proportion of pathogenic microorganisms can be removed by SSFs, including bacteria, protozoan oocysts, cercariae and schistosomes [31,39].

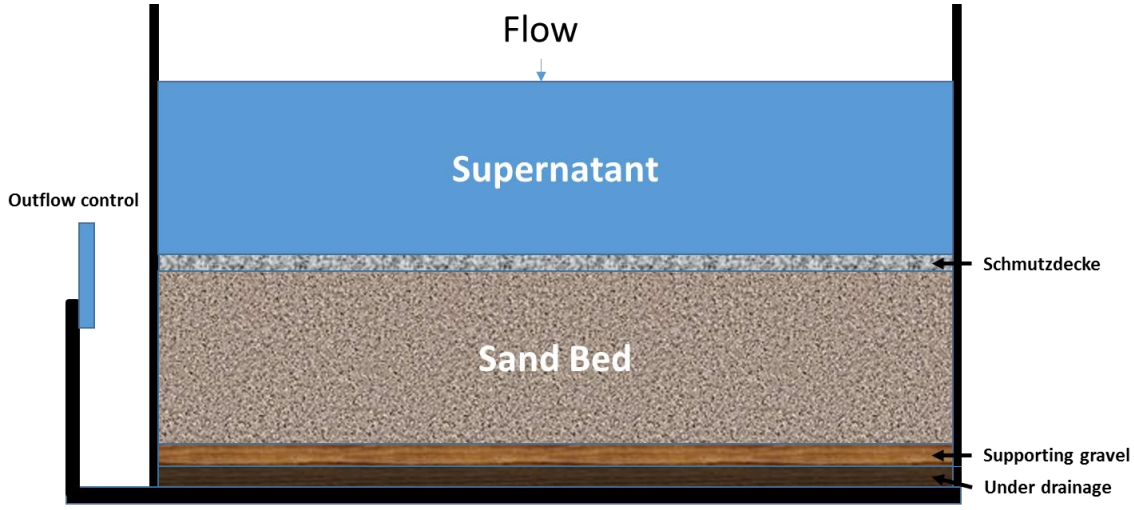

Figure 2-10 Schematic representation of a typical SSF

Generally, the water standing head in a SSF filter is around 100~150 cm and media depth is 0.6~1.2 m [110]. A thin layer of supporting gravel supports the sand layer. A thin biofilm, called *schmutzdecke*, grows at the top of the sand layer which is essential in the filtration performance. In addition, SSF filtration rate is usually 0.1~0.3 m/h and the effective size (D_{10}[1]) of the sand is 0.1~0.3 mm [40]. However, fine sand used in SSF can always cause the problem of clogging [49]. In recent years, coarse sand with D_{10} above 0.3 mm was also tried in SSF. Table 2-3 lists a number of studies using coarse sand in SSFs.

[1] D_{10} is the diameter at which 10 % of the sand's mass is comprised of particles with a diameter less than this value.

Table 2-3 SSF studies using coarse sand

Effective size (mm)	Uniformity coefficient[1]	
0.39	2.78	[240]
0.17 and 0.52	Not specified	[243]
0.45	1.3	[244]
0.6	1.8	[46]
0.55	5.6	[33]

Although it is one of the earliest water treatment process, SSF has some advantages that still make it a promising technology nowadays [239]:

- The delivered water does not support after growth in the distribution system and no other chemicals are needed and added.
- The simple design of SSF makes it possible to use local and cheap materials for construction. The cost of operation mostly lies in the filter cleaning, mechanically or manually, which makes it much cheaper than other treatment techniques (e.g. activated sludge, UV, coagulation-flocculation and sedimentation).
- In water-short areas, SSF has the additional advantage of not requiring the regular backwashing, avoiding waste of water.
- The sludge storage, dewatering and disposal are much easier to deal with and waste is usually accepted by farmers as useful dressing for land. Mixture of sand and organics is further suitable for conditioning heavy clay soils.

In addition, small/household-scale SSFs with intermittent flow mode as the biofilter are widely used as single treatment processes in developing countries [32,245].

[1] Uniformity coefficient: D_{60}/D_{10}

SSF also has some limitations. Capital cost may be high where land is limited. In cold places, water freezing may occur during winter and affect performance, therefore, structural precautions may be needed [239]. For large flowrates, low filtration rates (0.1~0.3 m/h) may be not appropriate due to the requirement of large surface areas [31].

2.3.2 PPCP removal in slow sand filtration

Compared with the CW, fewer studies have been conducted on PPCP removal using SSF alone. In one study from Escolà Casas and Bester (2015) [31], SSF was used (sand size: 0.210~0.297 mm) to remove diclofenac, propranolol, iopromide, iohexol and iomeprol, achieving removal of 41, 94, 58, 57 and 85 %, respectively. Because diclofenac and propranolol are usually recalcitrant to biodegradation by activated sludge, SSF could potentially be used to remove PPCPs in effluents from the activated sludge reactors of small WWTP. Nakada et al. (2007) [36] investigated the removal efficiencies of 24 PPCPs during sand filtration (retention time 1 hour, effective size not specified) and ozonation in a WWTP. Results showed inefficient removal of the PPCPs during sand filtration, probably due to the compounds low hydrophobicities. But when combined with ozonation, high removal (>80 %) was achieved for all the target compounds except carbamazepine and diethyltoluamide. In a study removing estrone, estriol and 17α-ethinyl estradiol, a household-scale SSF (effective size not specified) showed low removal efficiencies for all three compounds (all below 15 %), while removal increased to 98 % when household bleach was added [27]. Pompei et al. (2016) [32] also used household-scale SSF (effective size at 0.21 mm) to treat natural water, finding that diclofenac, naproxen, ibuprofen and methylparaben were fully removed, while benzophenone-3 and paracetamol were found at varied concentrations. Moreover, Hollender et al. (2009) [45] studied the removal efficiency of 220 micropollutants in a WWTP upgraded with post-

ozonation followed by sand filtration, finding no additional elimination by the sand filtration except for N-nitrosodimethylamine.

From limited studies shown above, it can be seen that PPCP compounds usually cannot be removed thoroughly during conventional SSF processes. Therefore, process optimization or further treatment/pre-treatment can be investigated to enhance the performance of this eco- and cost-friendly technique.

2.3.3 Mechanisms of slow sand filtration on PPCP removal

In SSF, the sand bed remains wet throughout operation due to continuous inflow and ripening process occurs, during which the *schmutzdecke* forms [246,247]. Treatment mechanisms involving in SSF are attributed to both physico-chemical and biochemical processes, among which predation, scavenging, adsorption and bio-oxidation as microbiologically mediated purification mechanisms have been hypothesised or assumed to occur within the filter [240]. Besides, mechanical mechanisms include absorption, diffusion, screening and sedimentation [39].

Usually there are two mechanisms involving in PPCP elimination in sand filtration: biodegradation and adsorption [31]. HRT and the compound residence time are related to biodegradation, while sorption mainly depends on the compounds properties and medium surface area.

2.3.3.1 Biodegradation

Biodegradation is thought to be an important pathway for PPCP elimination in biosand filtration processes. HRT determines the contact time between PPCP chemicals and microbes within the *schmutzdecke* and sand bed. Aerobic processes appeared to be the most efficient way for the removal of many PPCPs. Apart from that, other

mechanisms involved are not clear [31]. In the study using SSF (sand size: 0.210~0.297 mm) to remove 7 PPCP compounds which is mentioned above (Section 2.3.2), it was considered that removal of several compounds must be attributed to the biodegradation, since their high hydrophilicity meant they were not adsorbed onto the sand [31]. Yet mechanisms or microbes involved in SSF biodegradation have not been fully explained.

Within the *schmutzdecke* and sand bed, microbes derived initially from the influent water multiply selectively and use the deposited organic matter as food. Microbial activity occur mostly within the *schmutzdecke* and gradually decreases with sand depth as the food becomes scarcer. Depending on the filtration rate, below a certain sand depth, though microbial activity are small, biochemical reactions still take place [239,248]. Degradable organics are oxidized by microbes to provide the energy for metabolism and growth. In this way the degradable organic matter present in the influent is gradually broken down and converted into water, carbon dioxide, sulphates, nitrates, phosphates and other relatively innocuous inorganic salts, which are discharged in the effluent [239].

However, unlike degradable compounds (such as glucose) which can be used as energy sources by microbes in the filter, PPCP compounds are not food for general microbes and can only be degraded by microbes with certain degrading genes, which makes the biodegradation process slow [28]. In the sand filter, different types of microbes can be found at various depths, indicating that different PPCP compounds are degraded at different depths.

For satisfactory degradation of PPCPs, sufficient contact time between sand bed and water should be allowed to increase the degradation rate, which can be achieved by keeping filtration rate down. Then, as oxidation rate inside microbial cells are highly related to temperature, and the temperature cannot be too low as it affects enzyme activities. Low temperature not only influences PPCP degradation, but also decreases

filter performance. At low temperatures, the metabolism of bacteria slows down and activities of some bacteria predators such as protozoa and nematodes sharply drop, because of which nutrient removal decreases and some pathogens may survive during the process. Hence water quality may deteriorate [239]. In addition, PPCPs can be biodegraded under aerobic and/or anaerobic conditions (Section 2.5.1.2), and generally biodegradation of PPCPs is enhanced more under aerobic than anaerobic conditions [249]. Usually, the average oxygen content of effluent should not be allowed to fall below 3 mg/L in order to avoid anaerobic conditions [239]. Thus enough oxygen should be available and aeration can be applied under special circumstances [49,250].

While microbes in SSF process the PPCPs biodegradation, PPCPs may also influence the microbial community as well. Pompei et al. (2016) [32] injected 2 μg/L mixed PPCPs in the influent of a household-scale intermittent SSF, finding that the filter performance was not affected by PPCPs in influent water, but more bacterial species were present in the period with no PPCPs than during the PPCP added period, suggesting that the PPCPs affected the microbial community and structure.

2.3.3.2 Adsorption

Compared to biodegradation, adsorption could be excluded as the dominant removal mechanism in SSF removing PPCPs [31]. Adsorption to the sand media is not a significant mechanism since the PPCP removal do not correlate with adsorption potential as measured by the octanol-water distribution coefficient [251]. In the study by Zearley and Summers (2012) [244], adsorption of PPCP compounds into the filter biomass was also not significant and the maximum biomass adsorption capacity was reached within 2 h of operation for all PPCP compounds. Compared with adsorbents such as GAC and

graphene, sand is not a porous material and has much lower surface area, which considerably limits the adsorption capacity.

In comparison with particle pollutants, PPCPs range in trace concentrations and are dissolved in water. Generally, two mechanisms contribute to the adsorption process: *Van der Waals force* and *electrostatic attraction* [239].

Van der Waals forces operate universally and can occur between the PPCP compound molecule and sand surface. But this force is weak and decreases with the sixth power of the distance. However, once the contact has been made, the attraction is considerably more effective holding molecules to surfaces, since the distance between the centres of masses is very small. Van de Waals forces can also occur between PPCP molecules and thus multi-layer adsorption may form onto sand surfaces.

Electrostatic attraction operates between electrical charges and is inversely proportional to the square of the distance. Usually sand is made of mineral quartz, which gives the surface a negative charge and it is thus able to attract positively charged chemicals. Interestingly, during the initial maturation process, positively charged substances may accumulate on some sand grains, then oversaturation occurs with a reversal of charge, making the grain and attached substances positive and thus able to remove negatively charged compounds. Once started, the reversal of charge continues throughout the filtration process.

One main drawback of sand as the SSF medium is that the surface area is small, consequently rendering the adsorption process insignificant. By biodegradation only, PPCPs generally cannot be thoroughly removed, hence improvements of conventional SSFs are required.

2.3.4 GAC in slow sand filtration for PPCP removal

2.3.4.1 Overview of GAC filtration

Granular activated carbon is a porous medium with a large surface area widely used as an adsorbent in water/wastewater treatment [46]. Porous property of GAC provides a large surface area for physical adsorption as well as chemical adsorption if functional groups exist, which makes GAC as the most applied adsorbent for drinking water treatment with low to moderate content of organic matter or wastewater treatment [47,252]. However, if the concentrations of PPCP compounds are high, competition for adsorption sites of GAC may occur and removal decrease consequently, depending on the compounds and the GAC properties [46,253].

Compared with other adsorbents such as graphene, GAC is cheaper, but more expensive than sand medium. In practice, GAC filtration is generally used in tertiary water treatment process alone. When combined with SSF, series SSF-GAC columns (Figure 2-11-A) or dual-layer filters (Figure 2-12-B) are usually implemented.

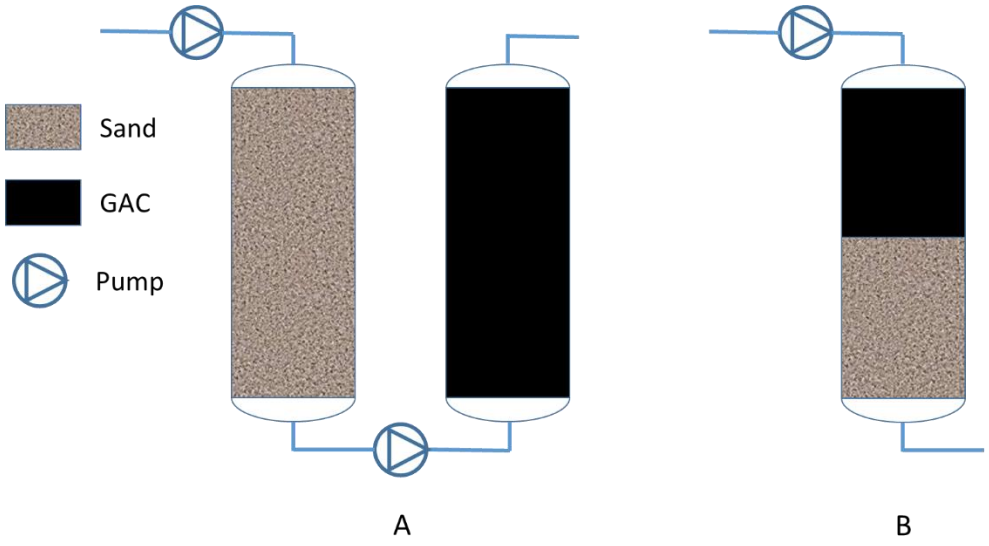

Figure 2-11 Schematic representations of two practical SSFs with GAC units (A, series sand-GAC unit [46]; B, dual-layer filter [47])

2.3.4.2 Series slow sand filtration-GAC system

This type of system consists of several serially connected tanks. Capital and maintenance costs are usually high. Rizzo et al. (2015) [46] investigated 4 PPCP compounds (namely caffeine, carbamazepine, ibuprofen and diclofenac, 1 mg/L) using sand filtration (effective size at 0.6 mm) followed by a GAC reactor (surface area at 875 m^2/g). In the early stage, the removal by GAC was about 62 % and these decreased as time increased. After a 14 hour process time, around 24 % constant removal was reached. The authors attributed the low efficiency in PPCP removal to the competition among the PPCP compounds for adsorption sites. Reungoat et al. (2011) [254] compared removal of 57 PPCP compounds using SSF (effective size not specified) and GAC filter (surface area at 1,146 m^2/g), showing that GAC had a good potential for the removal of dissolved organic carbon (35~60 %) and PPCPs (>90 %), while limited improvement of effluent quality was achieved by SSF. Similar results were also obtained by Paredes et al. (2016) [255] who used coarse sand (particle size at 1~2 mm) and GAC (surface area not specified) to remove 18 PPCPs. Organic matter, ammonium and nitrate were removed better by GAC than by sand. Carbamazepine, diazepam and diclofenac were only removed due to adsorption by GAC. No influence of filtration rate (empty bed contact time in the study) and type of secondary effluent were observed on GAC performance.

2.3.4.3 Dual-layer system

Dual-layer media (GAC-sand) filtration was also investigated by several researchers. However, putting GAC above the sand can cause quick clogging of micropores due to screening of particles on the top layer of GAC, lessening the GAC adsorption performance. McKie et al. (2016) [256] studied a pilot drinking water treatment plant utilizing ozonated lake water. Filters consisted of 50~150 cm GAC (surface area not

specified) over 15~50 cm of sand (effective size not specified). Without coagulant, the filter removed two of the nine compounds by more than 50% (average removal was 39 %). With the addition of 0.2 mg Al^{3+}/L PACl, the biofilter reduced PPCP on average removal of 45 %. Increasing PACl to 0.8 mg Al^{3+}/L improved average reduction to 70 %, with eight of the nine compounds reduced by 50 % or more. Altmann et al. (2016) [47] compared dual-layer media (GAC-sand, downflow) with GAC filter (upflow) to remove 15 PPCP compounds from wastewater. The dual-media filter used 1.4 m GAC (surface area not specified) and 0.6 m quartz sand (0.7~1.1 mm). With coagulant before filtration, both filters achieved effluent concentrations of 0.1 mg/L total phosphorus and 1 mg/L total suspended solid. In addition, both filters presented similar removal for most PPCPs. How to minimise the cost (lessen GAC usage) while ensuring acceptable performance is clearly worth investigating.

GAC can enhance the elimination of PPCP in water. But the service life and handling of GAC also need to be considered. The service life of GAC varies considerably depending on the influent type, filtration rate, pH and GAC type and size [244]. Bayer et al. (2005) [257] established a model-based methodology determining optimal refill strategies for GAC reactors based on economic or ecological criteria, and 10 years were assumed. However, GAC service life of weeks to several months for disinfection by-product control was suggested [252]. After the service life, the GAC needs to be reactivated for regeneration. Thermal and chemical reactivations are two commonly used processes [240,258]. Whichever method to use, the cost is much higher than that for sand cleaning which occurs by scrapping and washing.

2.3.4.4 GAC sandwich slow sand filtration

2.3.4.4.1 Concept

GAC sandwich SSF was first designed by M. Bauer at Thames Water Utilities Ltd, United Kingdom in order to consistently meet the standards for pesticides removal which conventional SSFs could not provide, and to avoid the construction of GAC contactors [48]. Four options were given to improve the conventional SSF: complete sand replacement; GAC above sand; GAC below sand; GAC sandwich (Figure 2-12). Effective size of sand and GAC were 0.3 mm and 0.7 mm, respectively.

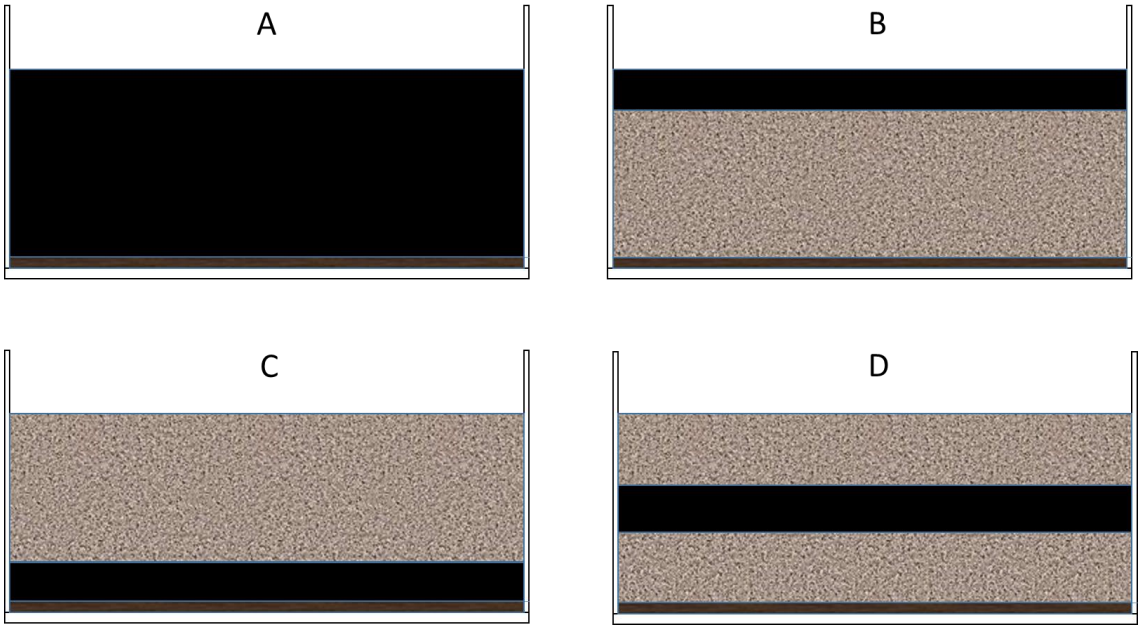

Figure 2-12 Four options for the improvement of conventional SSF from M. Bauer (Black: GAC; Brown: sand. A, All GAC; B, GAC at top; C, GAC at bottom; D, GAC in the middle)

Option A was rejected because it would involve a loss of existing SSF capacity (replacing fine sand medium with much coarser GAC) and reduce work output. Regular

surface cleaning and GAC reactivation were also required. Hence capital cost would increase greatly. Option B was rejected for similar reasons as option A due to mechanical attrition during the process being assessed as high. Option C was also rejected as there was concern about the possibility of GAC fines and biological entities entering effluent and passing into the supply.

Option D as GAC sandwich SSF was finally chosen. Compared with single medium filters, the GAC sandwich SSF is multi-functional: the upper layer of sand ensures the biological treatment process and host on its top a *schmutzdecke* which plays an important role in water purification. The middle layer, GAC, acts as a non-backwashed adsorbent which can remove contaminants that cannot be biodegraded in the *schmutzdecke*. In addition, the lower sand layer minimises the potential of biological entities and GAC fines entering the filtrate [48].

2.3.4.4.2 First trial of GAC sandwich filtration

Firstly, small scale pilot (2 m × 1 m filter) trials were carried out at filtration rate between 0.1 m/h and 0.3 m/h for 42 months (results not shown) [48]. Media comprised 450 mm sand, 150 mm GAC and 150 mm sand from top to bottom. Then full-scale trials (100 m × 30 m filter) were conducted at filtration rates of 0.1~0.3 m/h. Media comprised 450 mm sand, 150 mm GAC and 300 mm sand from top to bottom. Parameters including 20 pesticides (e.g. atrazine), organics (e.g. TOC), physical (e.g. turbidity), biological (e.g. chlorophyll a) and microbiological (e.g. total coliforms) were monitored.

Little difference of headloss development was found between the GAC sandwich SSF and control bed (conventional SSF). No pesticides were detected in the filtrate from the full-scale sandwich SSF, whereas various pesticides were found in filtrate of the control SSF. TOC removal was 60 % after six months operation, 40 % after twelve

months and finalising at 30~40 % thereafter, compared with the control bed at a mean removal of 20 %. Other parameters showed marginally better results than the control bed.

2.3.4.4.3 Advantages of GAC sandwich filtration

Compared with series SSF-GAC columns or dual-layer filters, GAC sandwich SSF needs less costs in capitals, operation and maintenance. Besides, it was also thought GAC sandwich SSF may provide better performance than GAC adsorbers [48]. Filtration rate at 0.3 m/h can provide better contact between micropollutants and media, which is 5~15 m/h for GAC adsorbers. The presence of sand layer above GAC layer should biologically reduce TOC loading, enabling maximal adsorption for micropollutants onto GAC. Another advantage lies in the longer GAC life cycle (2~4 years) in GAC sandwich SSF which remains undisturbed and may provide a more selective environment for micropollutant elimination. The bottom sand layer also can provide a physical barrier which prevents fines from entering effluents.

A preliminary cost of GAC sandwich SSF filter versus a conventional adsorber was also evaluated by M. Bauer (Table 2-4) [48]. GAC sandwich SSF was found more cost-saving than GAC adsorber overall, cost of which was reduced by the removal of the adsorber facility and inter-process pipework and tunnels.

As shown above, GAC sandwich SSF has been used to remove pesticides and some physico-chemical and bacteriological parameters, but have not been employed to remove DEET, PAR, CAF and TCS. Besides, various GAC depths were not investigated. Moreover, Bauer et al. (1996) [48] only used common fine sand (effective size at 0.3 mm) but coarse sand was not tried. In order to lessen the possibilities of filter bed clogging and further improve the filter performance [49], therefore, the effects of GAC layer depth and coarse sand use on PPCP removal is worth investigating.

Table 2-4 Relative costs of GAC adsorbers vs GAC sandwich SSF filter [48]

Item		Relative cost for adsorbers	Relative cost for GAC sandwich SSF
Capital costs	Civil	High	Low
	Mechanical	High	Low
	Electrical	High	Low
	GAC supply	Medium	High
Operating costs	Manpower	Low	Medium
	Plant maintenance	Low	Low
	Power	High	Low
	Water	Medium	Low

2.3.5 Combination of constructed wetland and slow sand filtration

2.3.5.1 Concept

Constructed wetland and slow sand filtration systems are usually used separately in tertiary treatment process of WWTPs. As for SSF-CW system, Gunes and Tuncsiper (2009) [38] investigated a SSF and HSSF-CW system in series for small community wastewater treatment (Figure 2-13).

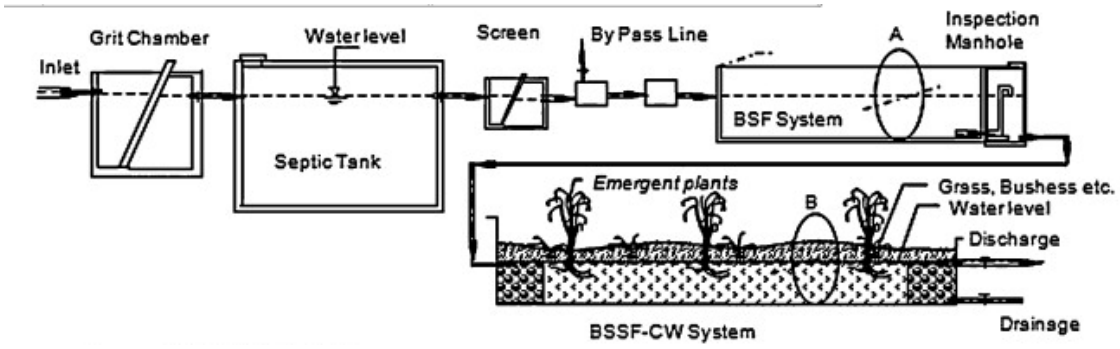

Figure 2-13 Series SSF-CW system [38]

This system was used to treat wastewater in the Village of Ileydagi, Turkey. A 14-month period of operation was employed. The average removal of the BOD, total nitrogen and total phosphorus were 97 %, 85 % and 69 %, respectively. There was a strong correlation (R^2=0.81~0.97) between the removal and loading. Performance of the combined treatment system was 5 % with removal higher during the summer period than during the winter. However, this study did not investigated PPCP compound removal using the combined system.

There are some possible drawbacks of SSF-CW system. SSF can only receive influent water within certain water quality limits of turbidity (usually < 10~20 NTU, Nephelometric turbidity units) [39]. Influent water with high turbidity and TSS can cause quick clogging of the filter. Besides, rich nutrients in influent may also generate excessive biomass accumulation, which may link to headloss development [40], thus lessening service life. In contrast, CWs as primary, secondary and tertiary treatment steps receiving various types of water have been successfully implemented [41]. However, as microbes play an important role in CW system, microbes usually exist in effluents, while high proportion of pathogenic microorganisms were proved to be removed by SSFs, including bacteria, protozoan oocysts, cercariae and schistosomes [31,39]. So it can be more suitable for SSF to be placed after CW unit.

To the author's knowledge, there is also no comprehensive study on the CW-SSF system. Some researchers reported the adsorption of PPCPs onto soil, sediment and matrix by CWs but substrate is not real SSF system [10,41]. Dubey (2014) [259] proposed a model (Figure 2-14) combining CW and SSF, which the tank acts as both CW tank and SSF tank. Water flows vertically down to the tank bottom.

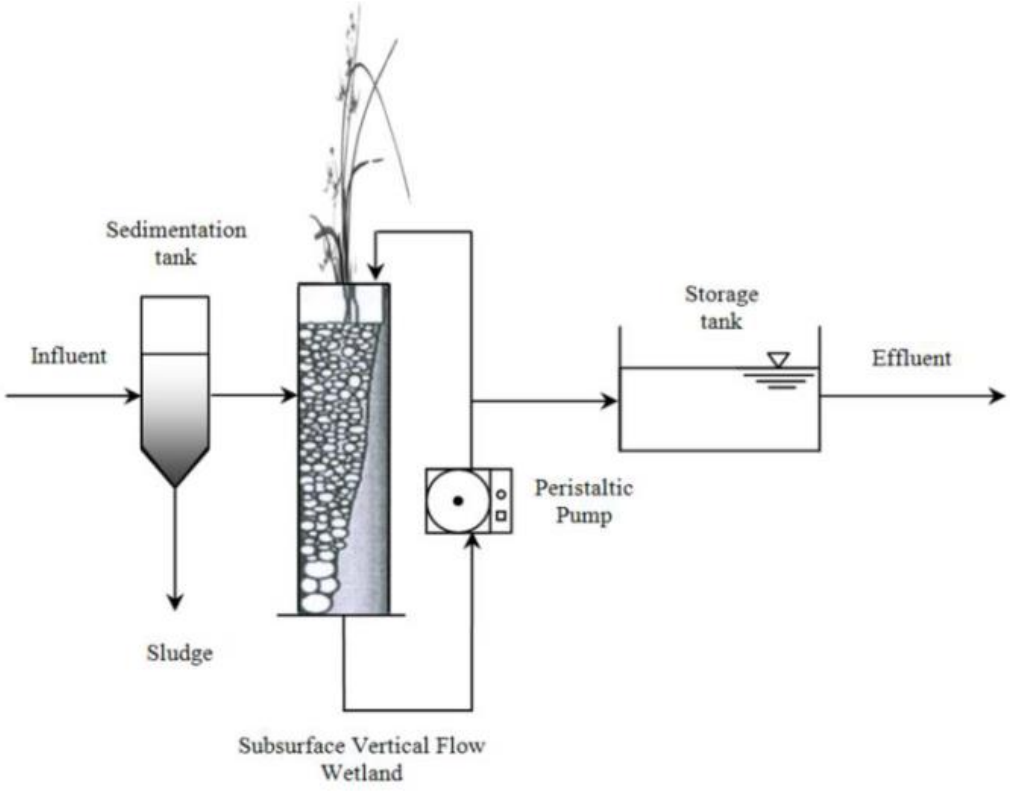

Figure 2-14 One combined model of CW and SSF by A. Dubey [259]

However, this system has some disadvantages. Plant roots insert into the sand layer and may negatively influence the healthy formation of the *schmutzdecke,* which is significant in SSF performance. Then, in order to clean the sand bed, certain bed plants must be removed or disturbed and the CW system must then be affected. If a combined medium is used, sand bed cleaning can be more complicated. Besides, this model can only include VSSF-CW but not all CW types.

In addition, CW-SSF system has never been used for treating PPCPs before either. So whether this combined system is able to effectively remove the selected PPCP compounds is worth investigation.

2.3.5.2 Constructed wetland-slow sand filtration system as cost-effective technique

Constructed wetland and slow sand filtration systems are regarded as cost-effective techniques since very little electricity and chemicals are required during the operation. However, there is no systematic economic study on combined CW-SSF system costs. What is more, very few studies have been carried out to systematically compare the CW and SSF costs with other treatment techniques. The main reasons are due to the different capital costs (e.g. size, materials, chemicals, lands and construction), maintenance and operating costs, human labour costs and energy costs, as well as different water types in different countries and regions [165,260,261].

Zhang et al. (2014) [113] conducted a comparison of the capital and operational costs for a traditional WWTP and CWs in China and Colombia from published studies (Table 2-5). Results showed that the costs of treatment and operation and maintenance (O/M) for CW systems are much cheaper than the conventional WWTP processes. For the CWs in China and Columbia, although the design capacities and capital cost vary considerably, O/M cost is around 0.012-0.014 USD/m^3, while conventional WWTPs cost 0.151-0.2465 USD/m^3. For the construction cost, the CW systems do not present an apparent advantage. The unit capital cost is around 82-225.72 USD/m^3, compared with 246-657 USD/m^3 in conventional WWTPs. As for the treatment cost, the CW system in Beijing China was calculated at 0.0223 USD/m^3 [262], only one-thirtieth of the cost at 0.7717 USD/m^3 [263] for conventional WWTP.

Table 2-5 Comparison of cost requirements between CWs and WWTPs, part of summary from Zhang et al. (2014) [113]

	Design capacity (m^3/d)	Total capital cost (USD)	Unit capital cost (USD/m^3)	Treatment cost (USD/m^3)	O/M* cost (USD/m^3)	Energy cost (USD/m^3)
Conventional WWTPs			246-657		0.151-0.2465 [264]	
				0.7717	0.6362 [263]	0.1036
CW in Bogota Savannah, Colombia	65	14,672	225.72		0.0134 [265]	
CW in Dongying, China	100,000	8.2 million	82		0.012 [266]	
CW in Beijing, China	200	32,616	163.08	0.0223	0.014 [262]	

* O/M, Operation and Maintenance

Among tertiary treatment technology, adsorption by GAC is one of the most cost-effective techniques. In the Table 2-4, a costs comparison between GAC adsorbers and GAC sandwich SSF filter shows GAC sandwich SSF filter has much less relative costs than GAC adsorption. Gupta et al. (2012) [267] summarized the costs of tertiary wastewater chemical technologies (Table 2-6).

Table 2-6 Costs of wastewater tertiary treatment technologies [267]

Technology	Costs (USD per one million litres of treated water)
Distillation	15~2000
Crystallization	50~150
Evaporation	15~200
Solvent extraction	250~5000
Oxidation	100~2000
Precipitation	20~500
Ion Exchange	50~200
Micro- and ultra-filtration	15~400
Reverse osmosis	20~450
Adsorption	20~150
Electrodialysis	15~400

From Table 2-6 shown above, it can be seen that adsorption only costs 20~150 USD per one million litres of treated water, compared with 15~5000 USD per one million litres of treated water by other tertiary treatment technologies, making adsorption a very cost-effective technique. Since GAC is the most commonly-used adsorbent in adsorption

process, it can be relatively concluded that the GAC sandwich SSF is also cost-friendly as sand is much cheaper than GAC.

From limited reported studies, CW and GAC sandwich SSF systems were regarded as cost-effective water treatment technologies due to their simplicity, relatively low costs of construction, operation, maintenance and management. Hence, their combination mode could also be an alternative choice to engineers and practitioners, especially in the developing areas. However, limited costs information from published studies indicates more detailed research on cost analysis can be conducted.

2.4 Summary

In this chapter, PPCPs, constructed wetland and slow sand filtration were reviewed and discussed, respectively. The key points are summarized as follows:

- Risks and contamination situation of PPCPs in aquatic environments indicated the broad pollution of PPCPs and the importance of PPCP treatment. However, current water treatment techniques are either not effective/efficient or expensive.
- DEET, PAR, CAF and TCS as ubiquitous and largely used PPCP compounds are introduced. The pollution situation and inadequate removal of these compounds during the general water treatment process indicates the significance of more effective removal.
- Greater duckweed as promising CW plant has not been used to treat target PPCP compounds (i.e. DEET, PAR, CAF and TCS) before, which is worth investigating. SF-CW type was selected not only because Greater duckweed belongs to free floating plant species, but also due to the popularity (easy to run and clean) of this CW variant.

- ST-CW system has been used to remove PPCPs but CW-ST has not been explored before, which can be studied for this area. Compared to ST-CW system, this variant can also lessen the potential of decaying plants materials from entering the effluent.
- The lack of studies using SSF dealing with PPCPs suggests deeper insight and enhancement to this technique for PPCP removal.
- It is shown that GAC sandwich SSF is a good choice due to the advantage of being a simple and cost-friendly process. Moreover, different GAC layer depths and coarser sand have not been investigated in any GAC sandwich SSF study, which are worth investigating.
- The performance and effectiveness of CW-SSF system on PPCP removal have not been reported before. This system has better influent water adaptability than SSF-CW system. Thus it can be more compatible in water/wastewater treatment system. So, this type of combined system is promising and must be studied.

CHAPTER 3 GENERAL METHODOLOGY

3.1 Introduction

This chapter gives the general methodology details of the whole thesis, including target PPCPs characteristics, chemicals, materials and equipment, extraction and detection methods of target PPCPs, determination of chemical oxygen demand (COD), total organic carbon (TOC), cations, anions, pH, conductivity, redox potential, dissolved oxygen (DO), preliminary treatment of Greater duckweed and filtration media, determination of *Escherichia coli* (*E.coli)* and other microbes; and preparation of synthetic wastewater.

