Removal of selected pharmaceuticals and personal care products in wastewater treatment

processes

By

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Abstract

Pharmaceuticals and personal care products (PPCPs) are a group of emerging environmental disrupting contaminants. PPCPs and their residues are widely detected in surface water, groundwater, and sewage treatment plants (STPs) due to their universal consumption, low human metabolic capability, and improper disposal. STPs are known as one of the major sources of PPCPs released into the environment while activated sludge is the significant process of PPCPs removal. Therefore, this study aimed to investigate the recent tendency of selected PPCPs in waste water matrix, elimination routes in STPs and propose an innovative method to improve its removal efficiency. The major tasks were (1) to establish an appropriate, sensitive and repeatable analytical method to detect selected PPCPs concentrations in different units of STPs, (2) to investigate the eliminate mechanisms of PPCPs in activated sludge treatment process, (3) to determine the PPCPs adsorption behavior on rice husk-derived biochar, and (4) to study the transformation routes of PPCPs under different redox conditions. The appropriate, sensitive and repeatable analytical method with a low detection limit was established for trace analysis of PPCPs in different water matrixes via liquid-liquid extraction (LLE), solid-phase extraction (SPE), and gas chromatography-tandem mass spectrometry (GC-MS/MS). The method established in this study was accurate and could be applied to a different water body. PPCPs were detected at the ranges of 89-657 and 0-58 ng/L in STPs inlet and outlet, respectively. The concentrations of PPCPs in the same city by different treatment units varied by 1-2 orders of magnitude. The removal efficiency ranged from -5% to >97% of each unit of local STPs in Hong Kong. Biodegradation and adsorption were considered as dominant removal mechanisms for selected PPCPs at environment relevant concentrations under aerobic conditions. In particular, octocrylene (OC) was mainly removed by adsorption. N,N-Diethyl-3-methylbenzamide (DEET),



benzophenone-3 (BP-3), homosalate (HMS), and triclosan were mainly removed by biodegradation process. The Biodegradation behavior of selected PPCPs under aerobic activated sludge can fit the first-order kinetics model well with the R^2 ranged from 0.94 to 0.98. The consistent k_1 ranged from 0.10 to 0.21. The adsorption of five PPCPs on rice husk-derived biochar performed well in Milli-Q water with all removal rate >80%. Therefore, the conclusion of the high potential of rice husk of adsorbed PPCPs could be drawn. Especially for BP-3, more than 99% has been adsorbed removed. Under different redox conditions, all target pollutants removal performance could have a positive response to the redox value increase. The pH and redox values showed a negative relationship with each other. The bacterial community was more active under the oxidation condition than that under the reduction condition. For triclosan, the oxidation condition may increase the formation of triclosan-methyl. The addition of rice huskderived biochar in activated sludge may increase the removal efficiency of PPCPs and decrease the PPCPs concentration in response to redox change.

Keywords: wastewater treatment plants, PPCPs, activated sludge, biochar, removal efficiency



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List of abbreviations

ASP	Activated sludge process		
BP-3	2-Hydroxy-4-methoxybenzophenone		
BSTFA	Regent N, O-Bis(trimethylsilyl)trifluoroacetamide		
DCM	Dichloromethane		
DEET	N,N-Diethyl-3-methylbenzamide		
DO	Dissolved oxygen		
EA	Ethyl acetate		
EPS	Extracellular polymeric substances		
HMS	Homosalate		
HRT	Hydraulic retention times		
MeOH	Methanol		
GC-MS/MS	Gas chromatography-tandem mass spectrometry		
LLE	Liquid-liquid extraction		
LOQ	Limit of quantitation		
OC	Octocrylene		
PPCPs	Pharmaceuticals and personal care products		
SRT	Sludge retention times		
STPs	Sewage treatment plants		
QA	Quality assurance		
QC	Quality control		
Redox	Reduction and oxidation		



SPE	Solid-phase extraction		
USEPA	US Environmental Protection Agency		

Chapter 1 Introduction

1.1 Background

Nowadays, pharmaceuticals and synthetic personal care products (PPCPs) been classified as a group of contaminants that can be widely detected in natural waters. Extensive researches on PPCPs in water has been conducted for several decades. The first study related to PPCPs of the United States Environmental Protection Agency (USEPA) on conventional, non-conventional, and toxic pollutants in the water began in 1982. PPCPs have presented in surface water, groundwater, drinking water sources, and wastewater matrix at the level of nanogram per liter (ng/L) to microgram per liter (µg/L) (Behera et al., 2011). Some residues also presented in treated wastewater since the STPs are not designed to remove PPCPs. The discharge criteria generally including organic substances and COD requirements (Dai et al., 2015; Tsang, 2015). Therefore, impropriate treated wastewater has been identified as one of the major sources of PPCPs releasing to the aquatic environment (Dey et al., 2019; Yang et al., 2017). The widespread use of PPCPs and their residues in different environmental media has led to great concern due to the potential harm to ecological systems and human health. Previous studies found that veterinary diclofenac may have negatively affected the population and diversity of birds, including the steppe eagle in South Africa and vulture in India (Cuthbert et al., 2016; Galligan et al., 2014; Sharma et al., 2014). In addition, several metabolites and transformation products of STP wastewater form together with parent compounds due to various chemical reactions during treatment (Zepon Tarpani and Azapagic, 2018). The detection of PPCPs in wastewater or drinking water has increased in recent years, partly due to advances in analytical techniques and routine monitoring to completely understand the occurrence of these



contaminants and the correlation with the environmental impact and human health. The environmental life of pentachlorophenol and its metabolites vary with their original degradation in the environment and related to their natural degradation degree in the environment (USEPA, 2013). The USEPA has categorized pharmaceuticals and hormones in its Contaminant Candidate List for safe drinking water (USEPA, 2009).

1.1.1 Classification of PPCPs

The production and application of PPCPs are for medical purposes and to improve the living standards for both human beings and animals. But it is also defined as a general term for a class of organic pollutants. These compounds including antibiotics, hormones, analgesics, anti-inflammatory drugs, blood lipid regulators, β -blockers, and cytostatic for pharmaceuticals; and preservatives, bactericides, insect repellents, fragrances, and sunscreen UV filter for personal care products (Table 1.1) (Dey et al., 2019). For pharmaceuticals, a large number of studies have been targeted well in recent years (Aymerich et al., 2016; Papageorgiou et al., 2016). Therefore, only commonly detected PCPs were discussed in detail for occurrence and removal study.

For the groups of personal care products, benzophenone-3 (BP-3), homosalate (HMS), octocrylene (OC) are commonly consumed sunscreen UV filter species. Synthetic polycyclic musks including galaxolide (HHCB) and toxalide (AHTN) with more production and application than the nitro group in recent years. N,N-diethyl-m-toluamide (DEET) is the main active ingredient of insect repellents and regularly detected. Triclosan and triclocarban are the two typical antimicrobial agents frequently presented in wastewater. Parabens are typical preservatives, which are widely applied in cosmetics, personal hygiene products, food, and



medicine. They are very effective in preventing the growth of fungi, bacteria, and yeast that can cause deterioration of the product.

Order		Typical classes	Representative
			compounds
1a	Pharmaceutical	Broad-spectrum antibiotics	Penicillin
1b		Hormones	Estriol
1c		Non-steroidal anti-	Ibuprofen
		inflammatory drugs	
1d		β-blockers	Metoprolol
1e		Blood lipid regulators	Gemfibrozil
2a	Personal care	Bactericides	Triclosan
	products		
			Triclocarban
2b		Insect repellents	DEET
2c		Sunscreen UV filters	BP-3
			HMS
			OC
2d		Preservatives	Parabens
2e		Synthetic musks	AHTN
			ННСВ

 Table 1.1 The classifications of common PPCPs and their representative compounds

1.1.2 Pathway of PPCPs in environment

PPCPs can enter the environment through a variety of pathways (Figure 1.1), including STP, industrial services, hospitals, aquaculture facilities, runoff from fields to surface waters, and runoff into the soil through animal husbandry and manure applications (Boxall et al., 2012). The PPCPs consumed in daily life mainly enter STPs through the sewage collection system. In the treated sewage, PPCPs residues in the sludge can also release into the environment through landfill and disposal. Therefore, uncompleted treated wastewater is identified as one of the major sources of PPCPs released into the environment. The existing PPCPs in surface water can enter



the drinking water treatment plant through the inlet of the water treatment plant and may enter human daily life in the tap water supply system (Jiang et al., 2013). Residues and metabolism of PPCPs can enter the environment through natural hydrological cycles. Some pharmaceutical ingredients that are not fully metabolized by humans and animals are excreted from the body through feces and urine and finally discharged into the sewage system (Jiang et al., 2019). Personal care products (PCPs), including shampoos, shower gels, toothpaste, sunscreens, cosmetics, and hand sanitizers, can be released into sewer systems and surface waters through human daily washing activities. In addition, swimming and other water recreation activities may also contribute to discharge of PPCPs (e.g. UV filters) (Yang et al., 2017). Other PPCPs exposure pathways include the disposal of unconsumed pharmaceuticals to landfills, veterinary pharmaceuticals runoff in farms, disposal of improperly treated carcasses and irrigation using reclaimed water (Bottoni and Caroli, 2018).





Figure 1.1 The pathway of PPCPs in the environment

1.1.3 Environmental and health risks

The distribution of PPCPs is widely around the world and their residues in various environmental media raise great worries due to the potential harm to the ecological system and human health. In terms of persistence, toxicity, and bioaccumulation, the effects of PPCPs on the environment and human beings are a major concern in the field. Many PPCPs can dissipate rapidly in the environment, but their widespread application has led to their accumulation in the aquatic environment and severe ecological impacts on aquatic organisms. (Kostich et al., 2014). Commonly detected PPCPs in STPs, including sewage effluent and reclaimed water, is caused



by their universal consumption, low human metabolic capability, improper disposal, and biologically active structures (Borova et al., 2014; Chen et al., 2013). In artificial wastewater treatment matrices, PPCP can partially or incompletely biodegrade. Thus, excreted metabolites may become secondary contaminants because the major components are further altered in the receiving water body (Tanoue et al., 2012). When applying reclaimed water from sewage sludge as an organic fertilizer, these pollutants may be taken as nutrients by plants (Cardinal et al., 2014; Jiang et al., 2013; Overturf et al., 2015). Experimental results have been used to demonstrate the conclusion that PPCPs are found in the tissues of plants when using compressed activated sludge in soil or using sewage for irrigation (Chen et al., 2014). The individual PPCP has little impact on human health, however, the accumulation effects of PPCP can be hazardous and unpredictable (Rajapaksha et al., 2015). Toxic pathological effects of the sunscreen UV filter, BP-3, on coral planulae in Hawaii and the U.S. Virgin Island were also investigated. BP-3 poses a danger to coral reef protection and threatens their resilience to climate change (Downs et al., 2016). Martins et al. (2017) found that frog embryo exposure to triclosan may exert adverse effects on the early life stages of frogs. 4-MBC may also induce oxidative stress and trigger apoptosis in marine copepod *Tigriopus japonicus*, resulting in developmental, reproductive, and lethal toxicity. Other results showed that environmentally relevant concentrations of BP-3 can negatively impact freshwater insects (caddisfly) (Campos et al., 2017). Ho et al. (2016) reported that triclosan exposure at 250 g/L does not have any effect on normal embryogenesis or organogenesis; however, concerns about possible damage to lipid metabolism persist. Human beings' exposure to PPCPs through drinking water, plant tissue, and fish due to manure amendments, wastewater irrigation, and sludge disposal have been discussed in recent years (Gaffney et al., 2015; Mottaleb, 2015; Prosser and Sibley, 2015). In recent



research, PPCPs were identified in human breast milk, blood, and children's urine (Frederiksen et al., 2017; Li et al., 2013; Yin et al., 2012). In addition, the existence of benzyl paraben and BP-4 was the first evidence of their accumulation in the placenta. Parabens and UV filters have been proven to accumulate in the human placenta, which suggests potential mother-fetus transfer (Valle-Sistac et al., 2016). This result was further studied by subsequent research. Fifteen tissue samples from randomly selected individuals were analyzed (Vela-Soria et al., 2017). However, no federal regulations for PPCPs in drinking or natural waters currently exist. According to the USEPA, the adverse effects on human fitness associated with pentachlorophenol and personal care products in drinking water have not been confirmed, and the contamination of PPCPs remains a serious concern (USEPA, 2015; USEPA, 2018). The first guideline established for PPCPs management for the Environmental Risk Assessment of Human medicines was published by the European Medicines Agency (EMA, 2006). Thus, the occurrence of polychlorophenol and its relationship with human health and the environment must be fully understood during routine monitoring. Given manure amendments, wastewater irrigation, and sludge disposal, human exposure to PPCPs through dietary intake has been discussed in recent years (Gaffney et al., 2015; Mottaleb, 2015; Prosser and Sibley, 2015). Current research work on PPCPs mainly focuses on determining the environmental concentration and environmental behavior. Research on its environmental effects and ecological risks is still in its infancy, especially for reproductive toxic effects and population dynamics under low-dose long-term exposure (Richardson and Ternes, 2017). Existing PPCPs toxicity data are derived from the toxicity database and different literature which lead the test species and the final value of the experiment is quite different.



Therefore, aquatic organisms (fish, large) should be characterized by different trophic levels. The toxicity characterization of sputum phytoplankton truly reflects the environmental and ecological risks of PPCPs in regional water environments (Wilkinson et al., 2016).

1.2 Innovation and objectives of the study

This work aimed to analyze the present situation of selected PPCPs and elimination routes in sewage treatment plants (STPs) and water matrix. To establish an appropriate, sensitive and repeatable analytical method for tracing low concentrations selected PPCPs belonging to three different classes in different units of the wastewater treatment processes. The analytical method was successfully applied in determining occurrence and transformation routes of multiple PPCPs in wastewater treatment processes and study dominant elimination mechanisms of PPCPs in the secondary process, and further, understand the removal performance of combined biochar and biological treatment under different redox conditions.

The innovation of the study including:

- To investigate the removal mechanisms of 5 PPCPs (3 classes) in activated sludge process simultaneously;
- (2) To explore the feasibility of PPCP removal using rice husk-derived biochar; and
- (3) To study the removal of PPCPs by activated sludge and biochar under different redox conditions



The aims and objectives of this study expressed as follows:

(1) Establish an appropriate, sensitive and repeatable methodology for five common detected PPCPs from the low magnitude of three different classes in STPs.

Liquid-liquid extraction (LLE), solid-phase extraction (SPE), and gas chromatography-tandem mass spectrometry (GC-MS/MS) were combined to establish an appropriate methodology to determine five PPCPs belonging to three classes (including insect repellents, bactericides and UV filters). The parameter of analytical procedures including method detection limit, recovery rate, repeatability, and limitation of quantitation was optimized. This analytical method has been successfully applied in order to investigate the concentrations of PPCPs from different wastewater treatment units in two local STPs.

(2) Determine the occurrence and removal efficiency of selected PPCPs in two local STPs, namely, Shatin and Taipo.

The analytical method has been applied in the study of the occurrence of PPCPs from each wastewater process, including influent, primary treatment, secondary treatment, and effluent. The removal efficiency of primary treatment, secondary treatment and UV disinfection were also investigated.

(3) Study the elimination routes of five commonly detected PPCPs at environmentally relevant concentrations.

The removal mechanism for these PPCPs was investigated through lab-scale batch experiments which simulated the polite scale aerobic tank in STP. The pseudo-first-order model for low concentration removed by biodegradation behavior was applied also.



(4) Determine the elimination mechanisms of target pollutants under different redox conditions with biochar.

Biochar adsorption kinetic study was established in the last part of the work. The kinetic study of PPCPs on rice husk-derived biochar was investigated. The biological removal of selected PPCPs was determined under different redox windows, including + 200, 0, and -200 mv.

The adsorption of five PPCPs at environmentally relevant concentrations under different redox conditions was systematically investigated. Special work involved the following tasks: (a) characterization of rice husk-derived biochar, (b) adsorption kinetics study of five selected PPCPs on rice husk-derived biochar with different dosages, (c) the relationship between redox conditions change and pH value, (d) the removal behavior differences between biological removal and biological removal combined with rice husk-derived biochar, and (e) the impact of pH on the biological and biochar removal rates.



Chapter 2 Literature review

According to the specific chemical categories of pollutants, a series of treatment methods have proven to be effective in reducing the concentration of PPCPs in STPs. However, in general, the residues in the environment cannot be ignored given that STPs are one of the major sources of PPCPs release in the water matrix. This chapter will discuss the commonly detected compounds, occurrence and fate of selected pollutants in STPs, and limitations of existing treatment technologies.

