Application of high rate nitrifying trickling filters on the removal of ammonium and chemicals of concern

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SUMMARY

The treated water is an important source for water supplement, particularly in some arid or semi-arid areas. To protect the public health and the environment, the reliability of water treatment has to be guaranteed. Ammonium has been recognized as a typical pollutant in water source, because it can increase the consumption of chloride during water treatment. The ability of the high rate nitrifying trickling filter (NTF) for ammonium removal at low concentrations has been identified. With the increase of the energy crisis, it is important to consider the energy consumption on the NTF design.

This thesis compared the nitrification performance in two NTFs, with different aspect ratios (height: diameter) and the same packing media specific surface area. The effect of some operational parameters on nitrification performance for the two NTFs was also taken into consideration.

A laboratory-scale NTF system, consisting of two filters with different aspect ratios and the same effective media surface area, was constructed in Flinders University, South Australia. The NTFs were operated at the same environmental conditions (e.g. temperature and pH).The influent ammonium concentrations for both NTFs were maintained low. The inorganic nitrogen profiles of short- and long-term observation in both NTFs showed high similarity. The typical operational parameters (e.g. pH, total alkalinity and dissolved oxygen) exerted the similarly effects on the nitrification performance in both NTFs. These results demonstrated that the aspect ratio of the filter had insignificant effect on nitrification performance in the NTF.

The nitrifying bacteria in the NTF also have been known to be able to biodegrade some chemicals of concern (CoC), which are prevalently known as organic contaminants in water sources. These organic contaminants drifting into the environment are mainly because of the inadequate treatment in conventional wastewater treatment plants (WWTPs) and the improper drainage from industries, hospitals or households. Biological treatment process is considered to be an efficient approach for the removal of the organic contaminants. Little is known about the efficiency of a fixed-bed NTF for chemical removal. In order to remove ammonium and the CoC at the same time, the high rate fixed-bed NTF was applied in this study.

This thesis investigated the feasibility of the high-rate NTF for the removal of some

CoC. These CoC were from a variety of classifications, including caffeine (stimulant), benzotriazole (detergent additive), N, N-diethyl-m-toluamide (insect repellent), 17α-ethynylestradiol (hormone), acetaminophen (analgesic agent), atrazine (herbicide), trimethoprim (antibiotic) and bisphenol A (plasticizer). A laboratory-scale NTF system, consisting of four parallel NTFs (0.6 m bed depth and 0.15 m in diameter), was constructed in Flinders University, South Australia. The results showed that biodegradation was the main removal mechanism for all the investigated CoC. The removal efficiency for CoC ranged from 27% (bisphenol A) to 98% (caffeine) after 12 hours recirculation.

This thesis also investigated effect of nitrification rate in the NTF to the removal efficiency for CoC and the effect of CoC challenge to the nitrification performance in the NTF. The results demonstrated that the nitrifying-enhanced NTF was able to improve the removal efficiency for most of the investigated CoC. The largest removal efficiency improvement was observed for acetaminophen.

This research further investigated the effect of exogenous organic carbon (sucrose) to the removal efficiency for CoC in the NTF. The addition of exogenous organic carbon might generate other bacteria species (e.g. heterotrophic bacteria) in the NTF. The removal efficiency for CoC ranged from 20% to 90%. High removal efficiency of >80% was observed for ACE, BPA, TRI and EE2. The addition of sucrose improved the removal efficiency of the NTF for most of the CoC.

This study revealed that the NTF aspect ratio had insignificant influence on the nitrification performance, and this is an important criterion for the NTF design. The feasibility of a high-rate NTF for CoC removal has been confirmed in this study. The enhancement of nitrification rate and addition of exogenous organic carbon might improve the efficiency of NTF for CoC removal.

DECLARATION

I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

Lei Mai

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Abbreviations

ACE	acetaminophen
AOB	ammonium oxidising bacteria
ATZ	atrazine
BEZ	benzotriazole
BOD	biological oxygen demond
BPA	bisphenol A
CAF	caffeine
CoC	chemicals of concern
DBPs	disinfection by-products
DEET	N, N-diethyl-m-toluamide
DO	dissolved oxygen
EDCs	endocrine disrupting compounds
EE2	17α-ethynylestradiol
HPLC	high performance liquid chromatograph
HRT	hydraulic retention time
MBR	membrane bioreactor
NAS	nitrifying activated sludge
NH_4-N	ammonium-nitrogen
NO_2-N	nitrite-nitrogen
NO_3-N	nitrate-nitrogen
NOB	nitrite oxidising bacteria
NTF	nitrifying trickling filter
PAC	powdered activated carbon
PPCPs	pharmaceuticals and personal care products
PVC	polyvinylchloride
SD	standard deviation
SRT	solid retention time
STPs	sewage treatment plants
TOC	total organic carbon
TRI	trimethoprim
WWTP	wastewater treatment plant

1 INTRODUCTION

1.1 General introduction

It is generally considered that the availability of clean and safe water is not only a big problem, but an escalating one that is fuelled by population increases, the contamination of many water resources and cyclical drought in some arid or semi-arid areas. It is also generally agreed, that this problem (and its causes) will affect the future prosperity of most countries. As the demands for clean, safe water rise, the need to ensure the availability of sufficient fresh water for the hydrological cycle will eventually compel greater efforts in water resource management through recycling and the reuse of municipal and industrial wastewater (Henry and Heinke, 1989). Therefore, wastewater reuse is a continuing vital component in many areas of water resource management and implementation. The potential applications of reclaimed water vary, falling into the principal categories for water reuse: irrigation, industrial reuse, groundwater recharge, recreation, and potable reuse (Metcalf and Eddy, 2003); however, they are dependent on the reliability of water treatment to protect the public health and the environment. To be reused, wastewater usually needs to be adequately treated and disinfected to minimise the adverse risk to public health and the exposure to water containing human pathogens. But in some developing countries with poor wastewater treatment technologies and little funding support, a large percentage of illness is attributed to an inadequate and inappropriate water supply (Henry and Heinke, 1989). The high pollution load and the varied of contaminants in wastewater always cause treatment difficulties, increasing the cost of meeting the water reuse standard.

Ammonium, in particular, is one of the most prevalent nutrient pollutants in contaminated waters. The discharge of excessive amounts of ammonium into the surface water can cause eutrophication and can be toxic:: to aquatic organisms (Tekerlekopoulou and Vayenas, 2007). Moreover, the presence of ammonium in the wastewater increases the chlorine requirement during disinfection process, because of the extra chlorine consumption to oxidise ammonium before chlorination (van den Akker et al., 2008). Therefore, it is necessary to eliminate it to reduce the risk to the public and environmental health and ensure efficient chlorination disinfection (Metcalf and Eddy, 2003).