For the whole experimental structure, the detection and extraction method of target PPCP compounds was first developed to fulfil the need of this study. Then CW and SSF systems on target PPCP removal were studied and optimized separately. At last, CW and SSF were serially connected to test the removal performance and effectiveness of this combined system. The specific operation details and schematic representations of target PPCP compounds method development, CW experiments, GAC sandwich SSF experiments (with study of adsorption kinetics and isotherms) and CW-SSF experiments can be found in Chapters 4, 5, 6 and 7.

3.2 Target PPCPs and relevant characteristics

The properties and relevant characteristics of the target PPCP compounds (DEET, PAR, CAF and TCS) of this thesis are shown in Table 3-1.

Table 3-1 Target PPCPs and their relevant characteristics

Compounds	Abbreviation	Molecular formula	Molecular weight	CAS No.	Category	Type	Log Kow	Predicted No Effect Concentration (PNEC, μg/L)	Solubility (mg/mL, 25℃)*
Diethyltolua-mide	DEET	$C_{12}H_{17}NO$	191.27	134-62-3	repellent	neutral	2.02	71.3[115]	0.912
Paracetamol	PAR	$C_8H_9NO_2$	151.16	103-90-2	analgesic	acidic	0.46	1[131]	14.0
Caffeine	CAF	$C_8H_{10}N_4O_2$	194.19	58-28-2	stimulant	neutral	-0.07	151[76]	21.6
Triclosan	TCS	$C_{12}H_7Cl_3O_2$	289.54	3380-34-5	antibacterial	acidic	4.76	121[76]	0.01 (20℃)

* data from United States National Library of Medicine

3.3 Chemicals, materials and equipment

Chemicals, materials and equipment used in this research are shown in Table 3-2 and Table 3-3, respectively.

Table 3-2 Chemicals and materials used in this thesis

Chemicals & Materials	Producer
Glucose	Sigma-Aldrich
Ammonium chloride	Fisher Scientific
Calcium chloride hydrate	Fisher Scientific
Ferric chloride	Fisher Scientific
Magnesium sulphate heptahydrate	Alfa Aesar
Dipotassium phosphate trihydrate	Sigma-Aldrich
Potassium sulphate	Fisher Scientific
Diethyltoluamide (DEET)	Sigma-Aldrich
Paracetamol	Sigma-Aldrich
Caffeine	Sigma-Aldrich
Triclosan	Sigma-Aldrich
Diethyltoluamide (DEET) standard	Sigma-Aldrich
Paracetamol standard	Sigma-Aldrich
Caffeine standard	Sigma-Aldrich
Triclosan standard	Sigma-Aldrich
Methanol	Fisher Scientific
Ethanol	Fisher Scientific

Acetonitrile	Fisher Scientific
Acetone	Fisher Scientific
Hydrochloric acid	Fisher Scientific
Sodium hydroxide	Fisher Scientific
Eosin methylene blue (EMB) agar	Sigma-Aldrich
M-ColiBlue24® agar	Hach
Lysogeny broth (LB)	Sigma-Aldrich
Nutrient broth	Sigma-Aldrich
Phosphate buffer solution (PBS)	GIBCO
Bleach	Domestos
E. Coli (ATCC 11775)	Sigma-Aldrich
Greater duckweed	Claremont Aquatics Leyland
Acrylic tube (clear, extruded)	Plastic Shop
Altec tubing	Altec
PVC Solva (solvent flex) tubing	Agilent
Constructed wetland container	Taylor-Davis
Aerator	AllPondSolutions
Cellulose Acetate Membranes (0.45 μm)	Waters
COD TNT test kit (0~1500 mg/L)	Hach
Strata X SPE cartridge (6cc/200mg)	Phenomenex
Oasis HLB Cartridge (6cc/200mg)	Waters
Supel™-Select HLB SPE cartridge (6cc/200mg)	Sigma-Aldrich
Sand	Mineral Marketing
Granular activated carbon (GAC)	Chemviron Carbon
Gravels	Progenitive Filtration

Table 3-3 Equipment used in this thesis

Equipment	Model
Gas chromatography-mass spectrometer (GC-MS)	PerkinElmer Clarus 500
Automatic solid phase extraction (SPE) system	Dionex Autotrace 280
TOC machine	Shimadzu TOC-L
Ion chromatography (IC)	Dionex ICS 1100
Spectrophotometer	Camspec M550
Brunauer–Emmett–Teller machine	Quantachrome autosorb-iQ_2
Scanning Electron Microscopy	JSM-6700F
Centrifuge machine	Fisher Scientific accuSpin^{TM} 3R
Rotary mixer	Designed by CEGE, UCL
COD digestion reactor	Hanna C 9800
COD colorimeter	Hach DR/890
Autoclave	Astell Classic
pH meter	Mettler Toledo SevenMulti
DO meter	Jenway 9200
Ultra-pure water machine	Ondeo Purite IS
Deionized water machine	Ondeo Purite Select
Lab oven	LTE OP250
Incubator	Stuart S150
Light intensity meter	Rectifier SKKH 72/20E

3.4 The extraction and detection of target PPCPs

Four target compounds were extracted and detected simultaneously. Establishment of this methodology is shown in Chapter 4. For each aqueous sample, 500 mL water was filtered through 0.45 μm cellulose acetate membrane filters (Whatman, United Kingdom) before SPE. Then sample pH was adjusted to around 3.0 using 1 mol/L HCl and NaOH solutions. The SPE cartridges (Waters Oasis HLB, 200mg/6cc) were conditioned using 10.0 mL methanol, 10.0 mL ultrapure water and 5.0 mL ultrapure water with the pH adjusted to 3.0, successively. After conditioning stage, samples were passed through cartridges using automatic SPE system at the flow rate of 5 mL/min. Cartridges were then rinsed with 10 mL ultrapure water and dried under gentle nitrogen gas for 30 min to evaporate the water left in it. After drying, cartridges were eluted with 2 × 4 mL acetonitrile. The elutes were collected in glass tubes and concentrated to below 0.5 mL under gentle nitrogen gas and later reconstituted to a volume of 0.5 mL with acetonitrile. Final treated samples were stored at -20 ℃ in the dark and analysed by GC-MS within 40 days.

GC-MS was equipped with an Electron Capture Detector GC and a Quadrupole MS detector. All target compounds were separated by an Rxi® – 5ms column (30 m × 0.25 mm, 1.0 μm). For the GC parameters, the injection volume was 3 μL splitless and injection temperature was set at 275 ℃. Helium was used as the carrier gas at the flow rate of 2.5 mL/min. For MS parameters, the source temperature and inlet line temperature were 200 ℃ and 290 ℃, respectively. 70 eV was used as the ionization energy. Dwell time was set at 0.02 second and the temperature programming was from 100 ℃ (hold for 2 min) to 300 ℃ (hold for 5 min) at the rate of 20 ℃ /min. The MS analysis was performed in the Electron Ionization (EI) mode. For each target compound, three diagnostic (m/z)

ions were selected as shown in Table 3-4. For PPCP samples, triplicate samples were tested.

Table 3-4 Diagnostic (m/z) ions of target compounds

Compounds	Diagnostic (m/z) ions		
DEET	119	91	190
PAR	109	151	43
CAF	194	109	55
TCS	288	290	218

3.5 Determination of COD, TOC, cations and anions

COD concentrations of triplicate water samples were determined by using Hach COD TNT digestion vials (HACH colorimeter method 8000). Each 2.0 mL water sample was pipetted into digestion vial and vials were inverted several times. Then vials were heated for 2 hours under 150 ℃. After digestion, vials were inverted several times while still warm. COD concentration then was read by COD colorimeter after vials have cooled to room temperature.

TOC concentrations of triplicate water samples were determined by TOC-L machine. Furnace temperature was set at 680 ℃ (developed by Shimadzu Company).

Ion chromatography method was used to detect and measure the concentrations of nitrite, nitrate, ammonia and phosphate. Triplicate samples were filtered using 0.45 μm cellulose acetate membrane before injection. For anion, the analytical column was IonPac AS23 4mm and guard column was IonPac AG23. Suppressor was AMMS 300 4 mm.

Eluent solution was consisted of 4.5mmol/L Na_2CO_3 with 0.8 mmol/L $NaHCO_3$ at the flow rate of 1ml/min. For cation, analytical column was IonPac CS12A 4 mm and guard column was IonPac CG12A 4 mm. Suppressor was CMMS 300 4 mm. Column temperature was set at 30 ℃. Eluent was 20 mmol/L methane sulfonic acid at the flow rate of 1 ml/min. For both cation and anion determinations, column temperature was set at 30 ℃.

3.6 Determination of pH, conductivity, redox potential and dissolved oxygen

General water parameters, pH, conductivity and redox potential, were determined using Mettler Toledo SevenMulti meter (method APHA 9221). Probe head was immersed in the water samples until the readings were stable.

DO concentrations were read by Jenway 9200 meter. Probe head was immersed in the water samples and it was stirred gently until the reading was stable (meter protocol).

All readings were conducted three times and average values were calculated.

3.7 Treatment of fresh Greater duckweed

To ensure the consistency of Greater duckweed in different laboratory-scale tests, plants were pre-treated before being used. Greater duckweed was placed in commercial hydrophyte nutrient solution after purchase. They were immersed and washed 10 times in water (7 times tap water and 3 times deionized water) to remove dust, small stones and insects. As *E.coli* (ATCC 11775) was one experimental factor in CW experimental design (Chapter 5), pre-treatment can also wash down existing *E.coli* and other attached microorganisms, to reduce the background effect from plants as much as possible. *E.coli*

attaching to water-cleaned Greater duckweed was left 24 hours in a sterile wastewater and, at the end abundance of *E.coli* in wastewater was found to be 2~7 CFU/100 mL (method 3.10).

3.8 Sterilization of Greater duckweed

Sterilization of Greater duckweed was used in batch CW test (Chapter 5) to verify the role of plants. Based on the study from Oyebanji et al. (2009) [268], a treatment using diluted bleach was conducted as sterilization process. Greater duckweed was washed first as explained above. 0.1 % bleach solution was prepared using sterile deionized water from commercial bleach (5 %). Then plants were immersed in diluted bleach for 5 mins and rinsed by sterile deionized water for 4 times. Then sterilized plants were stored in sterile containers and used as soon as possible. Experimental outcome of this method is shown in Appendix 1.

3.9 Properties and treatment of filtration media

Sand, GAC and gravels (2~5 mm) were washed clean by tap water and then rinsed by deionized water for 5 times to remove dust. Then they were dried at 105 ℃ in oven overnight and stored in sealed containers after cooling. The general parameters of sand and GAC used in present study are shown in Table 3-5.

Table 3-5 General parameters of sand and GAC used in this research.

	Sand	GAC
Effective size	0.60 mm	0.58 mm
Uniformity coefficient	1.4	1.7
Porosity	38.6 %	58.6 %
Sphericity	95 %	53 %
Density	2634.7 kg/m^3	1616.2 kg/m^3

3.10 Selective plate counting method for quantification of the abundance of *E.coli*

Eosin methylene blue (EMB) agar was used to quantify the abundance of *E.coli* in the tests associated with CW experiments. 35.96 g EMB agar was suspended in 1000 ml deionized water. The liquid was mixed until suspension was uniform and sterilized by autoclaving at 121℃ for 15 mins. Then 10 × fold serial water sample dilutions were prepared and 100 μL of each diluted sample was directly spread onto EMB plates. The plates were placed at 30 °C for 24 hours in the incubator. For each dilution, triplicate counting was performed. After 24 hours, metallic purple-black colonies were counted and then colony-forming units (CFU) were calculated in per 100 mL samples.

3.11 M-ColiBlue24® method for determination of total coliforms and *E.coli* abundance

M-ColiBlue24® method was employed to determine the total coliforms and *E.coli* abundance (method 10029, USEPA). This method was used in the tests associated with GAC sandwich SSF experiments. Absorbent pad was placed in a sterile petri dish. 2 mL m-ColiBlue24® agar was pipetted onto the petri dish. 100 mL water sample was filtered by a sterile membrane. Then membrane was placed onto the petri dish using sterile forceps. After the dish lid was re-placed, petri dish was inverted and incubated at 35 ℃ for 24 hours. After incubation, red and blue colonies indicated total coliforms and blue colonies specifically indicated *E. coli*. Final colony-forming units (CFU) were calculated in per 100 mL samples.

3.12 Preparation of synthetic wastewater

The synthetic wastewater used for SPE method establishment and CW tests (i.e. CW batch test, CW verification test, CW and CW-ST continuous tests, CW-SSF test) was made based on the recipes from Liu et al. (2013) and Zhang et al. (2012) [216,269]. In CW batch test, three *E.coli* (ATCC 11775) levels (none, 1×10^4 and 1×10^6 CFU/100 mL) were used to prepare the synthetic wastewater [34,270]. For other CW tests, 1×10^6 CFU/100 mL *E.coli* level was used. In addition, DEET, PAR, CAF and TCS solutions were mixed in synthetic wastewater to reach a final concentration of 25 μg/L. The recipe is shown Table 3-6.

Table 3-6 Recipe of synthetic wastewater used for the CW tests

Compound	Concentration (mg/L)
Glucose	300
Ammonium chloride	80
Calcium chloride hydrate	7.3
Ferric Chloride	0.05
Magnesium sulphate heptahydrate	4.5
Dipotassium phosphate	12.8
DEET	0.025
Paracetamol	0.025
Caffeine	0.025
Triclosan	0.025
E. Coli (11775)	None, 1×10^4 , 1×10^6 CFU/100 mL

The synthetic wastewater used in the Sandwich GAC SSF tests was prepared based from the adjusted results from the continuous CW tests, which is shown in Table 3-7.

Table 3-7 Recipe of synthetic wastewater used for the GAC Sandwich SSF tests

Compound	Concentration (mg/L)
Glucose	40
Ammonium chloride	7.43
Calcium chloride hydrate	7.3
Ferric Chloride	0.05
Magnesium sulphate heptahydrate	4.5
Dipotassium phosphate	6.0
DEET	0.025
Paracetamol	0.025
Caffeine	0.025
Triclosan	0.025
E. Coli (11775)	1×10^6 CFU/100 mL

This chapter describes the general methodology details of the entire thesis. As there is no method reported for simultaneous determination of DEET, PAR, CAF and TCS using GC-MS, along with the attempt to simplify SPE process, a new detection method was optimized, which is shown in the next chapter.

CHAPTER 4 SIMPLIFIED EXTRACTION AND QUANTIFICATION METHOD OF SELECTED PPCPS

4.1 Introduction

In this chapter, four selected PPCP compounds (DEET, paracetamol, caffeine and triclosan) were analysed using SPE and GC-MS procedures. This work has developed a cost-friendly simplified method combing SPE with GC-MS to analyse selected PPCP compounds. Relevant purification and detection conditions were optimized without conditioning and equilibration stages for SPE and without derivatization for GC-MS. Reliability and reproducibility of the SPE methodology have been further tested using tap water, natural surface water and synthetic wastewater.

4.2 Experiment

4.2.1 Optimization of target compounds in gas chromatography mass spectrometry detection

Gas chromatography was equipped with a Quadrupole MS detector. All target compounds were separated by an Rxi®-5ms GC column (30 m × 0.25 mm, 1.0 μm). Standard solutions of each target PPCP compound were prepared at 1 mg/mL using methanol [76]. Each 1 mg/mL standard solution was injected into GC-MS separately and target compounds were identified and peak times were determined using full-scan mode

(50 ~ 300 m/z). Initial temperature programming was set as 70 ℃ (hold for 2 min) to 300 ℃ (hold for 10 min) at the heating rate of 10 ℃/min. Initial carrier gas flow rate was set at 1 mL/min. Three diagnostic (m/z) ions were selected for each target compound under selected ion recording (SIR) mode (Table 3-4).

Later, a mixed standard solution (25 μg/mL) was injected into GC-MS and target compounds were detected and quantified by the MS system under Selected Ion Recording (SIR) mode. The injection volume was 3 μL splitless [67,90]. For the GC, the injection temperature was set at 275 ℃. Helium was used as the carrier gas. For the MS, the source temperature and inlet line temperature were 200 ℃ and 290 ℃, respectively. 70 eV was used as the ionization energy. The MS analysis was performed in the Electron Ionization (EI) mode. In order to have the optimal GC-MS parameters and to shorten total detection time, three carrier gas flow rates (i.e. 1, 2 and 3 mL/min), two temperature heating rates (i.e. 20 and 25 ℃/min) and two dwell time (i.e. 0.020 second and 0.200 second) were tested and compared [271,272].

4.2.2 Optimization of extraction of target compounds from water

Water samples were filtered through 0.45 μm cellulose acetate membrane filters (Whatman, United Kingdom) before pre-treatment and 100 μL of 250 μg/mL mixed standard solution prepared in methanol was added into 500 mL water samples. Then the pH of samples was adjusted to different pH (i.e. 2.0, 3.0, 5.0 and 7.0) using 1mol/L HCl and NaOH solutions. Three types of SPE cartridges (i.e. Supelco HLB, Waters Oasis HLB and Strata X) were tested. Sorbents of Oasis HLB and Strata X both contain polymeric reversed-phase, while Supelco HLB is a kind of hydrophilic modified styrene polymer particle platform (from product specifications). SPE cartridges were conditioned successively using 10.0 mL methanol, 5.0 mL ultrapure water and 5.0 mL ultrapure water

with the pH adjusted same of the water samples. For the Supel™-Select HLB SPE cartridge (6cc/200mg), as suggested from manufacturer instruction, cartridge was conditioned with 10.0 mL ethyl acetate, 10.0 mL methanol, 5.0 mL ultrapure water and 5.0 mL ultrapure water with the pH adjusted if ethyl acetate was used as eluent. Then samples were passed through cartridges using automatic SPE system at different flow rates in dark. When this step finished, cartridges were rinsed with 10 mL ultrapure water and dried under gentle nitrogen gas to evaporate the water left in it. Then cartridges were eluted with 2 × 4 mL different solvents. Methanol, acetonitrile and ethyl acetate were tested respectively since they are widely employed in the SPE process as eluents [67,92,273,274]. The elutes were collected in glass tubes and concentrated below 0.5 mL under gentle nitrogen gas and later reconstituted to a volume of 0.5 mL with the same solvent. Final treated samples were stored at -20 ℃ in the dark and analysed by GC-MS within 40 days.

In addition, method validation using Oasis HLB cartridge (6cc/200mg) with and without conditioning and equilibration processes were also conducted after the optimization of whole procedure. Method validation test was carried out at two concentrations (0.25 μg/L and 25 μg/L) using tap water, natural water (Regent's Park lake, London, United Kingdom) and synthetic wastewater, respectively. For SPE method optimization, triplicates samples were conducted. For method validation, five parallel samples were used.

4.3 Results and discussion

4.3.1 Optimization of gas chromatography mass spectrometry procedure

4.3.1.1 Initial method trial

Figure 4-1 gives the chromatograms of individual compound of 1 mg/mL under the full-scan mode (50 ~ 300 m/z). Total time for each injection was 35 mins. It also shows that retention times of the four target PPCP compounds were different and there was no overlap of response peaks to each other existed.

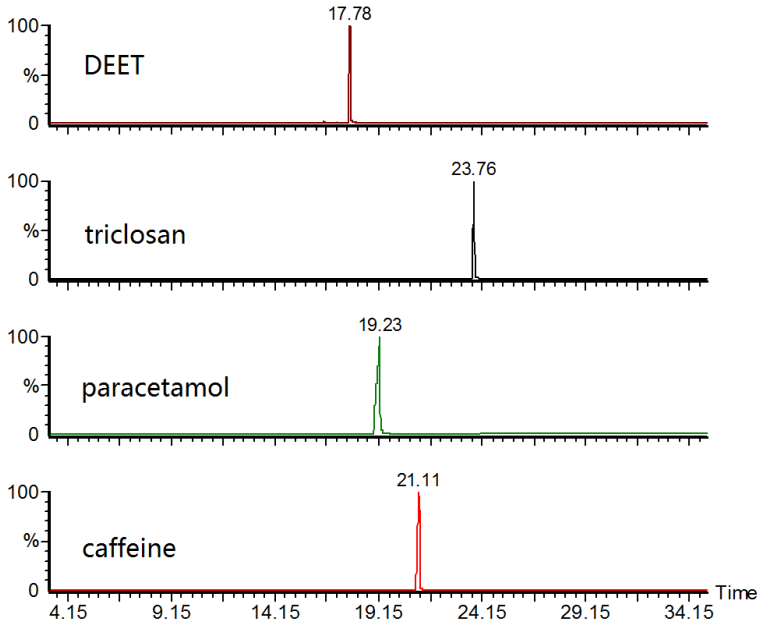

Figure 4-1 Chromatograms of individual compounds at 1 mg/mL under full-scan mode (Full-scan mode: 50 ~ 300 m/z; Temperature programming: 70 ℃ (2 min) to 300 ℃ (10 min) at rate of 10 ℃/min; Carrier gas flow rate: 1 mL/min; Concentration: 1 mg/mL; Peaks from top to bottom: DEET, TCS, PAR and CAF)

Mixed 25 μg/mL standard solution was injected into GC-MS under SIR mode using diagnostic (m/z) ions shown in Table 3-4. It can be seen that four target compounds could be separated thoroughly but the solvent peak was high (at time 3.42 min). So, 4.5 min was set as solvent delay time (Figure 4-2).

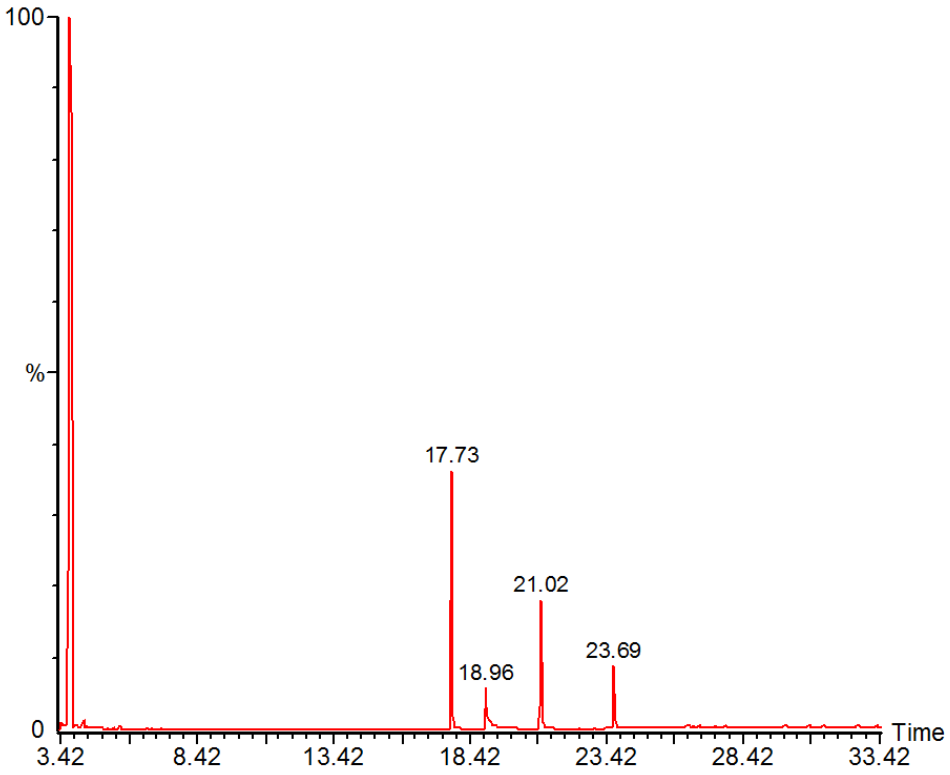

Figure 4-2 Chromatogram of mixed 25 μg/mL standard solution under SIR mode

(SIR mode; Temperature programming: 70 ℃ (2 min) to 300 ℃ (10 min) at rate of 10 ℃/min; Carrier gas flow rate: 1 mL/min; Dwell time: 0.200 second; Concentration: 25 μg/mL; Peaks from left to right (min): solvent peak, 17.73: DEET; 18.96: PAR; 21.02: CAF; 23.69: TCS)

4.3.1.2 Carrier gas flow rate optimization

In addition to the initial 1 mL/min, the flow rates 2 mL/min and 3 mL/min of carrier gas helium were further tried at start temperature of 100 ℃. Figure 4-3 shows the chromatograms of the mixed target compounds at carrier gas flow rates of 1, 2 and 3 mL/min.

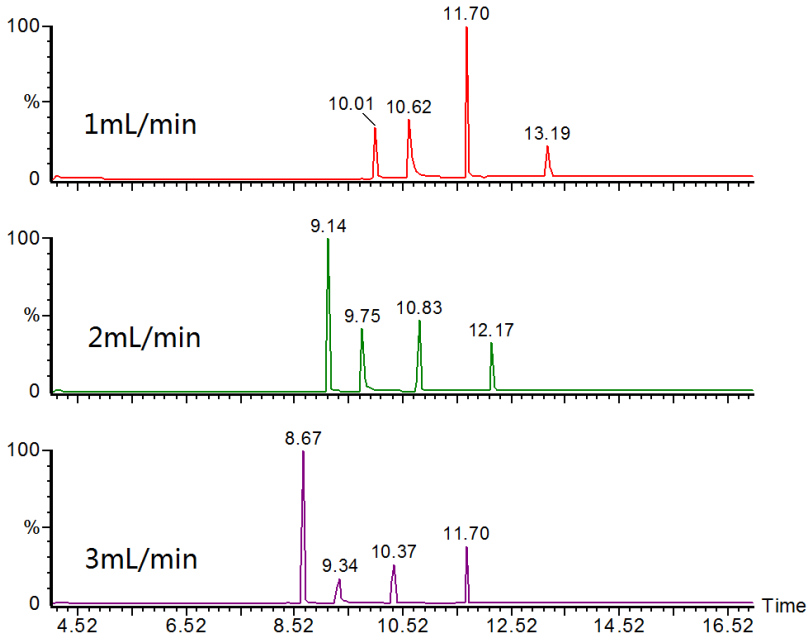

Figure 4-3 Chromatograms of mixed 25 μg/mL standard solution at different carrier gas flow rates

(SIR mode; Temperature programming: 100 ℃ (2 min) to 300 ℃ (10 min) at rate of 10 ℃/min; Dwell time: 0.200 second; Concentration: 25 μg/mL; Peaks from left to right: DEET, PAR, CAF, TCS)

From Figure 4-3, it can be seen that at 2 mL/min and 3 mL/min flow rates, four target compounds were also separated and response peaks came out earlier than that at 1 mL/min. However, by comparing the peak areas, under 3 mL/min, the response areas of

PAR and CAF were smaller than 2 mL/min, while response areas of DEET and TCS at 2 mL/min were small than at 3 mL/min. Usually, sharper peak and bigger response area indicate better LODs in chromatography [275]. Faster carrier gas flow rate also gets shorter detection time. So, in present study the final carrier gas flow rate was set at the median numeric, 2.5 mL/min.

4.3.1.3 Temperature programming optimization

To further shorten the whole procedure time, another two temperature programming were tested from 100 ℃ (hold for 2 min) to 300 ℃ (hold for 5 min) at the heating rates of 20 and 25 ℃/min, respectively. Figure 4-4 shows chromatograms at two temperature programming.

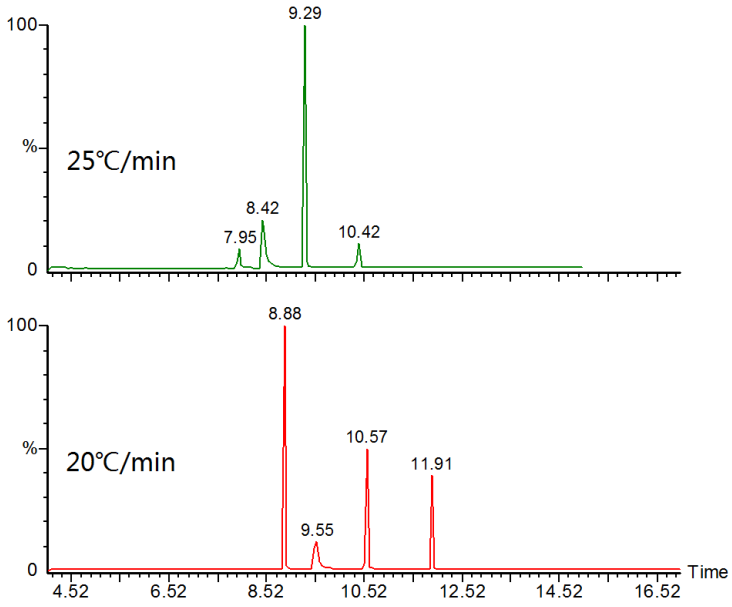

Figure 4-4 Chromatograms of mixed 25 μg/mL standard solution at two-temperature programming (25 ℃/min and 20 ℃/min)

(SIR mode; Temperature programming: 100 ℃ (2 min) to 300 ℃ (5 min); Carrier gas flow rate: 2.5 mL/min; Dwell time: 0.200 second; Concentration: 25 μg/mL; Peaks from left to right: DEET, PAR, CAF, TCS)

At 25 ℃/min heating rate, although target compounds could be separated, response peaks of DEET and TCS were clearly weaker than those at the heating rate of 20 ℃/min. The reason for this may be due to insensitiveness of the detector scanning (loss of resolution) to diagnostic (m/z) ions caused by the fast passing-through rate [276]. Hence, 100 ℃ (hold for 2 min) to 300 ℃ (hold for 5 min) at the rates of 20 ℃/min was chosen.

4.3.1.4 Dwell time optimization

As shown in Figure 4-4, the response of PAR (retention time: 9.55 min) was not as good as the other three compounds. Sharper peak usually gives better LODs. Dwell time is the time spending in scanning targets. Reducing dwell time accelerates the scanning frequency of the detector, therefore it can improve the target responses. Figure 4-5 shows chromatograms of target compounds under dwell time: 0.020 second and original 0.200 second.

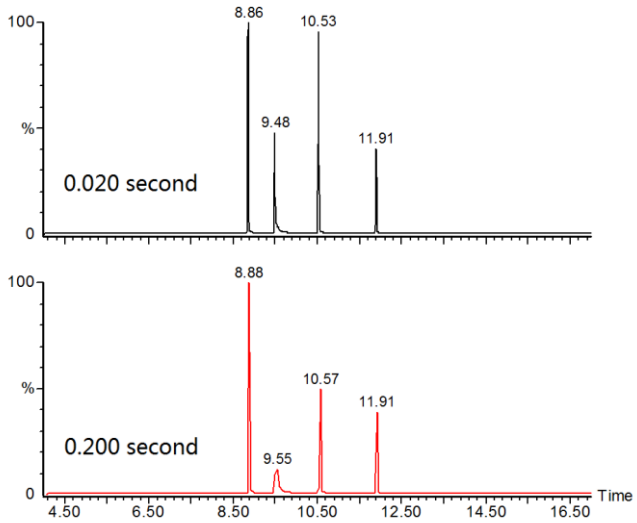

Figure 4-5 Chromatograms of mixed 25 μg/mL standard solution at two dwell times (SIR mode; Temperature programming: 100 ℃ (2 min) to 300 ℃ (5 min) at rate of 20 ℃/min; Carrier gas flow rate: 2.5 mL/min; Dwell time: 0.200 second; Concentration: 25 μg/mL; Peaks from left to right: DEET, PAR, CAF, TCS)

Under 0.020 second dwell time, peaks of PAR and CAF were visibly shaper than under 0.200 second. Using faster dwell time can accelerate the detector scanning frequency, which can avoid missing target fragments and consequently improve signal responses [277]. Thus, 0.020 second dwell time was applied in the final optimization. The final chromatogram of optimization (Figure 4-6) is shown below:

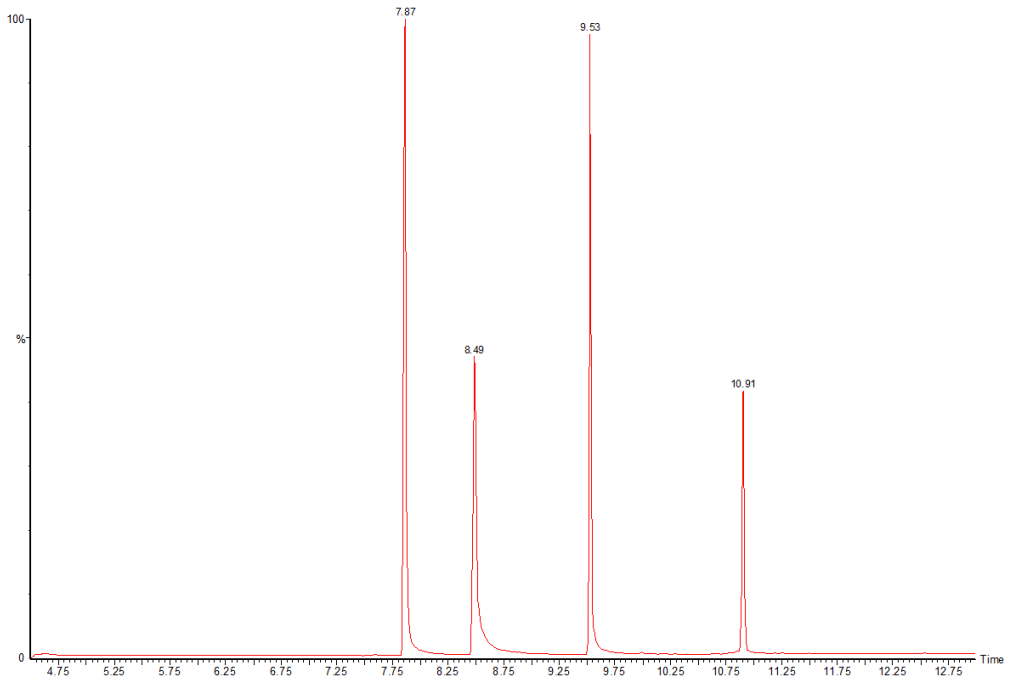

Figure 4-6 Optimized chromatogram of mixed 25 μg/mL standard solution

(SIR mode; Temperature programming: 100 ℃ (2 min) to 300 ℃ (5 min) at rate of 20 ℃/min; Carrier gas flow rate: 2.5 mL/min; Dwell time: 0.020 second; Concentration: 25 μg/mL; Peaks from left to right (min): 7.87: DEET; 8.49: PAR; 9.53: CAF; 10.91: TCS)

In the GC-MS procedure, no derivatization step was used, which gives simpler and faster detection and quantification approach [67,90]. In order to compensate the low sensitivity because of no derivatization, 3 μL splitless sample injection volume was

applied [67]. The LODs and LOQs (limits of quantification) of this method is shown in Table 4-5 (Section 4.3.4). Good target compounds response, short detection time and good LODs can fulfil daily detection demand, indicating this is a time-saving and simple GC-MS detection method.

4.3.2 Optimization of solid phase extraction process

Compared with traditional liquid-liquid separation-extraction method, SPE has become more popular in recent years for trace-level contaminant analysis [15]. Apart from the characteristics of the cartridge sorbent and features of target compounds, pH of samples, sample loading rate and eluents type all can influence SPE performance [278,279].