2.1 Occurrence and removal efficiency of PPCPs in sewage

N,N-diethyl-m-toluene amide (DEET) is the active ingredient in commonly used insect repellents, which can be commercially obtained worldwide because of its popularity among customers in the past 30 years. Several studies have recently reported the environmental-related concentration and fate of DEET, especially in lakes, rivers, and soil. It is also known that this substance poses a potential hazard to aquatic and terrestrial organisms. The concentration of DEET in sludge is the highest, accounting for 40%–62% of the total concentration. DEET mainly exists in the form of dissolution (detection frequency >92%) in the original inflow and final effluent (Veach and Bernot, 2011). Compared with the effluent (402 g/day), the sludge cake content (17 g/day) is much lower. The removal efficiency rates of primary treatment, A^2/O tank, and secondary treatment are 4.9%, 25%, and 90%, respectively (Gao et al., 2016). Modeling the fate of the environment may reveal that DEET flow into the environment is retained in the receiving water (~79%) (Weeks et al., 2012).



Triclosan is used in toothpaste, polymeric cutting boards, and functional clothes against bacteria. About 500 t/year of triclosan are used in Europe (Tato et al., 2018). After consumption of daily life, triclosan will eventually enter the wastewater. Therefore, wastewater treatment plants need to treat considerable concentrations of triclosan $(1-10 \ \mu g/L)$ in untreated wastewater. The removal rate of triclosan in activated sludge is high at 85%-95%; one-third of this percentage can be attributed to sorption to sludge, and the residual is due to biodegradation (Armstrong et al., 2017; Atar et al., 2015). In that case, 24.1% and 27.2% triclosan were adsorbed on the generated sludge, and 60% of the triclosan loaded were biotransformed. The formation of by-products (2, 4-dcp) during chlorination and UV disinfection resulted in triclosan losses of up to 9.9% and 13.0% respectively (Tohidi and Cai, 2017). The results showed that photodegradation and biodegradation of triclosan occurred. Triclosan has the highest photolysis rate in surface water, whereas the ratio of biodegradation in wastewater is higher than that compared with surface water (Durán-Álvarez et al., 2015). Anaerobic and aerobic sludge digestion processes can remove 23.0%-56.0% of triclosan. About 7.4% of triclosan in aerobic digestion is transformed into methyl triclosan. Triclosan may undergo transformation/degradation in STPs. Some byproducts such as 2,4-dichlorophenol, 2,8-dichlorodibenzodioxin, and methyl triclosan are considered toxic/persistent compounds. Ho et al. (2016) reported that exposure to 250 g/L triclosan does not have any effects on normal embryogenesis or organogenesis; however, triclosan may impair lipid metabolism and adversely affect the early life stages of frogs.

Environmental residues are an important but unquantified source of exposure to UV filters. Salicylates, cinnamates, and anthranilates are considered safe and non-irritating sunscreen ingredients in a chemical sunscreen. The frequency and concentration of organic UV filters in PCPs change with time. A survey analyzed concentrations of more than 20 organic UV filters.



The most frequently occurring UV filters is OC from 50 selected PCPs (account for 43%) (Manová et al., 2013). Benzophenone-type UV filter can absorb or reflect UV radiation, and they are widely applied in PCPs and synthetic polymer products (Manová et al., 2013). Some BPs may be as much as 10% of the product weight. BP,4-methoxybenzophenone and 4benzoylbiphenyl are used as inhibitors to prevent the degradation of polymers and pigments, such as plastics, packaging materials, glassworks, and textiles (Sankoda et al., 2015). BP-3 (≥80%) is often detected in inlet and outlet waters with the concentration ranges from 23 to 1290 and 18 to 1018 ng/L (Tsui et al., 2014). The toxic and pathological effects of the sunscreen UV filter, BP-3, on coral planulae in Hawaii and the Virgin Islands in the United States were investigated. BP-3 poses a hazard to coral reef conservation and threatens the resiliency of coral reefs to climate change (Downs et al., 2016). Martins et al. (2017) found that frog embryo exposure to 4-methyl benzylidene camphor (4-MBC) leads to developmental malformations (up to 3%). marine copepod T. japonicus suffers reproductive problems and lethal toxicity since UV filter restudies may induce oxidative stress and trigger apoptosis. Risk assessment indicates that at actual environmental concentrations, UV filters shows a serious pressure to marine crustaceans and ecosystems (Chen et al., 2018). Other results showed that environmentally relevant concentrations of BP-3 can negatively impact freshwater insects (caddisfly) (Campos et al., 2017). Some analytes were detected in N influent samples. BP-3 and OC concentration were at the range of 4–163 and 12–390 ng/L. The concentration tendency indicated that the UV filter was discharged to STP showed a higher load during the summer period. The temperature was positively correlated with the measured OC and BP-3 concentrations. However, BP-3 and OC were showed low concentrations in some effluent samples. The removal efficiency of BP-3 and OC in these plants was 64% to >99% and 94% to >99%, respectively (Magi et al., 2013). In another case, HMS accounted



for about 78% of the total numbers of UV filters detected, with an average concentration (ng/m³) ranges 9.3 to 55.7 in summertime and fourfold in winter (ranges from 5.76 to 11.46) in secondary treatment process in urban areas (Shoeib et al., 2016). In addition to the physicochemical information of UV filters, seasonal degradation pathways and metabolites need to be further understood to help investigate their environmental distribution and fate.

2.2 Limitation of current treatment technologies in STPs

2.2.1 Typical physical processes

Typical physical processes including sedimentation, adsorption, and membrane filtration have been applied in water/wastewater treatment plants to remove pollutants. Sedimentation is a traditional water treatment process to remove suspended solids by gravity. The settling performance is determined by the velocity of water in the sedimentation tank and retention time of water in the tank. For PPCPs removal, sedimentation presents relatively low efficiency as some PPCPs are hydrophilic (Dey et al., 2019; Yang et al., 2017). However, sedimentation can remove target PPCPs attached to solids such as stones or sands. The adsorption behavior becomes evident under porosity, abrasion resistance, and materials with small pore diameters such as activated carbon or nanoparticles (Van Wieren et al., 2012). PPCPs were removed by granular activated carbon and powdered activated carbon adsorption in the post-treatment system, and no conversion products were produced (Kassotaki et al., 2016; Rodriguez et al., 2016). PPCPs can be removed by activated sludge process (ASP) through adsorption (Ebele et al., 2017). The removal rate of PPCPs during sludge adsorption varies. For example, Li and Zhang (2010) found that the removal rate of three kinds of fluoroquinolones by sludge adsorption can reach 80%. The performance of sulfonamides can be negligible as they are highly water-soluble



compounds. The disadvantage of this process is that it creates a potential pathway for PPCPs into the environment by releasing sludge directly or applying it to farmland as fertilizer (Van Wieren et al., 2012). Membrane filtration systems rely on physical mechanisms based on size exclusion, adsorption onto the membrane, and charge repulsion to eliminate PPCPs (Yangali-Quintanilla et al., 2011). Pressure-driven membrane processes NF and RO are used in water treatment plants. Some PPCPs groups usually show significant removal, but these membranes are slightly permeable to relatively small contaminants (Al-Rifai et al., 2011). After treatment, triclosan removal efficiency can reach 80% at pH 8, whereas that of acetaminophen reaches only 30%-40%. These performance differences are believed to have relevance to their distinct molecular weight ratio and hydrophobicity. Acetaminophen is hydrophilic (log $K_{OW} < 1$) and has a smaller molecular percentage than chosen membranes, whereas triclosan is highly hydrophobic (log K_{ow}> 4) and nearly twice the size of the acetaminophen molecule (Garcia-Ivars et al., 2017). NF can achieve removal efficiencies higher than 60% for diclofenac, naproxen, and 17aethinylestradiol, whereas RO technology can eliminate about 95% of the proportion (Urtiaga et al., 2013). The main elements that limit the large-scale application of the membrane are high energy consumption and scaling (Löwenberg et al., 2014; Rodriguez et al., 2016).

Activated carbon is commonly used to reduce broad-spectrum dissolved organic substances from the liquid phase. This huge flexibility in activated carbon appropriations is due to its extensive physical surface properties and chemical properties of commercially and/or specially treated carbon materials (Mohan et al., 2014). Farming and wood secondary products have been studied as cheap and reproducible sources of activated carbon production, but they are often accompanied by treatment problems (Yahya et al., 2015). Given the different shapes of activated carbon, it can be divided into granular activated carbon and powdered activated carbon. In a



large-scale pilot study in which PAC was applied in STP, six PPCPs (including ibuprofen, paracetamol, and estrone) were poorly to moderately removed (<60%) (Mailler et al., 2015; Teixeira et al., 2019).

2.2.2 Typical chemical processes

Advanced oxidation processes (AOPs) including ozonation, UV oxidation, and Fenton and Fenton-like (conventional process) processes, which are used in the removal of PPCPs, are discussed in this section. Ozone is one of the most widely used and most studied AOP methods in PPCPs removal. The mechanism of ozonation is primarily based on the generation of hydroxyl radicals; therefore, the ozonation rate of PPCPs is highly dependent on the concentration of hydroxyl radicals. Currently, ozone treatment can be combined with other methods as pre-treatment in drinking water. The O³⁻ based AOPs used are as follows: O₃/UV, O₃/H₂O₂, and O₃/US/FeSO₄.

Ozone production process utilizes high energy with a very minimal conversion of 1%–2% in air and 4%–8% in oxygen. Around 85% of energy is wasted as heat, and the reactor should be protected from overheating. Another problem with ozone gas is its short half-life, which is around 3–8 days in air or 15–20 min in the water at 20 °C–25 °C (Bagheri and Mohseni, 2015; Lee et al., 2012). Moreover, the high cost and strong toxicity of some intermediate products have restricted the widespread use of advanced oxidation (Al-Rifai et al., 2011). Fenton oxidation processes offer a promising application for the removal of PPCPs in wastewater. Similar to the ozonation process, the generated highly oxidizing hydroxyl species are responsible for the degradation of organic pollutants (Bokare and Choi, 2014). Fenton oxidation processes have gained popularity in the field of chemical treatment processes for wastewater. Hydroxyl species can be generated easily compared with that in the ozonation process. A previous study



investigated the photo-Fenton decomposition of β-blockers and found that the initial compounds and intermediates are moderately toxic (Veloutsou et al., 2014). In other studies, Fenton oxidation was applied to remove PPCPs and pharmaceuticals (Annabi et al., 2016; Mackul'ak et al., 2015). UV light treatment is also one of the AOPs. Currently, this method is used alongside with H_2O_2 for the removal of PPCPs (Guo et al., 2018; Yang et al., 2016). UV can destroy chemical bonds of organic pollutants through photolysis. Photolysis alone has low efficiency in degrading organic structures, but it can effectively eliminate toxic and refractory organic compounds in wastewater with the aid of H_2O_2 (Lai et al., 2017). However, H_2O_2/UV treatment suffers from the high cost of H_2O_2 , including acquisition, transportation, and storage (Bagheri and Mohseni, 2015). Full mineralization of PPCPs can be achieved by prolonged exposure to UV light and large amounts of energy, resulting in a general by-product that is more polar and watersoluble than the parent compound (Yang et al., 2016).

2.2.3 Typical biological processes

Activated sludge originates from biological/chemical treatment in STPs. The sludge contains several organic, inorganic, and microbial substrates separated from the liquid phase during treatment. The digestion mode for removing organic pollutants can be divided into two types: aerobic digestion and anaerobic digestion. The differences can be found in Table 1. Activated sludge can rapidly degrade triclosan (61%–91%) (Chen et al., 2015). Compared with other processes, the main removal mechanism of PPCPs is most often biological (45%), followed by adsorption in activated sludge tank (33%) and UV radiation (22%) (Salgado et al., 2012).

The main limitation of the ASP is the disposal problem, which may lead to further pollution of the environment. The sludge amount is hoped to increase from 11.5 million tons to 13 million



tons from 2010 to 2020 in Europe (Kelessidis and Stasinakis, 2012). The disposal routes, including incineration, landfill, and composting, vary from country to country. However, the agriculture sludge reuse rates in Denmark and Sweden are 50% and 25%, respectively; in these countries, 50% is landfilled or allocated to construction work (Kelessidis and Stasinakis, 2012; Malmborg and Magnér, 2015). If not eliminated properly, the PPCPs residues in sludge are released to the environment through the land application (Martín et al., 2015). Membrane bioreactors (MBRs) for wastewater treatment involve suspended growth biological treatment methods (usually activated sludge) and membrane filtration equipment (usually low-pressure microfiltration or ultrafiltration membrane). For most groups of PPCPs, the removal efficiency is relatively high. Chtourou et al. (2018) found that UF-MBRs can efficiently remove triclosan by 89.7%. However, considering the cost of membrane materials and the energy requirements associated with pollution prevention, membrane pollution remains a major challenge in advancing MBR technology. Dealing with high-strength wastewater containing high concentrations of pollutants often results in clogging of the membrane due to membrane characteristics, biomass, and operation conditions (Sabrina et al., 2012). Biofilm is one of the main technologies for biological wastewater treatment, which is based on the principle of soil self-purification development. In pilot-scale research, two UV filters achieved >50% removal efficiency of nine pharmaceuticals through biofiltration (McKie et al., 2016). Biofilters have great potential for removing organic micro-contaminants because of their low space requirements, low energy input, and low levels of by-products formation (Chen and Patel, 2012). Biofilters may potentially be used for in situ biological regeneration to extend the life of pollutants previously adsorbed on filter media due to their biotransformation (Cecen and Aktas, 2012). For example, a previous study applied zebra mussels (Dreissena polymorpha) in the



biofiltration process for PPCPs removal in wastewaters (Binelli et al., 2015, 2014). For advanced treatment technologies, chemical and physical processes are combined with biofiltration. For example, slow sand filters and granular activated carbon are combined with biofiltration to enhance the treatment efficiency of PPCPs from STPs or water reuse purposes (Azzeh et al., 2015; Paredes et al., 2016; Pompei et al., 2017; Rattier et al., 2014). Biologically active filtration has been combined with the ozonation process for PPCPs removal. The ability of ozone to improve the biodegradability of organics and remove organics by biological filtration was evaluated via biodegradable dissolved organic carbon analysis method (Lee et al., 2012). However, in this process, the acute toxicity changes in the combined process were estimated using luminescent bacteria. The ozone oxidation inhibition rate increased from 9% to 15%. The concentration of carbonyl compounds (e.g., aldehydes and ketones) as by-products also increased by 58%, thereby increasing toxicity (li et al., 2015).



Figure 2.1 A simple flow diagram of conventional STPs



Compound	Influent (ng/L)	Effluent (ng/L)	Removal efficiency (%)	Region	References
BP-3	232	34	85	Hong Kong	(Tsui et al., 2014)
HOMO (HMS)	262	153	41	Hong Kong	(Tsui et al., 2014)
OC ÓC	8	0	>99	Hong Kong	(Tsui et al., 2014)
DEET	600-1200	60-624	69 ± 21	China	(Li et al., 2013)
	66	40	40	China	(Wang et al., 2014)
Triclosan	892	202	77	India	(Subedi et al., 2017)
	2300	48	>90	USA	(Yu et al., 2013)
	547	112	79	Korea	(Behera et al., 2011)

Table 2.1 Occurrence of selected PPCPs in sewage treatment plants


Chapter 3 Materials and method for tracing PPCPs in wastewater treatment process

3.1 Background and objectives

The premise of research on PPCPs is to have sensitive and reliable detection methods. Because the environmental samples are complex systems, there is a wide variety of compounds that are easily coupled to impurities in sewage samples. Therefore, it is very important to establish an effective pretreatment method for extracting target substances and effectively removing impurities. The PPCPs in the environment is mostly of ng/L-µg/L, it is normally to apply an enrichment process before detection. Establish an appropriate, sensitive and repeatable analytical method for qualifying selected PPCPs in different wastewater treatment processes is urgently needed. The common method applied for sample extraction and enrichment in the water sample is SPE (Rapp et al., 2017). Through the selective retention mechanism of the cartridge in the solid phase extraction column, the impurity purification process can be completed simultaneously in the extraction process. In addition, to reduce the effectiveness of inorganic salt, LLE was also applied for this study. Recently, GC-MS/MS has been widely applied for determining low levels (ng/L) pollutants in environmental samples (Abdul Mottaleb et al., 2015; López-Serna et al., 2018; Mottaleb, 2015). GC-MS/MS performs well in sensitivity and separation efficiency than other commonly used techniques. The detection limit of GC-MS/MS is significantly reduced compared with that of other technologies. To date, the simultaneous analysis of multiple PPCPs in environmental water by GC-MS /MS is still limited because the properties of various substances, such as multiple polarities, solubility, acid dissociation constant



(pk_a), partition coefficient (K_{ow}), and stability, may seriously affect simultaneous and subsequent analysis under acidic and alkaline conditions. The objectives of Chapter 3 were (1) to establish an accurate and efficient method for the trace analysis of five commonly detected PPCPs in each unit of STP; (2) to apply this analytical method to study the concentrations of selected PPCPs from different wastewater treatment processes; and (3) to apply this method to a batch experiment study, which will be discussed in detail in the following chapters.