With the development of technology, the usage of biologically active organic chemicals has increased in industries, hospitals and households. Relatively high concentrations of these organic chemicals were detected in wastewaters (Sim et al., 2011). The inadequate treatment and improper discharge of the wastewater resulted in the contamination of the receiving water systems (Bendz et al., 2005, Verlicchi et al., 2010), and further contaminated the drinking water, because some of the receiving water systems are the sources of drinking water (Benotti et al., 2009). This emerging water contamination problem is caused by the incidence of biologically active organic contaminants, which were named as chemicals of concern (CoC) in this study, including endocrine disrupting compounds, pharmaceuticals and personal care products.

Although little is known about the influence on human health or the environment of all emerging contaminants, some of the contaminants have been identified as having potentially acute or chronic impact on aquatic organisms (Metcalf and Eddy, 2003). For example, Hayes et a. (2010) reported that the presence of atrazine (a herbicide that is often used in agriculture industry) in the surface water would cause the feminisation on male frogs. Hence, organic pollutants are of some interest to the water industry (Snyder et al., 2003) and it is desirable to remove these contaminants to meet water reuse criteria and standards. Current water treatment technologies could be optimised to get higher quality of the effluent water and to be more financial-effective. Therefore, a low-cost and high-efficiency treatment system is expected to be built to remove both the nutrients and chemicals of concern (CoC). It is significantly important to protect the environmental and public health and to provide clean and safe water for reuse.

1.2 Nitrifying trickling filter process

1.2.1 Background

Increasingly, water resource management in Australia and China includes the reuse of treated wastewater for non-potable application. In 2008, South Australia reused 30% and 22% of its treated wastewater generated in metropolitan and country areas respectively (SA Water, 2008). Chlorination is widely used as the disinfectant, but ammonium present in treated wastewater increases the chlorine demand, which increases the risk of under- or over- dosing of chlorine. The former may compromise disinfection and the latter increases the risk of forming potentially carcinogenic disinfection by-products (DBPs) in organically rich wastewaters. Notwithstanding the risk to public health, the presence of ammonium significantly increases the cost of disinfection. At Glenelg (Adelaide, South Australia) wastewater treatment plant (WWTP) the mean concentration of ammonium (2001/2003) in the treated effluent was 6.87 mg NH_4-N L^{-1} (Wilkinson et al., 2003). A similar concentration in the 11GL of reuse water would require an additional 760 T of chlorine, which at $1550/T equates to a cost of $1.2m per year — due only to ammonium-driven chlorine demand. Therefore, it is vital to optimise ammonium-N removal from wastewater to improve chlorination efficiency.

One of the commonly used pathways to decrease the chlorine demand during chlorination process is nitrification, which can oxidise the ammonium-nitrogen to less chlorine required nitrate-nitrogen (Yang et al., 2007). The nitrifying bacteria are responsible for nitrification in the wastewater treatment (see Section 1.2.2.2). Comparing with the external aeration for the water in a tank, the column-based aeration system can provide more oxygen availability for the microorganisms in the biofilm (Miladinovic and Weatherley, 2008). In this case, a nitrifying trickling filter (NTF) column, which facilitated with passive aeration, is considered to be a cost- and energy- efficient approach to achieve effective nitrification. van den Akker et al. (2008) reported that high ammonium removal efficiency was observed in a 3-metre NTF. The primary energy usage in their study was to pump the water to the top of the 3-metre NTF. A shorter NTF will save the energy for pumping water, while require larger plant area. Therefore, the aspect ratio of the NTF requires to be considered to better design the WWTP. The nitrification performance of the NTFs with different aspect ratios was compared in this study to better understand the influence of aspect ratio on NTF performance.

1.2.2 Nitrifying trickling filters

Historically, NTFs have been applied for the removal of nitrogen in the nutrient-rich wastewater; hence, they are generally used in the pre-treatment section of WWTPs. The nitrification performance of a NTF has been widely studied and optimised from many aspects, including design and operating parameters and conditions (Eding et al., 2006).

1.2.2.1 Selection of packing media

The nitrifying bacteria are attached on the surface of the packing media in the NTF. Therefore, the packing material is a significantly important portion of the NTF construction. Many different packing materials are used as support media for the bacteria in the NTFs, such as artificial grass, Kaldnes rings, Norton rings, plastics, polystyrene, rubber and stones. As well, the nitrification performances were assessed when using these packing materials (Lekang and Kleppe, 2000, Naz et al., 2015). Important parameters for the choice of packing material are generally void ratio, specific surface area, weight, homogeneous water flow and economics (Lekang and Kleppe, 2000). Considering all of these parameters, in researching ammonium-N removal from potable water, van den Akker (2008) employed polypropylene (2H Plastics, Victoria Australia) as NTF packing material. With a high specific surface area, the cheap plastic polypropylene presented an area to volume ratio of 240 m^{-2} m^{-3}, was lightweight and with a 95% void ratio, and the 60° channels could provide a better water flow (van den Akker, 2008). Therefore, polypropylene filling material for NTFs was the first choice in this study.

1.2.2.2 Biofilm in NTFs

Biofilm in NTFs is formed by the microorganism population accumulating and attaching to the surface of the packing media (Wuertz et al., 2003). With the wastewater flows across the filter, many bacteria attach and grow on the packing material surface, the dominant bacteria being ammonium-oxidising bacteria (AOB) and nitrite-oxidising bacteria (NOB). In the filter, ammonium is oxidised to nitrite by AOB and the nitrite is further oxidised to nitrate by NOB. Both AOB and NOB populations develop and grow naturally and slowly within the biofilm on the packing material within the filters. Figure 1.1 (Liu and Liptak, 1997) shows the oxidation process on the biofilm.

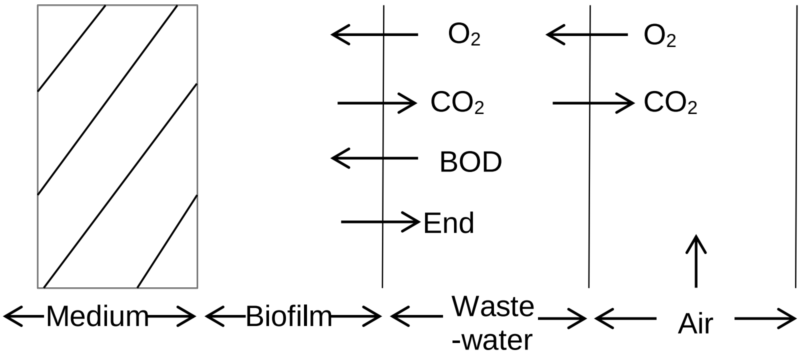


Figure 1.1 A schematic representation of the biological film in a trickling filter.