4.3.2.1 pH optimization

Because the four target compounds are either acidic or neutral, four pH values, 2.0, 3.0, 5.0 and 7.0 were selected to optimize the pH of water samples. Initially, samples were passed through the three tested cartridges at the rate of 5 mL/min and 2 × 4 mL ethyl acetate were used as eluent [280], results of which are shown in Table 4-1:

It can be seen from Table 4-1 that DEET achieved good recoveries by using the three cartridges (74.6~96.5 %) but PAR recoveries were very poor and PAR recoveries using the Supelco HLB cartridge were zero. Although PAR came out under all pH values using Strata X cartridge, recoveries were all below 50 %. Grujic et al. (2009) [281] found the optimal pH for PAR extraction was 4.5 (60 %), only 20 % higher than other pH (3, 6, 7.5) tested. Weigel et al. (2004) [117] tested seven types of SPE cartridges and found recoveries of PAR were all below 72 % at pH of 7.8. Poor PAR recovery means further improvements should be carried out. As for the other two compounds (i.e. CAF and

Table 4-1 Recoveries of target PPCP compounds using different pH modified samples (n=3)

		DEET		PAR		CAF		TCS	
	pH value	Recovery	RSD**	Recovery	RSD	Recovery	RSD	Recovery	RSD
Supelco HLB	pH=2	94.8%	2.3%	0.0%	n.a.*	62.6%	1.1%	84.1%	2.7%
	pH=3	90.9%	8.9%	0.0%	n.a.	66.4%	0.6%	87.4%	2.4%
	pH=5	96.5%	1.2%	0.0%	n.a.	54.4%	1.2%	85.9%	3.6%
	pH=7	90.0%	2.3%	0.0%	n.a.	58.7%	3.5%	71.2%	1.2%
Waters Oasis HLB	pH=2	86.1%	2.3%	0.0%	n.a.	68.8%	4.1%	82.6%	0.3%
	pH=3	84.8%	0.7%	17.3%	1.1%	89.8%	2.7%	83.7%	1.2%
	pH=5	92.5%	4.5%	0.0%	n.a.	49.3%	1.0%	89.7%	2.3%
	pH=7	90.5%	2.3%	0.0%	n.a.	49.4%	0.5%	83.8%	3.4%
Strata X	pH=2	85.0%	5.3%	13.8%	1.4%	86.3%	1.3%	49.7%	0.2%
	pH=3	93.7%	0.6%	42.8%	0.3%	87.7%	1.5%	82.5%	2.9%
	pH=5	74.6%	0.4%	19.2%	4.1%	86.6%	0.2%	62.7%	3.2%
	pH=7	80.3%	1.7%	17.3%	0.3%	84.0%	1.2%	62.7%	1.8%

* n.a. not available

** RSD, relative standard deviation

TCS), Strata X cartridge also achieved overall better recovery (above 80 %) of CAF than other two cartridges, though the best recovery was 89.8 % using Oasis HLB at pH of 3.0. However, Strata X was not quite suitable for TCS extraction as the overall recovery was about 20 % lower compared with the other cartridges. Overall, pH of 3.0 was the optimal among tested pH values, and this was obvious for CAF using Oasis HLB and for TCS and DEET using Strata X (Table 4-1). Therefore, pH of 3.0 was chosen for the parameter pH.

4.3.2.2 Sample loading rate optimization

Sample loading rate is another essential factor for improving SPE performance. Target compounds may not be adsorbed onto the sorbent of cartridge under a fast loading rate as time may not be sufficient for adsorption or exchange occurring [82]. Conversely, if the loading rate is too slow, it may also be time-consuming for SPE when treating samples with large volume. Sample loading rates usually vary a lot due to the properties of samples, ranging from 2 ml/min to 15 ml/min [2,3,273,280]. In this study, at sample pH of 3.0, three sample loading rates, namely 2, 3, and 5 mL/min, were tested for improving target compounds recoveries. Results are shown in Table 4-2 below.

At the three loading rates, PAR recovery (0 %) did not increase using Supelco HLB cartridge, indicating this cartridge is unsuitable for PAR. The poor paracetamol recovery may be attributed to sorbent overload or the eluent was not suitable for both sorbent and compound [282,283]. For the other three target compounds, except for CAF at 3 and 5 mL/min using Supelco HLB (recoveries of 65.7 % and 69.4 %, respectively), all others achieved recoveries higher than 70 %. However, at 2 mL/min loading rate, recoveries of the four compounds were all obviously lower (around 20~30 %) than 3 and 5 mL/min using Strata X cartridge (Table 4-2). This phenomenon was also reported by Guo et al.

Table 4-2 Recoveries of target PPCP compounds at different sample loading rate (n=3)

		DEET		PAR		CAF		TCS	
	Flow rate	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
Supelco HLB	2 mL/min	109.3%	5.2%	0.0%	n.a.*	73.8%	2.5%	86.6%	2.3%
	3 mL/min	92.8%	3.6%	0.0%	n.a.	65.7%	1.2%	82.6%	1.2%
	5 mL/min	90.9%	1.0%	0.0%	n.a.	69.4%	1.6%	87.4%	0.9%
Waters Oasis HLB	2 mL/min	89.6%	2.3%	28.1%	1.8%	101.1%	0.9%	83.7%	3.1%
	3 mL/min	91.4%	1.8%	26.9%	3.2%	102.0%	0.3%	81.8%	0.8%
	5 mL/min	85.8%	0.7%	21.9%	2.3%	93.8%	3.6%	86.8%	0.9%
Strata X	2 mL/min	75.6%	0.7%	23.2%	1.7%	80.3%	0.3%	60.6%	0.2%
	3 mL/min	104.6%	0.9%	41.8%	0.8%	101.0%	2.1%	89.4%	3.2%
	5 mL/min	100.4%	1.1%	47.9%	2.5%	94.4%	3.9%	94.5%	4.1%

* n.a. not available

(2011) [284]. Here it could be assumed that, apart from sorbent and compound chemical properties, under faster flow rate, the target compound might be more likely to have possibility to “run into” or “collide” the sorbent to increase the “capture” probability, but this needs further study. Apart from this point, no obvious difference on recoveries was observed among different sample loading rates, which indicated 5 mL/min was appropriate.

4.3.2.3 Eluent type optimization

Satisfying recoveries were achieved for DEET, CAF and TCS. In order to increase the PAR recovery, three different eluents (i.e. ethyl acetate, methanol and acetonitrile) were tested. Results are shown in Table 4-3.

For PAR, similar to ethyl acetate, methanol was found not to improve the recovery by the Supelco HLB cartridge. However, by using acetonitrile, the recovery rose to 16.7 %. Similar improvements also occurred to other two types of cartridges, especially the Oasis HLB cartridge which significantly increased recoveries from 21.3 % to 95.6 %. For Strata X cartridge, recovery of paracetamol increased from 47.9 % to 78.5 %. Significant recovery increase suggests that the poor recovery of PAR in previous tests may be due to the fact that eluent type was not suitable for washing targets down from sorbent. In terms of DEET, CAF and TCS, acetonitrile provided recoveries as good as methanol and ethyl acetate (except for TCS, about 20 % lower than methanol and ethyl acetate of Supelco HLB cartridge). The recoveries of DEET, PAR, CAF and TCS using acetonitrile with Waters Oasis HLB cartridges were 104.9 %, 95.6 %, 107.2 % and 87.2 %, respectively. Thus, acetonitrile was selected as optimal eluent.

Table 4-3 Recoveries of target PPCP compounds using different eluents (n=3)

		DEET		PAR		CAF		TCS	
	Eluent	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
Supelco HLB	Ethyl acetate	90.9%	1.0%	0.0%	n.a.*	69.4%	1.6%	87.4%	0.9%
	Methanol	94.4%	0.2%	0.0%	n.a.	71.3%	1.2%	84.4%	3.1%
	Acetonitrile	118.0%	2.1%	16.7%	1.3%	93.0%	1.0%	68.6%	4.6%
Waters Oasis HLB	Ethyl acetate	87.4%	0.9%	21.3%	1.0%	89.8%	3.6%	83.8%	0.9%
	Methanol	80.8%	0.4%	51.4%	5.5%	102.0%	3.5%	73.4%	2.0%
	Acetonitrile	104.9%	3.0%	95.6%	2.3%	107.2%	1.7%	87.2%	2.0%
Strata X	Ethyl acetate	100.4%	1.1%	47.9%	2.5%	94.4%	3.9%	94.5%	4.1%
	Methanol	94.5%	1.3%	23.4%	0.9%	116.9%	0.8%	70.2%	1.7%
	Acetonitrile	100.5%	2.3%	78.5%	1.4%	98.6%	5.9%	88.3%	1.5%

* n.a. not available

4.3.3 Solid phase extraction process without conditioning and equilibration steps and method validation

25 μg/L and 0.25 μg/L mixed target compound samples (500 mL) were prepared with tap water, lake water and synthetic wastewater, respectively, which had five replicates. Since the aim of this method optimization was to find a simple, fast and cost-effective purification and detection way, SPE without conditioning and equilibration were also further performed to test the recoveries and RSDs of the four target compounds. Along with the method validation, results are shown in Table 4-4.

With conditioning and equilibration, method validation showed that recoveries were 81.9~99.5 % for DEET, 76.1~109.0 % for PAR, 88.1~106.6 % for CAF, and 87.5~105.2 % for TCS. Without conditioning and equilibration, recoveries of 74.9~110.4 % for DEET, 80.0~111.3 % for PAR, 97.7~106.3 % for CAF and 88.0~98.9 % for TCS were also achieved. T-test showed that no significant difference (p>0.05) was found between with and without conditioning and equilibration samples, indicating excellent performance by the Oasis HLB cartridge.

Waters Oasis HLB cartridge showed excellent performance even without conditioning and equilibration. Sorbent of the SPE cartridge usually has large chromatographic surface area and target compounds must be able to flow into and out of the sorbent pores to be chromatographically acted upon by the sorbent [285]. Since reversed-phase sorbent (e.g. Strata X) is usually hydrophobic which cannot be wetted by aqueous sample, it should be wetted first with organic solvent in order to let aqueous sample compatible. Then inorganic solvent (water) was used to replace the organic solvent

Table 4-4 Recoveries of target PPCP compounds in tap water, lake water and synthetic wastewater using Waters Oasis HLB cartridge with and without conditioning and equilibration (n=5)

With conditioning and equilibration	Tap Water				Natural Water				Synthetic Wastewater			
	25 μg/L		0.25 μg/L		25 μg/L		0.25 μg/L		25 μg/L		0.25 μg/L	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
DEET	99.5%	2.4%	96.7%	5.6%	99.0%	2.2%	81.9%	6.6%	94.5%	1.1%	97.8%	2.3%
PAR	94.2%	3.2%	109.0%	6.8%	76.1%	1.9%	98.3%	7.9%	102.3%	0.6%	92.3%	5.9%
CAF	99.2%	1.9%	106.6%	4.9%	96.4%	3.5%	101.1%	5.2%	88.1%	0.5%	99.4%	4.8%
TCS	87.5%	3.7%	105.2%	6.2%	93.8%	4.5%	91.3%	5.7%	93.0%	1.4%	97.5%	5.4%
Without conditioning and equilibration	Tap Water				Natural Water				Synthetic Wastewater			
	25 μg/L		0.25 μg/L		25 μg/L		0.25 μg/L		25 μg/L		0.25 μg/L	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
DEET	97.6%	2.4%	110.4%	10.5%	105.8%	4.9%	74.9%	1.3%	97.6%	0.2%	80.4%	1.5%
PAR	93.7%	3.0%	101.1%	6.2%	80.0%	3.7%	90.7%	7.4%	80.0%	3.7%	111.3%	7.3%
CAF	101.5%	2.4%	97.7%	5.0%	98.3%	3.7%	106.3%	0.6%	98.3%	3.7%	104.4%	9.4%
TCS	93.7%	1.8%	98.9%	0.7%	95.0%	5.6%	88.0%	3.0%	95.0%	5.6%	92.9%	6.6%

(typically too strong to retain targets) to ensure compounds in the sample can be retained [285]. Hence, conditioning and equilibration are generally regarded as an important step in SPE procedure, which is carried out by both organic solvent and ultrapure water, and pH adjusted ultrapure water if samples need to have pH modified, for activation of the sorbent [76,133,273]. As the sorbent of Waters Oasis cartridge is a water-wettable hydrophilic-lipophilic balanced polymeric phase of divinylbenzene-co-N-vinylpyrrolidone with both ion-exchange and reversed-phase properties, this means it possible to escape the conditioning procedure [285]. By avoiding conditioning and equilibration, the proposed method would be further simplified and shortened.

According to the EPA quality control criteria, the accepted recovery range of SPE is 70~130 % [286]. Hence, good recoveries of target compounds achieved in the present study indicate reliability and acceptability of this method. Importantly, without conditioning and equilibration, recoveries of target PPCP compounds lay in the same range with that conducting the steps. The exclusion of this step cannot only save time and solvents, but also can lessen the potential risks to human health caused by toxic solvents.

4.3.4 Quality control

Calibration curves, LODs, LOQs, and RSDs of GC-MS detection of target PPCP compounds are shown in the Table 4-5.

Table 4-5 Calibration curves with correlation coefficients (R^2), limits of detection (LODs), limits of quantification (LOQs) and relative standard deviations (RSDs) of GC-MS detection (n=5)

Target	Calibration curve	R^2	LODs (ng/L)	LOQs (ng/L)	RSDs of GC-MS		
					0.25 μg/mL	2.50 μg/mL	25.0 μg/mL
DEET	y = 32034x - 9425.7	0.9999	20.0	65.0	6.04%	4.07%	3.94%
PAR	y = 49739x - 24239	0.9991	160.0	500.0	5.03%	2.97%	3.28%
CAF	y = 82660x - 29887	0.9996	15.0	45.0	5.75%	1.85%	2.39%
TCS	y = 31696x - 19697	0.9986	15.0	50.0	4.67%	2.73%	2.05%

Calibration curves of the four target PPCP compounds were made through six concentrations (i.e. 0.25, 0.50, 1.00, 5.00, 25.00, 50.00 μg/mL) of mixed standard samples. It can be seen from Table 4-5 that mean correlation coefficients (R^2) of four calibration curves were 0.9999, 0.9991, 0.9996 and 0.9986, for DEET, PAR, CAF, and TCS, respectively, indicating excellent linear correlations of curves. The LODs of target compounds in GC-MS were 20.0, 160.0, 15.0 and 15.0 ng/L and LOQs were 65.0, 500.0, 45.0 and 50.0 ng/L for DEET, PAR, CAF and TCS, respectively, showing that this

method is suitable for routine test. Equipment RSDs of target PPCP compounds were conducted by seven replicates of standard solutions in GC-MS at three concentrations (i.e. 0.25, 2.50 and 25.00 μg/mL). The RSDs results ranged from 1.85 % to 6.04 %, showing good instrumental detection precision (Table 4-5).

4.4 Summary

This chapter gives the details for developing a simplified method of extraction and detection of selected PPCP compounds from water using GC-MS and SPE techniques. Derivatization process was avoided in the detection method, not only shortening the overall procedure time, but also lessening the toxicity caused by the derivatization reagents to the human health. In terms of SPE process, good target compounds recoveries without conditioning and equilibration steps were also achieved by using Waters Oasis HLB cartridge, being 74.9~110.4 % for DEET, 80.0~111.3 % for PAR, 97.7~106.3 % for CAF and 88.0~98.9 % for TCS. By skipping conditioning, equilibration and derivatization steps, methods of SPE and detection of GC-MS are significantly simpler and faster, and potential risks of toxic solvents to human health are also reduced.

Overall, the optimized simplified method established by this work can be summarised as Figure 4-7.

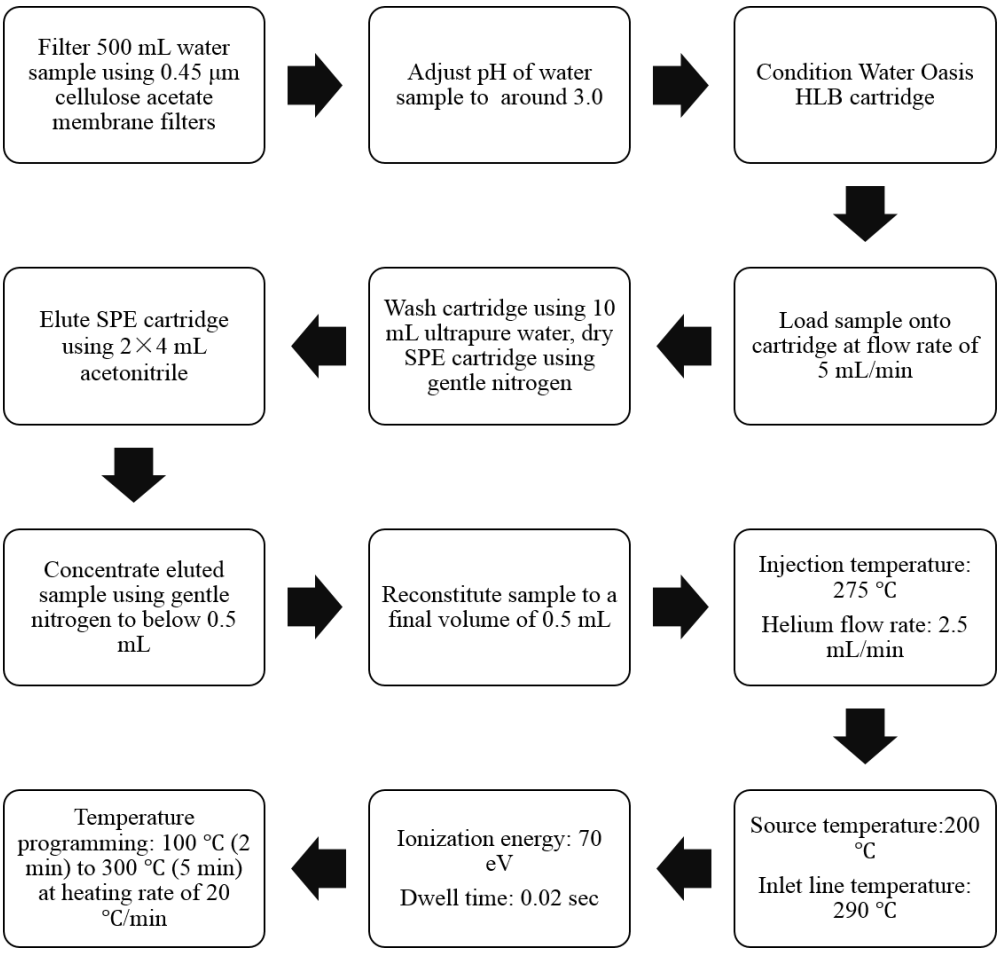

Figure 4-7 Flow chart of the extraction and detection method

For purification, pH of 3.0 was chosen as sample pH. Optimal sample loading rate was 5 mL/min. Acetonitrile was used as eluent. Oasis HLB cartridge achieved the overall best recoveries. With conditioning and equilibration, recoveries laid within the ranges of 81.9~99.5 % for DEET, 76.1~109.0 % for PAR, 88.1~106.6 % for CAF and 87.5~105.2 % for TCS.

For detection, helium at 2.5 mL/min was chosen as the carrier gas flow rate and the temperature programming was from 100 ℃ (hold for 2 min) to 300 ℃ (hold for 5 min) at the heating rate of 20 ℃/min. Dwell time of 0.020 second was applied and total detection time in GC-MS was 13 min.

CHAPTER 5 REMOVAL OF SELECTED PPCPS USING GREATER DUCKWEED CONSTRUCTED WETLAND

5.1 Introduction

In this chapter, the efficiency of Greater duckweed (*Spirodela polyrhiza*) based laboratory-scale free water CW was investigated to remove DEET, PAR, CAF and TCS from synthetic wastewater at high COD load (300 mg/L). Experiment consisted of batch and continuous modes. Batch tests were developed by the aid of orthogonal design [287] to optimize factors (i.e. light intensity, aeration, plant biomass and *E.coli* abundance) affecting PPCP removal. *E. coli* was used to represent bacteria abundance present in wastewater and to determine their effect on PPCP degradation [288,289]. Based on the results from orthogonal design, Duncan analysis was carried out to analyse results and select optimal factor levels and their combination. Then batch verification and continuous flow tests were experimented under the optimized factor levels. A test using CW tank followed by one ST tank at continuous mode was tested under the optimized conditions from batch test. In addition to the investigation of the target PPCP compound removal, other general parameters (e.g. COD, TOC) and their correlations between removal during treatment processes were also assessed.

5.2 Experiment

5.2.1 Batch test

For the CW tests, four factors were tested for the removal of target PPCP compounds, each has three levels. Light intensity (80, 160, ad 240 $\mu molm^{-2}s^{-1}$), oxygen (no aeration, intermittent and full aeration), plant biomass (0.25, 0.50 and 1.00 kg/m^2) and *E.coli* abundance (none *E.coli*, 1.0×10^4 and 1.0×10^6 CFU/100mL) were chosen as factors influencing the PPCP removal [10,193]. To minimise test run number, orthogonal design (four factors with three levels) was employed and conducted to reduce the number of runs, resulting in nine representative runs (CW1-CW9, Table 5-1).

In order to have deeper insight into the roles of photodegradation, biodegradation and plant degradation on target PPCP compounds removal, additional tests (ATs) were conducted (AT1-AT7, Table 5-1). AT1, 2 and 3 tests were carried out under three light intensity levels with no other factor levels for determination of light effect. *E.coli* effect was designed using AT4, 5 and 6 at three abundance levels in the dark without aeration and plants. To identify Greater duckweed's role, aseptic Greater duckweed plants were tested (AT7) under the same experimental condition of CW9. The sterilization process can be found in the Section 3.8. PPCP concentrations in the treated synthetic wastewater were quantified at the end.

Table 5-1 Orthogonal design of batch experiment and additional test (AT) sets

		Light intensity ($\mu molm^{-2}s^{-1}$)	Aeration	*E.coli* abundance (CFU/100mL)	Plant biomass (kg/m^2) (g)
CW	CW 1	160	Full	None	0.50, 20
	CW 2	240	Intermittent	None	1.00, 40
	CW 3	240	Full	1.0×10^4	0.25, 10
	CW 4	80	Full	1.0×10^6	1.00, 40
	CW 5	240	None	1.0×10^6	0.50, 20
	CW 6	160	Intermittent	1.0×10^6	0.25, 10
	CW 7	80	Intermittent	1.0×10^4	0.50, 20
	CW 8	160	None	1.0×10^4	1.00, 40
	CW 9	80	None	None	0.25, 10
AT sets	AT 1	80	None	None	None
	AT 2	160	None	None	None
	AT 3	240	None	None	None
	AT 4	None	None	None	None
	AT 5	None	None	1.0×10^4	None
	AT 6	None	None	1.0×10^6	None
	AT 7	80	None	None	0.25, 10, aseptic

Three litres of synthetic wastewater spiked with 25 μg/L PPCPs (Table 3-6) were placed in each CW tank and the experimental area was covered using reflective fabric, which made the light spread evenly upon the CW tanks. Schematic representation (Figure 5-1) and photos (Figure 5-2) are shown below.

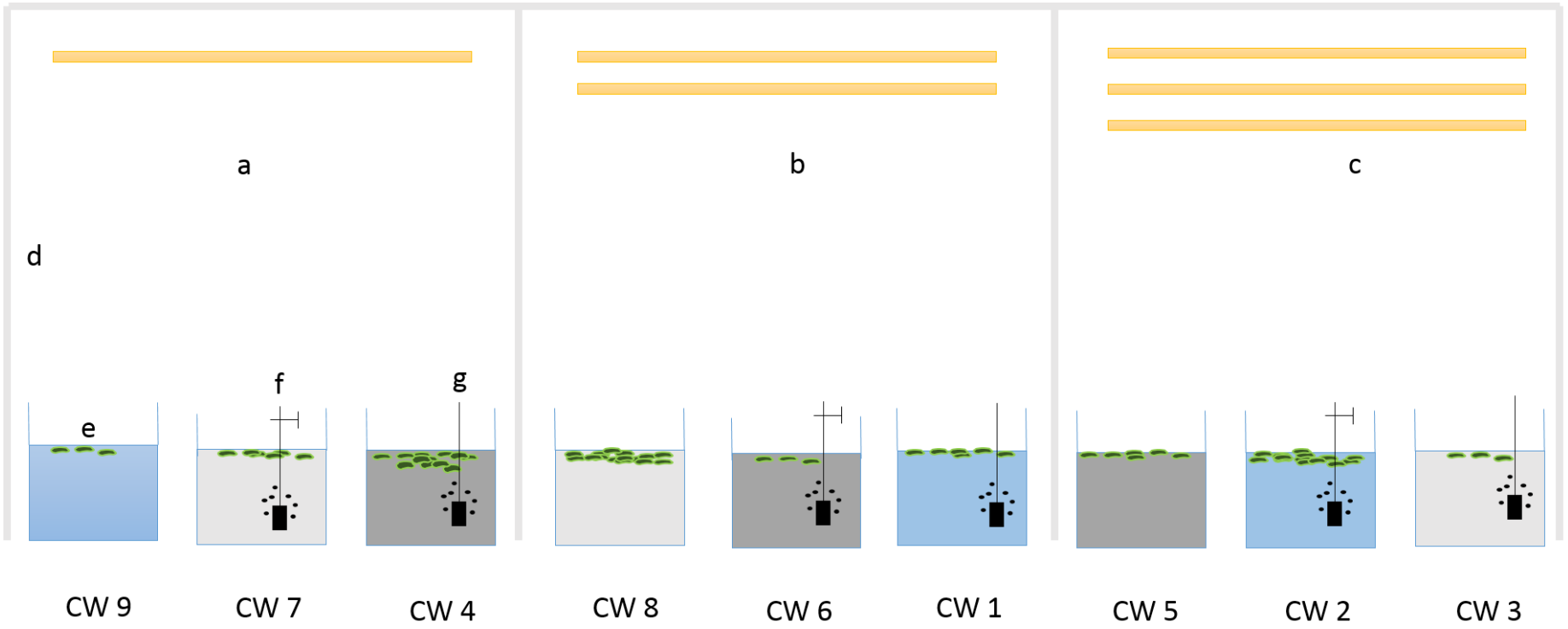

Figure 5-1 Schematic representations of the batch experiments a. low light intensity chamber. b. medium light intensity chamber. c. high light intensity chamber. d. reflective fabric. e. Greater duckweed. f. intermittent aerator. g. full aerator.

CW colour: blue: no bacteria; light grey: 1.0×10^4 CFU/100 mL bacterial abundance; dark grey: 1.0×10^6 CFU/100 mL bacterial abundance

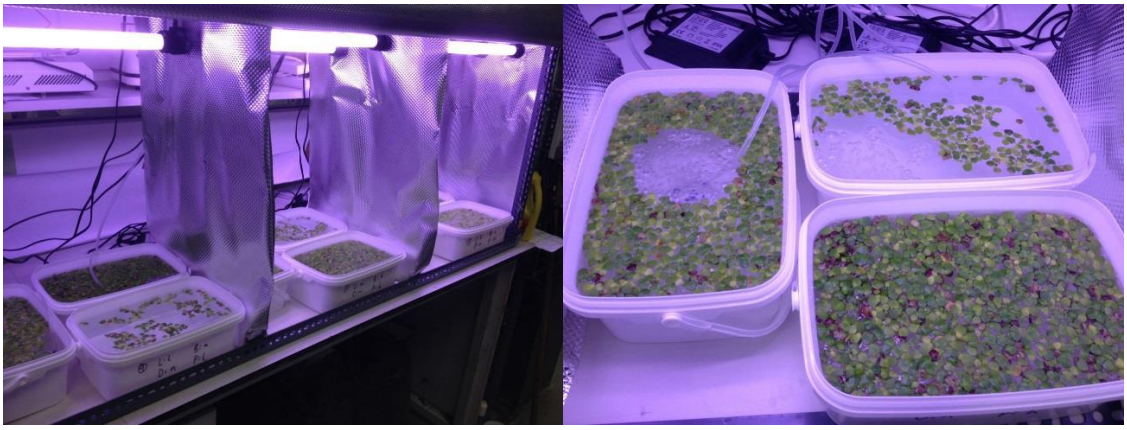

Figure 5-2 Photos of the batch CW test

As shown in the figures above, cleanly washed Greater duckweed was put into each CW tank. Aerators (output at 3.2 L/min) were placed in the water to supply DO and water DO reached saturation within 5 min. For intermittent aeration, aerators were switched on for 2 hours and then off for 2 hours. So, this cycle was repeated six times a day. Lights were placed on the top of the CW surface areas (50×40×70 cm) under the fabric in each chamber and light intensity was monitored by the light density meter. The lighting was left on for a period of 14 hours and off for 10 hours [290]. Batch test was conducted at laboratory-scale and the room temperature was around 23 ℃ constantly. In literatures, HRT in different types at different modes varies considerably from 1 to 12.9 days [220–222]. For the sake of practical sampling, the testing period (i.e. HRT) for the batch test was set at seven days. During this period, general parameters (i.e. pH, conductivity and redox potential) of each CW were measured at the same time each day (excluding weekend). DO concentrations were measured simultaneously in intermittent and full aerated CWs. After test ended, concentrations of PPCP compounds, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, COD and *E.coli* abundance of the final treated synthetic wastewater in each CW were determined. While in AT sets, only final PPCP compound concentrations were analysed.

5.2.2 Batch verification test

Based on the Duncan analysis of orthogonal design, high light intensity (240 μmolm^{-2}s^{-1}), full aeration, high plant biomass (1.00 kg/m^2) and high *E.coli* abundance (1.0×10^6 CFU/100mL) were chosen as optimum factor level combination. A batch verification test was carried out after batch test to verify the effect of the combined optimized factors on target PPCP compounds removal. Conditions including experimental apparatus and lighting were the same as in the batch test. The target PPCP concentrations, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, COD, TOC and *E.coli* abundance were determined at the end of the test (day 7). An additional control set using optimal factor level conditions without plants was also conducted to further verify the role of Greater duckweed in this system.

5.2.3 Continuous flow tests

5.2.3.1 Continuous flow constructed wetland test

The experimental conditions followed the optimal factor levels. The continuous flow CW consisted of one inflow tank, one CW tank (44×32×21 cm) and one outflow tank. 140 g fresh and cleaned Greater duckweed (1.00kg/m^2) was put into the CW tank. To prevent PPCP from photodegradation, inflow and outflow tanks were covered by black paper while the experimental area (100×40 cm) above the CW tank was covered by a reflective fabric [155]. Lights were placed above the CW surface area under the fabric. Aerators were placed evenly at the bottom of the tank to make sure DO was saturated in the CW tank. Figure 5-3 shows the photo of continuous CW system.

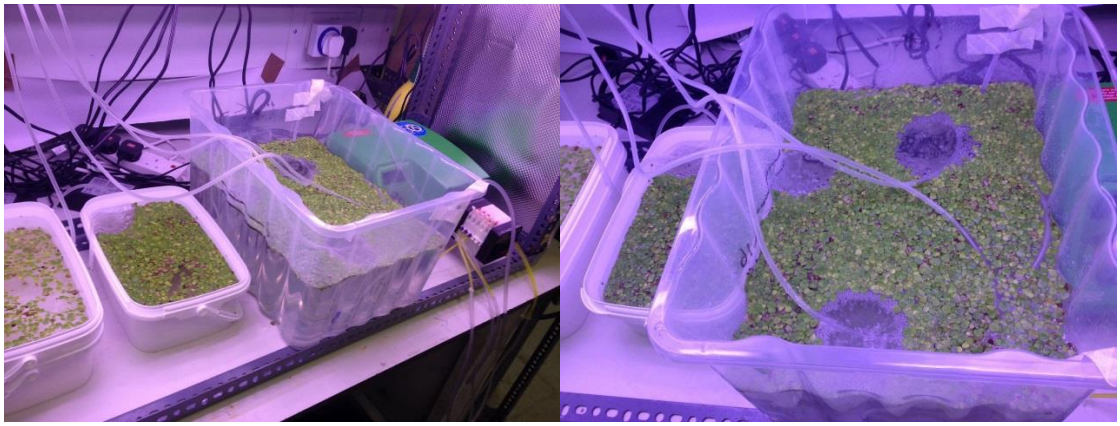

Figure 5-3 Photos of continuous CW system

Fourteen litres of synthetic wastewater spiked with the target PPCP compounds at 25 μg/L and 1.0×10^6 CFU/ 100mL *E.coli* were added into the CW tank. The HRT was set at 7 days (two litres of water in and out every day, actual HRT at 6.7 days due to water loss) and the peristaltic pump ensured the inflow and outflow of water was kept at 1.38 mL/min consistently. The system was operated for 4 weeks and was left under lighting for a period of 14 hours and 10 hours in darkness as the batch test. The room temperature was constantly around 23 ℃. To explore the stability of CW performance without aeration, at day 17 all aerators were removed after sampling. The inflow synthetic wastewater was freshly made every day. Both inflow and outflow tanks were sterilized by 70 % alcohol and antimicrobial each time before refilling. The pH, conductivity and redox potential of the treated synthetic wastewater and DO in the CW tank were measured from Monday to Friday each week. Samples were collected three times a week on Mondays, Wednesdays and Fridays for quantification of the PPCPs, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, COD, TOC and *E.coli* abundance.

5.2.3.2 Continuous flow with constructed wetland-stabilization tank test

The continuous flow CW-ST consisted of one inflow tank, one CW tank (32×22×17 cm), one ST tank (32×22×17 cm) and one outflow tank, successively connected by peristaltic pump (speed at 1.38 mL/min). Fresh and clean Greater duckweed (1.00kg/m^2, 70 g) was put in the CW tank. The area (100×40 cm) above the CW and ST tanks was covered by reflective fabric and inflow and outflow tanks were covered by black paper. Lights were put over the CW-ST area, and room temperature was constantly 23 ℃. For comparing this system with the continuous flow CW system, seven litres of the synthetic wastewater were initially added in CW and ST tanks separately. Aerators were evenly placed at the CW tank bottom. Figure 5-4 shows the photo of this continuous CW-ST system.

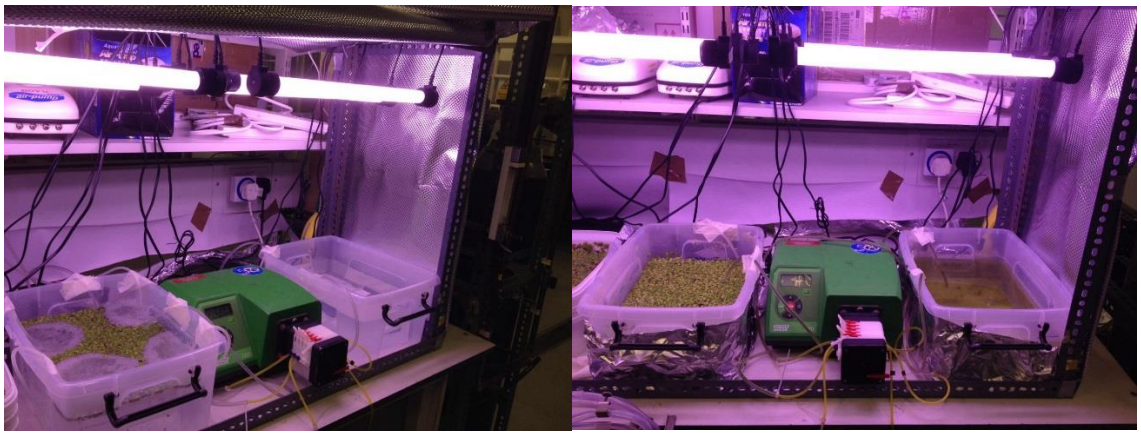

Figure 5-4 Photos of continuous CW-ST system

The total HRT of the system was set at 7 days (2 litres in and out every day, 3.5 days in CW tank and 3.5 days in ST tank, actual 6.9 days). The duration of this experiment (4 weeks) and aerator removal strategy (at day 17) were the same as for the continuous flow CW test. Every day, inflow synthetic wastewater was freshly prepared. Before reloading,

inflow and outflow tanks were cleaned and sterilized to avoid contamination as mentioned above. Sampling strategy and parameter monitoring were the same as for the continuous flow CW test.

Schematic representation of the continuous flow CW and CW-ST systems is shown in Figure 5-5.

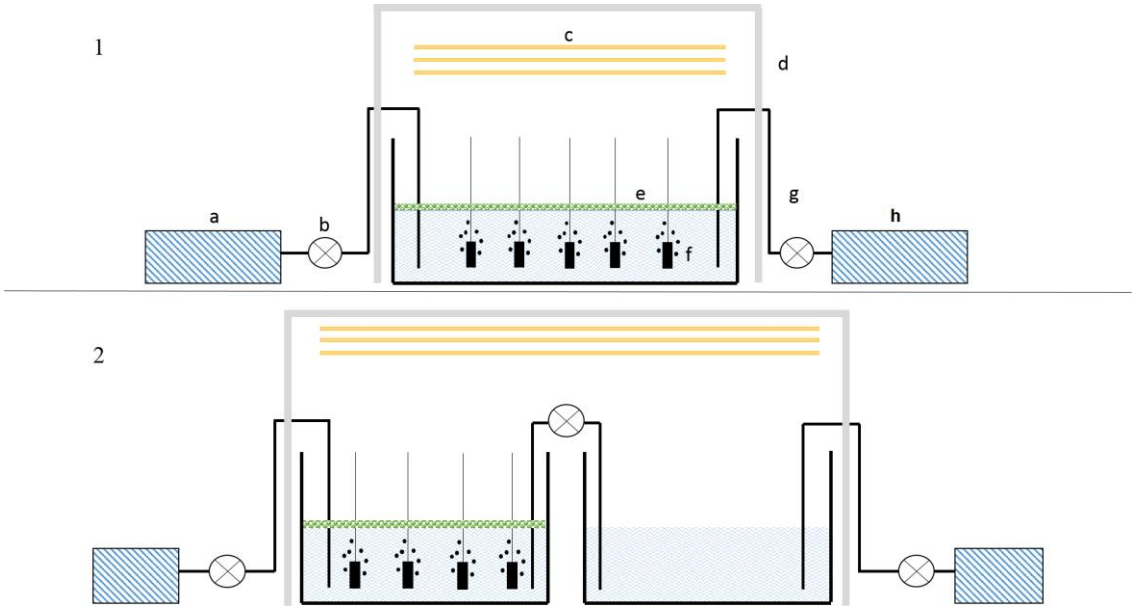

Figure 5-5 Schematic representations of the (1) continuous flow CW and (2) continuous flow CW-ST (a. inflow tank. b. peristaltic pump. c. lights. d. reflective fabric. e. Greater duckweed. f. aerators. g. peristaltic pump tubing. h. outflow tank.)