3.2. Materials and methods

3.2.1 Materials and chemicals

Analytical grade acetone, methanol (MeOH), dichloromethane (DCM), and ethyl acetate (EA) were purchased from ACS Company. Milli-Q water was prepared with a Merck[™] Ultrapure Lab Water System. The derivatization reagent, N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) + trimethylchlorosilane (TMCS) (99:1), was purchased from Sigma–Aldrich.

The standards of PPCPs, including N,N-diethyl-m-toluamide (DEET), 2,4,4'-Trichloro-2'hydroxydiphenyl ether (triclosan), 2-hydroxy-4-methoxybenzophenone (BP-3), 3,3,5trimethylcyclohexyl salicylate (cis- and trans- mixture (HMS), 2-ethylhexyl 2-cyano-3,3diphenylacrylate (OC), were all purchased from ACS Company with analytical grade (purity>98%). Isotopically labeled 2-hydroxy-4-methoxybenzophenone-2',3',4',5',6'-d5 (BP-d5) powder and benzophenone-d10 were obtained from Cambridge Isotope Laboratories (purity >99%), applied as surrogate standard and internal standard, respectively. Information on the physiochemical properties of the selected PPCPs is summarized in Table 3.1.



Pollutant	Another name	CAS No.	Molecular formula	Bulling point (°C)	log K _{ow} at pH=7;	MW (g/mol)	Structure
2,4,4'-Trichloro-2'- hydroxydiphenyl Ether	Triclosan	3380-34-5	C ₁₂ H ₇ Cl ₃ O ₂	120	4.76	289.54	
N, N-Diethyl-m- toluamide	DEET	134-62-3	C ₁₂ H ₁₇ NO	288 - 292	1.83/ 2.02	191.27	N N N N N N N N N N N N N N N N N N N
2-Hydroxy-4- methoxybenzophenone	Benzopheno ne-3	131-57-7	$C_{14}H_{12}O_3$	224 - 227	3.8	228.25	OH O H ₃ C, O
3,3,5- Trimethylcyclohexyl Salicylate (cis- and trans- mixture)	Homosalate	118-56-9	$C_{16}H_{22}O_3$	161 - 165	6.1	262.35	о Х
2-Ethylhexyl 2-Cyano- 3,3-diphenylacrylate,	Octocrylene	6197-30-4	C ₂₄ H ₂₇ NO ₂	218	6.9	361.48	N CH3
2-Hydroxy-4- methoxybenzophenone -2',3',4',5',6'-d5 (Surrogate)	Oxybenzone -(<i>phenyl-d</i> ₅)	1219798- 54-5	$C_{14}H_8D_6O_3$	-		-	
Benzophenone-d10 (I.S.)	-	22583-75-1	$C_{13}D_{10}O$	305		192.28	

Table 3.1 Summary of selected PPCPs and their physicochemical properties

3.3.2 Stock solution preparation

Standard solutions of each individual PPCPs (100 mg/L) were calculated and dissolved in acetone. The standard solutions were stored in amber glass bottles to avoid photocatalysis and maintained at 4°C for no more than 2 months. The calibration curve was prepared by a mixture of individual standards containing the concentrations from 1 μ g/L to 1 mg/L (six points) based on the concentrations detected usually in STPs. The surrogate and internal standard solutions



were also prepared in 100 mg/L acetone for stock. All glass bottles and test tubes were washed in Decon 90[™] Liquid Detergent (Decon Laboratories[™]) for 24 h and kept in the furnace for 4 h at 550 °C before use to avoid possible organic contamination.

3.3.3 Sample collection and preparation

The sampling was conducted from May to August 2017. Influent, primary sedimentation, secondary sedimentation, and after UV disinfection wastewater samples were collected from Taipo and Shatin, which are two traditional local STPs of Hong Kong. All the 4 L amber glass bottles were pre-cleaned to avoid possible contaminations. The operation parameters of two local STPs and sampling locations can be found in Table 3.2 and Figure 3.1. Both two STPs are secondary treatment plants, the sewage source composition is slightly different.

All samples were transported to the laboratory at 4 °C. The supernatant samples were filtered through a 0.2 µm cellulose nitrate membrane. Filtrates were stored in the dark at 4 °C, then pretreated (SPE) within 24 h. The operation conditions of the STPs are provided in Table 3.2. Both Taipo and Shatin are secondary treatment plants. The sewage composition is slightly different, Shatin is mainly treated domestic wastewater and Taipo is treated for the mixture of domestic and introital wastewater.

Table 3.2 S	ampling	sewage	treatment	plants	operation	parameters
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Name	Plant type	Population Equivalent	Major land use (nearby)	Average daily flow (m ³ /day)	HRT (h)	SRT (day)
Shatin	Major Secondary	600,000	Residential	250,000	19	15
	Secondary treatmen (1) screening of coar suspended matter (4	t processes including rse material; (2) settle) biological treatment	ement of grit particles; (t of sewage	(3) primary sedime	ntation of	
Taipo	Major Secondary	370,000	Industrial Residential	94,300	16	20



(Source: https://www.dsd.gov.hk/TC/Home/index.html)



Figure 3.1 Sampling locations of two STPs

3.3.4 Solid-phase extraction

A standard mixture of 100 ng/mL of each standard in acetone, the surrogate standard of 1 mg/L oxybenzone-(*phenyl-d*₅) in acetone, and internal standard of 1 mg/L of benzophenone-*d*10 in acetone were prepared. SPE cartridge was obtained from Oasis HLB (6 mL, 500 mg, Waters). The procedures were presented in following section:



1) Added 100 μ L of 1 mg/L surrogate standard to 250 mL of water sample;

2) Preconditioned the cartridge with 6 mL of DCM/MeOH (4:1 $^{v}/_{v}$), 6 mL of 5% acetone in hexane at a rate of 1 drop per second, and 6 mL of Milli-Q water;

3) Loaded the sample with a flow rate of about 1 drop/s;

4) Reconditioned the HLB cartridge using 15 mL of Milli-Q water and evaporate it to dry under vacuum

5) Eluted the HLB cartridge with 15 mL of eluant of DCM/MeOH (4:1 $^{v}/_{v}$)

6) Evaporated the eluant under 45°C water bath and dry the eluent with N₂ gas

7) Dissolved the concentrated sample with 5% acetone in hexane to 1.5 mL

8) Added 20 µL of internal standard and evaporate it to dryness

9) Reconstituted the extract in 100 μ L of BSTFA+1% TMCS and incubate the mixture in 70 °C oven for 1 h.

10) Prepared for GC-MS/MS analysis

All experiments were carried out in duplicate. The 250 mL Milli-Q water was applied as a blank sample, and control groups were spiked with a standard solution mixture of selected PPCPs, which omitted SPE procedures. All other steps were the same. This method was modified from the literature (Li and Zhang, 2010; López-Serna et al., 2018).

3.3.5 GC-MS/MS analysis

The GC-MS/MS device was purchased from Agilent Technologies (7010 GC/MS Triple Quad). The column was a DB-5 ms Ultra Inert with a length of 30 m, 0.25 mm ID, and 0.1 μ m film thickness for PPCPs analysis. The operation parameters were as follows: injection volume of 1 μ L, oven heater of 300 °C, interface temperature of 280 °C, pressure of 11.65 psi, total flow of



44 mL/min, septum purge flow of 3 mL/min, gas saver of 20 mL/min after 5 min, injection pulse pressure of 20 psi until 0.25 min, and purge flow to split vent of 40 mL/min at 1 min. The temperature program was as follows: 120 °C held for 1 min, ramp 1 from 15 °C to 180 °C, ramp 2 from 8 °C to 260 °C, ramp 3 from 20 °C to 300 °C, and held for 15 min. Time segment 1 was from 9 min to 10.5 min, segment 2 was from 13 min to 14.8 min, segment 3 was from 15 min to 16 min, and segment 4 was from 18.5 min to 20 min. For optimal accuracy, each chromatographic run was divided into four-time segments for improving the data collection precision of MS (Table 3.3).

Pollutants	Retention time (min)	<i>m/z</i> (dwell time, msec)	Time
			Segment
DEET	9.481	119 (100)	1
		190 (50)	
		191 (50)	
I.S.	10.005	110 (100)	1
		192 (50)	
		193 (50)	
HMS	13.967	195 (100)	2
		196 (50)	
		193 (50)	
Surrogate	14.608	290 (100)	2
-		291 (50)	
		247 (50)	
Triclosan	15.114	200 (100)	3
		347 (50)	
		345 (50)	
BP-3	14.642	151 (100)	3
		227 (50)	
		228 (50)	
OC	19.938	249 (100)	4
		204 (50)	
		250 (50)	

Table 3.3 Ions monitored and SIM acquisition windows for the GC-MS determination





Figure 3.2 GC-MS chromatogram of 10 mg/L mixture standard target pollutants

3.3.6 Quantification

The internal standard method was applied in this study. About 20 μ L of 50 μ g/L internal standard was added to water samples before instrumental analysis. Compound identification was confirmed by GC retention time and qualifier ions (usually molecular ion and one or two fragment ions) as shown in Table 3.2. The ratio of the standard solution concentration to the IS concentration was used as the ordinate of the standard curve. The selected PPCPs compounds were quantified by comparing peak areas of the most intensive ion of each compound with the peak area of the internal standard.



3.3 Results and discussion

3.3.1 Limit of quantitation (LOQ) and repeatability

LOQ is defined as all acceptance criteria and quantitative values within $\pm 20\%$ of the target concentration. If the average within this range is within 20%, the researchers generally consider the GC-MS control values to be acceptable. The value can be quantitated based on the signal-to-noise approach. The signal-to-noise ratio was determined by comparing measured signals from samples with known low concentrations of analyte with those of blank samples and by establishing the minimum concentration at which the analyte could be reliably quantified. A typical signal-to-noise ratio is 10:1 (Hao et al., 2007).

The recovery rate was calculated as follows:

Recovery (%) = $\frac{b}{a} \times 100$

Where a: concentration of theoretical spiked concentration.

b: concentration of surrogate in the derivatized sample

A 10 ng/mL QC sample was used to evaluate analysis repeatability. The results were obtained from mutually independent tests, which used the same method to aliquots of the same sample under the same conditions (e.g. same operators and same equipment at the same laboratory over a short time period). Moreover, 20 μ L of the 50 μ g/L surrogate was added to the sample prior to instrumental analysis.

 Table 3.4 PPCPs recovery from ultrapure Milli-Q water spiked mixture standard

Compound	Units	Batch DI Blank	Recovery (%)
BP-3	ng/L	< MDL	101-105



DEET	ng/L	< MDL	92-102
HMS	ng/L	< MDL	85-96
OC	ng/L	< MDL	89-102
Triclosan	ng/L	< MDL	94-104
I.S.	ng/L	< MDL	89-97

Note: DI blank represents ultrapure Milli-Q water field blank samples

Table 3.5 The linearity range, correlation coefficient (R^2) , recovery, repeatability, MDL, and LOQ of the target compound

Compound	Correlation coefficient (R ²)	Repeatability (RSD), n=5 ^b (ng/L)	MDL (ng/L)	LOQ (ng/L)
DEET	0.998	5.6	0.1	0.56
BP-3	0.997	5.9	0.05	0.32
HMS	0.998	4.0	0.08	0.28
OC	0.996	7.6	0.06	0.25
Triclosan	0.999	4.2	0.07	0.35

a: Concentration range is 1 ng/L to 1000 ng/L

b: calculated as 10 times the standard deviation of their responses in procedural blanks (b=5) divided by the slope of calibration curves

3.3.2 Method detection limit (MDL)

The defined method detection limit (MDL) was the minimum measured concentration of the substance, and the difference between the measured concentration and the method blank result was reported with a 99% confidence level following the method of USEPA (USEPA 2016). The



mean determined concentration plus three times the standard deviation of a set of method blanks were calculated.

3.3.3 Method application for sewage sample from different treatment processes

The concentrations of the selected PPCPs in influent, primary sedimentation, secondary sedimentation, and effluent from both Taipo and Shatin STPs were determined by the developed analytical method in August 2017. The sample collection and pretreatment can refer to the above sections.

	DEET		BP-3		HMS		OC		Triclo	san
	Shatin	Taipo	Shatin	Taipo	Shatin	Taipo	Shatin	Taipo	Shatin	Taipo
Influent	118.0	89.1	334.3	292.0	657.1	142.3	125.2	66.3	586. 6	791.3
Primary treatment	123.9	87.2	66.7	78.8	197.6	25.6	66.6	23.1	174. 3	228.1
Secondary treatment	24.7	20.9	14.1	23.6	63.2	5.1	36.7	8.1	55.8	63.8
After UV disinfection	21.8	18.8	12.3	22.2	55.6	4.9	33.7	7.8	53.0	58.7

Table 3.6 The concentration of target pollutants in two local STPs





Figure 3.3 Removal efficiency of selected PPCPs in Shatin STP





Figure 3.4 Removal efficiency of selected PPCPs in Taipo STP

In this study, the concentrations of different units in STPs and removal efficiency of each process were studied. For DEET, the ranges varied from 21.8 to 118 and 18.8 to 89.1 ng/L in Shatin and Taipo, respectively. This slight difference between the two plants may be due to the different sewage sources composition of the two plants. Shatin treated more residential sewage than Taipo, which resulted in more DEET detected in Shatin. The removal efficiency in secondary treatment was the highest. Similarly, concentrations dropped significantly below 20–36 ng/L after the second treatment step. Effluents ultimately contained 20–23 ng/L DEET (Aronson et al., 2012). Stinson (2007) compared DEET removal in four secondary STP treatment



plants, and the elimination rates were 55%–99%, 78%–99%, and 90%–99% (the median removal rate was 24%).

The concentration of BP-3 ranged from 12.3 to 334.3 and 22.2 to 292 at the level of ng/L in Shatin and Taipo, respectively. The HMS and OC concentrations varied from 55.6 to 657.1, 55.6 to 142.3, 33.7 to 125.2, and 7.8 to 66.6 ng/L. BP-3 is one of the dominant UV filters in the water matrix. The inlet load is arranged in the order of BP-3 > OC. The concentrations of treated wastewater (STP sewage) are quite low, and BP-3 and OC have also been detected in lakes and rivers in central Switzerland (Limmat), receiving inputs from STP and recreational activities (Balmer et al., 2005). In another study, UV filters at OC and HMS were detected in water during three sampling periods, with concentrations ranging from 34 to 2128 at ng/L level, for a total removal rate of 28%-43%. It was indicated that UV filters are not eliminated during treatment and can be released into the environment by water reuse process (Li et al., 2007). This concentration can be lower than that in other regions. For example, the total concentrations of UV filters over the three sampling seasons were 62.9–412 (surface water), 122–5055 (STP inlet), 108–2201 (STP outlet) ng/L (Ekpeghere et al., 2016). In Canada, UV filters and stabilizers were also studied in 9 STPs; results indicated 483 and 76.2 ng/L in the STP inlet, 28.4 and 4.84 ng/L in the STP outlet, and 2750 and 457 ng/g (dry weight) in biological solids (Lu et al., 2017). The median concentration of all detectable UV filters is <250 ng/L. BP-3 has more threat to fish than OC, and a high bleaching risk in Hong Kong's aquatic recreation districts has been reported (Tsui et al., 2014). Biological treatment is the dominant unit to the removal of UV filter compounds in STP in the previous study (Zhao et al., 2017).

As a commonly detected compound in STPs, triclosan has been studied extensively. The concentration ranged from 53 to 586.6 and 58.7 to 791.6 at the ng/L level in the two local plants.