1.2.2.3 Other operational parameters

Most of the nitrification studies on lab-scale NTFs (Pearce and Edwards, 2011, Tekerlekopoulou and Vayenas, 2003) or full-scale plants (Almstrand et al., 2011) were conducted at relatively high ammonium nitrogen concentration. Little is known about the nitrification rate when operating under low ammonium nitrogen concentration (<5 mg L^{-1}), which is commonly experienced in reclaimed wastewater. Uniquely, research at Flinders University on a three-meter high NTF (van den Akker, 2008, van den Akker et al., 2006, 2008, van den Akker et al., 2004, van den Akker et al., 2003) had demonstrated for the first time, nationally and internationally, that NTFs were able to operate under lower ammonium concentration at flow rates higher than those used by conventional wastewater applications. And the results also illustrated that there was a potential for additional nitrifying capacity at the bottom bed depths of the NTF. This brings the thought that the potential additional nitrifying capacity at the bottom depths might be available if the filter was shorter. But little is known about the nitrification performance of a shorter NTF comparing with a taller one.

Also investigated was the impact of the ammonium-N hydraulic surface loading (mg NH_4-N m^{-2} d^{-1}) and the organic carbon loading rates on nitrification (van den Akker, 2008, van den Akker et al., 2006). The high flow rate (L min^{-1}) can obtain better gaseous mass (oxygen and carbon dioxide) diffusion throughout the NTF than low flow rate. Sufficient oxygen and carbon dioxide transfer can escalate the nitrifying activity of the nitrifying microorganisms, which are aerobic and autotrophic organisms, and further enhance the nitrogen oxidation in the NTF (Boller et al., 1994). Therefore, high flow rate was applied in the NTFs in this study. Maintaining ammonium-N hydraulic surface loading the same (same flow rate, specific surface area and influent ammonium concentration), the aspect ratio (height to diameter) will be an important parameter for NTF design.

1.2.3 Process selection

The polypropylene filled NTF is a low-cost operating system that is relatively easy to manage and which requires relatively infrequent maintenance (Pearce and Edwards, 2011). Because the bacteria which are responsible for nitrification are aerobic, effective oxygen transformation is significantly important. The passive aeration was used in the high-rate NTF to achieve sufficient oxygen transfer (van den Akker, 2008). The only power required was to transport water to the top of the filter by pump, so the aspect ratio (height: diameter) may be one of the significant parameters for the filter design (Pearce, 2004, van den Akker, 2008). Thus, one goal of this study was to understand the role of filter aspect ratio on ammonium oxidation. The research on the influence of aspect ratio will also provide information on the relative importance of the design loading parameters of filter infiltration rate and substrate surface area loading.

Furthermore, in the NTF (van den Akker et al., 2008), *Nitrosomonas spp* and other highly aerobic bacteria have been identified as organisms with the potential to degrade CoC, including pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs) (Roh et al., 2009, Shi et al., 2004). The population and activity of the nitrifying bacteria in the NTF may influence the chemical removal efficiency. Moreover, Larcher and Yargeau (2013) reported that 17α-ethynylestradiol can also be degraded by heterotrophic bacteria. The addition of exogenous organic carbon source can generate heterotrophs and promote the growth of heterotrophs in the NTF (van den Akker et al., 2010). Therefore, another aim of this study was to optimise the operational parameter to improve the effectiveness of the NTF for to remove CoC from wastewaters.

1.3 Chemicals of concern in waters

1.3.1 Definition of chemicals of concern

Chemicals of concern (CoC) are a series of compounds, which are persistent contaminants when discharged into the environment. The CoC pollution in the aquatic environment is an emerging environmental issue that is of growing concern to public health and the ecosystem world-wide. The CoC generally include endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), and the chemicals related to this research are from variety of classifications. Some of the important characteristics are listed in Table 1.1.

1.3.1.1 PPCPs

The PPCPs can originate from prescription and non-prescription medication (through human usage and excretion and/or veterinary application): fungicides, herbicides, insecticides, disinfectants, fragrances, preservatives and other personal care products (Daughton and Ternes, 1999, Ying et al., 2004). Among the chemicals listed in Table 1.1, caffeine (CAF), benzotriazole (BEZ), trimethoprim (TRI) acetaminophen (ACE) and N, N-diethyl-m-toluamide (DEET) are some typical PPCPs.

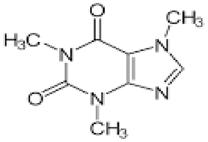
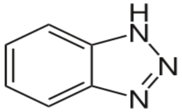
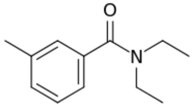
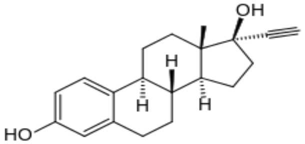
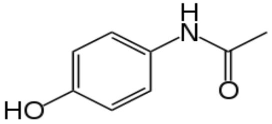
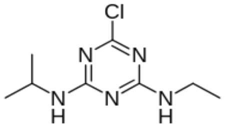
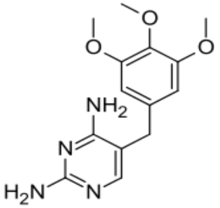
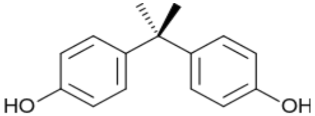
Generally, PPCPs are found in raw sewage from domestic usage, industries, hospitals and other waste sources as well as in the effluents of some WWTPs, which are not constructed for complete PPCPs removal (Behera et al., 2011, Ellis, 2006). As a consequence, the treated water that contains PPCPs discharged to surface water sources entering the environment (Boyd et al., 2003) could potentially contaminate the water environment of living organisms.

1.3.1.2 EDCs

Endocrine disrupters are emerging organic chemicals that have interference to the proper functioning of the endocrine system (Damstra et al., 2002). Normal biological function can be blocked by the presence of EDCs, which can bind to receptors on cell surfaces instead of a natural hormone thereby blocking the action of the hormone (Orchinik and Propper, 2005). In a review study to investigate the environmental fate of EDCs in Australia, Ying and Kookana (2002) found that a wide range of compounds possess endocrine disrupting activity. These include natural and synthetic hormones (e.g. β-estradiol, ethynylestradiol), pesticides (e.g. DDT, atrazine), phenols (e.g. bisphenol A) and other chemicals. Included in Table 1.1, atrazine (ATZ), bisphenol A (BPA) and 17α ethynylestradiol (EE2) are three of the typical EDCs, which are commonly detected in the raw wastewaters as well as the surface waters. Kidd et al. (2007) reported that the presence of EE2 can cause feminization of some male fish and have adverse impact on the sustainability of the population of some wild fish in the aquatic environment.

Bolong et al. (2009) reported that the many pathways by which EDCs entering the environment, for instance, via municipal sewage, industrial wastewaters, landfill and also the effluent discharges from WWTPs, which were not designed to remove these organic contaminants. With increasing usage of chemicals and the development of the organic chemical detection technologies, the reports about organic contaminants at low concentrations in natural water systems have increased (Benotti et al., 2009). This becomes an emerging environmental problem to the water industry, and has drawn increasing concern to the society.