5.2.4 Statistical Analysis

Orthogonal design was performed by using IBM SPSS Statistics 22 for planning the experiments. Duncan analysis was used for the orthogonal result evaluation [287].

ANOVA (analysis of variance) and correlation tests were conducted by using IBM SPSS Statistics 22, and *p*-value<0.05 was considered statistically significant.

5.3 Results and discussion

5.3.1 Batch experiment

5.3.1.1 Target compounds removal

Figure 5-6 illustrates the removal of target PPCP compounds in final treated water of batch test and concentrations of target compounds are shown in Table 5-2, including both orthogonal design sets and AT sets.

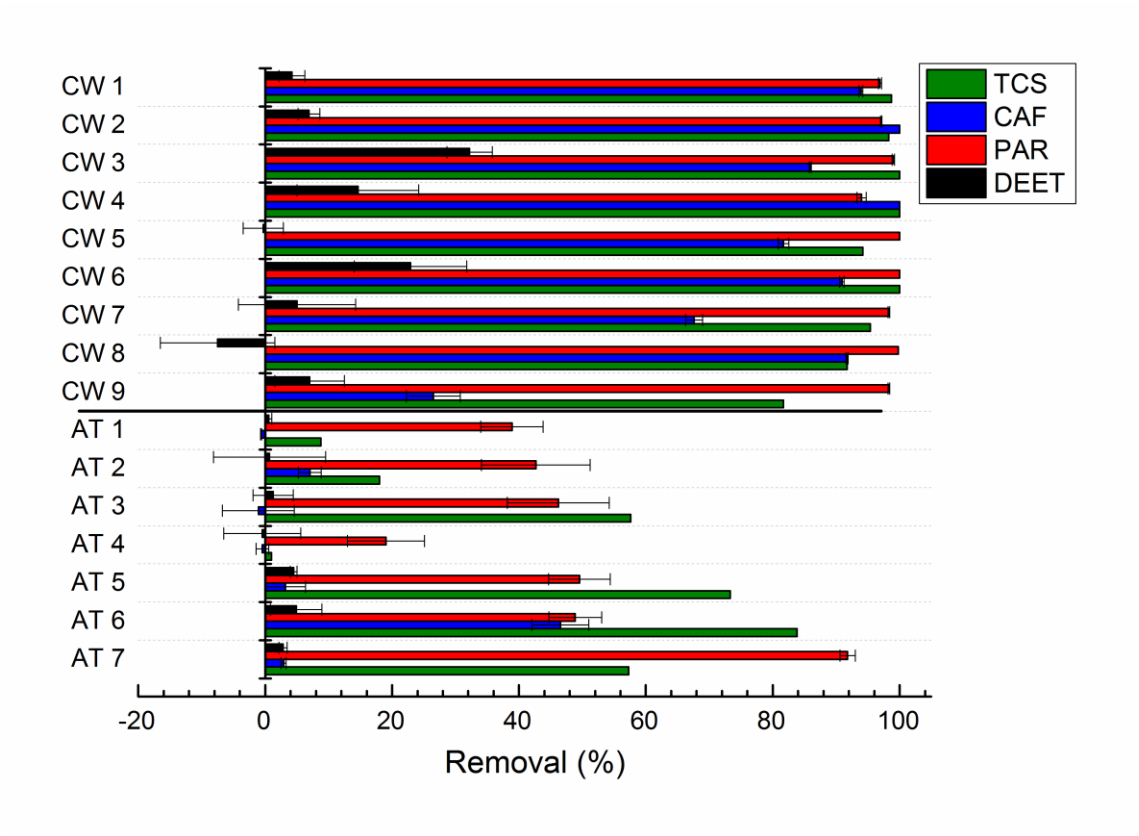

Figure 5-6 Removal of the target PPCP compounds in batch and ATs tests

(Initial target PPCP concentration: 25 μg/L)

Table 5-2 Concentrations and removal of target compounds in batch test and AT sets

		DEET			PAR			CAF			TCS			Average removal
		Con(μg/L)	RSD	Removal	Con(μg/L)	RSD	Removal	Con(μg/L)	RSD	Removal	Con(μg/L)	RSD	Removal	
CW	CW 1	23.95	0.51	4.2%	0.77	0.06	96.9%	1.52	0.07	93.9%	0.32	0.01	98.7%	73.4%
	CW 2	23.29	0.43	6.8%	0.74	0.03	97.0%	n.d.	n.a.	100.0%	0.43	0.03	98.3%	75.5%
	CW 3	16.94	0.89	32.2%	0.24	0.05	99.0%	3.52	0.04	85.9%	n.d.	n.a.	100.0%	79.3%
	CW 4	21.36	2.39	14.6%	1.49	0.18	94.0%	n.d.	n.a.	100.0%	n.d.	n.a.	100.0%	77.2%
	CW 5	25.08	0.79	-0.3%	n.d.*	n.a.**	100.0%	4.57	0.21	81.7%	1.45	0.03	94.2%	68.9%
	CW 6	19.33	2.22	22.7%	n.d.	n.a.	100.0%	2.3	0.09	90.8%	n.d.	n.a.	100.0%	78.4%
	CW 7	23.76	2.31	5.0%	0.44	0.03	98.2%	8.11	0.34	67.6%	1.15	0.07	95.4%	66.5%
	CW 8	26.88	2.26	-7.5%	n.d.	n.a.	100.0%	2.09	0.04	91.6%	2.07	0.37	91.7%	69.0%
	CW 9	23.24	1.37	7.0%	0.42	0.03	98.3%	18.36	1.06	26.6%	4.57	0.21	81.7%	53.4%
AT sets	AT 1	24.86	0.12	0.6%	15.28	1.23	38.9%	25.16	0.02	-0.6%	22.81	0.75	8.8%	11.9%
	AT 2	24.83	2.21	0.7%	14.34	2.14	42.6%	23.24	0.45	7.0%	20.5	0.22	18.0%	17.1%
	AT 3	24.69	0.79	1.2%	13.45	2.01	46.2%	25.27	1.42	-1.1%	10.6	1.23	57.6%	26.0%
	AT 4	25.12	1.52	-0.5%	20.24	1.52	19.0%	25.11	0.25	-0.4%	24.76	0.42	1.0%	4.8%
	AT 5	23.88	0.14	4.5%	12.62	1.22	49.5%	24.2	0.79	3.2%	6.68	0.12	73.3%	32.6%
	AT 6	23.78	1.02	4.9%	12.79	1.04	48.8%	13.37	1.12	46.5%	4.04	0.20	83.8%	46.0%
	AT 7	24.30	0.16	2.8%	2.06	0.30	91.8%	24.27	0.10	2.9%	10.67	0.41	57.3%	38.7%

Mixed target compounds were spiked into synthetic wastewater to reach a concentration of 25 μg/L

*n.d. not detected ** n.a. not available

From the results it can be seen that PAR, CAF and TCS achieved relatively better removal than DEET in the batch tests. For PAR, CWs 5, 6 and 8 showed no detectable PAR and the other CWs' removal ranged from 94.0~99.0 %, indicating excellent PAR (p<0.01) removal by the batch-scale CW system. All CAF concentrations were below 10 μg/L (not detected in CWs 2 and 4) except for CW9 (18.36 μg/L), with removal between 67.6~100.0 %. Very good TCS removal was also achieved and final TCS concentrations varied from 0~4.57 μg/L (removal between 81.7~100 %). However, DEET concentrations in the final treated wastewater were still high. The lowest concentration of DEET was 16.94 μg/L in CW3 (32.2 % removal) and the highest was 26.88 μg/L in CW8 (-7.5 %). The negative removal of DEET in CWs 5 and 8 might be due to no removal with system water evaporation which led to increasing remaining concentrations [11]. Generally, DEET removal by wetlands and other *Lemnaceae* species (*L. minor* or *L. punctata*) were found to be none or very poor [2,170]. Interestingly, be using Greater duckweed, DEET in the present CW system showed higher removal (up to 32.2 % in CW3). Overall, the average target compounds removal lay in the range of 53.4 % to 79.3 % in batch CW test.

Light effect on PPCP removal was investigated in AT1, AT2 and AT3 (Table 5-2). PAR concentration in this batch test decreased from 15.28 μg/L to 13.45 μg/L with light intensity increasing from 80 to 240 $\mu molm^{-2}s^{-1}$, indicating that photodegradation was one of the mechanisms responsible for PAR elimination. This is in agreement with the findings of Yamamoto et al. (2009) [291] that PAR is photodegradable. TCS removal also increased from 8.8 % to 57.6 % gradually with increased light intensity, and TCS photodegradation agrees well with the findings of Aranami and Readman (2007) [155]. In contrast, DEET demonstrated not to be light sensitive (only 1.2 % removal at highest at light intensity of 240 $\mu molm^{-2}s^{-1}$), supporting its poor degradation from CW1-CW9 in

batch test. In addition, CAF also behaved recalcitrant (7.0 % at highest at light intensity of 160 $\mu molm^{-2}s^{-1}$) under visible light, confirming the findings by Arfanis et al. (2017) [292] and Trovó et al. (2013) [293] who found CAF degradation by photocatalysis or photo-Fenton processes, but not under natural light.

*E.coli'*s effect on target PPCP removal was studied in AT4, AT5 and AT6 (Table 5-2). It is found that *E.coli* biodegradation of PAR was moderately effective (compared with 19.0 % removal without *E.coli* addition) but no significant difference of removal (49.5 % in AT5 and 48.8 % in AT6) was found between the two *E.coli* abundance levels. CAF behaved reluctant under visible light but showed more degradation by using *E.coli* from 3.2 % (AT5) to 46.5 % (AT6) when *E.coli* abundance increased from 1.0×10^4 CFU/100mL to 1.0×10^6 CFU/100mL. *E.coli* also favoured TCS elimination (removal of 73.3~83.8 %). No significant difference between light and *E.coli* effect ($p>0.05$) was found, though 83.8 % removal achieved by *E.coli* (AT6) was higher than the 57.6 % by light (AT3). For DEET, *E.coli'*s effect was found to be weak and the highest removal of 4.5 % was observed in AT6. Generally, biodegradation of PAR, CAF and TCS was suggested as one of degradation mechanisms by other researchers [132,159,294]. The present results show that pure cultures of *E. coli* (ATCC 11775) was capable of degrading the concentration of 25 μg/L target PPCP compounds in this experimental system. Degradation of organics (e.g. phenol) by *E.coli* (e.g. ATCC 33456) and other pure bacterial strains (e.g. ATCC 11172) were observed before [295,296]. In the present study, *E.coli* (ATCC 11775) was found capable of degrading certain PPCP compounds. This suggests to further investigate the biodegradation mechanisms of PPCPs inside cells.

AT7 and CW9 had same experimental conditions and tested factor levels. The only difference was aseptic plants was used in AT7. AT1 was conducted under the same light intensity as AT7 and CW9 while without plants. AT1 showed 0.6 %, 38.9 %, -0.6 % and

11.9 % removal for DEET, PAR, CAF and TCS, respectively, while AT7 (light and aseptic plant) achieved removal of 2.8 %, 91.8 %, 2.9 % and 38.7 % for DEET, PAR, CAF and TCS respectively. Higher removal in AT7 than AT1 indicated that Greater duckweed contributed to removal of the target PPCPs ($p<0.05$), especially PAR (52.9 %) and TCS (26.8 %). Besides, removal of DEET, PAR, CAF and TCS were 7.0 %, 98.3 %, 26.6 % and 81.7 % in CW9, respectively. Removal of AT7 lay within the removal range of CW9 and AT1, indicating that both plants and associated microbes attaching to plants contributed to the PPCP degradation. Generally, roles of plants in CWs include direct uptake of organic contaminants and creation of favourable conditions (e.g. biofilm anchorage) for their removal [28,41]. In addition, studies of planted CWs showing significant better performance than unplanted beds were also reported [35,220]. Good removal in current batch CW system indicated Greater duckweed-based CW is promising in treating contaminants.

5.3.1.2 Orthogonal Duncan analysis

Table 5-3 shows the orthogonal Duncan analysis results for individual target compounds removal. For results, *p* value indicates the significance level of the factor to target variable (removal). Statistical data of each factor shows the influence of each factor level to target variable (removal). A higher value indicates more influence, hence higher removal.

Table 5-3 Duncan analysis results of individual target compound removal for the batch test

DEET				PAR			
Light intensity	low	medium	high	Light intensity	low	medium	high
p=0.208*	0.089**	0.065	0.129	p<0.01	0.969	0.989	0.987
Aeration	none	intermittent	full	Aeration	none	intermittent	full
p<0.01	-0.003	0.116	0.169	p<0.01	0.994	0.984	0.967
E.coli abundance	none	1×10^4	1×10^6	*E.coli* abundance	none	1×10^4	1×10^6
p=0.214	0.061	0.099	0.124	p<0.01	0.974	0.991	0.981
Plant biomass	low	medium	high	Plant biomass	low	medium	high
p<0.01	0.207	0.029	0.046	p<0.01	0.991	0.984	0.969

CAF				TCS			
Light intensity	low	medium	high	Light intensity	low	medium	high
p<0.01	0.647	0.922	0.892	p<0.01	0.924	0.968	0.975
Aeration	none	intermittent	full	Aeration	none	intermittent	full
p<0.01	0.666	0.862	0.933	p<0.01	0.982	0.979	0.996
E.coli abundance	none	1×10^4	1×10^6	*E.coli* abundance	none	1×10^4	1×10^6
p<0.01	0.735	0.817	0.909	p<0.01	0.929	0.957	0.981
Plant biomass	low	medium	high	Plant biomass	low	medium	high
p<0.01	0.678	0.811	0.972	p<0.01	0.939	0.961	0.967

* p, statistical factor significance to the removal of target compound. p>0.05, no significance; p<0.05, significant; p<0.01, highly significant.

** 0.129 (high light intensity) > 0.089 (low light intensity) > 0.065 (medium light intensity), meaning high light intensity level has the best effect on DEET removal compared with the other two levels. A higher value indicates more removal.

For individual PPCP compounds, high light intensity favoured DEET and TCS degradations, while medium light intensity significantly decreased (p<0.01) PAR and CAF concentrations. CAF also achieved the highest removal (7.0 %) under medium light intensity in the AT sets, which was in accordance with the findings from the batch AT tests that medium light intensity favoured CAF degradation most. Except for PAR, the other three compounds were removed under full aeration mostly. Most efficient removal of PAR was without aeration (p<0.01). Oxygen is essential to bioactivity in CW system and usually regarded favouring PPCPs degradation [28]. In present batch test, without aeration, DO concentrations in the water were above 4 mg/L, indicating aerobic conditions and this is in agreement with Jim et al. (2006) [154] who found PAR to be degraded aerobically. As for *E.coli* biodegradation, abundance of 1.0×10^6 CFU/100 mL helped to remove DEET, CAF and TCS considerably. However, 1.0×10^4 CFU/100 mL *E.coli* abundance favoured PAR reduction, confirming the AT set results in Table 5-2 (AT4, AT5 and AT6). As for plant biomass, CAF and TCS were removed most under high level but low level for DEET and PAR. Greater duckweed is a floating plant with leaves spreading on the water surface. More plants on the water surface can reduce photodegradation because of less light penetration. Therefore, it may be assumed that higher removal of DEET and PAR under low plant biomass may be due to higher photodegradation effect. However, high plant biomass favoured CAF and TCS decrease mostly, which may be ascribed to effects of plant uptake and/or plant roots which provide adherent substrate and habitat for microbes to biodegrade organic matters [193].

Table 5-4 presents the results based on average removal of the four PPCP compounds.

Table 5-4 Duncan analysis results of average PPCP removal for the batch test

Average removal in each CW			
Light intensity	low	medium	high
p<0.01*	0.657	0.736	0.746
Aeration	none	intermittent	full
p<0.01	0.637	0.735	0.766
E.coli abundance	none	1×10^4	1×10^6
p<0.01	0.675	0.716	0.748
Plant biomass	low	medium	high
p<0.01	0.696	0.704	0.739

* p, statistical factor significance to the removal of target compound. p>0.05, no significance; p<0.05, significant; p<0.01, highly significant.

From the Table 5-4 above, results of the orthogonal Duncan analysis on average target PPCP compounds removal in each tested CW showed that under the combination of high light intensity, full aeration, high abundance of *E.coli* and high plant biomass, average PPCP removal could significantly increase (p<0.01). Because the removal of the four PPCP compounds in batch test varied a lot and the Duncan analysis on individual target compound removal showed different optimal factor combinations for each compound, in order to balance all PPCP removal and get the best optimum average removal, combined factor levels (240 $\mu molm^{-2}s^{-1}$ light intensity, full aeration, 1.00 kg/m^2 plant biomass and 1.0×10^6 CFU/100 mL *E.coli* abundance) were chosen to be used in following CW tests as the optimal conditions.

5.3.1.3 General water quality parameters

Concentrations and removal of COD, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-} and abundance change (log) of *E.coli* in final treated water of batch test is shown in Table 5-5.

Except for CW 7 (66.8 %), COD removal achieved around 90 % in other batch CWs, indicating good COD removal by the CW system. Ammonium removal varied from 10.6~83.3 % but increased by 55.3 % in CW 6. In CW5 and CW9, nitrate was not detected while removal in other CWs were 30.0~93.1 %. Besides, results showed that phosphate was removed 40.6~80.8 %, but nitrite was found in eight CWs (0.9~16.6 mg/L) and it was not detected in the synthetic wastewater. The increase of nitrite concentration in CW was also observed by Schaafsma et al. (1999) [297]. Although DO concentration indicates aerobic conditions in the water (Appendix 2), presence of nitrite suggests inadequate nitrification, which might have been caused by insufficient nitrobacteria (such as *Nitrobacter*), or due to more intense denitrification converting nitrate to nitrite [298]. *E.coli* abundance increased by 0.9~2.0 orders of magnitude in the final treated wastewater of all CWs, which is not in agreement with published work [299]. This might be due to the fact that a single microbe strain (*E.coli*) was inoculated into the synthetic wastewater, potentially generating a dominant microbial community. Besides, the lack of predators such as protozoa and high COD concentration (300 mg/L) may have favoured *E.coli* proliferation, causing an increase of *E.coli* abundance.

Other general parameters, including pH, conductivity, redox potential and DO, are shown in Appendix 2. DO concentrations in CWs 5, 8 and 9 without aeration decreased in the first three days and then increased to around 6 mg/L again. Oxygen consumption could increase under high organic load [300]. Apart from oxygen's natural diffusion from air to water, some aquatic plants may have the ability to transport oxygen from leaves to

Table 5-5 Concentrations and removal of COD, ammonium, nitrate, phosphate, nitrite and abundance change (log) of *E.coli* in final treated water of batch test.

CW	COD		Ammonium			Nitrate			Phosphate			Nitrite		*E.coli*
	Con(mg/L)	Removal	Con(mg/L)	RSD	Removal	Con(mg/L)	RSD	Removal	Con(mg/L)	RSD	Removal	Con(mg/L)	RSD	Abundance change (log)
1	33	88.9%	10.2	0.9	68.0%	16.8	1.4	30.0%	6.5	0.0	59.3%	5.7	0.5	n.a**
2	30	89.9%	5.3	1.0	83.3%	13.6	0.7	43.4%	3.1	1.1	80.8%	9.3	1.3	n.a
3	36	88.1%	12.1	1.5	62.4%	16.3	0.4	32.0%	4.8	0.2	70.0%	3.1	0.5	+1.8
4	27	91.0%	8.1	1.2	74.6%	16.2	1.4	32.5%	6.0	0.3	62.6%	16.6	0.8	+2.0
5	28	90.8%	15.8	2.5	50.4%	n.d.*	n.a.	100.0%	6.0	1.3	62.4%	0.9	0.1	+0.9
6	51	82.9%	49.5	0.6	-55.3%	3.5	2.4	85.5%	9.6	1.8	40.6%	3.3	0.5	+0.9
7	100	66.8%	15.6	0.6	51.0%	13.5	1.9	43.9%	8.2	1.6	48.9%	5.6	1.0	+1.2
8	31	89.8%	16.9	1.6	47.0%	1.7	0.6	93.1%	5.6	0.5	65.1%	4.7	0.2	+1.2
9	31	89.6%	28.5	1.0	10.6%	n.d.	n.a.	100.0%	6.1	0.1	62.3%	n.d.	n.a.	n.a

Initial concentrations of COD, ammonium, nitrate and phosphate were 300, 32, 24 and 16 mg/L, respectively, no nitrite detected.

* n.d. not detected. ** n.a. not available.

roots, increasing water DO level. Reddy et al. (1990) [301] found that two floating plants (i.e. *Hydrocotyle umbellata L.* and *Eichhornia crassipes*) increased DO concentration up to 6.1 mg/L. It is also found that another *Lemnaceae* species (*Lemna minor*) increased DO concentration during phytoremediation[302]. Hence, Greater duckweed as a floating plant of *Lemnaceae* species may potentially have this ability transporting oxygen.

5.3.2 Batch test verification

Batch test verification test result is shown in Table 5-6 below. Using optimal factor level combination from Duncan analysis of average removal, except for DEET, the other three PPCP compounds achieved more than 90 % removal in the batch verification test. Results showed that Greater duckweed-based CW was effective to remove 98.8 %, 96.4 % and 95.4 % of PAR, CAF and TCS, respectively at the batch scale, but it was less able to remove DEET (17.1 %) and *E.coli* (0.60 order of magnitude increased). In the none-plant control test, removal of DEET, PAR, CAF and TCS were 7.9 %, 84.4 %, 82.4 % and 84.2 %, respectively. AT set test in batch test indicated both plants and associated microbes played a part in eliminating target PPCP compounds (Section 5.3.1). The lower removal from current control test further demonstrates that Greater duckweed played a role in enhancing the removal of the PPCPs by potentially direct uptaking the PPCPs and/or by creating favourable conditions (e.g. biofilm anchorage) for their removal within the system [28,41]. Besides, removal of COD and TOC were 86.0 % and 84.9 %, respectively. Ammonium was not found in the final treated water, which may be attributed to the Greater duckweed ammonia preference uptake [42,43]. 30.0 % of nitrate and 62.0 % of phosphate were also removed, which agree well with other researchers [35,113,216]. Good performance of batch-scale CW test was achieved and suggested

Table 5-6 Concentrations and removal of target PPCP compounds, COD, TOC, ammonium, nitrate, phosphate, nitrite and abundance change (log) of *E.coli* in final treated water for the batch verification test

DEET			PAR			CAF			TCS		
Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal
20.73	1.22	17.1%	0.60	0.02	98.8%	0.91	0.01	96.4%	1.54	0.02	95.4%

DEET (control)			PAR (control)			CAF (control)			TCS (control)		
Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal
23.03	0.09	7.9%	3.90	0.04	84.4%	4.40	0.02	82.4%	3.95	0.04	84.2%

COD		TOC		Ammonium			Nitrate			Nitrite	
Con (mg/L)	Removal	Con (mg/L)	Removal	Con (mg/L)	RSD	Removal	Con (mg/L)	RSD	Removal	Con (mg/L)	RSD
42	86.0%	23	84.9%	n.d.*	n.d.	100%	18.31	0.26	30.0%	16.28	0.26

Phosphate			*E.coli*
Con (mg/L)	RSD	Removal	Abundance change (log)
3.46	0.04	62.0%	0.6

Mixed target compounds were spiked into synthetic wastewater to reach a concentration of 25 μg/L. Initial concentrations of COD, TOC, ammonium, nitrate and phosphate were 300, 150, 27, 26.2 and 9.1 mg/L, respectively, no nitrite detected.

* n.d. not detected.

further continuous flow test to be carried out, which is shown in the following sections.

5.3.3 Continuous tests

5.3.3.1 PPCP removal in continuous flow systems

Dynamic target PPCP concentration changes of continuous CW and CW-ST tests are shown in Figure 5-7. Table 5-7 gives the corresponding concentrations.

The final target compound removal by continuous CW system only were 32.6 %, 97.7 %, 98.0 % and 100 %, respectively, for DEET, PAR, CAF and TCS, compared to 43.3 %, 97.5 %, 98.2 % and 100 %, respectively, in the continuous flow CW-ST system (Table 5-7). As shown in Figure 5-7, the removal of PPCP compounds occurred as soon as the tests started in both systems. While DEET was present at the highest concentration in all samples, PAR and TCS concentrations decreased much quicker than DEET and CAF, demonstrating that PAR and TCS were easier to be removed by both continuous flow CW and CW-ST systems than the other two PPCP compounds. Although DEET concentrations decreased slowly with time, maximum removal was below 45 % (CW-ST system), confirming that DEET was recalcitrant from the batch experiments. The lowest DEET concentrations were 16.85 μg/L (day 26) in the continuous flow CW system and 14.17 μg/L (day 26) in the continuous flow CW-ST. When aeration stopped at day 17, DEET concentrations both increased from 21.82 μg/L to 23.65 μg/L in the continuous flow CW and from 16.37 μg/L to 18.17 μg/L in the continuous flow CW-ST, then declined again in two systems. In contrast, PAR and TCS removal did not show significant changes. CAF concentration in the continuous flow CW test fluctuated between 9.19 and 12.89 μg/L (day 17 to 22) then declined quickly to 1.11 μg/L. However, no increase of CAF concentration occurred in the CW-ST, and this may be attributed to

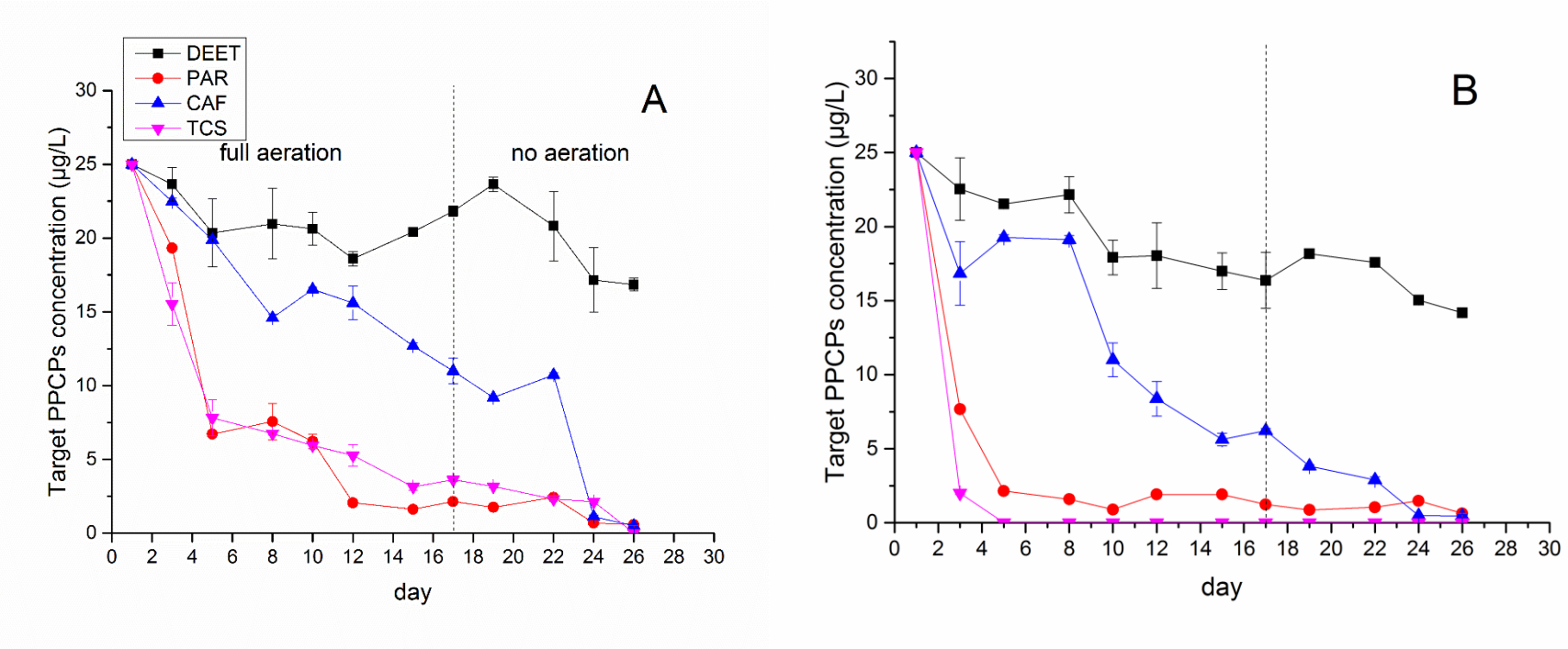

Figure 5-7 Concentrations of target PPCP compounds in the final treated water by (A) the continuous flow CW and (B) continuous flow CW-ST systems (day 1 to 17, full aeration; day 17 to 26, no aeration)

Table 5-7 Concentrations of target PPCP compounds in the continuous flow CW & CW-ST systems

Day	DEET				PAR				CAF				TCS			
	Continuous CW		Continuous CW with ST		Continuous CW		Continuous CW with ST		Continuous CW		Continuous CW with ST		Continuous CW		Continuous CW with ST	
	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD
1	25.00	0.00	25.00	0.00	25.00	0.00	25.00	0.00	25.00	0.00	25.00	0.00	25.00	0.00	25.00	0.00
3	23.64	1.12	22.53	2.11	19.33	0.12	7.67	0.14	22.48	0.23	16.84	2.14	15.53	1.45	2.00	0.10
5	20.35	2.30	21.53	0.18	6.71	0.14	2.15	0.13	19.88	0.14	19.27	0.18	7.81	1.21	n.d. *	n.a. **
8	20.97	2.40	22.15	1.23	7.56	1.23	1.59	0.01	14.59	0.23	19.12	0.28	6.75	0.11	n.d.	n.a.
10	20.64	1.12	17.91	1.17	6.21	0.47	0.90	0.08	16.53	0.14	11.00	1.14	5.93	0.23	n.d.	n.a.
12	18.60	0.48	18.04	2.21	2.05	0.09	1.91	0.08	15.60	1.15	8.38	1.17	5.26	0.74	n.d.	n.a.
15	20.42	0.25	16.99	1.23	1.61	0.02	1.91	0.09	12.69	0.19	5.62	0.42	3.13	0.21	n.d.	n.a.
17	21.82	0.36	16.37	1.89	2.14	0.11	1.24	0.12	10.99	0.86	6.22	0.15	3.62	0.11	n.d.	n.a.
19	23.65	0.47	18.17	0.07	1.74	0.11	0.87	0.01	9.19	0.12	3.82	0.09	3.16	0.09	n.d.	n.a.
22	20.82	2.36	17.59	0.24	2.42	0.02	1.04	0.02	12.89	0.13	2.89	0.21	2.30	0.01	n.d.	n.a.
24	17.16	2.18	15.04	0.11	0.68	0.18	1.49	0.03	1.11	0.11	0.48	0.02	2.13	0.10	n.d.	n.a.
26	16.85	0.45	14.17	0.10	0.58	0.04	0.63	0.02	0.50	0.13	0.46	0.11	n.d.	n.a.	n.d.	n.a.

Mixed target compounds were spiked into synthetic wastewater to reach a concentration of 25 μg/L

* n.d. not detected. ** n.a. not available.

the stable biodegradation in the ST tank as CAF is oxygen sensitive (orthogonal Duncan analysis result) and air oxygen may have continuously diffused into ST tank water from day 17 when aerators were turned off and removed. Oxygen may also be potentially transported from Greater duckweed leaves to roots, then into water. The sudden lack of oxygen could change the biotope of CW system, thus influencing the PPCP removal [28,303]. However, ANOVA analysis of the PPCP removal in CW and CW-ST systems both showed no significant differences (p>0.05) with and without aeration, indicating that the CW and CW-ST systems were robust enough to remove 25 μg/L of PPCP compounds in current system when the operational conditions changed.

As for the comparison of target compounds removal in two continuous systems, DEET concentrations in both systems did not decrease as quickly as the other three compounds (p<0.05). From day 12, DEET removal was higher in the continuous flow CW-ST system than those in the continuous flow CW until the end of the test. On the other hand, PAR concentrations in CW-ST system decreased quickly from 25 μg/L (day 1) to 0.90 μg/L (day 10) then fluctuated until the end of test. In contrast, PAR concentration in the continuous CW system did not show rapid decrease (p<0.05), but results from both systems showed no significant difference from day 12 to the end of the test (p>0.05). Compared to the other three compounds, except for day 8, CAF concentrations in both systems decreased more linearly with time but were higher in the CW system than in the CW-ST system. At day 26, CAF concentrations in both systems were below 0.5 μg/L. TCS concentration in CW-ST system decreased from 25 μg/L (day 1) to 0 (day 5) and then no TCS was detected in the following samples, probably due to the existence of ST tank which allowed more light penetration into the water for further TCS photodegradation [155]. For the continuous CW system, TCS concentrations decreased to 7.81 μg/L (day 5), and were eliminated gradually until day 26 when no

detectable amount was found. By using ANOVA test, removal of the four PPCP target compounds were significantly faster in the CW-ST system (p<0.05) than in the CW system only.

In CW and CW-ST systems, the total water volume (14 litres) and the HRT (7 days) were the same. However, the better removal of the target PPCP compounds occurred in the system with the adjunction of ST tank, which suggests that the use of ST tank not only ensured more direct light penetration for photodegradation process but also compensated the inadequate removal in the CW tank potentially caused by halving the HRT, and allowed more oxygen diffusion from air into ST tank water for biodegradation process. In the batch verification test, CW test achieved higher removal than control none-plant test (Section 5.3.2). Hence, current CW-ST system gives an optimal performance.

5.3.3.2 General water quality parameters

COD and TOC concentrations are shown in Table 5-8. ANOVA-test showed both COD and TOC degraded significantly faster in the CW-ST system (p<0.05) than in the CW system. When aeration stopped (day 17), both COD and TOC in two systems increased first and decreased again. The final concentrations of COD and TOC from the CW-ST treated water were 32 mg/L and 13 mg/L (at removal of 89.3 % and 91.3 %, respectively), compared to 62 mg/L and 22 mg/L (at removal of 79.3 % and 85.3 %, respectively) from CW system only.

Table 5-8 Concentrations and removal of COD and TOC in the continuous flow CW & CW-ST systems

Day	COD				TOC			
	Continuous CW		Continuous CW-ST		Continuous CW		Continuous CW-ST	
	Con (mg/L)	Removal	Con (mg/L)	Removal	Con (mg/L)	Removal	Con (mg/L)	Removal
1	300	0.0%	300	0.0%	150	0.0%	150	0.0%
3	288	3.9%	300	0.1%	107	28.5%	132	11.9%
5	215	28.3%	117	61.0%	79	47.3%	29	80.8%
8	76	74.7%	74	75.3%	18	88.1%	14	90.6%
10	82	72.6%	70	76.6%	33	78.2%	29	81.0%
12	131	56.4%	66	77.9%	51	66.2%	24	84.3%
15	65	78.2%	23	92.3%	27	82.0%	9	94.3%
17	69	76.9%	33	89.0%	43	71.3%	19	87.2%
19	174	41.9%	71	76.4%	64	57.6%	24	84.3%
22	205	31.7%	47	84.4%	89	40.7%	9	93.9%
24	106	64.8%	49	83.7%	37	75.6%	19	87.7%
26	62	79.4%	32	89.3%	22	85.2%	13	91.2%

Concentrations of NO_2^-, NO_3^-, NH_4^+, PO_4^{3-} and abundance change (log) of *E.coli* are shown in Table 5-9. Continuous flow CW system (up to 100 %) presented a higher ammonium removal than CW-ST (up to 96.2 %) and ammonium removal increased from day 10 to the last day (51.6 % to 100 %), probably because of the Greater duckweed's ammonia preference uptake and longer contact time. As an intermediate compound of nitrification and denitrification, nitrite in the continuous CW system varied greatly during the test period, with the final nitrite concentration at 6.4 mg/L. Nitrite was also present in

the CW-ST system since day 7 and from day 10, nitrite concentration declined gradually with time until 100 % removal was achieved. What is more, nitrate concentration in both two tested systems decreased at first and then increased but declined sharply after switching off the aerators. This may be explained by the fact that under anoxic condition, denitrification can be active, transforming nitrate to nitrite, then to nitrogen [304]. Both CW and CW-ST systems showed removal of phosphate within the range of 33~70 %. Phosphate concentrations declined in the first few days and then varied between 3 to 6 mg/L. This result agrees well with Lin et al. (2002) [305] who found phosphate removal of 32 % to 71 % in CW system only. The final concentrations of ammonium, nitrate and phosphate were higher in continuous CW-ST system than CW system, but the differences were all within 10 %. Besides, *E.coli* abundance in the final treated wastewater increased 0.5 order of magnitude in both continuous flow systems, due to the similar reason under batch tests (Section 5.3.1).