Unlike other PPCPs, the concentration of triclosan in Taipo was higher than that in Shatin. In another study in Hong Kong, the average concentration of Shatin STW previous reported value was 372.3 ng/L, with the least triclosan load in water. The mean influent concentrations in rainy and dry seasons were 329.4 ± 16.3 and 415.3 ± 18 ng/L (Tohidi and Cai, 2015). In sludge, the maximum triclosan concentration was $8.47 \mu g/g$, which indicated that activated sludge was the dominant removal mechanism of triclosan (Juksu et al., 2019). A similar conclusion was drawn in this study.

3.4 Summary

The occurrence of five commonly detected PPCPs in sewage treatment (influent, primary treatment, secondary treatment, and effluent) was determined by LLE, SPE, and GC-MS/MS. The method validation study results indicated that the five selected pollutants were separated well within 30.0 min. Thus, the whole method was precise and repeatable, and it could be applied in multiple wastewater matrices at a low detection limit. Five PPCPs were detected in the inlet and outlet samples of STPs at several sites by using this method. Experimental results showed that the method was effective (more than 50%) in monitoring PPCPs in different sewage substrates. The concentration of target pollutants varied even in the same city. Moreover, the results proved that biological treatment could remove most pollutants compared with primary treatment and UV disinfection.



Chapter 4. Removal routes of PPCPs in the activated sludge

4.1 Background and objectives

The present studies on PPCPs in STPs mostly focused on investigating the concentrations in water and sludge. However, the removal mechanism of each treatment process was usually determined as the basis of the on-site sampling results. Previous results revealed that efficiency varies from 20% to 99%. Target pollutants were mostly eliminated in the biological treatment process, but the removal mechanism of target pollutants in activated sludge remains unclear.

This chapter aimed to investigate the elimination routes of selected PPCPs in activated sludge under aerobic conditions. The main objectives were as follows: 1) determine the removal routes in ASP, including biodegradation, adsorption, volatilization, and hydrolysis of five PPCPs; and 2) conduct biodegradation kinetics studies on five PPCPs.

4.2 Materials and methods

4.2.1 Experimental set-up

A mixed slurry sample of aeration tanks from Shatin STPs was utilized for the batch experiment conducted with hydraulic retention time (HRT) of 10 h and sludge retention time (SRT) of 12 days. In the batch experiment, five reactors, also included the two controls reactors (2 L glass reactors) filled with 1.5 L of slurry sewage sampled from the biological treatment process were running simultaneously for 48 h at 25°C following five controls. The removal mechanisms for organic pollutants in activated sludge were biodegradation, adsorption, volatilization, and hydrolysis (Li and Zhang, 2010; Min et al., 2018). The duplicate reactors with



all removal routes were established. Treatment A included all four removal routes; treatment B comprised three removal mechanisms (adsorption, volatilization, and hydrolysis) because the biodegradation behavior was inhibited by 1% NaN₃ (Wu et al., 2009); treatment C considered only volatilization and hydrolysis as the removal mechanism, and treatment D was conducted to investigate the hydrolysis effect of PPCPs. Control E was responsible for investigating the impact of PPCPs on the microbial community activity. On the basis of the concentrations of each reactor, the removal routes could be calculated as follows:

Biodegradation = A - B

Adsorption = B - C

Volatilization = C - D

Hydrolysis = D

The standard solutions of target PPCPs were spiked into the rectors, each compound obtained a concentration of 100 μ g/L. Samples were obtained 12 times at 0, 0.25 h, 0.5 h, 1 h, 2 h, 5 h, 10 h, 15 h, 24 h, 36 h, and 48 h. All glass bottles were covered with foil film to avoid possible photolysis.

4.2.2 Sample preparation

In Chapter 3, the five commonly detected PPCPs were selected as target pollutants, namely, DEET, triclosan, BP-3, HMS, and OC. 5 mL of the liquor samples were grabbed by a glass syringe and centrifuged at 4000 rpm for 10 mins to separate the solid insoluble contaminants. 2 mL was collected into amber vials and rest filtered sample was discarded. The samples were then



filtered by a 0.2 μ m cellulose nitrate membrane. The treated samples were stored at 4 °C in dark and ready for extraction procedures. LLE was applied before SPE to decrease the salt concentrations in samples and the efficiency of SPE. The procedure was as follows:

1) Added with 5 mL of EA

2) Vortexed the mixture for 30 s

3) Centrifuged the mixture at 1500 rpm for 15 min

4) Collected the EA layer by using a glass dropper

5) Repeated steps (1) - 4) for two times

6) Combined the EA layer and evaporate it to dryness under N₂ steam

7) Reconditioned into 1 mL of 4% acetone in hexane and ready for SPE

8) Proceeded with GC-MS analysis.

4.2.3 Sample preparation and instrument analysis

The sample preparations including centrifugation, filtration with 0.2 µm cellulose nitrate membrane to sperate the bacteria in sludge and ready for preliminary concentrated and extraction processes (Li and Zhang, 2010). The pretreatment extraction of samples, including LLE, and SPE, were conducted as soon as possible after the sewage sample collected from the STPs (within 48h). The water samples were prepared in duplicate. GC-MS/MS (Agilent) was applied to analyze PPCPs using the selected ion monitoring mode. Detailed information on the analytical method was reported in the previous section.



4.2.4 Pseudo kinetics models

The following equations were performed for the Pseudo kinetics zero-order models, first-order models, and second-order models performed in equation (1), (2) and (3) to fit the biodegradation data.

Zero-order model:
$$\frac{dC}{dt} = -K_0$$
 (1)

First-order model:
$$\frac{dC}{dt} = -K_1 \cdot C$$
 (2)

Second-order model:
$$\frac{dC}{dt} = -K_2 \cdot C^2$$
 (3)

C₀: the concentration of selected PPCPs at time 0

Ct: the concentration of selected PPCPs at time t

Thus, half-lives (t_{1/2}), when $C_t = \frac{1}{2} C_0$, $t_{1/2}$ can be calculated as $\frac{C_0}{2 \cdot k_0}$, $\frac{\ln 2}{k_1}$, and $\frac{1}{k_2 \cdot C_0}$, respectively.

4.3 Results and discussion

4.3.1 Elimination mechanism of PPCPs in ASP

During the 48 h of investigation of the five target pollutants, hydrolysis and volatilization were ignored based on the results of treatments C and D with the removal efficiency around 1%. Only biodegradation and adsorption are discussed in detail in this section. The different performances of specific pollutants were investigated by comparing the physical and chemical characteristics of the target pollutants.





Figure 4.1 DEET removal routes in ASP



Figure 4.2 Triclosan removal routes in ASP



4.3.1.1 DEET

More than 79% of DEET can be removed by biodegradation, and adsorption contributes around 6% removal. The adsorption equilibrium was reached around 16 h in the ASP (Figure 4.1). On the basis of the estimated physical properties for DEET, DEET was not significantly adsorbed to sludge; its Henry's Law constant (2108 atm-m³/mol) suggested that it could not significantly volatilize during aeration (USEPA 2011). The study of bacteria degrading DEET indicated that in pure culture process, DEET may be transferred to identifiable metabolites. N,N-diethyl-mtoluamide-N-oxide, Nethyl-m-toluamide-N-oxide, and N-ethyl-m-toluamide were identified as three metabolites by the soil fungi (Cunninghamella elegans) study by Seo and coworkers (2005). N,N-diethyl-m-toluamide-N-oxide, Nethyl-m-toluamide-N-oxide were tested toxicity to Daphnia magna during the continuous time for 48 hours and 96 hours. N-ethyl-m-toluamide and DEET were found had similar toxicity with each other, whereas N,N-diethyl-m-toluamide-N-oxide was much less toxic than N-ethyl-m-toluamide. It was reported Pseudomonas putida DTB, which was able to utilize DEET as a sole carbon and energy source. DEET can transfer to 3methylbenzoate, followed by rapid conversion to 3-methylcatechol without metabolites appearing (Rivera-Cancel and coworkers, 2007).

4.3.1.2 Triclosan

In this study, approximately 71.4% of triclosan was biodegraded, and 24.8% of the pollutant was found to be adsorbed on sludge (Figure 4.2). Triclosan is relatively hydrophobic (log K_{ow} = 4.76), and its high sorption constant (log K_d = 4.3) suggests that triclosan will be absorbed onto sludge biomass (Singer et al., 2002). Therefore, biodegradation and sorption were considered as the mechanisms of triclosan removal. In a laboratory-scale study with a bioreactor, 75% of



triclosan was removed under aerobic conditions within 150 h (Chen et al., 2011). Sampling in the same STP (Shatin STP, Hong Kong), Tohidi and Cai (2015) found a sharp decrease in the triclosan concentration after biological treatment, thereby indicating the involvement of two probable processes: biodegradation of triclosan and sorption to biomass. Their results demonstrated that 79% of triclosan is biodegraded in a typical secondary treatment plant ASP, whereas 15% is adsorbed to the sludge. As a result, the 6% residues discharged into the receiving surface water (Luo et al., 2014; Singer et al., 2002). However, in another study, activated sludge's ability to biodegrade triclosan was reported to be dependent on biomass acclimatization, resulting in a mean biodegradation rate of 97% (Stasinakis et al., 2007). It was investigated that triclosan has been removed in the biodegradation process with different rates depending on the experiment conditions (Veetil et al., 2012). To conclude, both mentioned biodegradation and adsorption processes could be involved in triclosan reduction in ASP.





Figure 4.3 OC removal routes in ASP





Figure 4.4 BP-3 removal routes in ASP





Figure 4.5 HMS removal routes in ASP

4.3.1.3 UV filter

The transformation routes of UV filters in activated sludge are rarely studied (Figure 4.3-4.5). The biodegradation and adsorption rates of different kinds of UV filters vary. The biodegraded and adsorption rates of HMS, BP-3, and OC accounted for 40.5% and 12.9%; 72.3% and 17.7%, and 11.7% and 50%, respectively. The different results may be due to the hydrophobic coefficient and sorption constant. Compared with other studies, sorption onto biomass played a significant role in the removal of organic sunscreens. The removal of OC, the adsorption accounted for 52%–90% of the STP inlet removal rate. On the other hand, biodegradation played a dominant role in BP-3 (Liu et al., 2012a). The ranges of different studies were generally similar



and could be explained by high degradation rates (60%–90%) for the UV filter. Sorption onto sludge was the dominating factor driving elimination for OC with K_d values higher than 5000 L/kgSS (Kupper et al., 2006).

4.3.2 Biodegradation mechanism of PPCPs

It was known that pseudo-first-order degradation kinetics was observed for all compounds down to nanograms per liter level, the removal rates could be predicted for various reactor configurations (Tchobanoglous et al., 2003). Therefore, the reduce of sludge biomass will reduce the degree of biological removal efficiency. The sewage separation and source treatment are conducive to eliminating persistent micropollutants in the process of centralized end-of-pipe treatment. This has a positive effect on the typical reactor configuration of organic removal in municipal wastewater, and the deduction formula of predictive removal behavior allows the determination of the pollutant type according to their degradation (Joss et al., 2006).

The first-order R^2 and $t_{1/2}$ values ranged from 0.94 to 0.98 and 3.30 h to 6.93 h, respectively. In the comparison of the zero-, first-, and second-order models, the biodegradation kinetics of the five PPCPs matched the first-order kinetics model well (Figure 4.6-4.10). However, only a few studies provided information about the half-life of the selected PPCPs. A previous study estimated $t_{1/2}$ to be 54–86 h in activated sludge diluted 10 times (Chen et al., 2011). The biodegradation $t_{1/2}$ for BP-3 was 10.7 days in diluted activated sludge under oxic conditions (Liu et al., 2012b).





Figure 4.6 BP-3 biodegradation first-order model



Figure 4.7 DEET biodegradation first-order model





Figure 4.8 OC biodegradation first-order model



Figure 4.9 Triclosan biodegradation first-order model





Figure 4.10 HMS biodegradation first-order model

4.3.3 Sludge adsorption mechanisms of PPCPs

Activated sludge contains not only microbial cells, but also extracellular polymers (EPS), which are macromolecules composed of polysaccharides, proteins, proteins and nucleic acids (Tian et al., 2006). The anionic (e.g., $-COO^-$, $-SH^-$, $-SO_4^-$, $-HPO_4^-$) and cationic (e.g., $-NH_3^+$) represent a large number of functional groups, which are involved in adsorption of various organic compounds or other compounds (Wang et al., 2018). In the previous studies, it was reported the metal fixation ability and dye removal of EPSs from activated sludge (Maderova et al., 2016; Zhang et al., 2016). The bacteria are present at the isoelectric point in the activated sludge when the pH ranges 2-4. Therefore, their surface will be negatively charged at higher pH. Some pretreatment processes can alter the adsorption capacity of microbial biomass (e.g. autoclaving) because high-temperature treatment destroyed the cell leads to the surface area increasing of



biochar (Maderova et al., 2016). The potential for pollutants adsorbed on sludge needs to be further investigated to understand the interaction between PPCPs and EPS.

4.4 Summary

Selected PPCPs at environmentally relevant concentrations removal routes were studied in ASP with the major conclusions as follows:

It can be drawn to the conclusion that biodegradation and adsorption were the dominant removal mechanisms of selected pollutants, whereas volatilization and hydrolysis can be negligible. Kinetics study results indicated that the selected five PPCPs fitted the first-order model (R^2 : 0.942–0.980) with the rate constants ranging from 0.10 h⁻¹ to 0.21 h⁻¹ (Table 4.1). Removal mechanisms greatly affected by the physicochemical properties (e.g. acid dissociation constant, distribution coefficient between water and octanol) of specific compounds. The elimination routes can vary even the target pollutants belongs to the same group. Among the five target PPCPs, DEET, triclosan, and BP-3 were predominantly removed by biodegradation in the activated sludge system. OC was mainly removed by adsorption. Generally, they all be removed most in the sewage treatment process, but still existing after treated. Since the types of pollutants are constantly updated, it is necessary to improve existing treatment methods. Adding environmentally friendly new materials such as biochar to increase the absorption rate shows great potential. The hypothesis will be discussed in the following sections.



Zero-order kinetics: $C_t - C_0 = K_0 t$			First-order kinetics: $C_t = C_0 e^{-K_1 t}$				Second-order kinetics: $C_t = \frac{C_0}{1 + K_2 t}$			
Target pollutant s	C ₀ -C _t (µg/L)	$k_0 \ \mu g/(L \cdot h)$	R ²	C_0 - C_t (µg/L)	$k_1 (h^{-1})$	t 1/2 (h)	R ²	C0 (µg/L)	$ \begin{array}{c} K_2 \times \\ 10^{-3} \\ (L/\mu \\ g \cdot h) \end{array} $	R ²
BP-3	73.1	1.33	0.74	66.47	0.15	4.62	0.96	95.5	6.25	0.85
DEET	81.0	1.75	0.73	79.74	0.10	6.93	0.98	101.2	2.44	0.97
OC	11.8	0.25	0.68	12.68	0.11	6.30	0.97	99.5	2.56	0.96
Triclosan	75.2	1.50	0.65	76.45	0.14	4.95	0.98	105.3	6.18	0.87
HMS	41.3	0.71	0.68	35.99	0.21	3.30	0.94	100.5	4.21	0.92

 $t_{1/2}$ can be calculated as $\frac{C_0}{2 \cdot k_0}$, $\frac{\ln 2}{k_1}$, $\frac{1}{k_2 \cdot C_0}$ respectively.



Chapter 5 Removal of PPCPs in ASP under difference redox condition with biochar

5.1 Background and objectives

Biochar, like ordinary carbon, is the product of the pyrolysis of biomass energy raw materials. Its main component is carbon molecule has become a popular amendment in wastewater treatment. (Tan et al., 2016). The biochar with the properties of cost-effective pollutant stabilization, carbon sequestration, water retention, and enhanced enzyme and microbial activity (Gwenzi et al., 2017). Proper application of biochar plays an active role in mitigating global warming because it can stably 'lock' carbon for hundreds of years. More importantly, in addition to its wastewater and soil improvement function, some by-products produced in its production process are of great economic attraction.

The adsorption performance of biochar is affected by the biomass and pyrolysis process/temperature. During pyrolysis process, biochar produced at the temperature around 300 °C (low temperature) contains more oxygen-containing functional groups, while biochar produced at 500 °C - 700 °C (high temperature) contains a larger surface area and many micropore (Ahmad et al., 2014; Mohan et al., 2014), which influence their capacity for immobilization.