Table 1.1 Some of the important characteristics of selected emerging pollutants.

Compounds	Acronym	Structure	Classification	CAS NO.	pK_a	Log K_{ow}	Use / origin
Caffeine [f]	CAF		Stimulant	58-08-2	10.4 [a]	-0.07	Psychoactive drug
Benzotriazole [e]	BEZ		Detergent additive	95-14-7	8.37	1.44	Corrosion inhibitor
N, N-diethyl-m-toluamide [g]	DEET		Insect repellent	134-62-3	<2 [b]	2.18 [b]	Used to protect against insects
17α-ethynylestradiol [h]	EE2		Hormones	57-63-6	10.4 [c]	3.67 [d]	Used in oral contraceptive pills
Acetaminophen [i]	ACE		Analgesic agent	103-90-2	9.38 [b]	0.46 [b]	Pain reliever and antipyretic
Atrazine [j]	ATZ		Herbicide	1912-24-9	1.7 [b]	2.61 [b]	Herbicide in agriculture
Trimethoprim [f]	TRI		Antibiotic	738-70-5	7.12	0.91	Medical use for treatment of urinary tract infections
Bisphenol A [k]	BPA		Plasticizer	80-05-7	10.1 [c]	3.32 [d]	Plastic manufacture

[a] Qiao et al. (2011); [b] Westerhoff et al. (2005); [c] Yu et al. (2006); [d] Cirja et al. (2008); [e] Bahnmüller et al. (2015); [f] Pérez et al. (2005); [g] Ditzen et al. (2008); [h] Aris et al. (2014); [l] Pinkston and Sdelak (2004); [j] Djozan and Ebrahimi (2008); [k] Hernandez-Ruiz et al. (2012).

1.3.2 Background and occurrence of chemicals of concern (CoC) in waters

The global manufacture, distribution and usage of organic chemicals have increased. Coupled with developments in instrumentation for chemical analysis, it has resulted in the detection and identification of CoC in most areas of the environment all over the world. The CoC pollution has been detected in municipal wastewaters in the UK, Germany, Japan, in the surface waters of Germany and Japan, in drinking water of Germany (Kashiwada et al., 2002, Kuch and Ballschmiter, 2001, Rodgers-Gray et al., 2000, Ying and Kookana, 2002), and in the receiving waters in most other countries, such as South Korea, China and South America (Chen et al., 2012, Kim et al., 2007b, Solomon et al., 1996). Kosma et al. (2010) also reported the high PPCPs concentrations in the influent and effluent of the municipal and hospital WWTPs in Greece. However, the levels of these CoC in reclaimed waters vary, depending on the influent concentration and the treatment technology applied in WWTPs (Ying et al., 2004). Table 1.2 shows the occurrence and distribution of selected CoC in various water resources all over the world.

Table 1.2 Occurrence of the investigated CoCs in waters.

Compounds	Locations	Concentration in waters (ng L^{-1})			References
		Surface water	WWTP effluent	Sewage influent	
CAF	Portugal		437–4392	258–36160	(Salgado et al., 2011)
	US		≤1400	3300–130000	(Blair et al., 2013)
	Korea	10–194	23–776		(Kim et al., 2007b)
BEZ	Switzerland	100-6300			(Giger et al., 2006)
	Western Europe		7300		(Reemtsma et al., 2006)
DEET	US		18	220–4000	(Yang et al., 2011)
	Korea	2–69	6.4–60		(Kim et al., 2007b)
	USA	200	97		(Stackelberg et al., 2007)
EE2	UK		0.2–7		(Desbrow et al., 1998)
	Germany		1–15		(Ternes et al., 1999)
	Canada		9–42		(Ternes et al., 1999)
ACE	Korea	4.1–73	1.8–19		(Kim et al., 2007b)
	USA	<120	<36		(Stackelberg et al., 2007)
	France	<71	<45		(Vulliet et al., 2011)
ATZ	US	32–870	49–870		(Benotti et al., 2009)
	Italy	5			(Loos et al., 2007)
	Spain		18		(Rodriguez-Mozaz et al., 2004)
TRI	Korea	3.2–5.3	10–188		(Kim et al., 2007b)
	North America	<0.5–7900	2–212		(Pal et al., 2010)
	Europe	0–78.2	99–1264		(Pal et al., 2010)
	Asia and Australia	4–150	58–321		(Pal et al., 2010)
BPA	Germany	5–401	18–702		(Fromme et al., 2002)
	US	6.1–14	25		(Benotti et al., 2009)
	USA	<360	<220		(Stackelberg et al., 2007)

1.3.2.1 Occurrence of CoC in the influents and effluents at WWTPs

Caffeine, a stimulant that is used quite often in people's daily lives, was found at a relatively high concentration of 40.5 µg L^{-1}, while trimethoprim (used as antibiotic) was detected at concentrations of around 100 ng L^{-1} in raw sewage in Australia (Trinh et al., 2011). For most of the chemicals in raw waste waters and reclaimed waters, the concentration levels are usually in the range of parts per billion (µg L^{-1}) to parts per million (mg L^{-1}). Some pharmaceuticals, which have high consumption levels in humans and animals, were detected at concentration levels up to 6.3 µg L^{-1} in the sewage treatment plants, whereas concentration levels mostly in the ng L^{-1} range were detected ubiquitously in streams and rivers in Germany (Ternes, 1998). One of the main sources of organic pollutants in the aquatic environment is effluents from WWTPs. A study conducted in Portugal reported the concentrations in WWTP influent and effluent (see Table 1.2). It reported concentrations of PPCPs in WWTP influent were in the range of 0.05-100 µg/L and maximum 50 µg L^{-1} in the effluent (Salgado et al., 2011). One of the most commonly investigated compounds in urban raw wastewater is acetaminophen, which Verlicchi et al. (2012) found in concentrations of up to 246 µg L^{-1}, with an average concentration of 38 µg L^{-1}. In the same study, the highest concentration of trimethoprim in the secondary biological effluent was 6.7 µg L^{-1}.

In the WWTPs in the United States, Yang et al. (2011) found the concentration of some organic contaminants in primary effluent to be quite high, at an average concentration of 80 µg L^{-1} for caffeine and acetaminophen, followed by other chemicals at lower concentrations, such as DEET (1.5 µg L^{-1}), trimethoprim (0.61 µg L^{-1}) and EE2 (0.14 µg L^{-1}). However, a study conducted in Spain (Radjenović et al., 2009) detected a relatively lower concentration of acetaminophen in the sewage primary effluent (7.1–11.4 µg L^{-1}), with a mean value of 9.9 µg L^{-1}, a similar trimethoprim concentration (0.15–0.43 µg L^{-1}) was observed, with a mean concentration of 0.204 µg L^{-1}.