Table 5-9 Concentrations and removal of ammonium, nitrate, phosphate, nitrite and abundance change (log) of *E.coli* in the continuous flow CW & CW-ST systems

Day	Ammonium						Nitrate					
	Continuous CW			Continuous CW-ST			Continuous CW			Continuous CW-ST		
	Con (mg/L)	RSD	Removal	Con (mg/L)	RSD	Removal	Con (mg/L)	RSD	Removal	Con (mg/L)	RSD	Removal
1	27.0	0.0	0.0%	27.0	0.0	0.0%	26.0	0.0	0.0%	26.0	0.0	0.0%
3	n.d.	0.0	100.0%	2.1	0.6	92.1%	8.1	0.1	68.8%	3.9	0.0	85.0%
5	0.2	0.0	99.2%	16.1	0.2	40.3%	14.8	0.7	43.0%	1.4	0.0	94.8%
8	12.5	0.8	53.8%	13.4	0.4	50.3%	13.6	0.1	47.9%	n.d.	n.a.	100.0%
10	13.1	0.3	51.6%	1.8	0.0	93.2%	19.9	0.5	23.5%	3.0	0.0	88.5%
12	1.6	0.0	93.9%	2.3	0.1	91.4%	19.4	0.2	25.3%	7.6	0.2	70.9%
15	0.8	0.1	96.9%	2.8	0.1	89.6%	17.3	0.2	33.4%	10.0	0.1	61.5%
17	1.0	0.0	96.5%	1.0	0.1	96.2%	18.0	0.5	30.6%	12.7	0.0	51.2%
19	0.1	0.0	99.7%	4.8	1.0	82.1%	1.1	0.2	95.6%	5.4	0.0	79.2%
22	n.d. *	n.a. **	100.0%	12.4	0.2	54.2%	1.7	0.4	93.6%	3.4	0.1	87.0%
24	n.d.	n.a.	100.0%	2.6	0.4	90.5%	1.0	0.3	96.1%	4.8	0.2	81.7%
26	n.d.	n.a.	100.0%	2.6	0.2	90.2%	1.1	0.0	96.0%	2.6	0.1	89.8%

Day	Phosphate						Nitrite				*E.coli*	
	Continuous CW			Continuous CW-ST			Continuous CW		Continuous CW-ST		Continuous CW	Continuous CW-ST
	Con (mg/L)	RSD	Removal	Con (mg/L)	RSD	Removal	Con (mg/L)	RSD	Con (mg/L)	RSD	Abundance change (log)	
1	9.0	0.0	0.0%	9.0	0.0	0.0%	n.d.	n.a.	n.d.	n.a.	0.0	0.0
3	5.4	0.0	39.8%	5.1	0.0	43.3%	6.5	0.8	n.d.	n.a.	1.7	1.5
5	3.5	0.0	61.5%	5.8	0.3	35.2%	1.8	0.0	n.d.	n.a.	1.5	1.0
8	3.7	0.1	58.5%	6.0	0.3	33.3%	1.0	0.0	2.3	0.0	0.3	0.7
10	4.7	0.1	47.3%	4.7	0.2	47.6%	3.6	0.2	4.6	0.0	0.7	0.7
12	4.1	0.8	54.3%	4.5	0.0	49.7%	3.3	0.8	2.4	0.0	1.0	0.3
15	2.9	0.0	68.3%	5.0	0.1	44.9%	0.8	0.1	1.5	0.0	1.5	1.2
17	4.4	0.0	50.9%	5.3	0.1	40.6%	2.7	0.1	1.2	0.1	1.2	1.1
19	4.2	0.5	53.1%	5.5	0.2	38.5%	2.7	0.2	1.6	0.0	1.3	1.3
22	4.7	0.1	47.3%	6.3	0.9	30.5%	5.6	0.0	0.7	0.1	1.0	0.3
24	3.9	0.2	57.1%	4.5	1.4	50.5%	0.5	0.1	0.4	0.1	0.3	0.3
26	4.0	0.3	55.4%	4.7	0.1	47.8%	6.4	0.0	n.d.	n.a.	0.5	0.5

* n.d. not detected. ** n.a. not available.

Other general parameters monitored during systems operation, including pH, conductivity, redox potential and DO, are shown in Appendix 3. In CW-ST system, with aeration, DO concentration in the CW tank was higher than in the ST tank for the first 17 days. When aeration stopped, DO concentration in both continuous flow CW systems dropped to below 1 mg/L (anaerobic/anoxic condition), while DO in the ST tank remained above 2 mg/L and reached a stable value around 6 mg/L (day 22) when exchange equilibrium of oxygen between air and water achieved. DO concentrations in all tanks (CWs and ST) increased after day 22, and the ST tank presented the highest DO concentration (> 6 mg/L), suggesting that DO was being consumed more in the CW system. Since DO is essential for aquatic bioactivity, the addition of a ST tank to the CW can compensate the lack of DO in the CW tank potentially.

5.3.4 Correlation analysis

Correlation analysis between removal of parameters was carried out. Correlations between removal of target PPCP compounds and COD, TOC, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-} in continuous flow systems are shown in Table 5-10 below:

Table 5-10 Pearson's R values and *p* values in concentration correlation analysis between target PPCP compounds and COD, TOC, ammonium, nitrite, nitrate and phosphate in continuous flow CW & CW-ST systems

			COD	TOC	Ammonium	Nitrite	Nitrate	Phosphate
CW system	DEET	Pearson's R	0.651*	0.694*	0.466	-0.125	0.348	0.622*
		p value	0.022	0.012	0.126	0.699	0.267	0.031
	PAR	Pearson's R	0.770**	0.794**	0.683*	-0.088	0.451	0.832**
		p value	0.003	0.002	0.014	0.784	0.141	0.001
	CAF	Pearson's R	0.680*	0.684*	0.524	-0.115	0.679*	0.543
		p value	0.015	0.014	0.080	0.722	0.015	0.068
	TCS	Pearson's R	0.767**	0.818**	0.727**	-0.225	0.554	0.859**
		p value	0.004	0.001	0.007	0.482	0.062	3.4E-04
CW-ST system	DEET	Pearson's R	0.820**	0.739**	0.731**	-0.141	0.334	0.714**
		p value	0.001	0.006	0.007	0.662	0.289	0.009
	PAR	Pearson's R	0.821**	0.875**	0.712**	-0.355	0.819**	0.841**
		p value	0.001	1.9E-04	0.009	0.257	0.001	0.001
	CAF	Pearson's R	0.746**	0.674*	0.697*	-0.056	0.323	0.643*
		p value	0.005	0.016	0.012	0.864	0.306	0.024
	TCS	Pearson's R	0.707*	0.776**	0.748**	-0.302	0.853**	0.874**
		p value	0.010	0.003	0.005	0.340	4.2E-04	2.0E-04

* $p<0.05$, significant correlations

** $p<0.01$, highly significant correlations

It can be seen that both COD and TOC concentrations showed significant relationships ($p<0.05$) with all target PPCPs. COD correlated highly significantly ($p<0.01$) to PAR and TCS in the continuous flow CW system (R=0770, 0.767; $p=0.003$, 0.004 for PAR and TCS, respectively), and in the continuous flow CW-ST system. Also,

COD showed a significant relationship with DEET, PAR and CAF (R=0.820, 0.821, 0.746; p=0.001, 0.001, 0.005, respectively). Similar results were also found for TOC which showed a significant relationship with PAR and TCS in the continuous flow CW system (R=0.794, 0.818; p=0.002, 0.001, respectively), and DEET, PAR and TCS in the continuous flow CW-ST system (R=0.739, 0.875, 0.776; p=0.006, 1.9E-04, 0.003, respectively). Significant correlations (p<0.05) were also found between PPCPs and COD/TOC by Yoon et al. (2010) [6] and Wang et al. (2012) [306]. Compared with COD and TOC, nitrogen ions had weak correlation with the PPCPs. Ammonium concentrations only correlated to PAR and TCS in the continuous flow CW system while it had correlations with all four targets in the CW-ST system, having strongest correlations with DEET, PAR and TCS (p<0.01). Matamoros et al. (2007) [33] also observed significant positive correlations between ammonium and PPCPs in a vertical flow CW at pilot scale. Nitrate only correlated with CAF in the continuous flow CW (R=0.679; p=0.015), but PAR and TCS correlated more significantly with nitrate in the continuous flow CW-ST system (R=0.819, 0.853; p=0.001, 4.2E-04). However, nitrite concentrations fluctuated in both systems and no significant correlations were found between the four target compounds and nitrite (p>0.05). (Wang et al. (2015) [307] evaluated 28 PPCPs in urban river water samples and found most of them had positive correlations (p<0.05) with total nitrogen and total phosphorus concentrations. Chen et al. (2016) [221] also found positive correlations (p<0.05) between PPCPs with ammonium and phosphate in rural wastewater treatment wetlands. In this study, phosphate concentrations also showed a positive and significant correlation with the PPCPs, except for with CAF in the continuous CW system (R=0.001; p=0.068).

Apart from the correlations between target PPCP compounds and nutrients, correlations within target compounds removal were also investigated. Results are shown in Table 5-11.

Table 5-11 Pearson's R values and *p* values in concentration correlation analysis between target PPCP compounds in continuous flow CW & CW-ST systems

			DEET	PAR	CAF	TCS
CW system	DEET	Pearson's R	1	0.705*	0.717**	0.706*
		p value	n.a. ***	0.011	0.009	0.010
	PAR	Pearson's R	0.705*	1	0.784**	0.979**
		p value	0.011	n.a.	0.003	3.0E-08
	CAF	Pearson's R	0.717**	0.784**	1	0.806**
		p value	0.009	0.003	n.a.	0.002
	TCS	Pearson's R	0.706*	0.979**	0.806**	1
		p value	0.010	3.0E-08	0.002	n.a.
CW-ST system	DEET	Pearson's R	1	0.704*	0.953**	0.626*
		p value	n.a.	0.011	2.0E-06	0.030
	PAR	Pearson's R	0.704*	1	0.665*	0.981**
		p value	0.011	n.a.	0.018	2.1E-08
	CAF	Pearson's R	0.953**	0.665*	1	0.599*
		p value	2.0E-06	0.018	n.a.	0.040
	TCS	Pearson's R	0.626*	0.981**	0.599*	1
		p value	0.030	2.1E-08	0.040	n.a.

* $p<0.05$, significant correlations

** $p<0.01$, highly significant correlations

*** n.a. not available

Results showed all four target PPCP compounds had significant correlations with each other (p<0.05) statistically, having PAR the strongest correlation (R=0.979; p=3.0E-08) with TCS in the continuous flow CW system, and DEET with CAF (R=0.953; p=2.0E-06) in the continuous flow CW-ST system. Padhye et al. (2014) [308] carried out a study in an urban drinking water treatment plant and found a strong correlation (R=0.97) between PPCPs and endocrine disrupting chemicals, which demonstrated potential relations among micropollutant concentrations. Correlations between pharmaceuticals (carbamazepine and primidone, R^2 = 0.90) in drinking water sources were also reported by Guo and Krasner (2009) [309].

From the correlation analysis, significant relationships were found. Hence it can be assumed that removal of these contaminants may have similar degradation pathways and target PPCP compounds may also be used as carbon source. However, as removal of contaminants is associated with chemical property, treatment conditions and removal preference (e.g. ammonia for duckweed), statistical correlation does not always indicate "causal relationship" and mechanisms behind the correlations need further investigation [221].

5.4 Summary

Greater duckweed based laboratory-scale CW was used for degrading DEET, PAR, CAF and TCS at 25 μg/L in synthetic wastewater. Orthogonal design was used for the batch experiment planning.

- DEET was recalcitrant in the batch test. Based on the orthogonal Duncan analysis result, 240 $\mu molm^{-2}s^{-1}$ light intensity, full aeration, 1.00 kg/m^2 plant biomass and 1.0×10^6 CFU/100 mL *E.coli* abundance favoured the degradation of the PPCP

compounds (on average removal) in batch systems. Further batch verification test achieved 17.1 %, 98.8 %, 96.4 % and 95.4 % removal for DEET, PAR, CAF and TCS, respectively.

- In continuous flow systems, final PPCP removal achieved by the CW-ST system were 43.3 %, 97.5 %, 98.2 % and 100 % for DEET, PAR, CAF and TCS, respectively, compared to 32.6 %, 97.7 %, 98.0 % and 100 %, respectively, by the CW system. PPCP removal by the CW-ST system were significantly faster (p<0.05) than those by the single CW unit. Both continuous flow systems (CW and CW-ST) demonstrated treatment stability after aerators were switched off. Oxygen was considered an important factor in the CW performance and the lack of oxygen could be compensated by the addition of a ST tank downstream the CW tank.
- Correlation analysis showed a number of significant correlations (p<0.05) between PPCP compounds and general water parameters removal (e.g. COD, nitrate, phosphate), as well as between the four target compounds, in both continuous flow CW and CW-ST systems.
- COD and TOC concentrations were also better reduced in the CW-ST system. Removal of other nutrients varied in both continuous systems. However, high abundance of bacteria and insufficient removal (below 45 %) of DEET indicated further investigation is needed.

CHAPTER 6 REMOVAL OF SELECTED PPCPS USING GAC SANDWICH SLOW SAND FILTRATION

6.1 Introduction

In this chapter, the efficiency of the removal of the target PPCP compounds by GAC sandwich slow sand filter has been investigated. In the continuous CW test, good removal have been achieved. However, poor DEET removal, presence of nitrite and high abundance of microbes indicated incompleteness of the treatment and additional follow-up treatment is needed. Therefore, further slow sand filtration was carried out to improve the removal and novel technique, that is GAC sandwich SSF, was tried. In current experiment, three GAC sandwich SSFs using coarse sand were constructed with different GAC layer depths. In order to compare GAC sandwich filter performance with conventional filters, single medium filters with sand and GAC were also built. Their effectiveness in removing DEET, PAR, CAF and TCS was studied at different filtration rates, namely 5 cm/h, 10 cm/h and 20 cm/h. The adsorption kinetics and isotherms of DEET, PAR, CAF and TCS onto GAC were also investigated to give a deeper insight into GAC adsorption mechanisms.

6.2 Experiment

6.2.1 Chemicals and materials

Recipe of synthetic wastewater is shown in Table 3-7. Mixed PPCP solution (1 mg/mL) was added into the wastewater to reach a final concentration of 25 μg/L. A new synthetic wastewater solution was prepared every day. Acrylic columns have internal

diameter of 54 mm. General parameters of coarse sand and GAC are shown in Table 3-5. GAC particle was characterised by Brunauer–Emmett–Teller and Scanning Electron Microscopy. The surface area of GAC was about 556 m^2/g with microporous (<2 nm), mesoporous (2~50 nm) and macroporous (>50 nm) accounting for 80.0 %, 10.4 % and 9.6 % of the total pores, respectively (Figure 6-1).

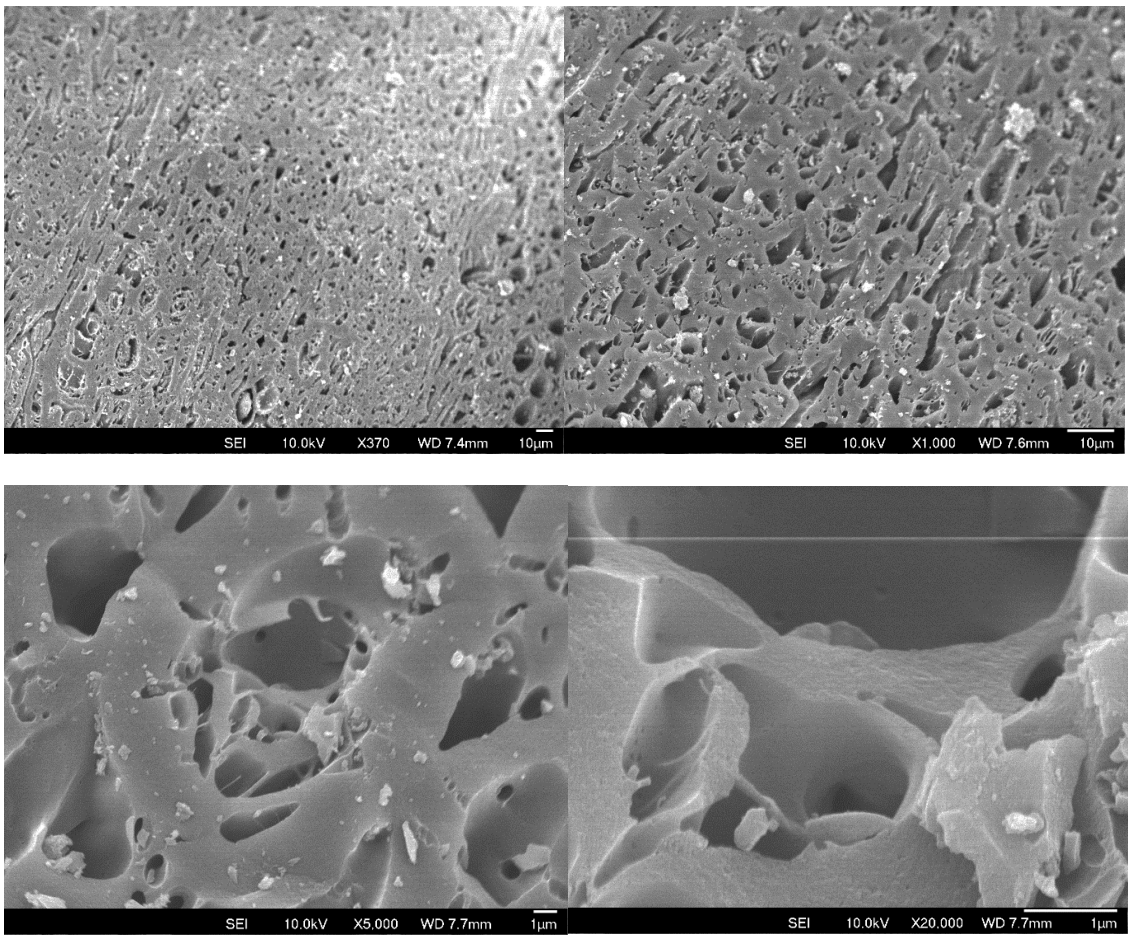

Figure 6-1 Scanning electron microscopy of GAC

(Top left: × 370 fold; top right: × 1,000 fold; bottom left × 5,000 fold; bottom right × 20,000 fold)

Infrared spectra analysis showed no specific functional groups existed on surface of GAC. Treatment of filtration media is shown in Section 3.9. Gravels (2~5 mm) used as supporting medium were also washed before use.

6.2.2 Filtration description and experiment design

Five filter columns were built, having each filter a total height of 65 cm with 3 cm of gravels and filter media depth of 50 cm. Overflow pipe was installed 5 cm above the filter media and effluent pipe was located 1 cm from the bottom. The effluent pipe had one valve to control the filtration rate. Filters were marked as number 1 to 5, which contained different media as respectively: 50 cm sand; 10 cm sand/10 cm GAC/30 cm sand; 10 cm sand/20 cm GAC/20 cm sand; 10 cm sand/30 cm GAC/10 cm sand; 50 cm GAC. Peristaltic pump was used to add synthetic wastewater into the filters. Influent tank was cleaned, and sample storage bottles were sterilized by 70 % alcohol every day. A schematic representation of the experiment arrangement is shown in Figure 6-2. Photo of the apparatus is shown in Figure 6-3.

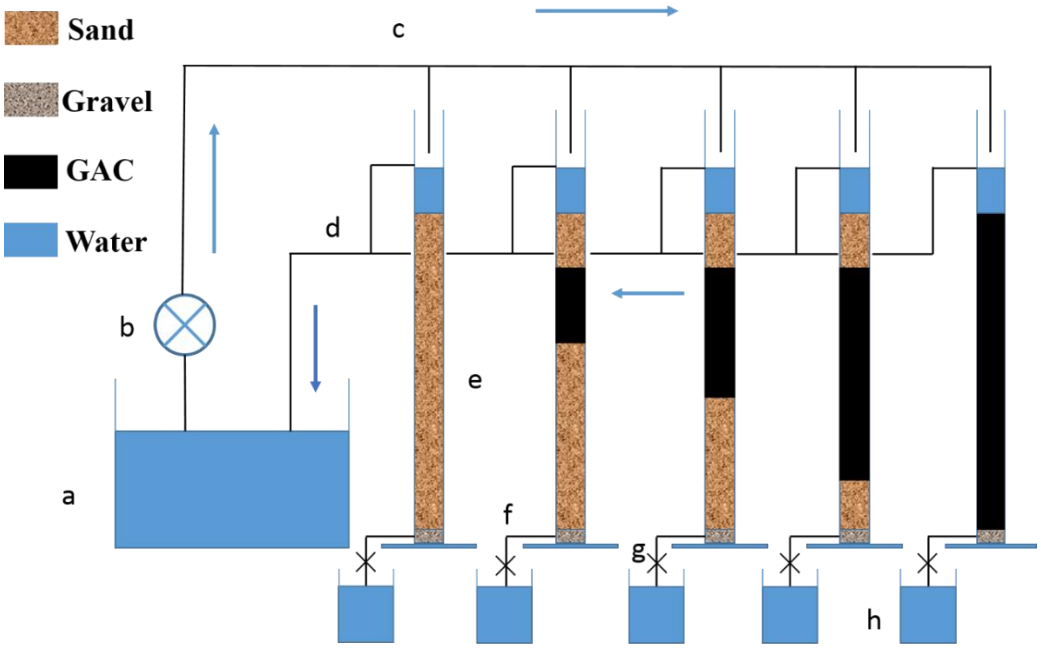

Figure 6-2 Schematic representation of the GAC sandwich SSF experiment.

(a) influent tank; (b) peristaltic pump; (c) influent pipe; (d) overflow pipe; (e) filter; (f) effluent pipe; (g) effluent valve; (h) effluent bottle.

Figure 6-3 Photo of the filtration experimental apparatus

This study was carried out in the Environmental Engineering Laboratory at UCL. Lake water from Regent's Park (London, United Kingdom) which had on average turbidity < 2 NTU and coliform and *E.coli* abundance around 7.6×10^3 and 1×10^2 CFU/100mL, respectively, was collected and stored in room temperature (around 23 ℃), and used for filter maturation before tests started. To evaluate the maturation period of the filters, effluent samples were initially collected on Mondays, Wednesdays and Fridays for the turbidity and total coliforms and *E.coli* abundance determinations. M-ColiBlue24® method was employed to determine total coliforms and *E.coli* abundance (method 10029,

USEPA). Slow sand filters reach maturation when turbidity of effluent is less than 1 NTU and removal of both total coliforms and *E.coli* are larger than 99 %, which took around 3 weeks in current study [310]. Photos of M-ColiBlue24® method at the beginning and end of filter maturation stage are shown in Appendix 4.

When filters were matured, synthetic wastewater contaminated with target PPCP compounds (25 μg/L) was filtered through the five filters. Three filtration rates, i.e. 5 cm/h, 10 cm/h and 20 cm/h, were tested successively without media cleaning. Although SSF filtration rate is usually recommended between 10 cm/h to 30 cm/h [40], 5 cm/h was also tested to explore whether target PPCP compounds could be removed maximally at lower filtration rate. Filtration rates of five filters were monitored twice a day and adjusted if needed. Influent flow rate was set at 20 mL/min, supernatant water level was maintained at 5 cm above media, and duration of each filtration run was 3 weeks for all filtration rates. Water temperature was around 23 ℃ constantly.

Replicate samples were collected twice a week, on Tuesdays and Fridays, for quantification of the target PPCP compounds, NO_2^-, NO_3^-, NH_4^+ and PO_4^{3-}, in the effluent. Also, pH, conductivity and redox potential of effluents were measured along with these samples. COD and TOC were determined once a week. Total headloss was also measured at the end of the test.

6.2.3 GAC adsorption kinetics and isotherms

As adsorption is the one of main mechanisms for removal of organics in wastewater treatment [311], adsorption kinetics of the four target PPCP compounds on GAC were determined to further explain the adsorption mechanisms. 0.500g GAC was placed in ten 500 mL glass bottles, respectively. Each glass bottle was filled with 500 mL synthetic wastewater spiked with 25 μg/L mixed target compound solution. Bottles were placed in

a rotary mixer (designed and manufactured by the workshop of the department) at the speed of 30 rpm. They were taken off from the mixer at 5 min, 10 min, 20 min, 30 min, 60 min, 120 min, 180 min, 300 min, 420 min and 660 min as recommended by Cao et al. (2013) and Kumar (2006a) [312,313].

For the adsorption isotherms, 10 mg, 30 mg, 50 mg, 100 mg, 200 mg, 300 mg, 400 mg and 500 mg GAC were placed in eight 500 mL glass bottles, respectively. 500 mL synthetic wastewater spiked with 25 μg/L mixed target compound solution was added in each bottle. Glass bottles were placed in the rotary mixer at the speed of 30 r/min. After 5 hours, bottles were removed down and triplicate samples were prepared for further treatment. Replicate samples preparation followed the analytical procedure.

6.2.4 Statistical analysis

ANOVA tests were carried out to assess the difference significance between sample concentrations and p-value < 0.05 was considered statistically significant. OriginPro 9.1 was used to develop all graphs. The data processing was conducted by Microsoft Excel 2013.

6.3 Results and discussion

6.3.1 Overview of the PPCP removal

Average removal of DEET, PAR, CAF and TCS are summarized in Table 6-1. The concentrations of DEET, PAR, CAF and TCS in the effluents of the five filters at each sampling day are shown in Table 6-2.

Table 6-1 Summary of average removal for individual and total PPCP compounds during the filtration process

Compound	Filtration rate*		Filter 1	Filter 2	Filter 3	Filter 4	Filter 5
DEET	5 cm/h	Average removal (%)	36.0	97.9	97.7	98.1	98.3
	10 cm/h	Average removal (%)	23.3	95.6	98.0	97.5	97.1
	20 cm/h	Average removal (%)	18.8	97.9	99.4	98.2	98.3
	Total average DEET (%)		25.7	97.2	98.4	98.0	97.9
PAR	5 cm/h	Average removal (%)	98.2	100	97.0	89.6	84.7
	10 cm/h	Average removal (%)	77.6	100	100	100	100
	20 cm/h	Average removal (%)	70.3	100	100	100	100
	Total average PAR (%)		81.4	100	99.1	96.7	95.2
CAF	5 cm/h	Average removal (%)	19.8	100	100	100	99.8
	10 cm/h	Average removal (%)	29.7	99.8	100	99.6	99.7
	20 cm/h	Average removal (%)	26.4	100	100	100	100
	Total average CAF (%)		25.3	99.9	100	99.9	99.8
TCS	5 cm/h	Average removal (%)	57.1	100	94.3	89.0	83.9
	10 cm/h	Average removal (%)	85.2	88.6	94.8	89.2	94.2
	20 cm/h	Average removal (%)	80.3	91.1	90.6	92.1	92.2
	Total average TCS (%)		74.2	93.2	93.2	90.1	90.1
Total average PPCPs at 5 cm/h (%)			52.8	99.5	97.3	94.2	91.7
Total average PPCPs at 10 cm/h (%)			53.9	96.0	98.2	96.6	97.8
Total average PPCPs at 20 cm/h (%)			48.9	97.3	97.5	97.6	97.6
Total average PPCPs for whole tests (%)			51.9	97.6	97.7	96.2	95.7

* Operation period for each filtration rate was three weeks.

Table 6-2 Concentrations of target PPCP compounds in the effluents during the filtration process

Filtration rate	DEET	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
	Day	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD
5 cm/h	2	16.07	1.01	0.56	0.01	0.60	0.01	0.64	0.11	0.55	0.01
	5	17.42	0.24	0.95	0.02	1.20	0.02	0.80	0.04	0.59	0.12
	9	18.04	0.15	0.40	0.01	0.52	0.04	0.32	0.03	0.42	0.02
	12	14.90	0.46	0.38	0.00	0.45	0.08	0.43	0.10	0.35	0.03
	16	15.38	1.21	0.48	0.04	0.35	0.09	0.31	0.02	0.29	0.04
	19	14.14	0.15	0.35	0.03	0.32	0.00	0.29	0.01	0.31	0.01
	Average	15.99	0.54	0.52	0.02	0.57	0.04	0.47	0.05	0.42	0.04
10 cm/h	23	17.56	0.26	1.04	0.10	0.47	0.00	0.76	0.04	1.18	0.01
	26	16.13	0.24	1.11	0.01	0.29	0.11	1.02	0.08	0.17	0.02
	30	18.76	0.45	1.10	0.11	0.28	0.02	0.21	0.00	0.88	0.07
	33	19.38	0.17	1.21	0.01	0.28	0.03	1.01	0.10	0.38	0.02
	37	21.82	1.56	1.11	0.00	1.41	0.20	0.35	0.00	1.32	0.10
	40	21.39	1.21	1.10	0.00	0.32	0.00	0.37	0.01	0.37	0.01
	Average	19.17	0.65	1.11	0.04	0.51	0.06	0.62	0.04	0.72	0.04
20 cm/h	44	21.23	0.12	0.90	0.02	0.21	0.00	1.28	0.08	0.80	0.02
	47	18.52	0.23	0.15	0.00	0.14	0.01	0.85	0.10	0.16	0.04
	51	18.99	0.24	0.60	0.04	0.10	0.01	0.18	0.00	0.15	0.01
	54	19.36	0.12	0.26	0.00	0.19	0.01	0.15	0.01	0.73	0.02
	58	21.75	0.56	0.62	0.01	0.12	0.02	0.07	0.00	0.67	0.03
	61	21.91	0.99	0.58	0.02	0.11	0.01	0.14	0.00	0.11	0.01
	Average	20.29	0.38	0.52	0.02	0.15	0.01	0.45	0.03	0.44	0.02
Total average DEET		18.49	0.52	0.72	0.02	0.41	0.04	0.51	0.04	0.52	0.03

Filtration rate	PAR	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
	Day	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD
5 cm/h	2	2.71	0.11	n.d.	n.a.	4.50	0.51	6.22	0.25	4.64	0.63
	5	n.d.*	n.a.**	n.d.	n.a.	n.d.	n.a.	5.42	0.42	5.11	0.12
	9	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	4.02	0.12	4.25	0.07
	12	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	4.52	0.23
	16	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	4.47	0.41
	19	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	0.45	0.02	n.d.	n.a.	0.75	0.09	2.61	0.13	3.83	0.24
10 cm/h	23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	26	5.98	0.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	30	6.70	0.14	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	33	7.88	0.86	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	37	5.46	0.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	40	7.61	0.31	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	5.61	0.30	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
20 cm/h	44	7.19	0.22	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	47	6.58	0.47	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	51	8.09	0.48	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	54	7.25	0.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	58	7.46	0.11	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	61	8.03	0.03	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	7.43	0.26	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
Total average PAR		4.50	0.19	n.d.	n.a.	0.25	0.03	0.87	0.04	1.28	0.08

Filtration rate	CAF	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
	Day	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD
5 cm/h	2	19.70	1.21	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	5	22.92	1.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	9	17.11	1.01	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	12	22.10	0.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.25	0.01
	16	20.35	0.85	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	19	18.20	0.47	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	20.06	0.83	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.04	0.00
10 cm/h	23	20.76	0.66	0.25	0.04	n.d.	n.a.	0.27	0.04	0.26	0.02
	26	17.28	0.97	n.d.	n.a.	n.d.	n.a.	0.38	0.01	0.20	0.03
	30	16.72	0.41	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	33	14.46	0.21	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	37	14.53	0.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	40	21.80	1.11	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	17.59	0.60	n.d.	n.a.	n.d.	n.a.	0.11	0.01	0.08	0.01
20 cm/h	44	20.54	1.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	47	19.25	1.45	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	51	17.15	0.11	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	54	17.23	0.03	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	58	17.52	0.78	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	61	18.79	0.01	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	18.41	0.60	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
Total average CAF		18.69	0.68	0.01	0.00	n.d.	n.a.	0.04	0.00	0.04	0.00

Filtration rate	TCS	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
	Day	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD	Con (μg/L)	RSD
5 cm/h	2	13.62	1.22	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	2.30	0.20
	5	15.12	0.14	n.d.	n.a.	n.d.	n.a.	2.71	0.74	11.01	1.45
	9	13.49	1.10	n.d.	n.a.	5.77	0.41	3.13	0.43	2.50	0.03
	12	13.12	0.56	n.d.	n.a.	2.76	0.21	3.38	0.23	4.49	0.23
	16	3.98	0.11	n.d.	n.a.	n.d.	n.a.	3.88	0.74	2.28	1.41
	19	5.00	0.11	n.d.	n.a.	n.d.	n.a.	3.38	1.01	1.63	0.03
	Average	10.72	0.54	n.d.	n.a.	1.42	0.10	2.75	0.53	4.04	0.56
10 cm/h	23	9.13	0.41	8.92	1.21	1.29	0.03	8.83	1.20	1.31	0.02
	26	2.72	0.06	1.10	0.01	1.24	0.09	1.06	0.03	1.16	0.14
	30	2.21	0.07	1.37	0.01	1.28	0.10	1.06	0.01	n.d.	n.a.
	33	2.24	0.12	1.62	0.04	1.46	0.01	1.26	0.00	2.54	0.02
	37	2.18	0.02	1.82	0.01	n.d.	n.a.	1.72	0.00	1.72	0.15
	40	3.70	0.04	2.21	0.11	2.51	0.31	2.32	0.04	2.01	0.11
	Average	3.70	0.12	2.84	0.23	1.30	0.09	2.71	0.21	1.46	0.07
20 cm/h	44	5.27	0.06	2.30	0.14	2.08	0.04	2.15	0.02	1.70	0.02
	47	3.44	0.21	2.24	0.21	1.97	0.01	1.73	0.01	1.92	0.01
	51	4.36	0.18	1.85	0.07	2.04	0.18	1.95	0.01	2.12	0.14
	54	3.71	0.04	2.60	0.09	2.03	0.11	2.10	0.21	2.16	0.17
	58	6.34	0.01	2.10	0.13	2.13	0.21	1.90	0.07	1.96	0.03
	61	6.44	0.07	2.28	0.11	3.84	0.22	2.02	0.02	1.91	0.04
	Average	4.93	0.10	2.23	0.13	2.35	0.13	1.98	0.06	1.96	0.07
Total average TCS		6.45	0.25	1.69	0.12	1.69	0.11	2.48	0.27	2.48	0.23

Mixed target compounds were spiked into synthetic wastewater to reach a concentration of 25 μg/L

* n.d. not detected ** n.a. not available

As shown in Table 6-1, total average removal of the four target compounds during the whole test were 51.9 %, 97.6 %, 97.9 %, 96.2 % and 95.7 % for Filters 1-5, respectively. No average target PPCPs removal difference was found between at 5 cm/h and 10/20 cm/h filtration rates (p>0.05). GAC sandwich filters (Filters 2-4) achieved noticeable higher removal than conventional slow sand filter (Filter 1) and total average removal of each compound were all above 90 %. DEET removal has been significantly improved compared with using Greater duckweed-based constructed wetland (< 45 %, Chapter 5). Good removal results found in present study indicate the applicability of GAC sandwich SSF for removing the target PPCPs. Details and discussion of individual compound are presented below.