Biochar shows great potential as a water remediation sorbent because of its raw materials widely availability, low cost and large surface area (Tan et al., 2015). Because the ability of biochar to remove various contaminants depends on their physical and chemical properties, which are strongly influenced by biomass composition, pyrolysis temperature process, and



pyrolysis conditions (Ahmad et al., 2014; Reddy and Lee, 2014; Yao et al., 2013). Therefore, selecting appropriate biochar for pollutant removal is essential for wastewater treatment applications. Another advantage of biochar application is that toxic metabolites produced by biotransformation are not exist during the adsorption process. For example, 4-cresol and 2,4-dihydroxybenzophenone are two metabolites of biodegradation of BP-3 under oxic and anoxic conditions. The biotransformation of BP-3 to 2,4-dihydroxybenzophenone by demethylation of the O-demethylation occurs in cultures under different redox conditions (Liu et al., 2012b). Therefore, biochar technology has minimal toxic effects and improved treatment efficiency. Rice husk is agricultural waste, but recent studies have transformed such solid waste into biochar for carbon sequestration. On the basis of the results of Chapters 3 and 4, adsorption can be one of the dominant mechanisms to remove target pollutants in sewage. Biochar was selected as the treatment technology to enhance adsorption efficiency.

Investigating the removal mechanisms of PPCPs under different redox conditions plays a significant role in determining wastewater treatment processes and predicting the fate of these selected pollutants once released into the environment, such as groundwater recharge, riverbank filtration, and flood condition. Also, the redox condition can affect the biochar removal performance by changing pH value in the solution (Liu et al., 2012). Different metabolites are produced under aerobic and anoxic conditions, such as BP-8 or DEET residues of N,N-diethyl-m-toluamide-N-oxide (Greskowiak et al., 2006). Therefore, the degradation behavior in both aerobic and anaerobic processes are different. In addition, under anoxic conditions, some pollutants are easier to remove than under aerobic conditions, although there is general evidence that higher oxidation potential under aerobic conditions is beneficial to its degradation.



The objective of Chapter 5 aims to investigate the removal behavior of five PPCPs under different redox conditions to understand the complete removal routes of PPCPs in full-scale STP. The impact of redox condition on pH, removal rate and microbial community were also been determined. In this section, the rice husk (agricultural waste) biochar produced at 550 C was applied as wastewater remediation material to study the difference of pollutants removal performance under redox conditions. A highly sophisticated automated biogeochemical microcosm system was utilized for a 56h continuous study.

5.2 Materials and method

5.2.1 Rice husk-derived biochar preparation

Biomass of rice husk was collected from Guizhou Province, China, washed with deionized water, air-dried. The sample then grounded and sieved under 1 mm metal sieve. Rice husk-derived biochars were produced at 550 °C with a heating rate of 7 °C min in accordance with the described method by Lou et al. (2016a, 2016b).

5.2.2 Rice husk-derived biochar adsorption of PPCPs kinetics study

The target pollutants and standard solution preparation method are the same as discussed in Chapter 3. A batch experiment was set up to determine the adsorption kinetics and removal efficiency of biochar in aqueous media. The rice husk-derived biochar was added into Milli-Q water with the dosages of 0.25%, 3%, and 5% in a 40 mL reagent glass bottle (Sophia and Lima, 2018). The final concentration of spiked target pollutants in solution was 100 μ g/L. A blank group (no PPCPs) and control group (no biochar) were also established for QC. The optimum pH



(pH 7–8) for PPCPs adsorption and shaking speed of 150 rpm were maintained during the kinetic experiment. The residence time was varied at 0, 15, and 30 min and 2, 4, 8, 10, 15, and 24 h. A 3 mL mixture was sampled by a syringe (10 ml) and filtered through a 0.45 cellulose membrane. After each run, the samples were analyzed for five PPCPs concentrations as described above. All samples were prepared and sent to GC-MS/MS for 48 h.

5.2.3 Removal kinetics of PPCPs under different redox condition with biochar

The study applied an automated biogeochemical microcosm system (bioreactor) which occupied an automatically pre-setting redox windows and a dynamic recording system. The mechanisms and technical details can be found in Yu and Rinklebe (2011). It has been applied for previous studies for soil remediation studies (Frohne et al., 2015; Rinklebe et al., 2016a). However, it is the first time that this system has been applied to the study of PPCPs in sewage. The simple scheme of the system can be found in figure 5.4. All microcosms were covered by aluminum foil to avoid possible photolysis. Two 2 L continuous glass stirred-tank reactors were coupled with 1.5 L of liquor collected from a conventional STP ASP tank in Wuppertal, Germany (Klärwerk Buchenhofen). The plant served around 360,000 residents, with a capacity of 3,564,455 m³ per year. Oxidizing conditions were considered as > 100 mV in this study. The E_H value of fresh activated sludge was 200 ± 30 mV as determined by testing with the E_H sensor from the system. Defined E_H (redox potentials) windows were examined from +200 mV to 0 mV and -200 mV, which were set 24 h before sampling and maintained by the automated flushing of N₂ and synthetic air/O₂.

Standard solutions of target PPCPs were pre-spiked into the rectors (final concentration for 100 μ g/L). All systems were covered by foil film to avoid possible photolysis. The kinetic study was



sampled at different times of 0, 1, 2, 3, 4, 8, 16, 24, 32, 40, 48, and 56 h. As explained in Chapter 4, five PPCPs (DEET, triclosan, BP-3, HMS, and OC) belonging to three were selected as the target pollutants. Subsequently, 5 mL slurry samples were collected by syringes. The samples were centrifuged for 10 min at 4000 rpm and filtered through 0.2 mm cellulose nitrate membranes (Whatman Inc., Maidstone, UK) immediately under N₂ atmosphere. In order to avoid any effect of oxygen, the entire sample separation was carried out in an anaerobic work station (MK3 Anaerobic WorkStation, Don Whitley Scientific, Shipley, UK), which maintained the oxygen concentration within 0%–0.1% automatically. The slurry samples were stored at 4 °C and prepared for extraction procedures. The sample preparation procedures were conducted as described in Chapters 3 and 4.

5.3 Results and discussion

5.3.1 Rice husk-derived biochar characterization

Selected properties of rice husk-derived biochar produced at 550 °C and pH 7.3 (pH determined in 1:20 soil-water suspension) are shown in Table 5.1. Biochars with high concentrations of Ca, K and Mg may promote specific π -interactions and increase the adsorption of aromatic compounds (Oh et al., 2013). Therefore, the main reason for biochar adsorption in this study is π -interactions and electrostatic attraction was believed to be the major adsorption mechanism. Scanning electron microscopy (Sem, Quanta 250 FEG) was performed to study the morphological and elemental composition of the rice husk-derived biochars produced (Figure 5.1) (Ahmad et al., 2014). Also, the Figure 5.2 indicated that the rice husk-derived biochar is very porosity and high potential and large number of surface area. Based on the BET analysis, the surface area is 1.37 m²/g and average pore size of 6.9 (d, mm) which is similar with the results from Leng et al. (2015).




5.3.1.1 Scanning electron microscope (SEM)

Figure 5.1 SEM-energy dispersive X-ray spectroscopy (EDX)

Table 5.1 Quantitative results of the rice husk-derived biochar samples

Element	Weight%	Weight %	Atom %	Atom %
Line		Error		Error
С	57.01	± 0.31	66.67	± 0.36
0	32.66	± 0.41	28.67	± 0.36
Na	0.18	± 0.03	0.11	± 0.02
Mg	0.12	± 0.04	0.06	± 0.02
Si	4.94	± 0.09	2.47	± 0.05
Κ	2.21	± 0.11	1.00	± 0.05
Ca	1.34	± 0.06	0.48	± 0.02
Total	100.00		100.00	





Figure 5.2 The SEM image of rice husk-derived biochar

5.3.1.2 Raman analysis of biochar structure

The ratios peak area (I) of the integrated intensity of major Raman bands indicates the alteration in biochar structure (crystalline or graphite-like carbon structures). The ratio (the I_D/I_G ratio) between the D band (1300 cm) and G band (1590 cm) of the material explains the ratio of defective structure to ordered structure (Li et al., 2006). The high I_D/I_G ratio normally represents a small number of ordered carbon structures in biochar. In this study, the I_D/I_G ratio values obtained as 0.89 which indicated that a relatively high percentage of structural defects (Teo et al., 2016).





Figure 5.3 Curve-fitting of a Raman spectrum of the rice husk-derived biochar

5.3.2 Rice husk-derived biochar adsorption of PPCPs kinetics study

The majority of previous studies applied 0.25%, 3%, and 5% rice husk-derived biochar dosages for wastewater and sewage treatment (Kalderis et al., 2017). In this work, the adsorption percentage ranged from 37.04% (0.25% biochar of DEET adsorption) to 99.21% (0.25% biochar of triclosan adsorption) (Figure 5.5-5.9). The standard derivation ranged from 0.002 to 7.42, which indicated that the experiment had good repeatability.



For DEET, the different biochar amounts changed the removal performance. The adsorption behavior occurred before 10 h. The removal rate increased with increasing biochar amount applied in the solution (5%> 3%> 0.25%). However, before 6 h, the removal rate of 3% biochar dosage was higher than that of 5% biochar dosage. Compared with sludge adsorption, UV filter is much easier adsorbed on biochar than biomass. BP-3 achieved the highest adsorption removal (~99%), and HMS and OC showed a good response to biochar adsorption. These results indicated that the different amounts of biochar exerted no significant effect on BP-3 removal. For HMS, the highest removal rate appeared in 0.25% biochar, which was opposite to that of OC. The performance for triclosan was highly similar to that for BP-3; that is, a high removal rate without any difference in biochar amount was obtained.

Hydrophobic interactions between the adsorbate and adsorbent can increase the removal ability. The amount of chlorophenol adsorbed increased with the increase of adsorbate and hydrophobicity of adsorbent (Yang et al., 2016). The O/C ratio (Table 5.2) indicates of the hydrophobicity of the biochar surface. Stronger the aromaticity and hydrophobicity of biochars the lower this ratio. It is due to the degree of carbonization and the loss of polar functional groups. (Kasozi et al., 2010). However, the ratio hypothesis cannot explain the adsorption capacity, suggesting that hydrophobicity is not the main mechanism. PPCPs, one kind of aromatic compounds, can be adsorbed onto the surface of biochar through a stable, non-covalent π donor-acceptor mechanism, which lies between the regions of the electron-absorbing atoms of Cl and the surface of biochar with high-density π -electrons (Inyang and Dickenson, 2015). Biochars prepared at 500 °C–700 °C usually have a non-uniform charge distribution, which leads to π -electron hotspots and a lack of surface areas (Zhu and Pignatello, 2005).



	Biochar	DEET	BP-3	HMS	OC	Triclosan
T 1 1	uosage	60.10/	00.00/	00.10/	07 50/	00.00/
Total removal	0.25%	63.1%	98.8%	98.1%	97.5%	99.2%
efficiency						
	3%	53.2%	98.5%	95.7%	97.7%	98.6%
	5%	68.5%	99.7%	95.4%	98.3%	98.3%
6 hours removal efficiency	0.25%	35.5%	99.4%	93.3%	97.6%	99.4%
ý	3%%	48.2%	98.8%	86.3%	94.8%	98.9%
	5%%	46.0%	99.%	81.1%	98.4%	98.8%

Table 5.2 The removal rate comparison of different biochar dosage



Figure 5.4 The simple scheme of microcosm





Figure 5.5 The adsorption kinetics study of rice husk-derived biochar on DEET





Figure 5.6 The adsorption kinetics study of rice husk-derived biochar on BP-3





Figure 5.7 The adsorption kinetics study of rice husk-derived biochar on HMS





Figure 5.8 The adsorption kinetics study of rice husk-derived biochar on OC





Figure 5.9 The adsorption kinetics study of rice husk-derived biochar on Triclosan

5.3.3 Removal kinetics of PPCPs under different redox condition with biochar

5.3.3.1 pH value and redox value comparation

During the whole experiment, pH value ranged from 5.80 to 8.14 for both activated sludge reactor and reactor with rice husk-derived biochar. The pH decreased with increasing $E_{\rm H}$. At the redox windows of +200 mv and -200 mv, the pH values were around 5.80 and 8.14, respectively. In general, biochar produced at the temperature of 550 °C, increases the pH because of the removal of -OH functional groups (Ahmad et al., 2014). It was known that pH is a key



environmental-related factor that affects microbial community activity in wastewater (Qambrani et al., 2017). Therefore, determine the relationship between pH and microbial activity is an essential parameter of PPCPs behavior in ASP.

5.3.3.2 Removal route of target pollutants under different redox condition

Previous studies rarely focused on the kinetics of PPCPs under different redox conditions from STPs. The performance of PPCPs removal under different redox conditions was affected by microbial community activity, biochar properties, and pH. The adsorption rates of all five PPCPs decreased compared with the adsorption experiment of biochar in Milli-Q water. This phenomenon is commonly investigated during the adsorption process of various pollutants (e.g. organic compounds, heavy metal) by carbonaceous materials (Alamin and Kaewsichan, 2016; Şener et al., 2016) and is due to the saturation of the available sorption sites on the adsorbent surface (Gao and Wang, 2007).

A previous study proved that pH and salinity play significant roles in biodegradation (Baena-Nogueras et al., 2017). pH decreases with increasing redox value. Alteration in E_H toward reducing conditions is commonly accompanied with an increase in pH (Rinklebe et al., 2016b; Shaheen and Rinklebe, 2017) possibly because of the production of CO₂ and organic acids from microbial activities and decomposing organic matter, and this finding might explain the low pH under oxidation conditions (Wang et al., 2013).

As shown in Figure 5.3.2 (a), redox and DEET concentration showed a negative correlation. Under oxidation conditions (+200 mv redox window), the activated sludge reactor was not as sensitive as the reactor with biochar. In addition, the adsorption rate increased compared with the reactor only added in activated sludge. In the three redox windows, a strong negative relation



was found between redox and DEET concentration. This result may be due to the fact that DEET is easily biodegraded, and its removal rate is related to microbial activity. This conclusion was similar to the conclusion in Chapter 4.

The group of UV filters, including BP-3, HMS, and OCs, could be removed by different redox conditions. HMS and BP-3 showed no significant differences. Similar results were reported for BP-3. Biodegradation of the BP-3 was studied in the lab-scale reactor to determine its removal routes under oxic and anoxic conditions. Biodegradation experiments were conducted in the reactors with ten times dilution of activated sludge and digested sludge. BP-3 can be degraded by microorganisms under different redox conditions. The biodegradation half-life for BP-3 had the following order: anoxic unamended (4.2 d) < sulfate-reducing (4.3 d) < Fe³⁺ reducing (5 d) < nitrate-reducing (8.7 d) < oxic (10.7 d). An interesting result indicated that anaerobic biodegradation is an important way to reduce BP-3 concentration (Liu et al., 2012b). Another study indicated the recalcitrance of OC to anaerobic degradation in mesophilic anaerobic biodegradation possibly occurred during stabilization digestion. However, because concentrations of selected pollutants were reduced in sludge stabilization water samples. The final biosolid still presents high concentrations of OC (465 ng/g) but remain lower than raw sludge (Ramos et al., 2016).

Triclosan can be removed efficiently under aerobic, anoxic, and anaerobic conditions (>70%). Biochar adsorption can increase the removal of triclosan in activated sludge. Sludge granulation affects the activity and accumulation of microorganisms, which is an important basis for the effective operation of a bioreactor (Neoh et al., 2016). In addition, granular sludge has abundant microbial morphology, in which microbial community constitutes a highly efficient metabolic network completed by a single microorganism (De Vrieze and Verstraete, 2016).



As shown in Figure 5.13, oxidizing conditions led to a slight removal efficiency than reducing conditions. Similar results could be found in other studies. Under different reduction and oxidation conditions, anaerobic and aerobic sludge digestion processes eliminated up to 23.0% and 56.0% of triclosan, respectively (Tohidi and Cai, 2017). Triclosan was removed to some degree (>50%) during anaerobic and anoxic treatments even though it was not significantly biotransformed in water matrix, indicating the presence of other removal mechanisms, such as sorption. Since triclosan is strongly hydrophobic (Log Downm = 3.95, 4.94) and is likely to adsorbed ($K_d = 3.61 \text{ L gss}^{-1}$) on sludge solids irrespective of the redox conditions (Inyang et al., 2016). In a laboratory scale bioreactor, diluted activated sludge removed 75% of triclosan in 150 hours under aerobic conditions, while no removal was observed under anaerobic or anoxic conditions. Under aerobic conditions, about 1% of triclosan-methyl is converted to triclosan. In contrast, the conversion observed under anoxic conditions (nitrate reduction) was less observed and none under anaerobic conditions (Chen et al., 2011;Suarez et al., 2010). Therefore, triclosan with the -methyl functional group can be regarded as the by-product of biodegradation of triclosan. Under oxygen-deficient conditions, triclosan was desorbed over time from anaerobic and anoxic sludge solids. It is assumed that the biotransformed of triclosan by sludge biomass is achieved by rapid adsorption on the sludge solids surface, and then diffusion and infiltration (absorption) into microbial cells (Tsezos and Wang, 1991). The concentration fluctuation indicated that by-products such as triclosan-methyl and triclosan could be converted to each other. Therefore, triclosan may be converted to triclosan-methyl under aerobic conditions.