Bisphenol A is widely used in plasticisers and polyvinyl chlorides (PVCs), consequently concentrations of bisphenol A in WWTP treated waters ranging from 0.088 µg L^{-1} to 11.8 µg L^{-1} in the influents and 0.006 µg L^{-1} to 4.09 µg L^{-1} in the effluents in Europe (Deblonde et al., 2011). Concentrations of caffeine and trimethoprim have been detected at range from <1 µg L^{-1} to 298 µg L^{-1} in the effluents of municipal, hospital, livestock and industrial WWTPs in Korea (Sim et al., 2011). In the sewage treatment plants of Germany, the concentration of trimethoprim has been detected at maximum 0.66 µg L^{-1} (Hirsch et al., 1999). Yang et al. (2011) found that after advanced treatment, the concentration of chemicals in the final WWPT effluent in the United States was quite low, with DEET and caffeine, for example, at maximum levels of 30 ng L^{-1} and 50 ng L^{-1} respectively (see Table 1.2). Ternes et al. (1999) compared the concentration difference of oestrogens in the effluent of the sewage treatment plants (STPs) in Canada and Germany, finding higher concentrations of 17α-ethinylestradiol (EE2) in effluent from Canadian STPs than from German STPs, with a median concentration of 0.009 µg L^{-1} and 0.001 µg L^{-1} respectively (see Table 1.2). A relatively low effluent concentration (0.45 ng L^{-1}) was obtained for EE2 after activated sludge treatment in STPs in Italy (Baronti et al., 2000).

However, another widely used chemical, benzotriazole (BEZ), which is frequently used as a corrosion inhibitor in household and industrial applications, has been observed in relatively high concentrations (a mean concentration of 7.3 µg L^{-1}) in the effluents (see table 1.2) and a mean concentration of 12 µg L^{-1} in the influents in some municipal WWTPs in Western Europe, owing to the poor removal efficiency (37%) during the treatment (Reemtsma et al., 2006, Reemtsma et al., 2002). In the same study, the removal of DEET was about 18% in Western Europe WWTPs, resulted in DEET effluent concentration of 1.2 µg L^{-1}. The removal efficiency of WWTPs varied for different chemicals, for instance, about 71% of BPA, 97% of CAF and 40–50% of TRI was removed in some European WWTPs (Deblonde et al., 2011). For ACE, the removal was >99% in a municipal WWTP in the USA. EE2 removal was ranging from 60% to 68% in the WWTPs in the U.K (Koh et al., 2009). While only up to 25% of ATZ was removed in the WWTPs in 14 European countries/regions (Luo et al., 2014b).

1.3.2.2 Occurrence of CoC in surface waters

Discharging effluent to receiving water bodies without adequate elimination of these chemicals in treatment plants, results in the contamination of surface waters and the environment. In an early study, very low concentrations of CoC were found in surface waters (e.g. up to 2.0 µg L^{-1} TRI) (Hirsch et al., 1999). A national reconnaissance launched in the US reported that at least one organic wastewater contaminant was detected in 80% of the selected 139 streams, at concentrations ranging from 0.001 µg L^{-1} to 6.0 µg L^{-1}, with the highest total concentration for the detergent metabolites (Kolpin et al., 2002). In the North Sea, CAF and DEET were found at concentrations as high as 16.1 ng L^{-1} and 1.09 ng L^{-1} respectively in research study conducted by Weigel et al. (2002).

As the usage of organic chemicals has increased, slightly higher concentrations of these chemicals have been subsequently found in surface waters. Kim et al. (2007b) investigated the occurrence of some chemicals in Korean surface waters (lakes and rivers), finding quite different concentrations from different chemicals (see Table 1.2). For example, the concentration of caffeine was as high as 194 ng L^{-1}, whereas the concentrations of ACE, DEET and TRI were relatively lower, at average concentrations of 33 ng L^{-1}, 22 ng L^{-1}, and 4.0 ng L^{-1}, respectively. In the upstream of a river in China, trimethoprim was one of the most frequently detected chemicals (occurrence >70%), with the average concentrations 0.77–18.77 ng L^{-1} (Qiao et al., 2011). ACE was found at concentrations of up to 71 ng L^{-1} (see Table 1.2) in the surface waters in France (Vulliet et al., 2011).

1.3.2.3 Occurrence of CoC in raw and treated drinking water

Variable concentrations of CoC were found in the raw drinking water of Seoul: high concentrations included ACE (11500 ng L^{-1}) and CAF (9680 ng L^{-1}); and relatively low concentrations of DEET and TRI at concentrations of 18 ng L^{-1} and 21 ng L^{-1}, respectively (Kim et al., 2007b) (see Table 1.2). Benotti et al. (2009) noted the occurrence of some pharmaceuticals and EDCs in US drinking water, including raw drinking water source and treated drinking water. As reported by Benotti et al. (2009) ATZ was frequently found in both source and treated waters at concentrations up to 870 ng L^{-1}, followed by DEET, which was observed at concentrations up to 110 ng L^{-1} in source water and 93 ng L^{-1} in treated water (see Table 1.2).

Organic compounds were frequently detected in stream water providing source water for drinking water treatment plants, which received the effluent discharge from WWPTs or STPs in the USA (Stackelberg et al., 2007). Among them, some compounds were detected a frequency of detection of more than 75% in all samples and the concentrations were reported relatively high, including DEET (0.2 µg L^{-1}), CAF (0.19 µg L^{-1}), ACE (0.12 µg L^{-1}) and BPA (0.36 µg L^{-1}) in the source water (see Table 1.2). Small quantities survived in the treatment process and were present in finished drinking water, at concentrations up to 0.06 µg L^{-1} (CAF), 0.22 µg L^{-1} (BPA) and 0.097 μg L^{-1} (DEET) (see Table 1.2).

The fate of these contaminants in drinking water treatment processes varied. In a drinking water biological filters system, 3 ± 3.6% of ATZ, 64 ± 29% of BPA, 80 ± 13% of CAF, 22 ± 17% of EE2 and 92 ± 7.4% of TRI with influent concentrations 9–500 ng L^{-1}, was removed (Zearley and Summers, 2012). In the drinking water treatment plants in the USA, the removal percentage for ACE and CAF was 98% and 88% respectively, a lower removal percentage of 76% for BPA and 35% for DEET (Stackelberg et al., 2007). The presence of these contaminants in the waters may have influence on the organisms in the aquatic environment as well as the potential impact on human health.

1.4 Potential Impact of CoC on organisms

In recent decades, a number of studies have been conducted to observe the adverse impact of some emerging organic pollutants on living organisms. Although in lower concentrations these chemicals might not cause acute toxicity, the potential exposure pathways of aquatic organism and humans to pollutants could exert adverse chronic risk, as pointed out by Ying et al. (2004). With the increased usage of reclaimed water and detection of CoC in waters and heightened public awareness of the issue, it is increasingly important to recognise the existing and potential impact of these pollutants on organisms. Table 1.3 shows some typical effects of CoC on organisms.