6.3.2 Comparison of filter performance on target PPCPs removal

6.3.2.1 Diethyltoluamide

Highest DEET effluent concentrations were found in Filter 1 (coarse sand only), ranging between 14.14 to 21.91 μg/L (Table 6-2, removal between 14.4 % and 43.4 %). By contrast, the effluent concentrations of DEET from the other four filters were all below 2.00 μg/L (removal higher than 94 %), achieving significantly better removal than that in Filter 1 (p<0.05). ANOVA test showed Filter 3 (10 cm sand/20 cm GAC/20 cm sand) presented the best performance for DEET removal than the other four filters (p<0.05). DEET is usually regarded as a recalcitrant [2,7] hydrophobic compound, but it can be biodegraded theoretically [41]. However, in the CW tests, it showed very limited biodegradation of DEET by Greater Duckweed in laboratory-scale. Thus, the low DEET removal in Filter 1 (sand only) indicates biodegradation in the sand filter and *schmutzdecke* was not effective even at low filtration rate of 5 cm/h. High removal of

DEET by Filters 2 to 5 suggest that the use of GAC in current study could significantly help increase removal performance, which is in accordance with the high DEET removal (100 %) found with GAC (surface area not specified) by Lin et al. (2016) [314].

6.3.2.2 Paracetamol

GAC-associated filters achieved significantly higher removal than Filter 1 ($p<0.05$) but no significant difference was found among the three sandwich filters ($p>0.05$). PAR was not detected in Filter 2 effluent during whole experimental period and it was only detected in the effluents of Filter 3 and Filter 4 during the first few days after maturation (Table 6-2). However, in Filter 5, PAR was found in the first 16 days while it disappeared from day 17, even when filtration rate was increased. Nonetheless, PAR was detected in Filter 1 (sand only) at day 2, then no detection occurred for a while, and from day 26, it was detected again until the end of the run, fluctuating from 5.46 (78.2 % removal) to 8.09 μg/L (67.6 % removal) (Table 6-2). These values are slightly larger than the findings (65.2 % highest removal) of Pompei et al. (2016) [32] who used a finer sand grain with effective size of 0.210 mm to remove a small PAR concentration of 2 μg/L from natural lake water by household SSF. Roberts and Thomas (2006) [132] investigated PAR removal in a WWTP and found its biodegradation by activated sludge to be effective. In the present work, it can be suggested that PAR elimination can occur by both biodegradation as demonstrated by Filter 1 and adsorption by GAC (Filter 5). Zhao et al. (2015) [159] treated 60 μg/L triclosan by constructed wetland and found triclosan-biodegradation bacteria abundance increased 9.36~31.37 %. Thus, it can be speculated that during the first few days of filtration process, PAR-preference microbes within SSF may thrive with contact of PAR and PAR elimination accelerated, as shown by Filters 1, 3 and 4.

6.3.2.3 Caffeine

No significant CAF removal difference was found between the four GAC-associated filters (p>0.05) but it was significantly higher than sand alone Filter 1 (p<0.05). CAF was not found in the effluent of Filter 3 during the whole experiment. CAF in effluents was observed in one sampling day (day 23) of Fiter 2 and two sampling days in Filter 4 and Filter 5 (days 23 and 26), all below 0.50 μg/L (Table 6-2). The sudden occurrence of CAF in effluents may be ascribed to the change of filtration rate, which is discussed in Section 6.3.3. Rizzo et al. (2015) [46] investigated the removal of CAF by conventional sand filtration coupling with graphene adsorption reactor (GAR, 890 m^2/g surface area) at flow rate of 4.4~5.3 mL/min and found 98.2 % of removal, having GAR adsorption played the most important role. More than 80 % removal of CAF was also found by using biological activated carbon filter (surface area not specified) [315]. Although CAF is regarded easily biodegraded [294,316], it was detected in all treated water samples of Filter 1 (only sand) with concentrations fluctuating between 14.46 and 22.92 μg/L (Table 6-2, removal from 8.3 % to 42.2 %), suggesting biodegradation in Filter 1 was not capable of removing CAF at 25 μg/L thoroughly in this study. Results also confirm that CAF can be adsorbed (Filters 2~5) with Filter 3 showing the highest efficiency of removal.

6.3.2.4 Triclosan

Compared to other three compounds, TCS behaved more recalcitrant. It was detected in all effluent samples of Filter 1, concentrations ranging from 2.21 to 15.12 μg/L (Table 6-2, removal from 91.3 % to 39.5 %). From day 23, TCS was detected in effluent samples of Filter 2 until the end of the filtration test. It was also detected in majority of the other three filters: 13 out of 18 sampling days of Filter 3, and 17 out of 18 sampling days of Filters 4 and 5. Rossner et al. (2009) [317] found 99.5 % TCS removal using coconut-

shell-based GAC CC-602 with surface area of 1160 m^2/g which is double than the GAC used in our work (i.e. 556 m^2/g). Although TCS removal in GAC-associated filters varied, the overall TCS removal of Filters 2, 3, 4 and 5 showed no significant difference statistically ($p>0.05$), but it was significantly different from Filter 1 ($p<0.05$). Generally photodegradation is regarded an important TCS elimination mechanism and biodegradation of TCS has been reported elsewhere [155,318]. In the present filtration systems, visible light was directly affecting the supernatant water layer and surrounding the filtration columns which were transparent. This may indicate that the removal of TCS in Filter 1 may have been by photo-biodegradation in the supernatant layer [319]. However, relatively low TCS concentrations in GAC-associated filter effluents indicated this compound can also be adsorbed by GAC.

In the present study, Filter 3 achieved overall highest removal and use of GAC significantly ($p<0.05$) enhanced removal performance compared to traditional SSF (Filter 1). At same filtration rate, more GAC volume ensures more adsorption time between GAC and contaminants. However, removal of target compounds using GAC sandwich filters in this experiment were not proportional with the GAC volume. Our results agree well with Feng et al. (2012) [320] who also found no direct proportion between contaminant removal and adsorption time. Also, Paredes et al. (2016) [255] used GAC contactors to remove PPCPs at different empty bed contact time but no direct correlations were found between organic pollutants and contact time, and influence of other factors including biological activity and loading rates were suggested as main causes.

6.3.3 Target PPCPs removal at different filtration rates

Comparisons of dynamic concentration changes of DEET, PAR, CAF and TCS during filtration process are shown in Figure 6-4 below:

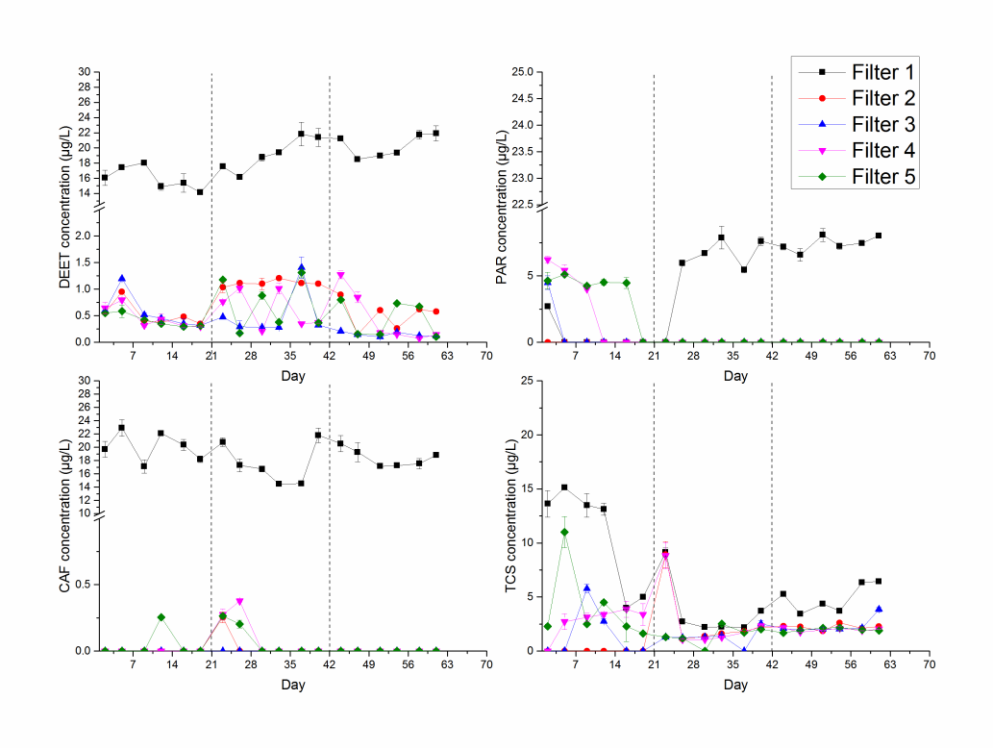

Figure 6-4 Comparisons of dynamic concentration changes of target PPCP compounds during the filtration process.

(day 1 to day 21, filtration rate at 5 cm/h; day 22 to day 42, filtration rate at 10 cm/h; day 43 to day 63, filtration rate at 20 cm/h)

From Figure 6-4, as expected, effluent concentrations of DEET in all five filters increased when filtration rate rose from 5 cm/h to 10 cm/h [244]. When filtration rate rose to 20 cm/h, effluent concentrations of DEET continued increasing in Filters 4 and 5, but dropped in Filter1, 2 and 3. However, despite the increase in effluent concentration when switching to two faster filtration rates, DEET concentrations did not increase considerably.

PAR was not detected at filtration rates of 10 cm/h and 20 m/h in all GAC-associated filters. However, at 10 cm/h, PAR was detected in Filter 1 at average concentration of 5.98 μg/L and rose to average 7.43 μg/L when filtration rate increased to 20 cm/h. This

demonstrated that Filter 1 (sand only) was not capable of efficiently removing 25 μg/L PAR at filtration rate faster than 10 cm/h, while GAC helped improving the filter efficiency considerably (p<0.05).

CAF was present in all effluent samples of Filter 1 and its concentration increased from 18.20 μg/L (day 19 at 5 cm/h) to 20.76 μg/L (day 23 at 10 cm/h) but interestingly did not increase when filtration rate rose to 20 cm/h (day 44). Also, CAF concentration in Filter 1 fluctuated with increase in filtration rate, but it was kept on average 17~20 μg/L. However, in the other filters, CAF only appeared when filtration rates were increased, then declined to zero again, which may be attributed to release/desorption effect when hydraulic pressure suddenly changed [46].

Compared to the other three compounds, TCS showed more resistance in GAC-associated filters. It was found in all effluent samples of Filter 1 (only sand) and Filter 5 (only GAC) at filtration rate of 5 cm/h, but the use of combination of sand and GAC showed a better TCS removal performance (p<0.05). When filtration rate changed to 10 cm/h, TCS effluent concentrations increased first (except for Filter 5 with only GAC) and decreased quickly again. No significant TCS removal difference (p>0.05) was found between 10 cm/h and 20 cm/h, although Filter 3 and Filter 5 achieved the highest average removal at these filtration rates (94.8 % and 92.2 %, respectively).

From the results above, it can be assumed that in GAC sandwich SSF system, the removal of target PPCPs may be due to both adsorption by the GAC layer (as shown by Filter 5) and biodegradation within the *schmutzdecke* and upper sand layer (as shown by Filter 1), and these are in accordance with Escolà Casas and Bester (2015) [31]. Apart from biodegradation, bio-sorption process such as electrostatic attraction and adhesion may also contribute to the removal of target compounds [239]. During the first few weeks, microbes within the *schmutzdecke* and upper sand layer may thrive gradually [40],

favouring the target PPCPs removal. When the filtration rate increased, the decline of PPCP removal by Filter 1 (only sand) could be ascribed to short contact time [321] and release/desorption effect [46]. But the subsequent decrease of PPCP concentrations within several days in GAC-associated filters suggests a fast system adaption to filtration rate changes (Table 6-2).

At 5 cm/h, Filter 2 achieved the highest average removal at 99.5 %, but the average PPCP removal in the other four filters at 5 cm/h were lower than at higher filtration rates (Table 6-1). Filter 3 achieved the highest average PPCP removal (i.e. 98.2 %) at 10 cm/h, but no significant difference was found between filtration rates of 10 and 20 cm/h for the three GAC sandwich filters (p>0.05). Hence, 5 cm/h is not recommended in the SSF process and 10~20 cm/h can be applied based on practical situation. In addition, the fluctuation of PPCP and high concentrations in the effluent of Filter 1 indicate that filter with coarse sand only (effective size of 0.6 mm) was not effective enough to remove PPCP (25 μg/L) in the present study. Reungoat et al. (2011) [254] studied pilot-scale WWTP filters and found that biosand filters showed limited PPCP removal and that biological activated carbon (BAC, 1,146 m^2/g surface area) removed 90 % of PPCP concentration. In the present study, GAC improved the PPCP compound removal but the average removal of Filter 5 (95.7 %, only GAC) was lower than that in Filter 2 (97.6 %), 3 (97.7 %) and 4 (96.2 %) (Table 6-1). Thus, our results suggest that biological activity within the *schmutzdecke* and upper sand layer of the sandwich filter have also played an important role for the target PPCP removal. Also, it can be suggested that the use of GAC in SSF could compensate both the inadequacies of single sand and GAC filters, and the GAC sandwich SSF could be a more appropriate option.

6.3.4 General parameters during filtration

The COD and TOC concentrations of the effluents in each filter are shown in Table 6-3.

Table 6-3 COD and TOC concentrations in the water effluent during the filtration tests

Week	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)
1	10	5.6	8	4.5	8	2.0	9	3.4	25	7.9
2	22	4.7	20	7.3	20	3.3	22	5.0	24	15.1
3	21	5.1	14	2.3	18	0.3	21	1.9	26	9.3
4	16	6.0	17	3.4	15	2.0	19	4.3	19	6.4
5	12	4.8	12	5.9	11	1.3	15	5.5	17	5.4
6	15	1.5	13	3.6	10	1.0	14	4.7	15	0.6
7	12	1.0	15	4.3	13	0.9	13	6.1	16	4.8
8	15	0.7	16	3.8	15	0.1	12	4.2	17	2.1
9	13	1.4	15	0.4	13	0.4	12	3.7	18	5.4

The initial concentrations of COD and TOC were 40 and 20 mg/L, respectively.

Concentrations of COD and TOC of influent synthetic wastewater were at 40 mg/L and 21±1 mg/L, respectively. The average removal of COD for the five filters were 62.2 %, 63.9 %, 65.8 %, 62.9 % and 50.8 %, respectively (Filters 1 to 5). TOC average removal were 84.5 %, 81.4 %, 90.3 %, 76.2 % and 68.3 %, respectively (Filters 1 to 5). Filter 3 (10 cm sand/20 cm GAC/20 cm sand) showed the best average removal for both COD and TOC. TOC removal was found to be around 50 % using GAC contactors [322]. Bauer et al. (1996) [48] found TOC removal from surface water in large scale GAC sandwich SSF around 30~40 % and on average 20 % in control slow sand filter. As glucose was used as carbon source to prepare the synthetic wastewater in the present study, higher TOC removal could be due to the fact that it is more degradable than other organics (e.g. humic substances) in real natural water [323,324].

The concentrations of NO_2^-, NO_3^-, NH_4^+ and PO_4^{3-} are shown in Table 6-4. Effluent pH was around 7.5~8.5, which lay within the range of discharge standards (6.5~8.5) reported by WHO-EM/CEH/142/E. Other general water parameters are shown in Appendix 5. Total headloss of all filters were below 2.0 cm during the whole experiment. No nitrite was detected except on only a few days. It was only found at the beginning of filtration run in Filter 2, and in 3 out of 18 sampling days in Filter 5. During the whole test, average removal of 97.7 %, 97.4 %, 99.7 %, 100 % and 99.9 % for nitrate and 92.5 %, 93.8 %, 95.1 %, 94.1 % and 94.5 % for ammonium were achieved in Filters 1 to 5, respectively, indicating very good nitrate and ammonium removal by all filters from synthetic wastewater. Ammonium was just detected at 5 cm/h and during the first few days of 10 cm/h. The highest concentration reached to 0.76 mg/L and exceed 0.5 mg/L limit suggested by EU Drinking Water Directive (98/83/EC). Adsorption of ammonium onto GAC and sand, and nitrate onto GAC were observed by Paredes et al. (2016) [255]. Besides, nitrification and denitrification can occur simultaneous in sand filtration and higher DO level transferred into the sand bed with faster filtration rates tend to enhance nitrification process [248]. So, it can be suggested that higher filtration rates (10 and 20 cm/h) promoted nitrification process transforming ammonium to nitrate. Denitrification microbes could therefore denitrify nitrate to nitrite, then to nitrogen [325]. Hence, apart from relatively low efficiency (no significant difference between 5 and 10/20 cm/h filtration rate on average target PPCP removal, Section 6.3.1), the presence of ammonium at slow filtration rates in the present study suggests inapplicability of filtration rate of 5 cm/h. Besides, due to Huisman and Wood (1974) [239], lower filtration rate of (e.g. 5 cm/h) may also result in unpleasant tastes and odours.

Table 6-4 Nitrite, nitrate, phosphate and ammonium concentrations in the effluents during the filtration tests

Nitrite	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
Day	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
2	n.d.*	n.a.**	1.18	0.24	n.d.	n.a.	n.d.	n.a.	1.50	0.31
5	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
9	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
12	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
16	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
19	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
26	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
30	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.20	0.02
33	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
37	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
40	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
44	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
47	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
51	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
54	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
58	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
61	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.08	0.02

Nitrate	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
Day	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
2	10.25	0.39	11.26	0.22	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
5	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
9	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
12	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
16	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
19	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
26	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
30	n.d.	n.a.	n.d.	n.a.	0.25	0.08	n.d.	n.a.	n.d.	n.a.
33	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
37	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
40	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
44	0.86	0.10	n.d.	n.a.	0.30	0.01	0.07	0.01	0.67	0.03
47	n.d.	n.a.	n.d.	n.a.	0.86	0.11	n.d.	n.a.	n.d.	n.a.
51	2.00	0.48	2.16	0.01	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
54	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
58	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
61	n.d.	n.a.	1.14	0.09	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.

Phosphate	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
Day	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
2	5.43	0.08	6.21	0.06	5.04	0.18	6.20	0.11	4.59	0.00
5	4.76	0.34	6.55	0.47	7.07	0.47	6.76	0.67	5.55	0.20
9	6.22	0.88	6.23	0.52	5.65	0.32	6.65	0.34	6.18	0.12
12	6.43	0.84	5.98	0.43	6.61	0.35	6.65	0.13	6.72	0.39
16	4.81	0.29	5.85	0.69	6.27	0.40	5.17	0.73	4.62	0.00
19	7.53	0.52	7.19	0.68	6.96	0.00	7.34	0.79	7.44	0.84
23	7.68	0.00	6.89	0.00	6.00	0.07	7.26	0.00	6.96	0.00
26	6.50	0.19	6.95	0.03	7.00	0.08	7.09	0.08	7.30	0.41
30	5.51	0.22	4.70	0.05	6.41	0.06	6.89	0.11	6.72	0.04
33	6.41	0.14	6.29	0.16	6.48	0.02	6.98	0.11	6.98	0.00
37	6.26	0.07	6.04	0.26	6.17	0.18	6.54	0.24	7.03	0.05
40	6.46	0.05	6.33	0.20	6.20	0.15	6.53	0.08	6.99	0.12
44	7.04	0.47	6.94	0.47	5.75	0.17	7.41	0.00	7.55	0.33
47	6.73	0.12	6.44	0.69	6.66	0.11	6.82	0.39	6.62	0.24
51	5.94	0.69	6.17	0.43	6.66	0.23	6.29	0.19	6.27	0.31
54	6.48	1.09	6.01	0.06	6.92	0.11	5.91	0.55	7.04	0.09
58	6.08	0.01	6.30	0.39	6.61	0.19	7.31	0.07	8.41	0.25
61	6.05	0.33	6.22	0.31	6.41	0.23	6.45	0.25	6.41	0.19

Ammonium	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
Day	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
2	0.43	0.01	1.00	0.02	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
5	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.76	0.02	0.22	0.02
9	0.31	0.04	0.43	0.11	0.39	0.04	0.42	0.01	0.27	0.05
12	0.42	0.01	n.d.	n.a.	0.23	0.02	0.34	0.05	0.51	0.02
16	0.37	0.14	0.40	0.16	0.51	0.03	0.37	0.04	0.53	0.01
19	0.49	0.04	0.41	0.05	0.49	0.01	0.21	0.01	0.32	0.01
23	0.32	0.03	0.55	0.10	0.58	0.06	0.58	0.09	0.57	0.02
26	0.28	0.08	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
30	0.35	0.01	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
33	0.43	0.11	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
37	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
40	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.04	0.01
44	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
47	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
51	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
54	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
58	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
61	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.

Initial concentrations of nitrate, phosphate and ammonium were 31.4, 7.2 and 2.5 mg/L, respectively.

* n.d. not detected ** n.a. not available

Compared to nitrogen compounds, average phosphate removal were much lower, at 13.3 %, 12.6 %, 11.4 %, 7.2 % and 7.9 % for Filters 1 to 5, respectively. Without any chemical dosing, up to 35 % total phosphorus removal was achieved by biological aerated filters [250]. Altmann et al. (2016) [47] found 80 % removal of phosphorus by a GAC (surface area not specified, upper layer)-sand (lower layer) filter for WWTP secondary effluent treatment but ferric chloride was added into the influent as coagulant. As biological activity mainly exists in the *schmutzdecke* and upper layer of the filter [40], microbial activity of building cell lipid bilayer using phosphorous may not be quick enough for efficient phosphate consumption. The low phosphate removal in the present study suggests other phosphate treatment processes (e.g. biological, coagulation, aeration) may be required.

Overall, for N and P removal, no significant difference (p>0.05) was found between filtration rates of 10 cm/h and 20 cm/h.

6.3.5 Kinetics of target PPCP compounds adsorption onto GAC

From Table 6-2, it can be seen that adsorption played an important role in the removal of the target PPCP compounds investigated in this study. Thus, to further understand the removal mechanisms, adsorption kinetics of the four target PPCP compounds at 25 μg/L onto GAC were investigated. Figure 6-5 shows the adsorption capacity (μg/mg) of the four target compounds by GAC within 660 min.

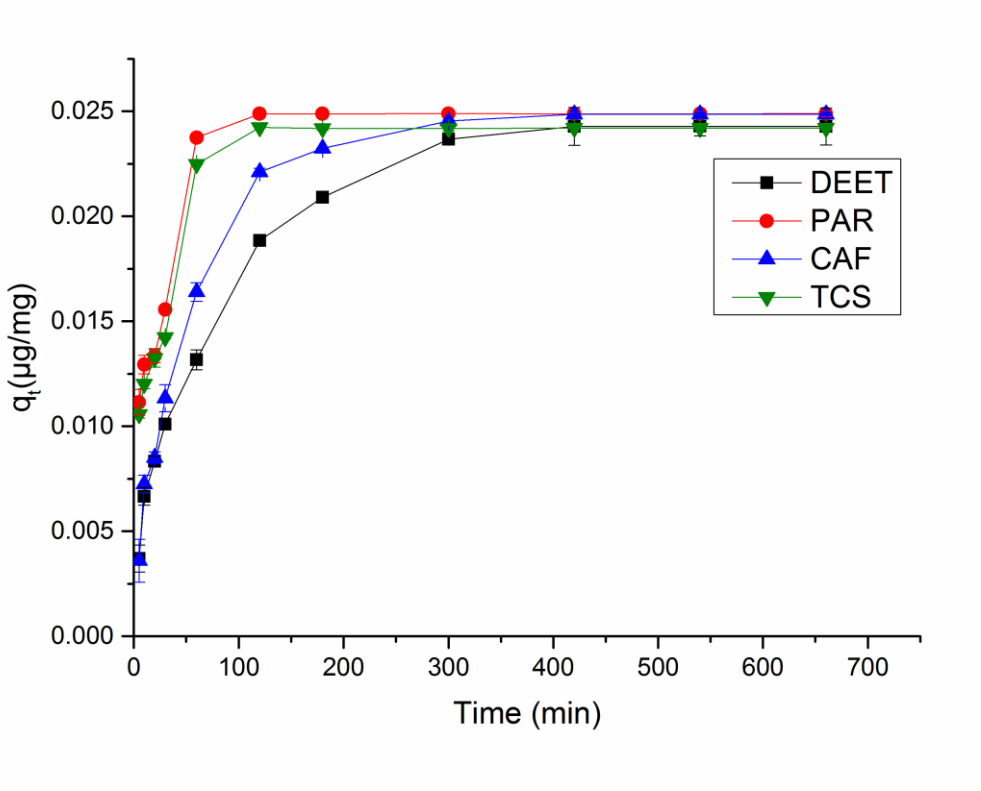

Figure 6-5 Adsorption kinetic plots of target PPCP compounds on GAC.

(Adsorption conditions: water temperature = 23 ℃; initial DEET, PAR, CAF and TCS concentration = 25 μg/L; GAC dose = 1 g/L)

At around 120 min, adsorption of PAR and TCS reached equilibrium, while DEET and CAF reached equilibrium at about 300 min. Maximum adsorption capacity was 0.025 μg/mg. From Figure 6-5, experimental adsorption capacity (q_e, Exp) of DEET, PAR, CAF and TCS about 0.0243, 0.0249, 0.0249 and 0.0242 μg/mg were read, respectively. Further kinetic modelling of the adsorption process of four target PPCP compounds onto GAC were carried out using Lagergren pseudo-first-order, pseudo-second-order and Elovich equations. These three models have been widely applied to describe the adsorption kinetics of pollutants from water onto adsorbents [312,326,327].

For Lagergren pseudo-first-order equation:

$$\frac{dq_t}{dt} = k_{p1}(q_e - q_t) \quad \text{(E. 7-1)}$$

Which can be rearranged to:

$$\log(q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303}t \quad \text{(E.7-2)}$$

Where *q*e and *qt* (μg/mg) are the adsorption capacities at equilibrium and time *t* (min), respectively. k_{p1} (min^{-1}) is the pseudo-first-order constant for this kinetic model.

For pseudo-second-order equation:

$$\frac{dq_t}{dt} = k_{p2}(q_e - q_t)^2 \quad \text{(E.7-3)}$$

Pseudo-second-order equation has different variations and based on the study of Kumar (2006) [328], five linear forms were chosen:

$$\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{1}{q_e}t \qquad (type\ 1) \quad \text{(E.7-4)}$$

$$\frac{1}{q_t} = \left(\frac{1}{k_{p2}q_e^2}\right)\frac{1}{t} + \frac{1}{q_e} \qquad (type\ 2) \quad \text{(E.7-5)}$$

$$\frac{1}{t} = \frac{k_{p2}q_e^2}{q_t} - \frac{k_{p2}q_e^2}{q_e} \qquad (type\ 3) \quad \text{(E.7-6)}$$

$$\frac{q_t}{t} = k_{p2}q_e^2 - \frac{k_{p2}q_e^2 q_t}{q_e} \qquad (type\ 4) \quad \text{(E.7-7)}$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_{p2}t \qquad (type\ 5) \quad \text{(E.7-8)}$$

and

$$V_0 = k_{p2}q_e^2 \quad \text{(E.7-9)}$$

Where *q*e and *qt* (μg/mg) are the adsorption capacities at equilibrium and time *t* (min), respectively. k_{p2} (mg/μg·min) is the pseudo-second-order constant for the kinetic model. V_0 (μg/mg·min) means the initial adsorption rate [329].

For Elovich equation [330]:

$$\frac{dq_t}{dt} = ae^{-\alpha q_t} \quad \text{(E.7-10)}$$

Which can be rearranged to:

$$q_t = \alpha \ln(a\alpha) + \alpha \ln t \quad \text{(E.7-11)}$$

Where q_t represents the amount of pollutants adsorbed at time *t*, *a* the desorption constant (μg/mg.min), and α the initial adsorption rate (mg/μg) [312,331,332].

Table 6-5 summarizes the fitted parameters of kinetic models of Lagergren pseudo-first-order and Elovich equations for adsorption of DEET, PAR, CAF and TCS onto GAC. The correlation coefficients (R^2) for the fitted Lagergren pseudo-first-order equation were 0.9511, 0.8652, 0.9459 and 0.5594 for DEET, PAR, CAF and TCS, respectively. Calculated q_e values were 0.0207, 0.7752, 0.0154 and 0.0037 μg/mg for DEET, PAR, CAF and TCS, compared to the experimental q_e at 0.0243, 0.0249, 0.0249 and 0.0242 μg/mg (Figure 6-5). For Elovich equation, the R^2 values of the fitted models for DEET, PAR CAF and TCS were 0.9796, 0.8542, 0.9582 and 0.8642, respectively. Usually these two equations describe diffusion and chemical adsorption models [333,334]. In present study, the calculated q_e and R^2 varied significantly, indicating Lagergren pseudo-first-order and Elovich equations not fit.

Table 6-5 Parameters for the kinetic models of Lagergren pseudo-first-order and Elovich equations for adsorption of target PPCP compounds on GAC

		Pseudo-first order equation			Elovich equation		
Compound	q_e, Exp (μg/mg)	q_e, Cal (μg/mg)	k_{p1} (min^{-1})	R^2	a (μg/(mg·min))	α (mg/μg)	R^2
DEET	0.0243	0.0207	0.0122	0.9511	78.27	0.0047	0.9796
PAR	0.0249	0.7752	1.7966	0.8652	2196.18	0.0032	0.8542
CAF	0.0249	0.0154	0.0111	0.9459	90.54	0.0048	0.9582
TCS	0.0242	0.0037	0.0076	0.5594	1689.36	0.0032	0.8642

Parameters of kinetic models of pseudo-second-order equation (five types) for adsorption of DEET, PAR, CAF and TCS on GAC are shown in Table 6-6.

Table 6-6 Parameters of kinetic models of pseudo-second-order equation for adsorption of target PPCP compounds on GAC

	DEET				PAR			
Type	q_e, Cal (μg/mg)	k_{p2} (mg/(μg·min))	V_0 (μg/(mg·min))	R^2	q_e, Cal (μg/mg)	k_{p2} (mg/(μg·min))	V_0 (μg/(mg·min))	R^2
1	0.0261	0.9338	6.361E-04	0.9983	0.0254	4.3645	2.816E-03	0.9994
2	0.0220	1.8149	8.784E-04	0.9806	0.0233	6.6209	3.594E-03	0.8061
3	0.0223	1.6410	8.985E-04	0.9806	0.0249	4.6707	2.896E-03	0.8061
4	0.0236	1.2585	7.009E-04	0.8961	0.0261	3.8167	2.600E-03	0.7377
5	-0.0002	82.701	3.308E-06	0.8005	0.0001	106.32	1.063E-06	0.5715
	CAF				TCS			
Type	q_e, Cal (μg/mg)	k_{p2} (mg/(μg·min))	V_0 (μg/(mg·min))	R^2	q_e, Cal (μg/mg)	k_{p2} (mg/(μg·min))	V_0 (μg/(mg·min))	R^2
1	0.0264	1.2081	8.420E-04	0.9990	0.0247	4.0913	2.496E-03	0.9994
2	0.0253	1.3310	8.520E-04	0.9833	0.0219	7.1407	3.425E-03	0.7892
3	0.0246	1.3211	7.995E-04	0.9833	0.0238	4.7731	2.704E-03	0.7892
4	0.0268	1.1119	7.986E-04	0.9282	0.0247	3.7652	2.297E-03	0.7005
5	-4.41E-05	45.163	8.763E-08	0.8466	0.0004	15.732	2.676E-06	0.4276

q_e, Exp (μg/mg) of DEET, PAR, CAF and TCS are 0.0243, 0.0249, 0.0249 and 0.0242 μg/mg, respectively

Among the five models, model Type 1 gave the best fitting level as R^2 values for DEET, PAR, CAF and TCS were 0.9983, 0.9994, 0.9990 and 0.9994, with corresponding calculated q_e of 0.0261, 0.0254, 0.0264 and 0.0247 μg/mg, respectively, which were much closer to the experimental q_e values than Lagergren pseudo-first-order fitted models. In the case of TCS, only Type 1 achieved higher than 0.9 of R^2 values, whereas other four types R^2 values were all below 0.8. Although calculated q_e values via Type 1 equation were not the nearest to experimental q_e, good linearization of Type 1 showed excellent fitting of the adsorption process, which could be used in adsorption prediction. Besides, calculated q_e of DEET and CAF by model Type 5 was negative, indicating this linearization model was not suitable in the present study. Kumar (2006) [328] also applied five types of linear pseudo second-order-rate model to fit the adsorption kinetics of methylene blue onto activated carbon, finding that experimental results fitted the model Type 1 best (all $R^2 > 0.9999$ at eight concentrations). Hussain et al. (2007) [335] investigated the adsorption kinetics of ammonia onto GAC and found it was well described by pseudo-second-order model ($R^2 > 0.93$). Moreover, Lu et al. (2014) [336] found the removal of oxidized sulphur compounds by GAC was well fitted to the pseudo-second-order model ($R^2 > 0.99$). Based on the results, the pseudo-second-order model (Type 1) fitted the data best.

6.3.6 Adsorption isotherms of target PPCP compounds onto GAC

In this experiment, distribution of target PPCP compounds were described by Freundlich and Langmuir isotherm models. Freundlich isotherm was widely used in water and wastewater treatment to describe the adsorption characteristics of the activated

carbon [337]. And Langmuir isotherm was commonly used to represent the data of sorption from solution [338,339].

For Freundlich isotherm:

$$q_e = K_f C_e^{1/n} \quad \text{(E.7-12)}$$

Which can be rearranged to:

$$\ln q_e = lnK_f + \frac{1}{n}\ln C_e \quad \text{(E.7-13)}$$

Where q_e represents the amount adsorbed per amount of adsorbent at the equilibrium (μg/mg) and C_e represents the equilibrium concentration (μg/L). K_f (μg/mg) and n (L/μg) are Freundlich constants which represent adsorption capacity and adsorption intensity, respectively [340].

For Langmuir isotherm:

$$q_e = \frac{q_{max} b C_e}{(1+bC_e)} \quad \text{(E.7-14)}$$

Which can be rearranged to:

$$\frac{1}{q_e} = \frac{1}{C_e q_{max} b} + \frac{1}{q_{max}} \quad \text{(E.7-15)}$$

Where q_e represents the amount adsorbed per amount of adsorbent at the equilibrium (μg/mg) and C_e represents the equilibrium concentration (μg/L). The Langmuir constants b (L/μg) and q_{max} (μg/mg) correspond to the energy of adsorption and maximum adsorption capacity [340].

Table 6-7 presents the parameters of Freundlich and Langmuir isotherm adsorption models of DEET, PAR, CAF and TCS onto GAC.

Table 6-7 Parameters of isotherm models of target PPCP compounds onto GAC

Compound	Freundlich model			Langmuir model		
	k (μg/mg)	n (L/μg)	R^2	q_{max} (μg/mg)	b (L/μg)	R^2
DEET	0.9129	0.4183	0.9646	-0.0886	-1.1265	0.9946
PAR	2.0660	0.5128	0.9879	-0.1294	-1.7430	0.9897
CAF	5.3672	0.2979	0.9857	-0.0455	-1.9841	0.9739
TCS	0.1176	0.2715	0.9801	-0.0388	-0.7077	0.9744

For Freundlich isotherm, R^2 of the fitted models were 0.9646, 0.9879, 0.9857 and 0.9801 for DEET, PAR, CAF and TCS, respectively. Adsorption capacity K_f (μg/mg) of PAR and CAF were 2.0660 and 5.3672, higher than those of DEET and TCS (0.9129, 0.1176). Usually the Freundlich constant *n* is higher than 1 [341–343]. Although not common, *n* lower than 1 was also observed in adsorption process [344]. In present study, the constant n for DEET, PAR, CAF and TCS were 0.4183, 0.5128, 0.2979 and 0.2715. Constant *n* lower than 1 is often observed at low concentration ranges (25 μg/L in present study) containing a polar functional group, which are in competition for adsorption sites with water [345]. All four target compounds contain polar functional group (e.g. hydroxyl, acyl, carbonyl), which may explain the values of *n* below 1 in fitted model of this study. PPCP adsorption isotherm fitting Freundlich model was also reported [346], suggesting GAC behaves as heterogeneous material consisting of not energetically equivalent sorption sites [347].

Langmuir isotherms of fitted models gave R^2 of 0.9646, 0.9879, 0.9857 and 0.9801 for DEET, PAR, CAF and TCS, respectively. Nevertheless, calculated q_{max} (μg/mg) for four PPCP compounds were all negative. Negative q_{max} has also been reported by other researchers [348–350]. Langmuir isotherm is widely used in adsorption process, but it tends to work better at high adsorbate concentrations while it reduces to Freundlich isotherm at low adsorbate concentrations [351]. In this experiment, the concentrations of adsorbates were relatively low (μg/L). Although fitted R^2 of models were all higher than 0.9, the negative calculated q_{max} (μg/mg) demonstrated inapplicability of Langmuir isotherm model for present study. So Freundlich isotherm was more suitable and could represent the distribution of adsorbed and unadsorbed target PPCP compounds in solution.