5.4 Summary

The permeability of PPCPs to microbial cell components is a function of the biodegradation rate and contact time of PPCP. If PPCPs are not biodegraded by the bacteria, the poorly absorbed PPCPs are easily desorbed from the sludge surface, then the adsorption efficiency of PPCPs on the sludge surface is weak and reversible. By the results of Chapter 5, it was found that triclosan can be removed efficiently (>70%) under oxidative and reduced conditions, but oxidizing conditions can enhance removal efficiency. 50% of triclosan can be removed by adsorption during oxidative and reduced treatments, while biotransformation was not significant. Triclosan is hydrophobic (Log Kow = 4.76) and favor its adsorption on sludge biomass and biochar. HMS (log Kow = 6.16) has the highest removal efficiency amongst the 5 PPCPs in different redox condition (99-101%). DEET achieved the highest removal rate under oxidative condition (200 mv, log Kow =1.83, 96.3%). Higher removal of OC (97.1%) was found under reduced condition (0 mv). No significant difference was observed in BP-3 removal under different redox conditions (possibly due to equilibrium between metabolites, e.g. BP-1 and BP-8). Chapters 4 and 5 studied the transformation and fate of PPCPs under anaerobic, anoxic and aerobic conditions. It is important to investigate the behavior of PPCPs under different redox conditions for determining wastewater treatment processes and predicting the fate of these selected pollutants once released into the environment, such as groundwater recharge, riverbank filtration and flood condition. Different metabolites are produced under aerobic and anoxic conditions, as previously reported pollutants, such as BP-8 or DEET residues of N,N-diethyl-mtoluamide-N-oxide. Therefore, the degradation behavior in anoxic and aerobic processes are different. In addition, under anoxic conditions, some pollutants are easier to remove than under



aerobic conditions, although there is general evidence that higher oxidation potential under aerobic conditions is beneficial to its degradation.





Figure 5.10 The pH and redox tendency within 56 hours





Figure 5.11 DEET concentration and redox correlation





Figure 5.12 BP-3 concentration and redox correlation





Figure 5.13 HMS concentration and redox correlation





Figure 5.14 OC concentration and redox correlation





Figure 5.15 Triclosan concentration and redox correlation



Elimination efficiency	Redox value	DEET	BP-3	HMS	OC	Triclosan
Total removal	+200 mv	95.3	81.1	99.4	81.1	56.9
	+200 mv with biochar	96.3	88.2	99.4	88.2	81.1
	0 mv	82.5	88.1	78.5	88.1	34.8
	0 mv with biochar	87.0	97.1	98.7	97.1	65.0
	-200 mv	79.1	96.1	98.1	96.5	62.2
	-200 mv with biochar	98.4	97.6	98.9	96.2	93.7
Removal rate after 16 h	+200 mv	86.8	79.6	98.2	79.6	57.9
	+200 mv with biochar	88.0	81.7	99.7	71.7	66.6
	0 mv	83.8	84.1	78.3	84.1	28.4
	0 mv with biochar	98.4	94.1	97.4	93.1	65.6
	-200 mv	79.7	97.0	98.9	97.0	62.8
	-200 mv with biochar	98.3	97.6	99.8	97.6	99.6

Table 5.3 The removal of efficiency of selected PPCPs under different redox condition



Chapter 6 conclusion and perspectives

6.1 Conclusion

PPCPs have become a great concern in the worldwide water environment because STPs usually cannot remove them completely. Therefore, this study aimed to analyze the current situation of the selected PPCPs in the water matrix and their elimination routes in various wastewater treatment processes.

An appropriate, reliable and sensitive method was applied to trace analysis selected five PPCPs in different wastewater treatment processes (influent, primary treatment, secondary treatment, and effluent). LLE and SPE were applied for efficient and reproducible to extract five PPCPs in both sewage and activated sludge slurry. The recovery rate, repeatability, MLQ, LOQ were also determined. The whole method was accurate and could be widely applied in water and slurry samples for selected commonly detected PPCPs.

The concentrations of DEET ranged from 21.8 to 118 and 18.8 to 89.1 at ng/L level in Shatin and Taipo, respectively. The concentrations of BP-3 ranged from 12.3 to 334.3 and 22.2 ng/L to 292 at ng/L level in Shatin and Taipo, respectively. The HMS and OC concentrations varied from 55.6 to 657.1, 55.6 to 142.3, 33.7 to 125.2, and 7.8 to 66.6 ng/L. The concentration of triclosan ranged from 53 to 586.6 and 58.7 to 791.6 ng/L in the two local plants. The same PPCPs concentrations in different treatment processes vary 1–2 orders of magnitude in the same region. The PPCPs' consumption patterns varied strongly affected by sewage source composition. PPCPs in wastewater were considered origin from human activity daily consumption.

In ASP, biodegradation and adsorption were investigated as dominant elimination mechanisms of selected pollutants. DEET, BP-3, and triclosan were predominantly removed by



biodegradation. The biological activity of the selected PPCPs under aerobic conditions fitted the first-order kinetics model well (K values: 0.10 h^{-1} to 0.21 h^{-1}).

The rice husk-derived biochar adsorption study of different PPCPs was established. The rice husk-derived biochar dosages of 0.25%, 3%, and 5% are commonly applied for wastewater and sewage treatments. In this study, the adsorption percentage ranged from 37.04% (0.25% biochar of DEET adsorption) to 99.21% (0.25% biochar of triclosan adsorption). The standard derivation ranged from 0.002 to 7.42, which indicated that the experiment had good repeatability. Hydrophobic interactions between the adsorbate and adsorbent can increase the sorption ability. The amount of chlorophenol adsorbed increased with the increase of adsorbate and hydrophobicity of adsorbent. The O/C ratio indicates the hydrophobicity of biochars are due to the greater degree of carbonization and the loss of polar functional groups. The redox study in the bioreactor indicated that the pH values ranged from 5.80 to 8.14 for both activated sludge reactor and reactor with rice husk-derived biochar. These results indicated that pH decreased with increasing $E_{\rm H}$.

The performance of PPCPs removal under different redox conditions was affected by microbial community activity, biochar properties, and pH value. In general, the adsorption rate of all five PPCPs decreased compared with the adsorption experiment of biochar in Milli-Q water. Since the pore is limited and competition adsorption of different compounds occurred when the wastewater composition is complicated. This phenomenon is typically observed in the adsorption of different species by carbonaceous materials. Oxic conditions can achieve higher removal efficiency than reducing conditions. For BP-3, no significant difference was observed between different redox conditions.



6.2 Perspectives

This work aimed to study the current situation of selected PPCPs and elimination routes in STPs and water matrix. The following recommendations are proposed for the next stage research:

First, the removal efficiency of an important unit for selected pollutants in wastewater treatment processes was investigated in this study. The method for the long-term trace analysis of PPCPs concentrations in sludge samples should be developed. Other pollutants should be monitored in future studies.

Second, although the selected PPCPs were removed by biodegradation efficiently, the byproducts of target pollutants should be monitored accordingly. Information about the metabolites and their corresponding transformation activities was limited. For example, the by-products of BP-3, including BP-1 and BP-8, are more toxic than BP-3. Isotope-labeled analysis should be applied during the trace analysis of these procedures.

Third, some UV filters exhibited high adsorption affinity to the inactivated sludge. FT-IR spectrometry should be utilized to understand the adsorption since the behavior is suspected to be relevant to EPSs.

Finally, the removal routes of the selected PPCPs under different redox conditions were studied. However, the microbial activity influenced by the redox condition should be determined later. Since the removal behavior of PPCPs in sludge is highly related to microbial activity. The interactions of the microbial community, pH, biochar, and PPCPs concentration under different redox conditions warrant further studies. Also, different types of biochar with the various modified method should be optimized for PPCPs removal. In terms of society and educational meaning, PPCPs are indispensable for improving human living standards. However, in order to



protect water resources and the marine environment from these kinds of pollutants, relevant departments may consider proposing alternative products. For example, DEET-free mosquito repellent and triclosan-free disinfectant were appeared in the commercial market. Therefore, in addition to efforts to improve the treatment efficiency of sewage treatment plants, there is still a long way to raise awareness of PPCPs.



References

- Abdul Mottaleb, M., Meziani, M.J., Abdul Matin, M., Musavvir Arafat, M., Wahab, M.A., 2015. Emerging micro-pollutants pharmaceuticals and personal care products (PPCPs) contamination concerns in aquatic organisms-LC/MS and GC/MS Analysis, in: ACS Symposium Series. pp. 43–74.
- Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere.
- Al-Rifai, J.H., Khabbaz, H., Schäfer, A.I., 2011. Removal of pharmaceuticals and endocrine disrupting compounds in a water recycling process using reverse osmosis systems. Sep. Purif. Technol. 77, 60–67.
- Alamin, A.H., Kaewsichan, L., 2016. Equilibrium and kinetic studies of sorption of 2.4dichlorophenol onto 2 mixtures: Bamboo biochar plus calcium sulphate (BC) and hydroxyapatite plus bamboo biochar plus calcium sulphate (HBC), in a fluidized bed circulation column. Polish J. Chem. Technol. 18, 59–67.
- Annabi, C., Fourcade, F., Soutrel, I., Geneste, F., Floner, D., Bellakhal, N., Amrane, A., 2016.
 Degradation of enoxacin antibiotic by the electro-Fenton process: Optimization, biodegradability improvement and degradation mechanism. J. Environ. Manage. 165, 96–105.
- Armstrong, D.L., Rice, C.P., Ramirez, M., Torrents, A., 2017. Influence of thermal hydrolysisanaerobic digestion treatment of wastewater solids on concentrations of triclosan,



triclocarban, and their transformation products in biosolids. Chemosphere 171, 609–616.

- Aronson, D., Weeks, J., Meylan, B., Guiney, P.D., Howard, P.H., 2012. Environmen500tal release, environmental concentrations, and ecological risk of N,N-diethyl-m-toluamide (DEET). Integr. Environ. Assess. Manag. 8, 135–166.
- Atar, N., Eren, T., Yola, M.L., Wang, S., 2015. A sensitive molecular imprinted surface plasmon resonance nanosensor for selective determination of trace triclosan in wastewater. Sensors Actuators, B Chem. 216, 6.
- Aymerich, I., Acuña, V., Barceló, D., García, M.J., Petrovic, M., Poch, M., Rodriguez-Mozaz, S., Rodríguez-Roda, I., Sabater, S., von Schiller, D., Corominas, L., 2016. Attenuation of pharmaceuticals and their transformation products in a wastewater treatment plant and its receiving river ecosystem. Water Res. 100, 126–136. 38–644.
- Azzeh, J., Taylor-Edmonds, L., Andrews, R.C., 2015. Engineered biofiltration for ultrafiltration fouling mitigation and disinfection by-product precursor control. Water Sci. Technol. Water Supply 15, 124–133.
- Baena-Nogueras, R.M., González-Mazo, E., Lara-Martín, P.A., 2017. Degradation kinetics of pharmaceuticals and personal care products in surface waters: photolysis vs biodegradation. Sci. Total Environ. 590–591, 643–654.
- Bagheri, M., Mohseni, M., 2015. Impact of hydrodynamics on pollutant degradation and energy efficiency of VUV/UV and H2O2/UV oxidation processes. J. Environ. Manage. 164, 114–120.
- Balmer, M.E., Buser, H.R., Müller, M.D., Poiger, T., 2005. Occurrence of some organic UV filters in wastewater, in surface waters, and in fish from Swiss lakes. Environ. Sci. Technol. 39, 953–962.



- Behera, S.K., Kim, H.W., Oh, J.E., Park, H.S., 2011. Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. Sci. Total Environ. 409, 4351–4360.
- Binelli, A., Magni, S., Della Torre, C., Parolini, M., 2015. Toxicity decrease in urban wastewaters treated by a new biofiltration process. Sci. Total Environ. 537, 235–242.
- Binelli, A., Magni, S., Soave, C., Marazzi, F., Zuccato, E., Castiglioni, S., Parolini, M., Mezzanotte, V., 2014. The biofiltration process by the bivalve D. polymorpha for the removal of some pharmaceuticals and drugs of abuse from civil wastewaters. Ecol. Eng. 71, 710–721.
- Bokare, A.D., Choi, W., 2014. Review of iron-free Fenton-like systems for activating H2O2in advanced oxidation processes. J. Hazard. Mater. 275, 121-135.
- Bottoni, P., Caroli, S., 2018. Presence of residues and metabolites of pharmaceuticals in environmental compartments, food commodities and workplaces: A review spanning the three-year period 2014–2016. Microchem J, 136, 2-24.
- Boxall, A., Rudd, M. A., Brooks, B. W., Caldwell, D. J., Choi, K., Hickmann, S., Innes, E., Ostapyk, K., Staveley, J. P., Verslycke, T., Ankley, G. T., Beazley, K. F., Belanger, S. E., Berninger, J. P., Carriquirborde, P., Corrs, A., Deleo, P. C., Dyer, S. D., Ericson, J. F., Gangé, F., Giesy, J. P., Gouin, T., Hallstrom, L., Karlsson, M. V., Larssom, D. G., Lazorchak, J.M., Mastrocco, F., McLaughlin, A., McMaster, M. E., Meyerhoff, R. D., Moore, R., Parrott, J. L., Snape, J. R., Murray-Smith, R., Servos, M. R., Sibley, P. K., Straub, J. O., Szabo, N. D. Topp, E., Tetreault, G. R., Trudeau, V. L., Van Der Kraak, G., 2012. Pharmaceuticals and personal care products in the environment: what are the big questions? Environmental Health Perspectives, 12



- Borova, V.L., Maragou, N.C., Gago-Ferrero, P., Pistos, C., Thomaidis, N.S., 2014. Highly sensitive determination of 68 psychoactive pharmaceuticals, illicit drugs, and related human metabolites in wastewater by liquid chromatography-tandem mass spectrometry. Anal. Bioanal. Chem. 406, 4273–4285. 0(9), 1221-1229.
- Campos, D., Gravato, C., Fedorova, G., Burkina, V., Soares, A.M.V.M., Pestana, J.L.T., 2017. Ecotoxicity of two organic UV-filters to the freshwater caddisfly Sericostoma vittatum. Environ. Pollut. 228, 370–377.
- Cardinal, P., Anderson, J.C., Carlson, J.C., Low, J.E., Challis, J.K., Beattie, S.A., Bartel, C.N., Elliott, A.D., Montero, O.F., Lokesh, S., Favreau, A., Kozlova, T.A., Knapp, C.W., Hanson, M.L., Wong, C.S., 2014. Macrophytes may not contribute significantly to removal of nutrients, pharmaceuticals, and antibiotic resistance in model surface constructed wetlands. Sci. Total Environ. 482–483, 294–304.
- Chen, G.Q., Patel, M.K., 2012. Plastics derived from biological sources: Present and future: A technical and environmental review. Chem. Rev. 112, 2082–2099.
- Chen, L., Li, X., Hong, H., Shi, D., 2018. Multigenerational effects of 4-methylbenzylidene camphor (4-MBC) on the survival, development and reproduction of the marine copepod Tigriopus japonicus. Aquat. Toxicol. 194, 94-102.
- Chen, W., Lu, S., Jiao, W., Wang, M., Chang, A.C., 2013. Reclaimed water: A safe irrigation water source? Environ. Dev. 8, 74–83.. Aquat. Toxicol. 194, 94–102.
- Chen, X., Nielsen, J.L., Furgal, K., Liu, Y., Lolas, I.B., Bester, K., 2011. Biodegradation of triclosan and formation of methyl-triclosan in activated sludge under aerobic conditions. Chemosphere 84, 452–456.