Table 1.3 The typical effects of CoC on organisms.

CoCs	Effects on living organisms
CAF	Chronic effects on rats (Gasior et al., 2000)
BEZ	Low toxicity and health hazard to humans, mutagenic in bacterial systems, also toxic to plants (Farré et al., 2008)
DEET	Acute effects on aquatic environment unlikely, but slightly toxic to fish and invertebrates (Costanzo et al., 2007)
EE2	Male fish failed to develop regular secondary sexual characteristics and egg fertilization (Länge et al., 2001, Parrott and Blunt, 2005)
ACE	Hepatic oxidative stress (Solé et al., 2010); decreased *C. dubia* offspring survival rate (Brun et al., 2006)
ATZ	Hermaphroditism in frogs (Hayes et al., 2002); reduced the growth rate of marine species (DeLorenzo and Serrano, 2003)
TRI	Growth-inhibiting toxicity on algae (Lützhøft et al., 1999)
BPA	Causes feminization due to its anti-androgenic activity (Sohoni and Sumpter, 1998)

1.4.1 Overview of CoC effects on the aquatic ecosystem

There is considerable evidence that some aquatic organisms exposed to sewage effluents containing PPCPs and EDCs are more sensitive than human beings to chemical contamination and are at risk of endocrine disruption, having been exposed to the contaminated environment for a very long time, even over their whole life cycle (Ying et al., 2004). However, a review by Fent et al. (2006) reported that acute toxicity to aquatic organisms was unlikely to occur at environmental concentrations, as the concentrations that cause acute toxicity are usually 100- to 1000-fold higher than the concentrations detected in the aquatic environment. Although the short-term acute toxicity of the CoC have not yet been determined, the chronic impact of the chemicals should not be ignored, since they will affect future generations of organisms (Ying et al., 2004).

For example, Hayes et al. (2010) took 3 years to investigate the toxicity of ATZ to some amphibians, and the results revealed that the endocrine system of ATZ-exposed male frogs (ATZ concentration of 2.5 ng L^{-1}) was affected, resulted in reduced spermatogenesis, feminisation and decreased breeding gland size. An eco-toxicological study of EE2 on fathead minnow conducted by Länge et al. (2001) revealed that exposure of male fish to EE2 at concentrations ≥4.0 ng L^{-1} inhibited the development of their normal secondary sexual characteristics (Table 1.3), no adverse effect was observed when the male fish exposing to ATZ concentrations less than 1.0 ng L^{-1}. Kidd et al. (2007) reported that the estrogens detected in the freshwater in Canada can affect the wild fish population and almost result in an extinction of some species in the lake. The pesticide-contaminated lakes in Florida have caused abnormalities of sex hormone development in young alligators, with permanent modification to alligators' reproductive system (Guillette Jr et al., 1994, Guillette et al., 2000). Feminisation and sexual disruption has been widely observed in wild fish, following exposure to hormonally active contaminants that appear to have originated in the discharges from STPs (Jobling et al., 1998). Similarly, the effects of ATZ on frog sexual development have been investigated by Hayes et al. (2002), hermaphroditism in frogs was observed when exposed to ATZ concentrations ≥0.1 ng L^{-1}. Further evidence revealed that some estrogens, which were regarded as endocrine disrupters, could cause intersex or other abnormalities in wildlife and have the potential to adversely affect human health (Birkett and Lester, 2010).

As summarised by Verlicchi et al. (2012), both acetaminophen (ACE) and trimethoprim (TRI) pose a medium risk to the aquatic environment, however when discharged at high loading rate, they would exert adverse effects on aquatic lives over long-term exposure because of the chronic and mixture toxicities.

1.4.2 Potential effects on human health

Reclaimed water is often reused for various applications, e.g. irrigation of agricultural land, sports ovals and even as source of potable water (Metcalf and Eddy, 2003). Some persistent organic pollutants that were incompletely removed during treatment processes enter the water environment and then potentially affect human health by bio-accumulation or bio-concentration, especially in the case of sensitive populations (e.g. children and pregnant women) (Zenker et al., 2014). Thus, even though the environmental concentrations of these CoC are much lower than the concentrations that can cause acute toxicity, the potential adverse effects should not be ignored or underestimated (Zenker et al., 2014).

Although apparent effects of low concentrations of CoC on human health have not been confirmed, the potential risk assessment is still a focus for researchers. Pomati et al. (2008) investigated the effect of environmental concentrations of some therapeutic drugs on human embryonic cells, finding that the mixture of these drugs at ng L^{-1} levels could block cell proliferation.

The CoC contaminate aquatic environments by chemicals spillage, direct disposal or the discharge of WWTP effluent (Farré et al., 2008). Those water bodies used as a drinking water source are especially of concern (Benotti et al., 2009). Acute toxicity, however, is unlikely to happen at environmental concentrations, because the concentrations of organic contaminants at which acute effects are observed are 100-1000 times higher than the residues found in aquatic water bodies (Farré et al., 2008). Reclaimed wastewater used for irrigation of plants, may also be an indirect route for human exposure to CoC by bio-accumulation (Zenker et al., 2014). Exposure of aquatic organisms to the contaminated waters over their life-cycle, may have an adverse impact on humans who consume those aquatic organisms (e.g. fish) as food (Daughton, 2008).

Damstra et al. (2002) pointed out that there was no scientific consensus that the extremely low organic pollutant levels found in many countries were hazardous to most human beings. However, although evidence of direct harm or acute toxicity is minimal, potential impact of CoC might yet be a major problem for the environment and public health (Daughton and Ternes, 1999, Ying et al., 2004). Further research is still needed to investigate the potentially adverse impact of CoC on human health in long-term intergenerational study (Daughton and Ternes, 1999, Ying et al., 2004).

1.5 Potential treatment technologies for removing CoC from waters

The main exposure pathways of CoC have been illustrated in Figure 1.2. Theoretically, if the chemicals could be completely removed in the treatment plants, then minimal quantity of CoC would be released to the surface waters or receiving waters. Except for those biologically resistant chemicals, most of the CoC are biodegradable. These chemicals may be partly or completely removed from various polluted water bodies or waste waters by conventional or advanced treatment technologies. There are a number of different technologies commonly used in the water treatment industries, including physicochemical treatment (Matamoros and Salvadó, 2013), biological treatment (Joss et al., 2006), oxidation (Margot et al., 2013), ultra-violet photolysis (Bahnmüller et al., 2015) and other conventional and advanced membrane treatments (Clara et al., 2005b, Trinh et al., 2012b). The removal efficiencies of CoC vary significantly, depending on the chemicals' characteristics and the treatment methods, and the elimination rates could range from ≤20% to 100% (Benner et al., 2013, Benotti et al., 2009, Bolong et al., 2009, Onesios et al., 2009). The possible treatment approaches and removal percentages of target chemicals are listed in Table 1.4.