At the end of the whole filtration process, no PAR and CAF were detected in the treated water by the GAC-associated filters, while DEET and TCS removal by GAC adsorption were less effective. Kinetic results showed that TCS had the lowest equilibrium capacity at 0.0242 μg/mg, followed by DEET, which had the equilibrium capacity of 0.0243 μg/mg. This phenomenon agreed well with the results found in the filtration process above (Section 6.3.2). Since TCS has larger molecular weight than other three compounds (Table 3-1) and the GAC used in the present study has 80 % of the pores comprised by microporous (< 2 nm), it might be because TCS molecule was larger to enter the GAC pores than other PPCP molecules, resulting in relatively lower removal [352,353]. Besides, DEET is usually regarded as a compound resistant to biodegradation [2] and its removal in Filter 1(sand only) was lower than the other three compounds at 10 and 20 cm/h. Thus, the good removal of DEET by GAC-associated filters indicated effective adsorption, which may be ascribed to hydrophobic property and interactions between GAC and DEET molecules [354–356]. In addition, the π–π dispersion, existence

of hydrogen bonds, release/desorption effect and electron distribution may have also influenced the adsorption performance and led to the fluctuations of treated water concentration [46,354,356,357]. It is noteworthy that, as shown by Filter 1 (sand only), removal of the target PPCP compounds also demonstrate that biodegradation processes were present in the filter. Hence, deeper biodegradation process and molecular-level adsorption mechanisms during GAC sandwich SSF filtration process can be further investigated.

6.4 Summary

The main conclusions drawn from this chapter are:

- The target PPCP compounds were significantly (p<0.05) removed by using GAC sandwich SSF than sand alone. Filter 2 (10 cm sand/10 cm GAC/30 cm sand) at 5 cm/h had 99.5 % average removal for the target PPCP compounds, but 5 cm/h led to slower filtration and ammonium was not effectively removed. Filter 3 (10 cm sand/20 cm GAC/20 cm sand) achieved the overall optimal average target PPCP removal (98.2 %) at 10 cm/h filtration rate.
- No significant difference of average PPCP removal was found between 10 cm/h and 20 cm/h filtration rates for three GAC sandwich filters (p>0.05). The removal of target PPCP compounds could be attributed to both adsorption (especially DEET and CAF) and biodegradation.
- Filter 3 (10 cm sand/20 cm GAC/20 cm sand) also showed better average removal of COD (65.8 %) and TOC (90.3 %), compared with the other filters. Nitrogen could be effectively removed by the GAC sandwich SSFs. No significant difference was found between 10 cm/h and 20 cm/h for nitrogen and phosphate removal (p>0.05).

- Type 1 pseudo-second-order model fitted best the adsorption kinetics of target PPCP compounds onto GAC. Adsorption isotherms of four target compounds at 25 μg/L can be described by the Freundlich model.
- Results of this laboratory-scale test show that GAC sandwich slow sand filter was an effective process for removing the target PPCPs from synthetic wastewater. This suggests that PPCPs may be effectively removed from wastewater by using a combination of sand with reduced GAC layer depth at tertiary treatment, potentially reducing operational costs. As filter performance at 5 cm/h filtration rate was found not satisfactory, 10~20 cm/h filtration rate is suggested based on the practical situation.

CHAPTER 7 REMOVAL OF SELECTED PPCPS BY GREATER DUCKWEED CONSTRUCTED WETLAND SYSTEM FOLLOWED BY GAC SANDWICH SLOW SAND FILTRATION

7.1 Introduction

By using continuous CW-ST system, good removal of PAR, CAF and TCS and improvement of system stability were achieved. But DEET (removal < 45 %) and high abundance of microbes were still present in the effluent of the system (Chapter 5). GAC sandwich SSF showed great improvement to DEET and microbial removal (Chapter 6). Filter of 10 cm sand/20 cm GAC/20 cm sand achieved the average four target PPCP removal (98.2 %) at 10 cm/h filtration rate. However, the two aforementioned treatment experiments were conducted using synthetic wastewater. Hence, in this chapter, combined CW-SSF system (CW-ST-GAC sandwich SSF) was built to investigate the performance of the removal of the target PPCP compounds using both synthetic wastewater and real environmental water. To author' knowledge, this is the first study investigating PPCP removal using CW followed by sandwich SSF system.

7.2 Experiment

7.2.1 Chemicals and materials

Acrylic column with internal diameter of 34 mm and length of 65 cm was used as filter column. Washing, treatment and properties of Greater duckweed, coarse sand, GAC and gravel can be found in Section 3.9.

Lake water collected from the Regent's Park, London, United Kingdom, was used as natural water which has on average turbidity < 2 NTU and COD of 15 ± 5 mg/L. Synthetic waste water with COD at 300 mg/L was prepared using the recipe in Section 3.12. For both two types of experimental water, mixed PPCP solution prepared with methanol was added into them to reach a spiked concentration of 25 μg/L before entering the treatment system.

7.2.2 Experimental design and description

A schematic and a photo representation of the experiment system are shown in Figure 7-1 and 7-2.

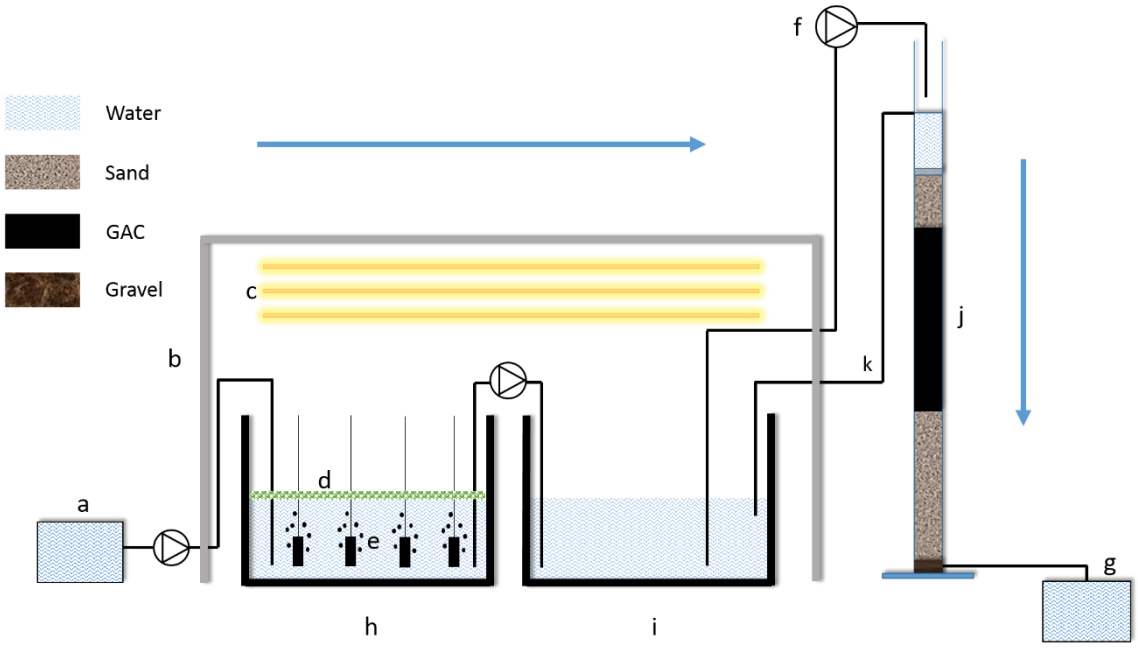

Figure 7-1 Schematic representation of the CW-SSF experimental system (a. influent tank; b. reflective fabric; c. lights; d. Greater duckweed; e. aerator; f. peristaltic pump; g. effluent tank; h. wetland tank; i. stabilization tank; j. GAC sandwich slow sand filter)

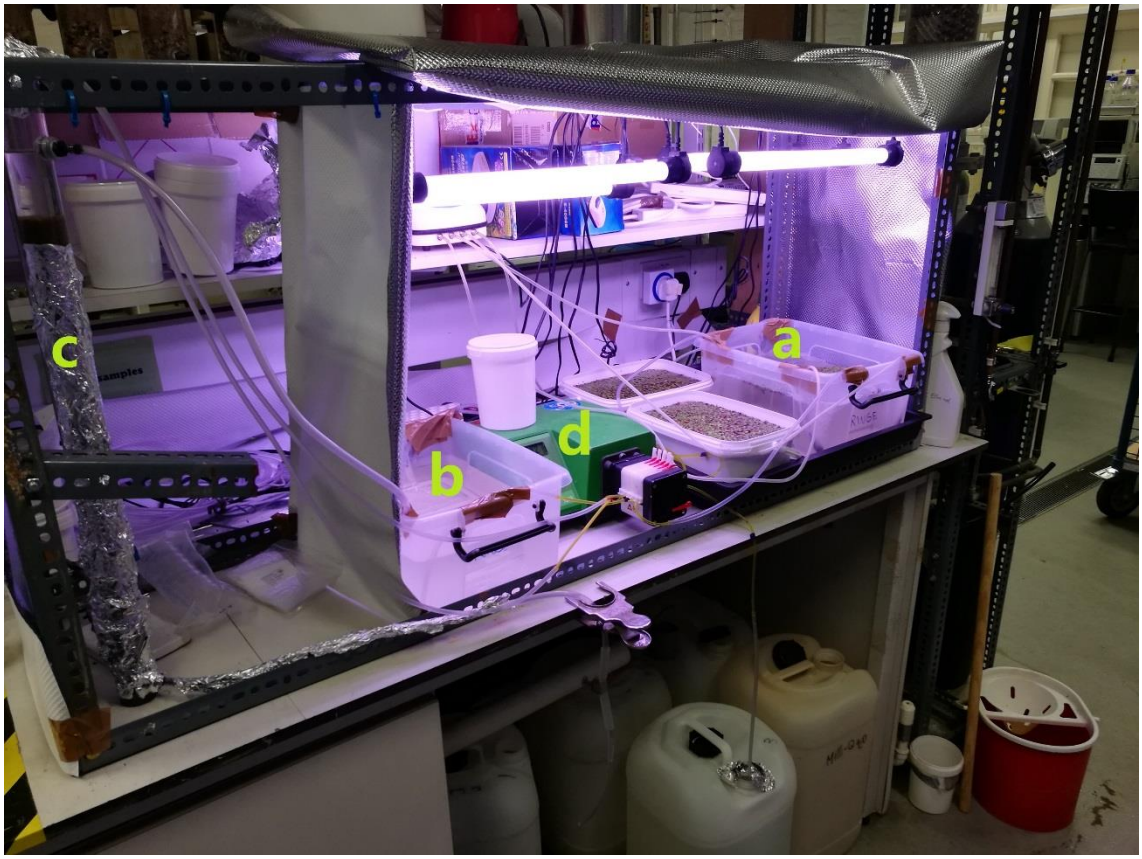

Figure 7-2 Photo of the CW-SSF experimental system (a. wetland tank; b. stabilization tank; c. GAC sandwich slow sand filter; d, peristaltic pump)

The system consisted of one influent tank, one CW tank (32×22×17 cm), one ST tank (32×22×17 cm), one GAC sandwich filter and one outflow tank, connected in series by peristaltic pumps. The area above the CW and ST tanks was covered by reflective fabric. The experimental conditions (full aeration in CW tank, 240 μmol$m^{-2}s^{-1}$ light intensity, 1.00 kg/m^2 plant density) used were the optimal parameter levels obtained in previous experiments (Chapter 5). Lights - which were left on for 14 hours and off for 10 hours each day - were placed above the CW-ST area. 70g of fresh and washed Greater duckweed were placed in the CW tank. Aerators (3.2 L/min output each) were evenly placed at the CW tank bottom and room temperature was maintained at 23 ℃. Seven litres of the water spiked with 25 μg/L target PPCP compounds were put in the CW and ST

tanks separately at the beginning of the test. Flow speed of the peristaltic pumps was set at 1.38 mL/min (HRT at 7 days).

GAC sandwich column was attached after the ST tank receiving CW-ST system effluent. Column height was 65 cm with 10 cm sand/20 cm GAC/20 cm sand/3 cm gravels from top to bottom. Effluent pipe which had one valve controlling filtration rate was located 1 cm above the column base. Filtration rate was set at 10 cm/h. Before the experiment began, lake water was filtered through sandwich filter for maturation, which is detailed in Chapter 6 and Appendix 4. After the maturation, filter was connected to CW-ST system.

For the synthetic wastewater, CW system was first operated alone for around one week until the COD of the effluent was stable at around 40 mg/L, then GAC sandwich filter was attached to the ST tank and test began. The purpose of leaving CW tank operating alone for a period was to ensure that the filter was not clogged quickly because of high COD concentration (300mg/L) as glucose is a highly degradable substance [323] and filter may be clogged soon due to vigorous microbial growth. For the natural water, test began immediately and peristaltic pumps were switched on after lake water was added into both CW and ST tanks.

Duration of each test was 4 weeks. In order to explore the system performance without aeration, at day 14 all aerators were removed. Filtration rate of GAC sandwich filter was monitored and adjusted twice every day. Samples were collected three times a week on Mondays, Wednesdays and Fridays to determine concentrations of PPCPs, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, COD and TOC. pH, conductivity and redox potential of effluent samples were also determined. At each sampling day, DO concentrations in both CW and ST tanks were detected. Total headloss of GAC sandwich SSF was measured at the end of the test.

7.2.3 Determination of selected PPCP compounds and general parameters

The extraction of target PPCP compounds from water and quantification method can be found in Section 3.4. Other general parameters, namely abundance of total coliforms and *E.coli*, concentrations of COD, TOC, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, DO, pH, conductivity and redox potential were measured using methods from Sections 3.5 and 3.6. For synthetic wastewater system, water samples from both ST tank and effluents were collected to determine the nutrient parameters.

7.2.4 Statistical analysis

ANOVA tests were carried out to assess the difference significance between sample concentrations and *p*-value < 0.05 was considered statistically significant. OriginPro 9.1 was used to develop all graphs. The data processing was conducted by Microsoft Excel 2013. Removal (%) of target PPCP compounds in natural water system were calculated using the equation below:

$$\text{Removal (\%)} = \frac{C_i + C_a - C_e}{C_i + C_a} \times 100\%$$

Where C_i (μg/L) is the influent concentration of target compounds from natural water. C_a is the added concentration (25 μg/L each compound) and C_e (μg/L) is the final concentration of the effluent.

7.3 Results and discussion

7.3.1 Synthetic wastewater system

7.3.1.1 Removal of target PPCP compounds

Concentrations and removal of the target PPCP compounds in effluents of synthetic wastewater system are shown in Table 7-1. The average concentrations of the four compounds were 0.97±0.02, 0.01±0.00, 0.14±0.00 and 0.68±0.10 μg/L, for DEET, PAR, CAF and TCS, with good average removal at 96.1 %, 99.9 %, 99.4 % and 97.3 %, respectively. From day 10, no PAR and CAF were detected in the effluent. Although DEET behaved as the most recalcitrant among the four compounds, removal of all PPCPs in the effluent were above 95 %. Both PAR and CAF were found at the first 8 days in the effluent, then disappeared afterwards.

Table 7-1 Concentrations and removal of target PPCP compounds in effluents of synthetic wastewater system

day	DEET			PAR			CAF			TCS		
	Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal
3	1.01	0.00	96.0%	0.05	0.01	99.8%	0.53	0.01	97.9%	0.85	0.22	96.6%
5	1.07	0.00	95.7%	0.05	0.00	99.8%	0.52	0.01	97.9%	0.78	0.01	96.9%
8	0.90	0.01	96.4%	0.05	0.00	99.8%	0.52	0.00	97.9%	0.88	0.05	96.5%
10	0.97	0.01	96.1%	n.d.*	n.a.**	100.0%	n.d.	n.a.	100.0%	0.75	0.02	97.0%
12	1.01	0.00	96.0%	n.d.	n.a.	100.0%	n.d.	n.a.	100.0%	0.79	0.04	96.8%
15	0.83	0.09	96.7%	n.d.	n.a.	100.0%	n.d.	n.a.	100.0%	0.45	0.03	98.2%
17	1.04	0.01	95.8%	n.d.	n.a.	100.0%	n.d.	n.a.	100.0%	0.49	0.01	98.0%
19	0.93	0.00	96.3%	n.d.	n.a.	100.0%	n.d.	n.a.	100.0%	0.33	0.01	98.7%
22	1.15	0.04	95.4%	n.d.	n.a.	100.0%	n.d.	n.a.	100.0%	0.45	0.02	98.2%
24	0.85	0.01	96.6%	n.d.	n.a.	100.0%	n.d.	n.a.	100.0%	0.85	0.05	96.6%
26	0.90	0.01	96.4%	n.d.	n.a.	100.0%	n.d.	n.a.	100.0%	0.89	0.02	96.4%
Average	0.97	0.02	96.1%	0.01	0.00	99.9%	0.14	0.00	99.4%	0.68	0.04	97.3%

Mixed target compounds were spiked into synthetic wastewater to reach a concentration of 25 μg/L

* n.d. not detected. **n.a. not available

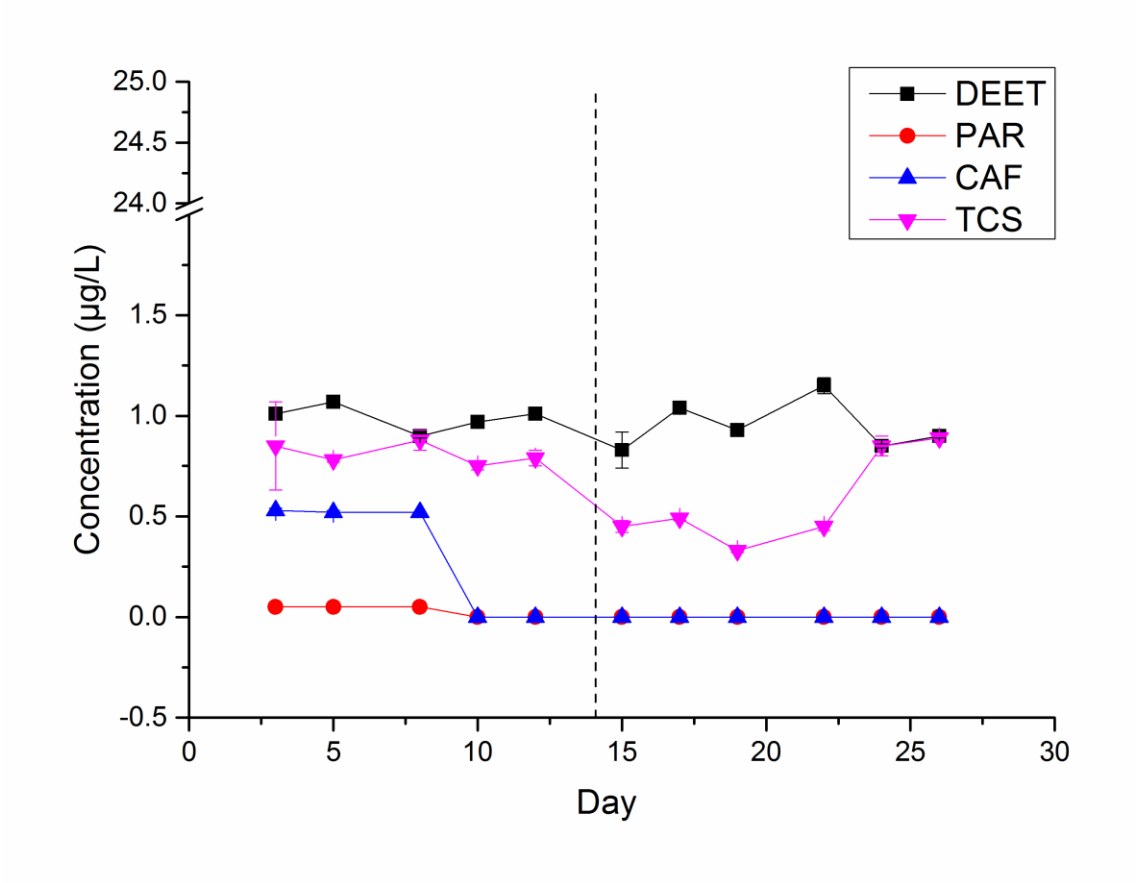

Figure 7-3 Concentrations of target PPCP compounds in the effluent during the synthetic wastewater treatment

(Initial concentration: 25 µg/L. day 1 to 14, full aeration; day 14 to 26, no aeration)

After switching off the aerators, environmental condition in CW system may change considerably due to DO decrease. Figure 7-3 shows the concentration dynamic changes during the treatment. However, no significant difference (p>0.05) of removal was found between aeration and non-aeration for DEET and TCS. Statistical significant differences (p<0.05) were observed for PAR and CAF but these two compounds were not detected during the non-aeration period. Although sudden decrease of DO concentration affecting microbial and plant activity [28,303] may weaken the biodegradation process in CW tank, continuous oxygen diffusion from air to water in CW and ST tanks and undisturbed removal in the filter ensured stability of the whole system.

7.3.1.2 General water parameters during the system operation

Since CW-ST system was first operated until COD concentration was around 40 mg/L (approximately one week) before the operation process began, concentrations of COD, TOC, nitrite, nitrate, phosphate and ammonium in both ST tank and effluent are shown in Table 7-2. Other general parameters are shown in Appendix 6.

Under aeration, both COD and TOC were detected at low level, with concentrations below 1 mg/L and 2 mg/L in the effluent, respectively. However, after switching off the aerators, COD and TOC concentrations increased both in ST tank and effluent, then decreased again in ST tank, which are in accordance with the previous CW-ST study (Chapter 5) and the reason can be attributed to the microbial structural changes [303]. Concentrations of COD and TOC in the effluent fluctuated until the test ended, with concentrations of 19±1 mg/L and 4.79±0.05 mg/L, respectively, at the day 26.

Compared with continuous CW-ST test (Chapter 5), a clearer trend of nitrogen compounds can be found in current test. Nitrification and denitrification can occur simultaneously in CW and SSF systems [248,298]. Under aeration, nitrification can be active [195]. Therefore, the increase of nitrite, decrease of nitrate and fluctuation of ammonium concentrations may be attributed to active nitrosation (e.g. *Nitrosomonas*, *Nitrosocystis*) converting ammonium to nitrite and less effective nitrobacteria activities (e.g. *Nitrospina*) converting nitrite to nitrate. When aeration stopped, no drastic change of nitrate and nitrite was observed except an increase of ammonium (day 19) concentration, which then decreased quickly again. Nitrite, nitrate and ammonium all presented concentration declines without aeration, and intense denitrification under anoxic/anaerobic conditions can be regarded as main cause [195]. At the last sampling day, no nitrite was found in the effluent and concentrations of nitrate and ammonium were 4.77±1.18 mg/L and 1.03±0.02 mg/L, respectively.

Compared to nitrogen, phosphate concentration fluctuated during the whole test. No significant difference (p<0.05) was found between with and without aeration. The average removal of phosphate was found to be 91.1 %, compared to 69 % in SSF-CW system [38], indicating good phosphate removal. Similar to CW-ST test results in Chapter 5, after switching off the aerators, DO concentration in CW tank drastically dropped to below 1mg/L, while it changed slightly in the ST tank and maintained above 6 mg/L until the end of the test. Similarly, DO concentration in CW tank increased 2.66 mg/L after 9 days while in CW tank of continuous CW-ST test it increased 2.98 mg/L after 8 days (Appendix 6). The final headloss of the filter was less than 1 cm.

Table 7-2 Concentrations of COD, TOC, nitrite, nitrate, phosphate and ammonium in ST tank and effluents of synthetic wastewater system

Day	COD				TOC				Nitrite			
	ST tank		effluent		ST tank		effluent		ST tank		effluent	
	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
initial	40	5	n.a.*	n.a.	17.18	0.47	n.a.	n.a.	1.15	0.01	n.a.	n.a.
3	29	3	<1	n.a.	12.02	0.21	0.69	0.07	1.67	0.02	1.80	0.10
5	12	2	<1	n.a.	3.96	0.01	0.84	0.04	5.57	0.03	5.79	0.11
8	6	2	<1	n.a.	4.34	0.03	1.71	0.04	6.56	0.04	6.18	0.01
10	9	1	<1	n.a.	3.76	0.09	1.56	0.02	10.79	0.04	6.27	0.03
12	12	1	<1	n.a.	4.56	0.14	1.90	0.05	8.39	0.05	5.73	0.05
15	42	2	<1	n.a.	8.79	0.02	1.35	0.09	5.10	0.05	5.12	0.22
17	107	5	16	2	20.56	0.01	3.80	0.04	4.26	0.06	n.d.**	n.a.
19	29	3	13	2	8.31	0.01	4.25	0.08	3.29	0.07	2.72	0.04
22	32	4	17	1	8.12	0.02	3.66	0.10	1.17	0.04	n.d.	n.a.
24	39	2	24	1	10.20	0.06	5.35	0.21	0.29	0.02	n.d.	n.a.
26	16	1	19	1	5.38	0.01	4.79	0.05	1.40	0.01	n.d.	n.a.
Day	Nitrate				Phosphate				Ammonium			
	ST tank		effluent		ST tank		effluent		ST tank		effluent	
	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
initial	34.65	0.08	n.a.	n.a.	9.30	0.57	n.a.	n.a.	6.12	0.08	n.a.	n.a.
3	33.10	0.30	25.62	0.14	9.30	1.20	4.23	0.04	5.21	0.41	0.17	0.02
5	25.26	0.07	14.17	7.66	5.70	0.06	4.48	0.17	2.42	0.07	n.d.	n.a.
8	24.15	0.17	23.01	0.12	7.26	0.01	7.57	0.03	5.19	0.24	2.01	0.00
10	18.35	0.04	11.55	0.01	7.08	0.02	6.43	0.06	3.51	0.21	4.97	0.11
12	15.65	0.12	11.60	0.03	6.74	0.03	8.26	0.05	5.33	0.07	5.03	0.14
15	11.12	0.15	11.90	0.72	3.28	0.04	7.03	0.32	4.99	0.23	1.13	0.17
17	7.04	0.00	n.d.	n.a.	7.13	0.03	2.96	0.02	6.24	0.47	1.61	0.48
19	2.66	0.01	1.93	0.27	9.23	0.07	6.70	0.01	11.75	2.45	6.19	1.47
22	4.45	0.04	2.85	1.44	8.26	0.05	7.60	0.09	3.91	0.14	3.80	0.01
24	2.55	1.32	n.d.	n.a.	7.46	0.02	6.57	0.09	1.67	0.05	1.54	0.03
26	7.73	1.38	4.77	1.18	5.76	0.01	6.68	0.05	5.82	0.52	1.03	0.02

*n.a. not available. **n.d. not detected

7.3.2 Natural water system

7.3.2.1 Removal of target PPCP compounds

The concentrations and removal of four target PPCP compounds are shown in Table 7-3. Dynamic changes of the concentration during the treatment are demonstrated in Figure 7-4. All four compounds were detected in the lake water, with concentrations of DEET at 0.88±0.32 μg/L, PAR at 0.26±0.21 μg/L, CAF at 0.72±0.37 μg/L and TCS at 3.54±1.84 μg/L. As DEET and TCS are synthetic organic compounds, occurrence of these two compounds in the water sampling area indicates the pollution is from human activities. From Table 7-3, it can be seen that by using CW-SSF system, removal of above 90 % were achieved for all compounds, with average removal at 95.9 %, 99.1 %, 98.1 % and 97.4 % for DEET, PAR, CAF and TCS, respectively, and high removal of DEET occurred as soon as test started, which can be attributed to efficient GAC adsorption (Chapter 6).

Table 7-3 Concentrations and removal of target PPCPs compounds in effluents of natural water system

Day	DEET			PAR			CAF			TCS		
	Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal	Con (μg/L)	RSD	Removal
lake water	0.88	0.32	n.a.*	0.26	0.21	n.a.	0.72	0.37	n.a.	3.54	1.84	n.a
1	0.97	0.00	96.3%	0.26	0.01	99.0%	0.66	0.04	97.4%	1.63	0.03	93.5%
3	1.05	0.03	96.0%	0.03	0.05	99.9%	0.51	0.01	97.9%	0.56	0.31	97.8%
5	0.86	0.01	96.7%	0.01	0.01	99.9%	0.58	0.06	97.7%	0.65	0.06	97.4%
8	1.05	0.02	95.9%	1.08	0.11	95.7%	0.54	0.09	97.8%	0.35	0.01	98.6%
10	1.03	0.02	96.0%	0.43	0.05	98.3%	0.67	0.09	97.3%	0.34	0.01	98.6%
12	1.05	0.06	95.9%	n.d.**	n.a.	100.0%	0.54	0.01	97.9%	0.42	0.10	98.5%
15	1.05	0.06	95.9%	n.d.	n.a.	100.0%	n.d.	n.a.	100.0%	0.29	0.02	99.0%
17	1.16	0.09	95.5%	n.d.	n.a.	100.0%	0.55	0.02	97.8%	1.75	0.04	93.9%
19	1.05	0.09	96.0%	n.d.	n.a.	100.0%	0.56	0.03	97.8%	0.60	0.02	97.9%
22	1.22	0.06	95.3%	0.75	0.16	97.0%	n.d.	n.a.	100.0%	0.14	0.00	99.5%
24	1.10	0.02	95.7%	0.14	0.01	99.5%	0.57	0.01	97.7%	0.25	0.02	99.1%
26	1.13	0.00	95.6%	0.11	0.02	99.6%	0.55	0.01	97.8%	1.25	0.03	95.6%
Average	1.06	0.04	95.9%	0.23	0.04	99.1%	0.48	0.03	98.1%	0.69	0.05	97.4%

* n.a. not available ** n.d. not detected

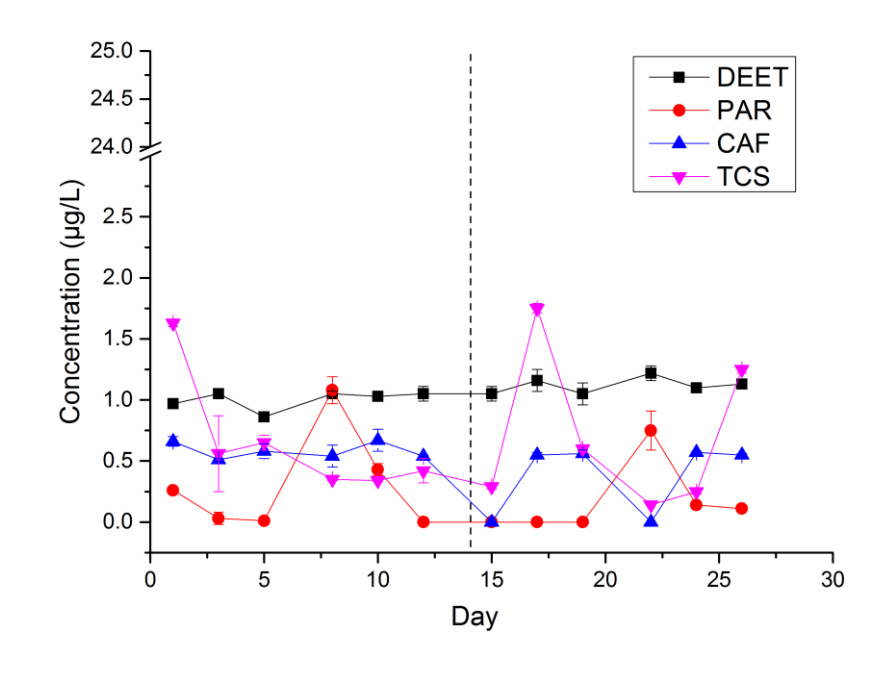

Figure 7-4 Concentrations of target PPCP compounds in the effluent during the natural water treatment

(Initial concentration: 25 µg/L. day 1 to 14, full aeration; day 14 to 26, no aeration)

Oxygen is an essential factor influencing plants and microbial activity and biotope of natural water system can differ a lot from synthetic wastewater system. At the day 14, aerators in CW tank were removed. Different from synthetic wastewater system, no significant difference (p>0.05) of other three compounds removal was observed between with and without aeration, except DEET (p<0.05). In the present study, though statistical significant difference was found (p<0.05), removal of DEET with aeration were just slightly higher than without aeration (Table 7-3). From Appendix 7, it can be seen that after switching off the aerators, DO concentrations dropped from above 8 mg/L to 5.32 mg/L in the CW tank and then increased again, while the ST tank concentration were more stable. Sudden change of DO could affect CW plants and microbes activity [303],

leading to PPCP removal fluctuations [28]. However, continuous adsorption in GAC sandwich SSF and continuous oxygen diffusion from air to water in CW and ST tanks for biodegradation ensured the stability of the system on PPCP removal. At the final sampling day of the experiment (day 26), concentrations of DEET, PAR, CAF and TCS were 1.06±0.04, 0.25±0.04, 0.48±0.03 and 0.69±0.05 μg/L, respectively.

7.3.2.2 General water parameters during the system operation

Table 7-4 summarizes the concentrations of COD, TOC, nitrate, phosphate, nitrite and ammonium in raw natural water and final treated effluents. While nitrite was not found, nitrate, phosphate and ammonium were detected in the lake water at concentrations of 0.07±0.01, 0.12±0.02 and 0.31±0.12 mg/L, respectively. Especially, high ammonium concentration at 19.56±0.18 mg/L was detected, which can be attributed to the fact that Regent's Park is a natural habitat for a variety of waterfowls and biologic excretion leads to high ammonium concentration. In addition, lake water had COD level at 20±5 mg/L and TOC at 1.67±0.18 mg/L.

During the treatment process, COD concentrations of effluent were kept below 1 mg/L and at day 22 concentration increased to 21 mg/L and then declined, whilst TOC dropped with fluctuation under aeration and increased to 1.10 mg/L (day 22), then declined again, having final concentration at 0.59 mg/L and removal of 64.7 %. In the continuous CW-ST test, after switching off the aerators, COD increased around 40 mg/L and then declined again about one week after, while TOC had the same trend. Sharp DO concentration decrease would influence dynamically stable aerobic microbial community and break ecological balance [303], hence affected nutrients removal. However, in the present research, re-decreased concentrations of COD and TOC demonstrated stability of this combined system.

Table 7-4 Concentrations of COD, TOC, nitrite, nitrate, phosphate and ammonium in influent and treated effluents of natural water system

Day	COD		TOC		Nitrite		Nitrate		Phosphate		Ammonium	
	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
Lake water	20	5	1.67	0.18	n.d.**	n.a.	0.07	0.01	0.12	0.02	19.56	0.18
3	<1	n.a.*	0.79	0.00	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
5	<1	n.a.	0.80	0.01	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
8	<1	n.a.	1.14	0.14	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
10	<1	n.a.	1.03	0.07	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
12	<1	n.a.	0.70	0.09	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
15	<1	n.a.	0.73	0.02	n.d.	n.a.	0.09	0.01	n.d.	n.a.	n.d.	n.a.
17	<1	n.a.	0.97	0.30	n.d.	n.a.	n.d.	n.a.	0.33	0.01	n.d.	n.a.
19	<1	n.a.	0.87	0.04	n.d.	n.a.	0.04	0.00	n.d.	n.a.	15.53	0.23
22	21	3	1.10	0.05	n.d.	n.a.	0.06	0.00	n.d.	n.a.	4.91	0.17
24	13	3	0.65	0.00	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.67	0.04
26	15	2	0.59	0.06	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.

* n.a. not available. **n.d. not detected

No nitrite was found in the final treated water. Nitrate was only found in several sampling days at very low concentrations after stopping the aeration and was totally removed thereafter. Phosphate was only detected at the day 17 at 0.33 mg/L. From the research of Gunes and Tuncsiper (2009) [38], total phosphorus was removed 69 % under the raw wastewater concentration of 8.94±3.97 mg/L by a SSF-CW system connected in series. Using GAC sandwich SSF, only around 10 % of phosphate was removed (Chapter 6), and 30~50 % of phosphate was removed by the continuous CW-ST system (Chapter 5). Compared to high influent concentration used in synthetic wastewater systems, low phosphate concentration (0.12±0.02 mg/L) existed in the raw lake water. No occurrence of phosphate in treated water by CW-SSF can be attributed to lower phosphate load. Ammonium was thoroughly removed under aeration condition (active nitrification) but appeared at 15.53±0.23 mg/L at day 19 after switching off the aerators (more intense denitrification under anaerobic condition), then gradually decreased to zero again at day 26 (recovered nitrification). Good nitrate and nitrite removal lie within the range of standards for drinking water quality (50 mg/L for nitrate and 0.5 mg/L for nitrite, EU Directive 98/83/EC).