- Chen, X., Vollertsen, J., Nielsen, J.L., Gieraltowska Dall, A., Bester, K., 2015. Degradation of PPCPs in activated sludge from different WWTPs in Denmark. Ecotoxicology 24, 2073–2080.
- Chtourou, M., Mallek, M., Dalmau, M., Mamo, J., Santos-Clotas, E., Salah, A. Ben, Walha, K., Salvadó, V., Monclús, H., 2018. Triclosan, carbamazepine and caffeine removal by activated sludge system focusing on membrane bioreactor. Process Saf. Environ. Prot. 118, 1–9.
- Cuthbert, R.J., Taggart, M.A., Saini, M., Sharma, A., Das, A., Kulkarni, M.D., Deori, P., Ranade, S., Shringarpure, R.N., Galligan, T.H., Green, R.E., 2016. Continuing mortality of vultures in India associated with illegal veterinary use of diclofenac and a potential threat from nimesulide. ORYX 50, 104–112.
- Dai, G., Wang, B., Huang, J., Dong, R., Deng, S., Yu, G., 2015. Occurrence and source apportionment of pharmaceuticals and personal care products in the Beiyun River of Beijing, China. Chemosphere 119, 1033–1039.
- De Vrieze, J., Verstraete, W., 2016. Perspectives for microbial community composition in anaerobic digestion: from abundance and activity to connectivity. Environ. Microbiol. 18(9), 2797–2809.
- Dey, S., Bano, F., Malik, A., 2019. Pharmaceuticals and personal care product (PPCP) contamination—a global discharge inventory. In Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology (pp. 1-26). Butterworth-Heinemann.
- Downs, C.A., Kramarsky-Winter, E., Segal, R., Fauth, J., Knutson, S., Bronstein, O., Ciner, F.R., Jeger, R., Lichtenfeld, Y., Woodley, C.M., Pennington, P., Cadenas, K., Kushmaro, A.,



Loya, Y., 2016. Toxicopathological Effects of the Sunscreen UV Filter, Oxybenzone (Benzophenone-3), on Coral Planulae and Cultured Primary Cells and Its Environmental Contamination in Hawaii and the U.S. Virgin Islands. Arch. Environ. Contam. Toxicol. 70, 265–288.

- Durán-Álvarez, J.C., Prado, B., González, D., Sánchez, Y., Jiménez-Cisneros, B., 2015. Environmental fate of naproxen, carbamazepine and triclosan in wastewater, surface water and wastewater irrigated soil - Results of laboratory scale experiments. Sci. Total Environ. 538, 350–362.
- Ebele, A.J., Mohamed Abou-Elwafa Abdallah, Harrad, S., 2017. Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment. Emerg. Contam.
- EMA, 2006. The European Medicines Agency in 2006.
- Frederiksen, H., Nielsen, O., Skakkebaek, N.E., Juul, A., Andersson, A.M., 2017. UV filters analyzed by isotope diluted TurboFlow-LC–MS/MS in urine from Danish children and adolescents. Int. J. Hyg. Environ. Health 220, 244–253.
- Frohne, T., Diaz-Bone, R.A., Du Laing, G., Rinklebe, J., 2015. Impact of systematic change of redox potential on the leaching of Ba, Cr, Sr, and V from a riverine soil into water. J. Soils Sediments 15, 623–633.
- Gaffney, V. de J., Almeida, C.M.M., Rodrigues, A., Ferreira, E., Benoliel, M.J., Cardoso, V.V., 2015. Occurrence of pharmaceuticals in a water supply system and related human health risk assessment. Water Res. 72, 199–208.
- Galligan, T.H., Amano, T., Prakash, V.M., Kulkarni, M., Shringarpure, R., Prakash, N., Ranade,S., Green, R.E., Cuthbert, R.J., 2014. Have population declines in Egyptian Vulture andRed-headed Vulture in India slowed since the 2006 ban on veterinary diclofenac? Bird



Conserv. Int. 24(3), 272-281.

- Gangadharan Puthiya Prajeesh Veetil, Vijaya Nadaraja, A., Bhasi, A., Khan, S., Bhaskaran, K.,
 2012. Degradation of triclosan under aerobic, anoxic, and anaerobic conditions. Appl.
 Biochem. Biotechnol. 167, 1603–1612.
- Gao, J., Huang, J., Chen, W., Wang, B., Wang, Y., Deng, S., Yu, G., 2016. Fate and removal of typical pharmaceutical and personal care products in a wastewater treatment plant from Beijing: a mass balance study. Front. Environ. Sci. Eng. 10, 491–501. d
- Gao, R., Wang, J., 2007. Effects of pH and temperature on isotherm parameters of chlorophenols biosorption to anaerobic granular sludge. J. Hazard. Mater. 145, 398–403.
- Garcia-Ivars, J., Martella, L., Massella, M., Carbonell-Alcaina, C., Alcaina-Miranda, M.I., Iborra-Clar, M.I., 2017. Nanofiltration as tertiary treatment method for removing trace pharmaceutically active compounds in wastewater from wastewater treatment plants. Water Res. 125, 360–373.
- Goel, A., Müller, M.B., Sharma, M., Frimmel, F.H., 2003. Biodegradation of nonylphenol ethoxylate surfactants in biofilm reactors. Acta Hydrochim. Hydrobiol. 31, 108–119.
- Greskowiak, J., Prommer, H., Massmann, G., Nützmann, G., 2006. Modeling seasonal redox dynamics and the corresponding fate of the pharmaceutical residue phenazone during artificial recharge of groundwater. Environ. Sci. Technol. 40, 6615–6621.
- Guo, K., Wu, Z., Yan, S., Yao, B., Song, W., Hua, Z., Zhang, X., Kong, X., Li, X., Fang, J., 2018. Comparison of the UV/chlorine and UV/H2O2 processes in the degradation of PPCPs in simulated drinking water and wastewater: Kinetics, radical mechanism and energy requirements. Water Res. 147, 184-194.

Gwenzi, W., Chaukura, N., Noubactep, C., Mukome, F.N.D., 2017. Biochar-based water



treatment systems as a potential low-cost and sustainable technology for clean water provision. J. Environ. Manage. 197, 732-749.

- Harikishore Kumar Reddy, D., Lee, S.M., 2014. Magnetic biochar composite: Facile synthesis, characterization, and application for heavy metal removal. Colloids Surfaces A Physicochem. Eng. Asp. 454, 96–103.
- Ho, J.C.H., Hsiao, C.D., Kawakami, K., Tse, W.K.F., 2016. Triclosan (TCS) exposure impairs lipid metabolism in zebrafish embryos. Aquat. Toxicol. 173, 29–35.
- Inyang, M., Dickenson, E., 2015. The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: A review. Chemosphere.
- Inyang, M., Flowers, R., McAvoy, D., Dickenson, E., 2016. Biotransformation of trace organic compounds by activated sludge from a biological nutrient removal treatment system. Bioresour. Technol. 216, 778–784.
- Jiang, J.Q., Zhou, Z., Sharma, V.K., 2013. Occurrence, transportation, monitoring and treatment of emerging micro-pollutants in waste water - A review from global views. Microchem. J. 110, 292–300.
- Jiang, X., Qu, Y., Zhong, M., Li, W., Huang, J., Yang, H., Yu, G., 2019. Seasonal and spatial variations of pharmaceuticals and personal care products occurrence and human health risk in drinking water-A case study of China. Sci. Total Environ., 694, 133711.
- Joss, A., Zabczynski, S., Göbel, A., Hoffmann, B., Löffler, D., McArdell, C.S., Ternes, T.A., Thomsen, A., Siegrist, H., 2006. Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme. Water Res. 40, 1686–1696.
- Kalderis, D., Kayan, B., Akay, S., Kulaksiz, E., Gözmen, B., 2017. Adsorption of 2,4dichlorophenol on paper sludge/wheat husk biochar: Process optimization and comparison



with biochars prepared from wood chips, sewage sludge and HOG fuel/demolition waste. J. Environ. Chem. Eng. 5, 2222–2231.

- Kasozi, G.N., Zimmerman, A.R., Nkedi-Kizza, P., Gao, B., 2010. Catechol and humic acid sorption onto a range of laboratory-produced black carbons (biochars). Environ. Sci. Technol. 44, 6189–6195.
- Kassotaki, E., Buttiglieri, G., Ferrando-Climent, L., Rodriguez-Roda, I., Pijuan, M., 2016. Enhanced sulfamethoxazole degradation through ammonia oxidizing bacteria cometabolism and fate of transformation products. Water Res. 94, 111–119.
- Kelessidis, A., Stasinakis, A.S., 2012. Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. Waste Manag. 32, 1186–1195.
- Kostich, M.S., Batt, A.L., Lazorchak, J.M., 2014. Concentrations of prioritized pharmaceuticals in effluents from 50 large wastewater treatment plants in the US and implications for risk estimation. Environ. Pollut. 184, 354–359.
- Kupper, T., Plagellat, C., Brändli, R.C., de Alencastro, L.F., Grandjean, D., Tarradellas, J., 2006.Fate and removal of polycyclic musks, UV filters and biocides during wastewater treatment.Water Res. 40, 2603–2612.
- Lai, W.W.P., Chuang, Y.C., Lin, A.Y.C., 2017. The effects and the toxicity increases caused by bicarbonate, chloride, and other water components during the UV/TiO2degradation of oxazaphosphorine drugs. Environ. Sci. Pollut. Res. 24, 14595–14604.
- Lee, C.O., Howe, K.J., Thomson, B.M., 2012. Ozone and biofiltration as an alternative to reverse osmosis for removing PPCPs and micropollutants from treated wastewater. Water Res. 46, 1005–1014.

Leng, L., Yuan, X., Zeng, G., Shao, J., Chen, X., Wu, Z., & Peng, X., 2015. Surface



characterization of rice husk bio-char produced by liquefaction and application for cationic dye (Malachite green) adsorption. Fuel, 155, 77-85.

- Li, B., Zhang, T., 2010. Biodegradation and adsorption of antibiotics in the activated sludge process. Environ. Sci. Technol. 44, 3468–3473.
- Li, W., Ma, Y., Guo, C., Hu, W., Liu, K., Wang, Y., Zhu, T., 2007. Occurrence and behavior of four of the most used sunscreen UV filters in a wastewater reclamation plant. Water Res. 41, 3506–3512.
- Li, X., Hayashi, J.I. and Li, C.Z., 2006. FT-Raman spectroscopic study of the evolution of char structure during the pyrolysis of a Victorian brown coal. Fuel, 85(12-13),1700-1707.
- Li, X., Shi, H., Li, K., Zhang, L., 2015. Combined process of biofiltration and ozone oxidation as an advanced treatment process for wastewater reuse. Front. Environ. Sci. Eng. 9, 1076– 1083.
- Li, X., Ying, G.G., Zhao, J.L., Chen, Z.F., Lai, H.J., Su, H.C., 2013. 4-Nonylphenol, bisphenol-A and triclosan levels in human urine of children and students in China, and the effects of drinking these bottled materials on the levels. Environ. Int. 52, 81–86.
- Liu, P., Liu, W.J., Jiang, H., Chen, J.J., Li, W. W., & Yu, H.Q., 2012. Modification of bio-char derived from fast pyrolysis of biomass and its application in removal of tetracycline from aqueous solution. Bioresour. Technol. 121, 235-240.
- Liu, Y.S., Ying, G.G., Shareef, A., Kookana, R.S., 2012a. Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant. Environ. Pollut. Elsevier, pp. 225–232.
- Liu, Y.S., Ying, G.G., Shareef, A., Kookana, R.S., 2012b. Biodegradation of the ultraviolet filter benzophenone-3 under different redox conditions. Environ. Toxicol. Chem. 31, 289–295.


- López-Serna, R., Marín-de-Jesús, D., Irusta-Mata, R., García-Encina, P.A., Lebrero, R., Fdez-Polanco, M., Muñoz, R., 2018. Multiresidue analytical method for pharmaceuticals and personal care products in sewage and sewage sludge by online direct immersion SPME onfiber derivatization – GCMS. Talanta 186, 506–512.
- Löwenberg, J., Zenker, A., Baggenstos, M., Koch, G., Kazner, C., Wintgens, T., 2014. Comparison of two PAC/UF processes for the removal of micropollutants from wastewater treatment plant effluent: Process performance and removal efficiency. Water Res. 56, 26–36.
- Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S., Wang, X.C., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, Science of the Total Environment. Elsevier. 473, 619–641.
- Mackul'ak, T., Mosný, M., Grabic, R., Golovko, O., Koba, O., Birošová, L., 2015. Fenton-like reaction: A possible way to efficiently remove illicit drugs and pharmaceuticals from wastewater. Environ. Toxicol. Pharmacol. 39, 483–488.
- Magi, E., Scapolla, C., Di Carro, M., Rivaro, P., Ngoc Nguyen, K.T., 2013. Emerging pollutants in aquatic environments: Monitoring of UV filters in urban wastewater treatment plants. Anal. Methods 5, 428–433.
- Mailler, R., Gasperi, J., Coquet, Y., Deshayes, S., Zedek, S., Cren-Olivé, C., Cartiser, N., Eudes, V., Bressy, A., Caupos, E., Moilleron, R., Chebbo, G., Rocher, V., 2015. Study of a large scale powdered activated carbon pilot: Removals of a wide range of emerging and priority micropollutants from wastewater treatment plant effluents. Water Res. 72, 315–330.
- Malmborg, J., Magnér, J., 2015. Pharmaceutical residues in sewage sludge: Effect of sanitization and anaerobic digestion. J. Environ. Manage. 153, 1–10.



- Manová, E., von Goetz, N., Hauri, U., Bogdal, C., Hungerbühler, K., 2013. Organic UV filters in personal care products in Switzerland: A survey of occurrence and concentrations. Int. J. Hyg. Environ. Health 216, 508–514.
- Martín, J., Santos, J.L., Aparicio, I., Alonso, E., 2015. Pharmaceutically active compounds in sludge stabilization treatments: Anaerobic and aerobic digestion, wastewater stabilization ponds and composting. Sci. Total Environ. 503–504, 97–104.
- Martins, D., Monteiro, M.S., Soares, A.M.V.M., Quintaneiro, C., 2017. Effects of 4-MBC and triclosan in embryos of the frog Pelophylax perezi. Chemosphere 178, 325–332.
- Maderova, Z., Baldikova, E., Pospiskova, K., Safarik, I., & Safarikova, M., 2016. Removal of dyes by adsorption on magnetically modified activated sludge. Int. J. Environ. Sci. Technol., 13(7), 1653-1664.
- McKie, M.J., Andrews, S.A., Andrews, R.C., 2016. Conventional drinking water treatment and direct biofiltration for the removal of pharmaceuticals and artificial sweeteners: A pilot-scale approach. Sci. Total Environ. 544, 10–17.
- Min, X., Li, W., Wei, Z., Spinney, R., Dionysiou, D. D., Seo, Y., & Xiao, R., 2018. Sorption and biodegradation of pharmaceuticals in aerobic activated sludge system: A combined experimental and theoretical mechanistic study. Chem Eng J., 342, 211-219.
- Mohan, D., Sarswat, A., Ok, Y.S., Pittman, C.U., 2014. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent A critical review. Bioresour. Technol. 160, 191–202.
- Mottaleb, M.A., 2015. Use of LC-MS and GC-MS Methods to Measure Emerging Contaminants
 Pharmaceutical and Personal Care Products (PPCPs) in Fish. J. Chromatogr. Sep. Tech. 06.
 Neoh, C.H., Noor, Z.Z., Mutamim, N.S.A., Lim, C.K., 2016. Green technology in wastewater



treatment technologies: Integration of membrane bioreactor with various wastewater treatment systems. Chem. Eng. J.

- Oh, S.Y., Son, J.G., Chiu, P.C., 2013. Biochar-mediated reductive transformation of nitro herbicides and explosives. Environ. Toxicol. Chem. 32, 501–508.
- Overturf, M.D., Anderson, J.C., Pandelides, Z., Beyger, L., Holdway, D.A., 2015. Pharmaceuticals and personal care products: A critical review of the impacts on fish reproduction. Crit. Rev. Toxicol. 45, 492–530.
- Papageorgiou, M., Kosma, C., Lambropoulou, D., 2016. Seasonal occurrence, removal, mass loading and environmental risk assessment of 55 pharmaceuticals and personal care products in a municipal wastewater treatment plant in Central Greece. Sci. Total Environ. 543, 547–569.
- Paredes, L., Fernandez-Fontaina, E., Lema, J.M., Omil, F., Carballa, M., 2016. Understanding the fate of organic micropollutants in sand and granular activated carbon biofiltration systems. Sci. Total Environ. 551–552, 640–648.
- Pompei, C.M.E., Ciric, L., Canales, M., Karu, K., Vieira, E.M., Campos, L.C., 2017. Influence of PPCPs on the performance of intermittently operated slow sand filters for household water purification. Sci. Total Environ. 581–582, 174–185.
- Prosser, R.S., Sibley, P.K., 2015. Human health risk assessment of pharmaceuticals and personal care products in plant tissue due to biosolids and manure amendments, and wastewater irrigation. Environ. Int. 75, 223-233.
- Qambrani, N.A., Rahman, M.M., Won, S., Shim, S., Ra, C., 2017. Biochar properties and ecofriendly applications for climate change mitigation, waste management, and wastewater treatment: A review. Renew. Sustain. Energy Rev. 79, 255–273.