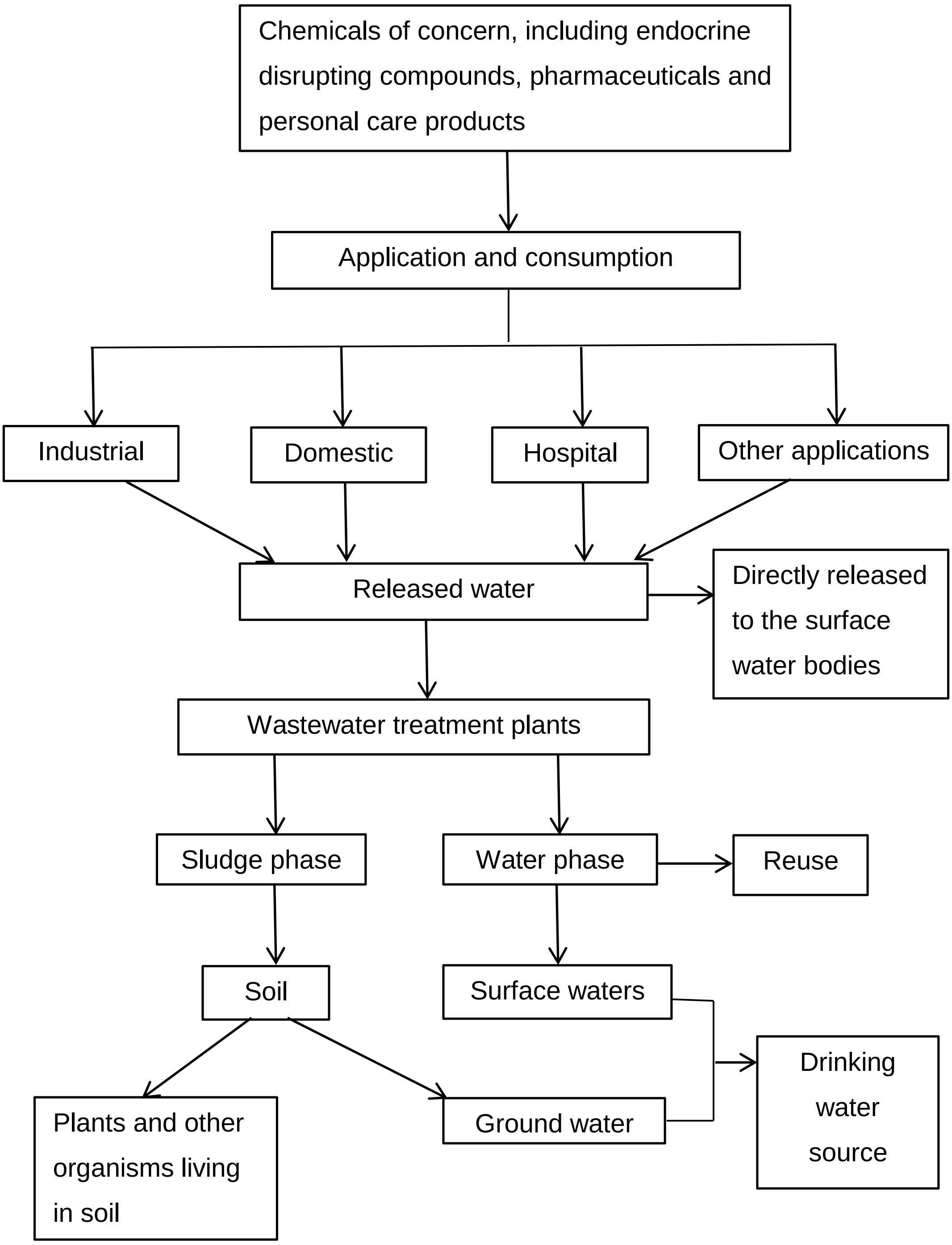


Figure 1.2 Theoretical distribution of CoC in the environment.

Table 1.4 Removal efficiencies of selected chemicals attributed to different treatment technologies.

Compounds	Removal	Treatment technologies	References
CAF	>90%	Membrane bioreactor	(Trinh et al., 2011)
	99.2%	Biological treatment	(Behera et al., 2011)
	>80%	Ponds, constructed wetlands	(Hijosa-Valsero et al., 2010)
BEZ	37±17%	Conventional activated	(Weiss et al., 2006)
	61±12%	Lab-scale membrane bioreactor	(Weiss et al., 2006)
	35%	Wastewater treatment plants	(Reemtsma et al., 2006)
DEET	>80%	Aerobic wetland	(Conkle et al., 2012)
	>90%	Activated sludge and membrane filtration	(Yang et al., 2011)
	25–75%	Granular activated carbon	(Stackelberg et al., 2007)
EE2	85.2±4.5%	Moving bed bioreactor	(Luo et al., 2014a)
	99%	Nitrifier enriched membrane bioreactor	(De Gusseme et al., 2009)
	50.4–99%	Powdered activated carbon	(Yoon et al., 2003)
ACE	96%	Activated sludge	(Yamamoto et al., 2009)
	>99%	Aerobic Batch inoculated with diluted activated sludge	(Yu et al., 2006)
	71.4±10.6%	Moving bed bioreactor	(Luo et al., 2014a)
ATZ	3±3.6%	Sand media biofilter	(Zearley and Summers, 2012)
	80%	Ozonation	(Upelaar et al., 2000)
	>95%	Biological granulated activated carbon reactor	(Herzberg et al., 2004)
TRI	24%	Membrane bioreactor	(Trinh et al., 2011)
	50%	Nitrifying activated sludge	(Batt et al., 2006)
	92±7.4%	Sand media biofilter	(Zearley and Summers, 2012)
BPA	>90%	Membrane bioreactor	(Trinh et al., 2011)
	77.8±8.8%	Moving bed bioreactor	(Luo et al., 2014a)
	33.3–99%	Powdered activated carbon	(Yoon et al., 2003)

1.5.1 Physicochemical Treatment

1.5.1.1 Coagulation and flocculation

Coagulation and flocculation processes in water treatment have been generally found to be capable of removing chemicals with a high octanol-water partition coefficient (log K_{ow}>6) and relatively low water solubility (Snyder et al., 2007a). As shown in Table 1.1, the log K_{ow} values of selected chemicals are lower than 6, indicating that using coagulation or flocculation to eliminate of these chemicals would be inefficient. Early investigation of the process of coagulation—flocculation in both pilot plants and drinking water treatment plants showed low level of removal of chemicals (Ternes et al., 2002). Removal evaluation experiments on antibiotics conducted by Adam et al. (2002) also revealed the poor removal rate of CoC by coagulation and flocculation processes. A bench scale experiment conducted by Westerhoff et al. (2005) observed < 25% removal of most EDC/PPCPs after metal salt coagulation (or flocculation) process. Further, the research results obtained by Bodzek and Dudziak (2006) demonstrated that the efficiency of coagulation was not good enough to eliminate steroidal sex hormones from waters completely.