Other general parameters (e.g. pH, DO) monitored are shown in Appendix 7. The system effluent pH was around 8.2~8.5, lying within the range (6.5~8.5) of discharge standards suggested by WHO-EM/CEH/142/E. Final DO concentrations in CW tank and ST tank were 6.16 mg/L and 7.11 mg/L, respectively, indicating aerobic environment. Change trend of DO concentration of this system agrees well with the previous tests (Chapter 5 and Section 7.3.1). Final headloss of the filter was less than 1 cm.

7.3.3 Comparison among different tested systems

7.3.3.1 Target compound removal

The average removal of target PPCP compounds in continuous CW, continuous CW-ST, GAC Sandwich SSF (Filter 3, 10 cm/h) and CW-SSF (synthetic wastewater and natural water) are compared in Table 7-5.

Table 7-5 Average removal (%) of target PPCP compounds in different tested systems

System	DEET	PAR	CAF	TCS	Average
Continuous CW	18.2	81.4	50.4	77.8	57.0
Continuous CW-ST	27.1	92.2	65.8	99.3	71.1
GAC sandwich SSF (Filter 3, 10cm/h)	98.0	100	100	94.8	98.2
CW-SSF (synthetic wastewater)	96.1	99.9	99.4	97.3	98.2
CW-SSF (natural water)	95.9	99.1	98.1	97.4	97.6

The average removal of total four target PPCP compounds were 57.0 %, 71.1 %, 98.2 %, 98.2 % and 97.6 % for continuous CW (synthetic water), continuous CW-ST (synthetic water) GAC sandwich SSF (Filter 3, 10cm/h, synthetic water), CW-SSF (synthetic wastewater) and CW-SSF (natural water) systems, respectively.

For the tests with synthetic wastewater, it can be seen that by using CW systems only, average removal of target PPCP compounds were apparently lower than other tested systems, especially DEET and CAF, removal of which were below 30 % and 70 % in continuous CW systems. Poor removal of DEET and CAF indicate the unsuitability of this single unit for these two compounds. High average removal of all four compounds

(mostly above 95 %) were achieved in GAC sandwich SSF and synthetic wastewater CW-SSF systems. As for the GAC sandwich SSF, under the filtration rate of 10 cm/h, average removal of DEET, PAR, CAF and TCS from synthetic wastewater were 98.0 %, 100 %, 100 % and 94.8 %, respectively. However, except TCS, removal of other three compounds (96.1 %, 99.9 % and 99.4 % for DEET, PAR and CAF, respectively) were slightly lower in the synthetic wastewater CW-SSF system (no significant difference, $p>0.05$). In the GAC sandwich SSF test, clean synthetic wastewater (COD at 40 mg/L) was used, while influent COD of the CW-SSF system was at 300 mg/L continuously. Plants and vigorous microbial activity existing in CW and ST tanks made water flowing into filter more complex in content than influent of GAC sandwich SSF test because of other substances (e.g. exudates and metabolic organic matters of plants and microbes). As adsorption was found to be the main mechanism of PPCP removal during GAC sandwich SSF (Chapter 6), the reason that removal of DEET, PAR and CAF by the CW-SSF system were slightly lower than by the GAC sandwich SSF system may be attributed to the competitive adsorption between target compounds and other substances from front units [358]. Moreover, since removal in two types of treatment systems were high while final concentrations of target compounds were at ng/L level, normal errors in quantification may be another reason (RSDs of instrument below 10 % in Section 4.3.4).

Compared with synthetic wastewater tested systems, natural water CW-SSF system represented more like real treatment situation. But no significant difference ($p>0.05$) was found between average removal of four PPCPs in natural water and synthetic wastewater systems. In contrast to synthetic wastewater, much more complex matrix (e.g. humic substance) existing in natural water may lead to competitive adsorption between target compounds and other substances onto adsorbents (GAC in current study) [358,359]. Besides, carbon resource of synthetic wastewater used was glucose, which can be more

degradable than other organic substances [323,324]. High concentration of glucose could favour microbial growth and activities, including PPCP-degradation microorganisms, accelerating target PPCP elimination, while natural water harbours less nutrients, therefore, relatively lower intensity of bioactivity may limit PPCP removal. However, high removal of four PPCP compounds (> 90 %) showed good performance of CW-SSF system treating natural water contaminated with target PPCPs.

By using CW-SSF system, adsorption (GAC), biodegradation (microbes), plant degradation (Greater duckweed) and photodegradation (mainly in ST tank) can be considered as the main mechanisms responsible for target PPCP compounds removal. All or several of these processes contributed to different compound degradation, leading to high removals. As for other technologies, Monsalvo et al. (2014) [360] conducted a study to remove trace organics using anaerobic membrane bioreactors, and found that the removal of DEET, CAF, PAR and TCS were 1.4 %, 76.9 %, 58.1 % and 90.2 %, respectively. In addition, except for CAF, removal of DEET, PAR and TCS were found all below 25 % in activated sludge tank-plate and frame/hollow-fibre membrane system [361]. In present study, obvious better removal of these four compounds were observed by CW-SSF system. Good average removal of four target PPCP compounds at all above 95 % indicate the potential applicability of current CW-SSF system dealing with trace contaminants.

7.3.3.2 Nutrients removal

The average removal of COD, TOC, ammonium, nitrate, phosphate and concentrations of nitrite in continuous CW, continuous CW-ST, GAC Sandwich SSF (Filter 3) and CW-SSF (synthetic wastewater and natural water) are shown in Table 7-6.

Table 7-6 Average removal (%) of COD, TOC, ammonium, nitrate, phosphate and concentrations of nitrite (mg/L) in different tested systems

System	COD	TOC	NH_4^+	NO_3^-	PO_4^{3-}	NO_2^-
Continuous CW	55.4	65.5	90.2	59.4	54.0	3.2
Continuous CW-ST	73.3	80.7	79.1	80.8	42.0	1.8
GAC sandwich SSF (Filter 3, 10cm/h)	65.8	93.7	96.1	99.8	11.4	0.0
CW-SSF (synthetic wastewater)	97.3	98.2	90.7	72.1	91.1	3.1
CW-SSF (natural water)	75.5	-8.6	90.1	75.7	75.0	0.0

From Table 7-6, it can be seen that CW-SSF system using synthetic water achieved the highest average removal of COD and TOC at 97.3 % and 98.2 %, respectively, compared to the other synthetic wastewater tests (55.4~73.3 % for COD and 65.5~93.7 % for TOC). It can be explained that the two biological treatment units make use of more carbon sources than single unit. Besides, good average phosphate removal of 91.1 % was much higher than just using GAC sandwich SSF (11.4 %) or continuous CW (42.0 ~ 52.0 %). As phosphorus is essential element building cell lipid bilayer, more phosphate removal in CW systems can be ascribed to plant-activity and more vigorous bioactivity in CW and ST tanks but biological activity mainly exists in the *schmutzdecke* and upper layer of the filter [40], resulting less phosphate consumption.

Because nitrification and denitrification are highly associated with environmental oxygen level, continuous CW-ST and CW-SSF tests are comparable for nitrogen removal since both two tests underwent aeration/non-aeration period. CW-SSF had more average ammonium removal (90.7 %) and higher average nitrite concentration (3.1 mg/L) while continuous CW-ST had better nitrate removal (80.8 %). It can be assumed that active nitrosation (e.g. *Nitrosomonas*, *Nitrosocystis*) converting ammonium to nitrite existed in

the CW-SSF system, which is in accordance with the findings in Section 7.3.1.2. However, although nitrogen removal varied between continuous CW-ST and CW-SSF systems, both of them showed higher removal than 40~50 % reported in other SF-CWs [171,175], probably due to Greater duckweed ammonia preference uptake [169] and nitrogen adsorption onto GAC [255].

In Table 7-6, it is noteworthy that average TOC removal was -8.6 % in natural water system (final removal at 64.7%). Since the TOC in the raw water was 1.67±0.18 mg/L and TOC concentration was below 2 mg/L during the whole process (Table 7-4), the fluctuation of concentration is acceptable as the TOC upper limit of drinking water is 5 mg/L (GB5749-2006). Although the removal of COD (75.5 %), ammonium (90.1 %) and phosphate (75.0 %) in the natural water system were lower than that in the synthetic wastewater system (97.3 %, 90.7 % and 91.1 %, respectively), no statistical significant difference (p>0.05) was found between average nutrient removal of synthetic wastewater and natural water systems. Besides, no nitrite was found during the whole experiment and ammonium removal was 90.7 %.

From the comparisons above, Greater duckweed (*Spirodela polyrhiza*) based free water CW-GAC sandwich SSF (CW-SSF) system presented good treatment performance of target PPCP compounds and nutrients from both high COD synthetic wastewater and real environmental water, as well as good stability. This combined system can compensate for the defects of single CW unit (e.g. poor DEET and CAF removal) or GAC sandwich SSF unit (e.g. poor phosphate removal, quick clogging), which can be a potential and suitable eco- and cost- effective water treatment technique.

7.4 Summary

In this chapter, CW-SSF system connected in series (CW-ST-GAC sandwich SSF) was investigated to remove selected target PPCP compounds from both synthetic wastewater and natural water.

- The average removal of four PPCP compounds from synthetic wastewater were 96.1 %, 99.9 %, 99.4 % and 97.3 %, respectively. Good removal also demonstrated treatment stability after aerators were switched off.
- All four compounds were detected in the lake water. By using CW-SSF natural water system, average removal of 95.9 %, 99.1 %, 98.1 % and 97.4 % for DEET, PAR, CAF and TCS, respectively, were found. No significant difference ($p>0.05$) of removal was observed between with and without aeration, except for DEET ($p<0.05$). Good removal of nitrite, nitrate and phosphate were observed during the whole test period from natural water.
- No significant difference ($p>0.05$) was found between average removal of four PPCPs and nutrients in natural water and synthetic wastewater systems. CW-SSF system connected in series not only showed good removal of the four target PPCP compounds, but also compensated for the disadvantages of single CW or GAC sandwich SSF units, suggesting it as a promising treatment technique for tertiary wastewater.
- Adsorption, biodegradation, plant degradation and photodegradation can be considered as the main mechanisms responsible for target PPCP compounds removal.

CHAPTER 8 CONCLUSIONS AND FUTURE WORK

8.1 Conclusion

A systematic investigation was conducted to evaluate CW and SSF on removing four PPCP compounds from water. Greater duckweed (*Spirodela polyrhiza*)-based free water CW and GAC sandwich SSF using coarse sand were both tried the first time to remove DEET, PAR, CAF and TCS. It is also the first time that CW and SSF units were connected in series to test the target PPCPs treatment performance. In this study, simplified SPE extraction and GC-MS detection methods of target compounds were developed to fulfil the needs of this research. Greater duckweed-based laboratory-scale free water CW system and GAC sandwich SSF with coarse sand system were initially studied individually using synthetic wastewater to optimize the removal of all target PPCPs. Then combined CW-SSF system in series was further investigated to test the performance of PPCP removal using both synthetic wastewater and natural water. Removal effects of photodegradation, biodegradation and plant degradation were assessed, adsorption kinetics and isotherms were investigated, and stability of CW-involved systems with/without aeration was studied. The main findings of the research can be concluded as follows:

- Optimization of GC-MS procedure

  Final carrier gas flow rate was set at the 2.5 mL/min. Temperature programming was optimized to 100 ℃ (hold for 2 min) to 300 ℃ (hold for 5 min) at the rate of 20 ℃/min; and 0.020 second of dwell time. Total GC-MS running time of one sample was less than 13 min. No derivatization process was involved.

- Optimization of SPE process

  The pH of the optimized sample 3.0. Sample loading rate was set at 5 mL/min. Acetonitrile was used as eluent. Oasis HLB cartridge achieved the overall best recover among all tested cartridges.

- SPE-(GC-MS) method validation

  With conditioning and equilibration, recoveries were 81.9~99.5 % for DEET, 76.1~109.0 % for PAR, 88.1~106.6 % for CAF and 87.5~105.2 % for TCS, respectively. Without conditioning and equilibration steps, good recoveries were also observed, using Waters Oasis HLB cartridge, being 74.9~110.4 % for DEET, 80.0~111.3 % for PAR, 97.7~106.3 % for CAF and 88.0~98.9 % for TCS, respectively. Both methods lie in the accepted recovery range.

- Batch scale CW tests

  Four factors (light, oxygen, plant and microbes) with three levels influencing CW performances were studied and orthogonal design was employed for the experiment design. DEET was found recalcitrant in the batch system while the other three compounds were photodegraded (PAR, TCS) and/or biodegraded (PAR, CAF, TCS). Greater duckweed contributed to removal of PAR (52.9 %) and TCS (26.8 %).

  Based on the orthogonal Duncan analysis, 240 $\mu molm^{-2}s^{-1}$ light intensity, full aeration, 1.00 kg/m^2 plant biomass and 1.0×10^6 CFU/100 mL *E.coli* abundance favoured the average removal of the PPCP compounds in the batch systems.

Verification test using optimized factor levels achieved 17.1 %, 98.8 %, 96.4 % and 95.4 % removal for DEET, PAR, CAF and TCS, respectively.

- Continuous flow CW tests

  For continuous flow systems, CW tests with and without adjunction of ST tank were both carried out using the optimized factor levels from the batch tests. Final PPCP removal achieved by the continuous flow CW system were 32.6 %, 97.7 %, 98.0 % and 100 %, respectively, for DEET, PAR, CAF and TCS, while in the continuous flow CW-ST system removal of 43.3 %, 97.5 %, 98.2 % and 100 %, respectively, were achieved. However, low removal of DEET indicated further investigation needed.

  PPCP removal by the continuous flow CW-ST system were significantly faster (p<0.05) than the removal by the continuous flow CW alone. Oxygen was considered an important factor in the CW system. After aerators were switched off, both continuous flow systems (CW and CW-ST) demonstrated treatment stability for PPCP removal. Continuous oxygen diffusion from air to water and potential oxygen transportation of plant leaves-roots-water can be regarded as main reasons. The lack of oxygen in the CW system could be compensated by the inclusion of a ST tank following the CW tank.

  Continuous flow CW-ST showed better COD, TOC and nitrite removal, while ammonium was removed more in continuous flow CW system. Both continuous flow systems gave removal of phosphate between 33 % and 70 %.

- Correlation analysis on continuous flow CW tests

In both continuous flow CW and CW-ST systems, correlation analysis showed a number of significant correlations (p<0.05) between removal of PPCP compounds and water nutrients. Removal of all four PPCPs showed significant correlations with each other (p<0.05) statistically, indicating removal of these contaminants may have similar degradation pathways. PAR had the strongest correlation (r=0.979; p=3.0E-08) with TCS in the continuous flow CW system, and DEET with CAF (r=0.953; p=2.0E-06) in the continuous flow CW-ST system.

- GAC sandwich SSF test

  GAC sandwich SSF significantly (p<0.05) enhanced the target PPCP compound removal compared with that using traditional slow sand filter. The overall optimal average target PPCP removal (98.2 %) was achieved at filtration rate of 10 cm/h by Filter 3 (10 cm sand/20 cm GAC/20 cm sand). Total average removal of the four target compounds during the whole operation were 51.9 %, 97.6 %, 97.9 %, 96.2 % and 95.7 % for Filters 1-5, respectively. DEET which was not efficiently removed by the CW system (< 45 %) was highly removed (> 95 %) using the GAC sandwich SSF.

  No significant difference (p>0.05) of average PPCP removal was found between 10 cm/h and 20 cm/h filtration rates for three GAC sandwich filters. In the GAC sandwich SSF system, the removal of target PPCPs could be attributed to both adsorption (especially DEET and CAF) and biodegradation.

  Compared with the other filters, filter 3 (10 cm sand/20 cm GAC/20 cm sand) showed better average removal of COD and TOC in this test. Nitrogen could be effectively removed by the GAC sandwich SSF systems. Due to probable insufficient microbial phosphate consumption, less than 15 % phosphate removal

was observed for all filters. No significant difference (p>0.05) was found between 10 cm/h and 20 cm/h for nitrogen and phosphate removal.

- Adsorption kinetics and isotherms

  Compared with Lagergren pseudo-first-order and Elovich models, Type 1 pseudo-second-order model fitted best the adsorption kinetics of target PPCP compounds (25 μg/L) onto GAC (Pearson R^2 value > 0.99). Adsorption isotherms of four target compounds at 25 μg/L could be described by the Freundlich model (Pearson R^2 > 0.96).

- Tests for the CW-SSF system in series using synthetic wastewater

  Good removal of four PPCP compounds from synthetic wastewater were achieved at 96.1 %, 99.9 %, 99.4 % and 97.3 %, respectively, on average. From day 10, no PAR and CAF was detected in the effluent. Because of continuous GAC adsorption and transportation of oxygen from air/plants to water for continuous biodegradation, after the aerators were switched off, removal of PPCPs did not change dramatically, demonstrating treatment system stability for the target PPCP removal.

  With no nitrite detected, at the end of the test, the concentrations of COD, TOC, nitrate, ammonium and phosphate were 19±1 mg/L, 4.79±0.05 mg/L, 4.77±1.18 mg/L, 1.03±0.02 mg/L and 6.68±0.05 mg/L, respectively.

- Test for the CW-SSF system in series using natural water

  All four compounds were detected in the lake where natural water was collected.

Good average removal of 95.9 %, 99.1 %, 98.1 % and 97.4 % for DEET, PAR, CAF and TCS from natural water were observed, respectively. Except for DEET (p<0.05), no significant difference (p>0.05) of removal was observed after the aeration stopped, indicating good system stability.

Good removal of nitrite, nitrate and phosphate were observed (only detected in a few days) and none of them was found in the effluent at the end of the test. COD and ammonium were effectively treated with aeration.

- Comparisons among tested systems

  Biodegradation from microbes and photodegradation from light contributed to target PPCPs removal in CW-associated systems. Plant degradation from Greater duckweed was proven also playing a role in degradation process, especially for PAR and TCS. In contrast, adsorption from GAC was more responsible for the removal in filtration system than biodegradation and photodegradation. The CW-SSF system combined the mechanisms from both two systems.

  Single CW and GAC sandwich SSF units both showed some limitations. DEET and CAF were not well removed (less than 70 % averagely) in continuous CW/CW-ST systems. Although GAC sandwich SSF achieved better target PPCP removal, phosphate was poorly removed (less than 12 % averagely) and can only receive influent with certain quality. CW-SSF system in series not only showed good removal of four target PPCP compounds and environmental stability, but also compensated for some shortcomings of single CW or GAC sandwich SSF unit, suggesting it as a potential water treatment technique (e.g. as tertiary wastewater treatment).

No significant difference (p>0.05) was found between average removal of four PPCPs (spike concentration at 25 μg/L) in natural water and synthetic wastewater systems.

With much fewer chemical and less electricity required than other techniques, CW-SSF in series can be regarded as eco- and cost-friendly water/wastewater treatment technology. Therefore, the applicability of this design concept will be of interest to researchers, engineers and practitioners working with PPCPs removal and water/wastewater treatment.

8.2 Future work

The following areas are recommended for future work:

- The pathway of target PPCP compounds in the Greater duckweed. Dordio et al. (2011) [362] assumed that 10,11-dihydro-10,11 epoxycarbamazepine is one of the possible routes of carbamazepine metabolism in the tissues of Typha spp. Since metabolisms of PPCPs in plant cells are complex processes, it is worthwhile to have a deeper understanding of the transformation or the accumulation mechanisms inside Greater duckweed tissues, as well as degradation by-products.

- Toxicity of target PPCP compounds to Greater duckweed. Toxicity of some PPCPs to plants were found [55,160]. The (co-) influence of target PPCP compounds on the Greater duckweed can be studied in the future, morphologically, genetically and physiologically.

- Microbial community structural changes in the CW-SSF system in series. Bacterial community variation was observed in both CW system and SSF system treating PPCP compounds before [32,159]. Knowing such changes can strengthen the understandings on how microbial communities vary (e.g. sensitivity, toxicity) under PPCPs treatment and potential influence to the system performance.

- Screening the PPCP-degradation microbes. Biodegradation was proved effective in both CW and SSF systems, which demonstrates some microbes are capable of eliminating target PPCP compounds. Just like some bacteria (e.g. ATCC 33456, ATCC 11172) were found able to degrade organics (e.g. phenol) [295,296], if these microbes can be screened out, they may be useful as engineering strains in water and wastewater treatment. Besides, degradation by-products can be also monitored and analysed.

- Deeper insight into the adsorption/desorption mechanisms [229,351] of target PPCP compounds onto GAC. The adsorption study was not deep enough to look into the GAC surface changes after adsorption. Studying desorption and using higher PPCP dose will help understand the mechanisms more.

- Service life of GAC sandwich SSF. In current study, GAC sandwich SSF did not reach the lifespan since concentration of target PPCP compounds were very low. Breakthrough curves of target PPCPs were not considered as in other studies [46]. Hence, longer testing time using higher concentration can be further studied.

- Economic evaluation of CW-SSF system. In the Chapter 2, a preliminary comparison of costs between CW/SSF with other techniques was briefly reviewed. A systematic study considering practical costs can be investigated and assessed.

- Experiments of this study were only carried out at laboratory-scale dealing with synthetic wastewater and natural water. Large-scale trial treating real wastewater can be conducted in the future.

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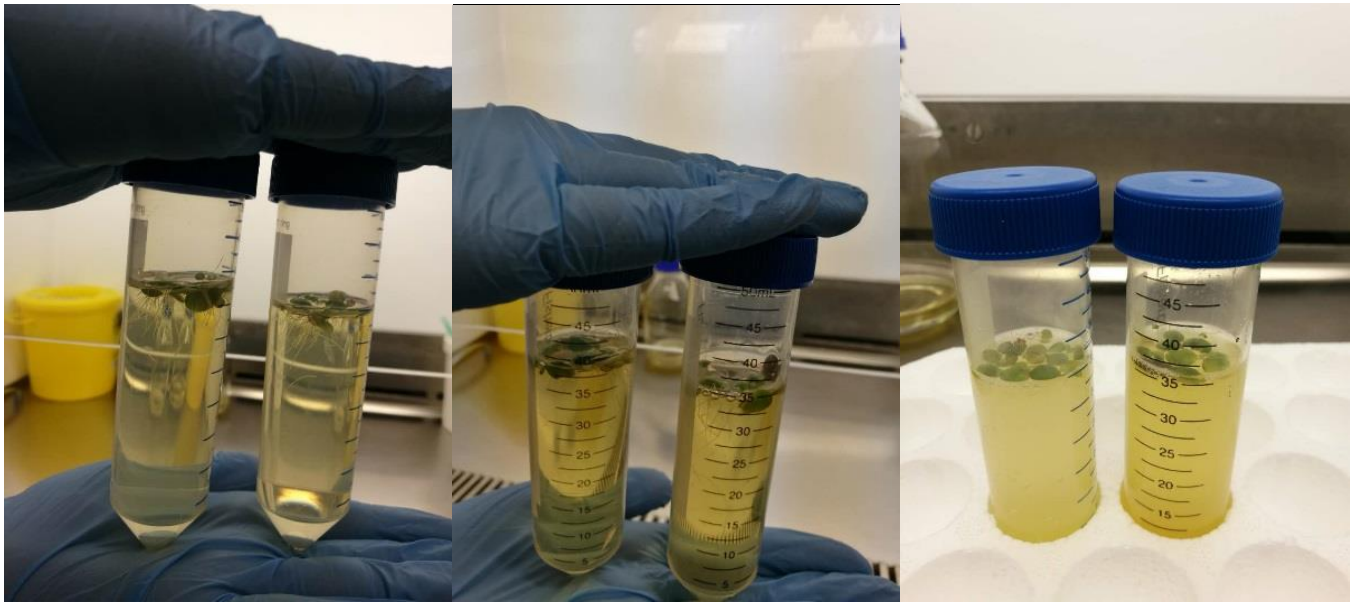
APPENDIX 1

Sterilization of Greater duckweed test

Several randomly selected plants were put in both LB broth and nutrient broth for 24 hours at 37 ℃, to verify the effectiveness of sterilization process. After incubation, clear broth indicated aseptic plants (negative). Broth control was done to verify tested broths were not contaminated.



Photos of tested Greater plants in LB broth and Nutrient broth after using 0.1 % bleach treatment

(Left: 24-h later nutrient broth after 0.1 % bleach treatment; middle: 24-h later LB broth after 0.1 % bleach treatment; right: plant control)

APPENDIX 2

pH, conductivity, redox potential and DO for the CW batch test

Day	CW1			CW2			CW3			CW4			CW5			
	pH	Conductivity (µS/cm)	Redox potential (mV)	pH	Conductivity (µS/cm)	Rredox potential (mV)	pH	Conductivity (µS/cm)	Redox potential (mV)	pH	Conductivity (µS/cm)	Redox potential (mV)	pH	Conductivity (µS/cm)	Redox potential (mV)	DO (mg/L)
1	8.15	785	32.3	8.07	798	4.7	8.20	793	35.0	8.25	792	-21.3	7.71	822	22.1	8.5
2	8.07	774	-35.5	8.02	782	-53.7	8.19	786	-72.4	8.10	783	-96.5	7.86	812	-52.3	6.0
3	7.76	753	-25.1	7.73	749	-45.5	8.00	837	-67.6	7.61	765	-74.8	6.93	776	-36.8	5.5
4	7.82	691	2.0	7.68	727	-10.4	7.91	787	-24.0	8.00	748	-37.3	6.93	753	-10.8	6.1
5	7.96	767	14.7	7.88	770	11.1	8.08	782	18.8	8.05	762	-15.5	7.65	764	3.0	6.1
8	7.97	787	25.7	7.95	797	16.9	8.10	791	21.0	8.02	793	-7.5	7.60	773	11.4	6.2

Day	CW6			CW7			CW8				CW9			
	pH	Conductivity (µS/cm)	Redox potential (mV)	pH	Conductivity (µS/cm)	Redox potential (mV)	pH	Conductivity (µS/cm)	Redox potential (mV)	DO (mg/L)	pH	Conductivity (µS/cm)	Redox potential (mV)	DO (mg/L)
1	8.09	799	7.6	8.14	795	12.7	7.59	815	7.5	8.13	7.49	800	-2.3	7.36
2	8.02	784	-69.2	8.10	788	-47.8	7.59	804	-69.3	6.21	7.69	797	-68.5	5.74
3	7.66	766	-51.2	7.80	785	-27.3	6.95	774	-48.4	4.4	7.05	789	-45.7	4.77
4	7.41	743	-10.7	7.71	745	-3.1	6.79	794	-23.4	5.29	7.22	768	-17.8	5.12
5	7.81	790	8.1	7.99	763	14.1	7.54	777	2.6	5.83	7.32	773	10.5	5.77
8	7.88	788	12.3	8.03	768	21.1	7.56	786	10.2	6.28	7.47	791	17.6	5.78

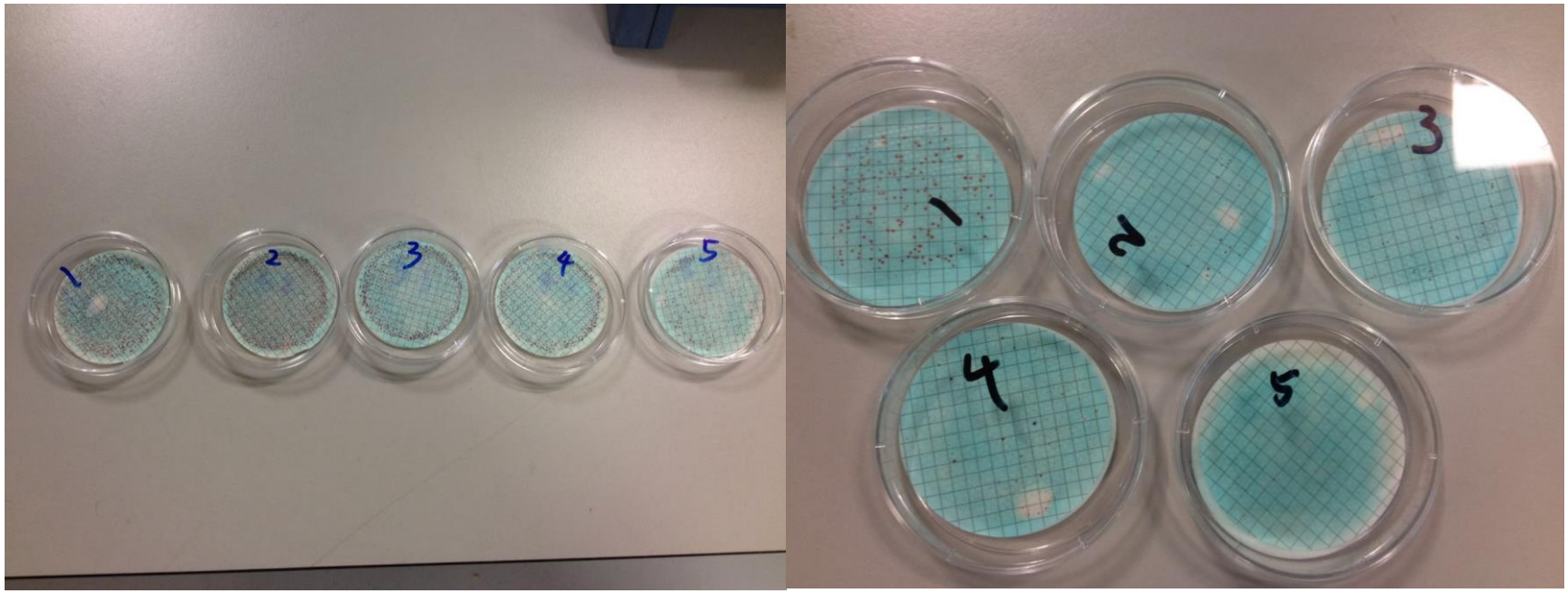
APPENDIX 3

pH, conductivity, redox potential and DO in the continuous flow CW & CW-ST systems

Day	pH		Conductivity (μS/cm)		Redox potential (mv)		DO (mg/L)		
	Continuous CW	Continuous CW-ST	Continuous CW	Continuous CW-ST	Continuous CW	Continuous CW-ST	Continuous CW	Continuous CW-ST (tank CW)	Continuous CW-ST (tank ST)
1	8.17	8.12	821	811	50.0	74.4	7.86	7.92	6.99
2	8.05	7.82	796	789	11.7	46.8	7.95	7.90	2.46
3	8.00	7.82	757	766	7.5	34.3	7.94	7.86	0.20
4	8.2	7.91	748	759	3.0	13.5	7.96	7.93	0.02
5	8.02	7.76	756	752	12.0	15.8	7.92	7.97	0.46
8	8.13	7.81	753	749	18.0	27.7	7.89	7.92	6.20
9	8.03	7.98	738	721	17.0	25.3	7.91	7.42	5.56
10	8.14	8.03	745	728	22.2	27.7	7.78	7.41	4.94
11	7.87	8.17	734	739	26.6	35.5	7.86	7.39	4.34
12	7.81	8.09	741	736	20.2	34.3	7.93	7.86	5.86
15	7.79	7.87	742	733	21.3	36.4	7.92	7.98	6.67
16	7.77	7.99	743	750	45.7	27.5	7.92	7.97	5.98
17	7.87	8.00	753	734	43.7	35.8	7.93	7.95	5.66
18	8.03	7.83	728	735	65.0	32.6	0.51	0.28	4.33
19	7.96	7.77	732	776	52.5	40.5	0.64	0.06	2.07
22	7.89	7.68	735	776	47.3	39.0	3.12	0.29	6.04
23	7.92	7.83	724	775	37.4	40.6	3.36	0.30	6.18
24	7.83	7.88	735	752	24.3	35.0	4.49	0.54	6.96
25	7.73	7.98	704	753	27.3	42.1	4.51	2.11	6.54
26	7.99	7.97	711	751	36.2	39.0	3.99	2.98	6.78

APPENDIX 4

Photos of M-ColiBlue24® method at the beginning and end of filter maturation stage



(Left: effluent of first day during maturation; right: effluent of day 22 during maturation. Red and blue colonies indicate total coliforms and blue colonies specifically indicate *E. coli*)

APPENDIX 5

pH, conductivity and redox potential in the effluents during the GAC sandwich SSF tests

Day	Filter 1			Filter 2			Filter 3			Filter 4			Filter 5		
	pH	Conductivity (µS/cm)	Redox potential (mv)	pH	Conductivity (µS/cm)	Redox potential (mv)	pH	Conductivity (µS/cm)	Redox potential (mv)	pH	Conductivity (µS/cm)	Redox potential (mv)	pH	Conductivity (µS/cm)	Redox potential (mv)
2	8.01	649	70.1	8.09	634	57.9	8.05	610	58.9	8.00	600	59.1	7.84	584	55.2
5	8.17	624	60.5	8.20	652	64.9	8.13	654	69.1	8.05	637	52.0	7.80	673	59.0
9	7.94	630	33.0	8.12	673	35.0	8.23	664	35.6	8.06	645	37.4	8.12	645	31.5
12	7.83	643	32.2	8.07	639	31.4	8.10	643	33.1	8.09	630	27.3	8.17	646	28.1
16	7.93	587	38.6	8.04	620	38.6	8.12	611	33.0	8.09	634	34.5	8.02	626	33.1
19	7.81	604	42.6	7.97	622	46.0	7.99	614	46.8	8.08	628	47.5	8.12	623	38.0
23	7.76	610	27.2	7.68	615	33.4	7.95	631	30.0	7.99	613	30.3	7.92	602	27.8
26	7.81	608	37.0	7.78	612	39.6	7.88	609	32.7	8.00	609	37.9	8.03	611	45.3
30	7.59	610	64.1	7.65	607	67.4	7.80	610	66.0	7.85	613	35.9	7.85	614	36.5
33	7.82	598	76.1	7.75	595	74.9	7.72	594	72.4	7.80	608	67.1	7.92	610	59.8
37	7.55	610	68.6	7.62	617	74.2	7.64	612	72.4	7.67	617	69.2	7.78	626	65.6
40	7.41	602	61.5	7.50	606	61.2	7.61	601	59.1	7.52	600	57.1	7.72	620	53.8
44	7.58	604	64.8	7.55	597	63.3	7.66	592	62.4	7.58	599	55.5	7.85	612	53.3
47	7.66	619	60.5	7.70	603	67.3	7.74	623	68.2	7.75	611	63.2	7.80	622	63.2
51	7.78	686	62.2	8.00	685	50.3	7.86	679	51.4	7.87	688	54.9	7.86	681	60.3
54	7.59	688	55.7	7.68	690	46.9	7.69	690	45.5	7.71	684	61.2	7.74	683	66.4
58	7.83	682	51.3	7.83	689	61.6	7.91	690	50.9	7.80	692	52.6	7.69	688	49.3
61	7.67	682	39.8	7.72	678	28.9	7.70	674	30.4	7.66	682	44.5	7.82	682	42.9

APPENDIX 6

pH, conductivity, redox potential and DO in the synthetic wastewater CW-SSF system

Day	pH	conductivity (μS/cm)	redox potential (mV)	DO (CW, mg/L)	DO (ST, mg/L)
1	8.22	750	22.6	7.86	7.64
3	8.05	700	96.6	7.83	5.84
5	8.04	755	48.5	7.82	6.50
8	8.05	796	22.9	7.77	6.76
10	8.09	789	24.5	7.70	6.53
12	8.07	753	25.0	7.75	6.66
15	8.03	811	18.0	1.40	6.37
17	8.02	750	18.4	0.74	6.30
19	8.02	746	16.2	0.99	6.32
22	8.05	729	31.9	1.29	6.33
24	8.04	730	26.7	2.66	6.19
26	8.05	704	24.3	4.43	6.22

APPENDIX 7

pH, conductivity, redox potential and DO in the natural water CW-SSF system

Day	pH	conductivity (μS/cm)	redox potential (mV)	DO (CW, mg/L)	DO (ST, mg/L)
1	7.97	1800	69.8	8.25	8.17
3	8.26	1085	29.6	7.98	6.86
5	8.18	1020	36.6	8.17	6.70
8	8.22	1013	22.1	8.19	7.05
10	8.29	1210	22.0	8.19	7.06
12	8.30	1263	92.8	8.20	7.02
15	8.25	1303	90.1	5.32	6.88
17	8.37	1154	93.3	5.26	6.81
19	8.27	1159	66.1	5.35	7.00
22	8.30	1163	65.7	6.04	7.55
24	8.23	1265	40.1	6.26	7.47
26	8.24	1270	41.8	6.16	7.11