- Ramos, S., Homem, V., Alves, A., Santos, L., 2016. A review of organic UV-filters in wastewater treatment plants. Environ. Int. 86, 24–44.
- Rapp-Wright, H., McEneff, G., Murphy, B., Gamble, S., Morgan, R., Beardah, M., & Barron, L., 2017. Suspect screening and quantification of trace organic explosives in wastewater using solid phase extraction and liquid chromatography-high resolution accurate mass spectrometry. J. Hazard. Mater., 329, 11-21.
- Rajapaksha, A.U., Vithanage, M., Ahmad, M., Seo, D.C., Cho, J.S., Lee, S.E., Lee, S.S., Ok, Y.S., 2015. Enhanced sulfamethazine removal by steam-activated invasive plant-derived biochar. J. Hazard. Mater. 290, 43–50.
- Rajapaksha, A.U., Vithanage, M., Lim, J.E., Ahmed, M.B.M., Zhang, M., Lee, S.S., Ok, Y.S.,
 2014. Invasive plant-derived biochar inhibits sulfamethazine uptake by lettuce in soil.
 Chemosphere 111, 500–504.
- Rattier, M., Reungoat, J., Keller, J., Gernjak, W., 2014. Removal of micropollutants during tertiary wastewater treatment by biofiltration: Role of nitrifiers and removal mechanisms. Water Res. 54, 89–99.
- Richardson, S. D., & Ternes, T. A., 2017. Water analysis: emerging contaminants and current issues. Aanl Chem., 90(1), 398-428.
- Rinklebe, J., Shaheen, S.M., Frohne, T., 2016a. Amendment of biochar reduces the release of toxic elements under dynamic redox conditions in a contaminated floodplain soil. Chemosphere 142, 41–47.
- Rinklebe, J., Shaheen, S.M., Frohne, T., 2016b. Amendment of biochar reduces the release of toxic elements under dynamic redox conditions in a contaminated floodplain soil. Chemosphere 142, 41–47.



- Rodriguez, E., Campinas, M., Acero, J.L., Rosa, M.J., 2016. Investigating PPCP Removal from Wastewater by Powdered Activated Carbon/Ultrafiltration. Water. Air. Soil Pollut. 227, 177.
- Sabrina, N., Mutamim, A., Zainon Noor, Z., Ariffin, M., Hassan, A., Olsson, G., 2012. Application of membrane bioreactor technology in treating high strength industrial wastewater: a performance review. DES 305, 1–11.
- Salgado, R., Marques, R., Noronha, J.P., Carvalho, G., Oehmen, A., Reis, M.A.M.M., 2012. Assessing the removal of pharmaceuticals and personal care products in a full-scale activated sludge plant. Environ. Sci. Pollut. Res. 19, 1818–1827.
- Sankoda, K., Murata, K., Tanihata, M., Suzuki, K., Nomiyama, K., Shinohara, R., 2015. Seasonal and Diurnal Variation of Organic Ultraviolet Filters from Personal Care Products Used Along the Japanese Coast. Arch. Environ. Contam. Toxicol. 68, 217–224.
- Şener, M., Kayan, B., Akay, S., Gözmen, B., Kalderis, D., 2016. Fe-modified sporopollenin as a composite biosorbent for the removal of Pb2+ from aqueous solutions. Desalin. Water Treat. 57, 28294–28312.
- Shaheen, S.M., Rinklebe, J., 2017. Sugar beet factory lime affects the mobilization of Cd, Co, Cr, Cu, Mo, Ni, Pb, and Zn under dynamic redox conditions in a contaminated floodplain soil. J. Environ. Manage. 186, 253–260.
- Sharma, A.K., Saini, M., Singh, S.D., Prakash, V., Das, A., Bharathi Dasan, R., Pandey, S., Bohara, D., Galligan, T.H., Green, R.E., Knopp, D., Cuthbert, R.J., 2014. Diclofenac is toxic to the Steppe Eagle Aquila nipalensis: Widening the diversity of raptors threatened by NSAID misuse in South Asia. Bird Conserv. Int. 24(3), 282-286.
- Shoeib, M., Schuster, J., Rauert, C., Su, K., Smyth, S.A., Harner, T., 2016. Emission of poly and perfluoroalkyl substances, UV-filters and siloxanes to air from wastewater treatment plants.



Environ. Pollut. 218, 595–604.

- Singer, H., Müller, S., Tixier, C., Pillonel, L., 2002. Triclosan: Occurrence and fate of a widely used biocide in the aquatic environment: Field measurements in wastewater treatment plants, surface waters, and lake sediments. Environ. Sci. Technol. 36, 4998–5004.
- Sophia, A., C., Lima, E.C., 2018. Removal of emerging contaminants from the environment by adsorption. Ecotoxicol. Environ. Saf. 150, 1–17.
- Stasinakis, A.S., Petalas, A. V, Mamais, D., Thomaidis, N.S., Gatidou, G., Lekkas, T.D., 2007. Investigation of triclosan fate and toxicity in continuous-flow activated sludge systems. Chemosphere 68, 375–381.
- Suarez, S., Lema, J.M., Omil, F., 2010. Removal of Pharmaceutical and Personal Care Products (PPCPs) under nitrifying and denitrifying conditions. Water Res. 44, 3214–3224.
- Subedi, B., Balakrishna, K., Joshua, D.I., Kannan, K., 2017. Mass loading and removal of pharmaceuticals and personal care products including psychoactives, antihypertensives, and antibiotics in two sewage treatment plants in southern India. Chemosphere 167, 429–437.
- Tan, X. fei, Liu, Y. guo, Gu, Y. ling, Xu, Y., Zeng, G. ming, Hu, X. jiang, Liu, Shao bo, Wang, X., Liu, Si mian, Li, J., 2016. Biochar-based nano-composites for the decontamination of wastewater: A review. Bioresour. Technol. 212, 318–333.
- Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere. 125, 70–85.
- Tanoue, R., Sato, Y., Motoyama, M., Nakagawa, S., Shinohara, R., Nomiyama, K., 2012. Plant uptake of pharmaceutical chemicals detected in recycled organic manure and reclaimed wastewater. J. Agric. Food Chem. 60, 10203–10211.

Tato, T., Salgueiro-González, N., León, V.M., González, S., & Beiras, R., 2018.



Ecotoxicological evaluation of the risk posed by bisphenol A, triclosan, and 4-nonylphenol in coastal waters using early life stages of marine organisms (Isochrysis galbana, Mytilus galloprovincialis, Paracentrotus lividus, and Acartia clausi). Environ. Pollut. 232, 173-182.

- Tchobanoglous, G., Burton, F.L., & Stensel, H.D., 2003. Metcalf & Eddy wastewater engineering: treatment and reuse. International Edition. McGrawHill, 4, 361-411.
- Teixeira, S., Delerue-Matos, C., Santos, L., 2019. Application of experimental design methodology to optimize antibiotics removal by walnut shell based activated carbon. Sci. Total Environ. 646, 168–176.
- Teo, E.Y.L., Muniandy, L., Ng, E.P., Adam, F., Mohamed, A.R., Jose, R. and Chong, K.F., 2016. High surface area activated carbon from rice husk as a high performance supercapacitor electrode. Electrochimica Acta, 192,110-119.
- Tian, Y., Zheng, L., Sun, D.-Z., 2006. Functions and behaviors of activated sludge extracellular polymeric substances (EPS): A promising environmental interest. J. Environ. Sci. 18, 420– 427.
- Tohidi, F., Cai, Z., 2017. Fate and mass balance of triclosan and its degradation products: Comparison of three different types of wastewater treatments and aerobic/anaerobic sludge digestion. J. Hazard. Mater. 323, 329–340.
- Tohidi, F., Cai, Z., 2015. GC/MS analysis of triclosan and its degradation by-products in wastewater and sludge samples from different treatments. Environ. Sci. Pollut. Res. 22, 11387–11400.
- Tsui, M.M.P., Leung, H.W., Lam, P.K.S., Murphy, M.B., 2014. Seasonal occurrence, removal efficiencies and preliminary risk assessment of multiple classes of organic UV filters in wastewater treatment plants. Water Res. 53, 58–67.



- Urtiaga, A.M., Pérez, G., Ibáñez, R., Ortiz, I., 2013. Removal of pharmaceuticals from a WWTP secondary effluent by ultrafiltration/reverse osmosis followed by electrochemical oxidation of the RO concentrate. Desalination 331, 26–34.
- USEPA, 2009. Pharmaceuticals and Personal Care Products (PPCPs). Frequently Asked Questions. Accessed on 15th April, 2016. <u>http://www.epa.gov/ppcp/faq.html</u>
- USEPA, 2013. Pentachlorophenol: health and environmental effects profile. [WWW Document]. URL <u>https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=42186</u>
- USEPA, 2018. PPCPs | US EPA [WWW Document]. URL https://search.epa.gov/epasearch/epasearch?querytext=ppcp&areaname=&areacontacts=&ar easearchurl=&typeofsearch=epa&result_template=2col.ftl (accessed 10.6.18).
- USEPA, 2016. Definition and Procedure for the Determination of the Method Detection Limit, Revision 2 [WWW Document]. URL https://www.epa.gov/cwa-methods/proceduresdetection-and-quantitation-documents
- USEPA, 2015. Contaminants of Emerging Concern including Pharmaceuticals and Personal Care Products [WWW Document]. URL https://www.epa.gov/wqc/contaminants-emergingconcern-including-pharmaceuticals-and-personal-care-products (accessed 10.6.18).
- Valle-Sistac, J., Molins-Delgado, D., Díaz, M., Ibáñez, L., Barceló, D., Silvia Díaz-Cruz, M., 2016. Determination of parabens and benzophenone-type UV filters in human placenta: First description of the existence of benzyl paraben and benzophenone-4. Environ. Int. 88, 243–249.
- Van Wieren, E.M., Seymour, M.D., Peterson, J.W., 2012. Interaction of the fluoroquinolone antibiotic, ofloxacin, with titanium oxide nanoparticles in water: Adsorption and breakdown. Sci. Total Environ. 441, 1–9.



- Veach, A.M., & Bernot, M.J., 2011. Temporal variation of pharmaceuticals in an urban and agriculturally influenced stream. Sci Total Environ. 409(21), 4553-4563.
- Vela-Soria, F., Gallardo-Torres, M.E., Ballesteros, O., Díaz, C., Pérez, J., Navalón, A., Fernández, M.F., Olea, N., 2017. Assessment of parabens and ultraviolet filters in human placenta tissue by ultrasound-assisted extraction and ultra-high performance liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1487, 153–161.
- Veloutsou, S., Bizani, E., Fytianos, K., 2014. Photo-Fenton decomposition of β-blockers atenolol and metoprolol; study and optimization of system parameters and identification of intermediates. Chemosphere 107, 180–186.
- Wang, B. Bin, Liu, X.T., Chen, J.M., Peng, D.C., He, F., 2018. Composition and functional group characterization of extracellular polymeric substances (EPS) in activated sludge: the impacts of polymerization degree of proteinaceous substrates. Water Res. 129, 133–142.
- Wang, D., Sui, Q., Lu, S.G., Zhao, W.T., Qiu, Z.F., Miao, Z.W., Yu, G., 2014. Occurrence and removal of six pharmaceuticals and personal care products in a wastewater treatment plant employing anaerobic/anoxic/aerobic and UV processes in Shanghai, China. Environ. Sci. Pollut. Res. 21, 4276–4285.
- Wang, Y., Tang, C., Wu, J., Liu, X., Xu, J., 2013. Impact of organic matter addition on pH change of paddy soils. J. Soils Sediments 13, 12–23.
- Weeks, J.A., Guiney, P.D., Nikiforovz, A.I., 2012. Assessment of the environmental fate and ecotoxicity of N,N-diethyl-m-toluamide (DEET). Integr. Environ. Assess. Manag. 8, 120–134.
- Wilkinson, J. L., Hooda, P. S., Barker, J., Barton, S., & Swinden, J., 2016. Ecotoxic pharmaceuticals, personal care products, and other emerging contaminants: A review of



environmental, receptor-mediated, developmental, and epigenetic toxicity with discussion of proposed toxicity to humans. Crit. Rev. Env. Sci. Tec., 46(4), 336-381.

- Wu, C., Spongberg, A.L., & Witter, J.D., 2009. Sorption and biodegradation of selected antibiotics in biosolids. J Environ Sci Heal A. 44(5), 454-461.
- Yahya, M.A., Al-Qodah, Z., Ngah, C.W.W.Z., 2015. Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. Renew. Sustain. Energy Rev. 46, 218–235.
- Yang, H., Hu, Y., Cheng, H., 2016. Sorption of chlorophenols on microporous minerals: mechanism and influence of metal cations, solution pH, and humic acid. Environ. Sci. Pollut. Res. 23, 19266–19280.
- Yang, X., Sun, J., Fu, W., Shang, C., Li, Y., Chen, Y., Gan, W., Fang, J., 2016. PPCP degradation by UV/chlorine treatment and its impact on DBP formation potential in real waters. Water Res. 98, 309–318.
- Yang, Y., Ok, Y.S., Kim, K.H., Kwon, E.E., Tsang, Y.F., 2017. Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: A review. Sci. Total Environ. 596, 303-320.
- Yangali-Quintanilla, V., Maeng, S.K., Fujioka, T., Kennedy, M., Li, Z., Amy, G., 2011. Nanofiltration vs. reverse osmosis for the removal of emerging organic contaminants in water reuse. Desalin. Water Treat. 34, 50–56.
- Yao, Y., Gao, B., Chen, J., Yang, L., 2013. Engineered biochar reclaiming phosphate from aqueous solutions: Mechanisms and potential application as a slow-release fertilizer. Environ. Sci. Technol. 47, 8700–8708.

Yin, J., Wang, H., Zhang, J., Zhou, N., Gao, F., Wu, Y., Xiang, J., Shao, B., 2012. The



occurrence of synthetic musks in human breast milk in Sichuan, China. Chemosphere 87, 1018–1023.

- Yu, K., Rinklebe, J., 2011. Advancement in soil microcosm apparatus for biogeochemical research. Ecol. Eng. 37, 2071–2075.
- Yu, Y., Wu, L., Chang, A.C., 2013. Seasonal variation of endocrine disrupting compounds, pharmaceuticals and personal care products in wastewater treatment plants. Sci. Total Environ. 442, 310–316.
- Zepon Tarpani, R.R., Azapagic, A., 2018. Life cycle environmental impacts of advanced wastewater treatment techniques for removal of pharmaceuticals and personal care products (PPCPs). J. Environ. Manage. 215, 258–272.
- Zhang, W., Cao, B., Wang, D., Ma, T., Xia, H., Yu, D., 2016. Influence of wastewater sludge treatment using combined peroxyacetic acid oxidation and inorganic coagulants reflocculation on characteristics of extracellular polymeric substances (EPS). Water Res. 88, 728–739.
- Zhu, D., Pignatello, J.J., 2005. Characterization of aromatic compound sorptive interactions with black carbon (charcoal) assisted by graphite as a model. Environ. Sci. Technol. 39, 2033– 2041.



Publications

Journal paper

Yang, Y., Ok, Y. S., Kim, K. H., Kwon, E. E., & Tsang, Y. F. (2017). Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: A review. Science of the Total Environment, 596, 303-320.

Conference paper

Yang, Y., Tsang, Y.F.* (2018, August). Removal of Selected Pharmaceuticals and Personal Care Products (PPCPs) using Bioreactors with Engineered Biochars. The 4th International Conference on Contaminated Land, Ecological Assessment and Remediation (CLEAR2018), Hong Kong.

Yang, Y., Ok, Y.S., Rinklebe, J., Tsang, Y.F.* (2019, March). Removal of Pharmaceuticals & Personal Care Products (PPCPs) Using Selected Sludge Bacteria and Biochars. E2S2-CREATE and AIChE Waste Management Conference, Singapore.

Yang, Y., Tsang, Y.F.* (2018, June). Occurrence, Sorption Behavior and Biodegradability of DEET in Wastewater Treatment Plants. The 2nd International Conference on Bioresources, Energy, Environment, and Materials Technology (BEEM2018), Gangwon, Korea.