1.5.1.2 Activated carbon

Powdered activated carbon (PAC) and granular activated carbon (GAC) are the most commonly used types of activated carbon for adsorption of CoC in water treatment process.

The adsorption efficiency of BPA and EE2 on PACs was investigated by Yoon et al. (2003), who found that PAC treatment was a feasible and efficient way to remove up to 99% of estrogenic chemicals from drinking water. They also reported that the removal performance varied from 31% to 99%, depending on the PAC type or dosage and the effect of organic matters. The high removal efficiency (>90%) obtained by Westerhoff et al. (2005) for many EDCs on PAC confirmed the ability of PAC to remove the chemicals from waters, furthermore, a higher removal was achieved at higher PAC dosage. Additionally, Boehler et al. (2012) illustrated that the application of PAC for organic contaminant removal from wastewater was an adequate technology in WWTPs with post-ozonation, attaining an elimination efficiency of >80%. Contrarily, there was only weak efficacy for adsorption of BEZ from raw wasters via activated carbon reported in a batch experiments (Reemtsma et al., 2010) (see Table 1.4).

GAC filtration treatment achieved 53% removal of organic compounds, with moderate removal of 25% to 75% obtained for both bisphenol A and DEET with post filtration concentrations of 0.014 μg/L and 0.071 μg/L, respectively (Stackelberg et al., 2007) (see Table 1.4).

Despite the moderate-to-high removal efficiencies of chemicals in activated carbon filtration processes observed by many researchers, Benner et al. (2013) suggested that activated carbon treatment might not be a sustainable technology due to the relatively high cost of the operation and maintenance. The indirect contamination might be caused by the improper disposal of the activated carbon, which just passed the contaminants from one medium to another (Ormad et al., 2008, Snyder et al., 2007b). The occupational safety and health also need to be considered because of the toxicity and characteristics (e.g. gasification) of activated carbon (Marsh and Reinoso, 2006).

1.5.2 Advanced Technologies

1.5.2.1 Membrane Filtration

Typical membrane filtration technology, including reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF), has been considered to be a promising method to remove organic contaminants with its wide application in water treatment industries (Bolong et al., 2009, Yoon et al., 2006).

NF membranes have the ability to extract small organic contaminants from the aqueous phase, an elimination efficiency ≥ 63% was obtained for the steroidal sex hormones, and the removal rate increased to > 81.5% when a coagulation—NF integrated system was applied (Bodzek and Dudziak, 2006). Another membrane filtration treatment study of organic chemicals at environmental concentration levels (2 to < 250 ng/L) was conducted by Yoon et al. (2006). The results from this study revealed that most of the compounds investigated were >40% removal for both NF and UF membranes, and the more hydrophobic group compounds achieved higher removal efficiency than the less hydrophobic ones, which indicated that hydrophobicity was one of the important factors in the NF and UF membrane treatment. Huang and Sedlak (2001) concluded that the RO process was an efficient way to remove hormones from municipal wastewaters. In this advanced treatment, >95% hormones were removed. In another study, NF/RO was similarly shown to be an efficient way to remove pollutants from surface water and groundwater (van der Bruggen and Vandecasteele, 2003). Viruses and bacteria were also able to be removed during this drinking water treatment process, which improved drinking water quality.

Given that the pollutants selected for the review presented here mostly have relatively low hydrophobicity (Table 1.1), membrane filtration is likely unsuited to their elimination from water bodies.

1.5.2.2 Ultra-Photolysis

Ying et al. (2004) concluded that the efficiency of the direct sunlight photolysis in natural water treatment systems for the removal of organic pollutants might be limited. A pilot plant to test for the removal of pharmaceuticals by using ozonation and ultra-violet (UV) disinfection in Germany was conducted by Ternes et al. (2003). The results showed no significantly higher removal efficiency with the addition of UV disinfection as a post-treatment process. However, for some chemicals, such as BPA, the removal efficiency was improved from 80 to 99% when applying GAC followed by UV treatment (Kleywegt et al., 2011). Thus, UV photolysis may be effective in the degradation of some chemicals in some instances.

1.5.2.3 Oxidation

Oxidation is generally used as an advanced treatment process, for instance, ozonation and chlorination are typical oxidation processes. In a drinking water treatment process for the removal of chemicals, chlorination accounted for only 32% of the elimination of target compounds from the aqueous phase, and some hydrophobic chemicals were largely oxidised during chlorination (Stackelberg et al., 2007).

Compared with chlorination, it appears that ozonation may obtain better efficiency. As Westerhoff et al. (2005) pointed out, ozone oxidised most compounds by >80%, with the exception of those that did not contain aromatic moieties (e.g. atrazine), small concentrations of additional H_2O_2 prior to ozonation could improve chemical oxidation by 5–15%. It has been suggested that decreased BEZ concentration following ozonation may make it mandatory to partly remove BEZ from the raw water sources (Reemtsma et al., 2010). A removal of >90% was achieved for BEZ by ozonation, which demonstrated that ozonation might be very effective in reducing BEZ concentration from contaminated waters (Weiss et al., 2006) (see Table 1.4). Further research has shown that 95% of TRI was removed at an ozone concentration of 5 mg/L (Lee et al., 2014).

Notwithstanding, oxidation by-products were generally detected after application of an advanced oxidation processes, although some pose less risk than the original parent compounds (e.g. EE2), others pose toxicity or health risk as serious as the target compounds (e.g. ATZ), which should be avoided in the water treatment process (Westerhoff et al., 2005).

1.5.3 Biological treatment

Biodegradation or biotransformation is generally considered to be the dominant mechanism in most of the emerging technologies for the removal of most organic pollutants either at laboratory-scale experiments (Fan et al., 2014) or in large pilot-scale WWTPs (Andersen et al., 2003). Typical biological removal technologies include activated sludge treatments (Johnson and Sumpter, 2001), membrane bioreactors (Trinh et al., 2012b), constructed wetlands (Conkle et al., 2012) and biological filters (Zearley and Summers, 2012).

Two mechanisms are recognised that contribute to the removal of CoC in biological treatment: sorption onto the sludge and biodegradation. The poor efficiency of primary treatment indicates that adsorption is insignificant for chemicals removal in WWTPs (Behera et al., 2011). Similarly, Gao et al. (2012) demonstrated that the contribution of sorption onto sludge was relatively insignificant (7%) for the tested chemicals. Generally, biodegradation was responsible for the removal of a majority of chemicals in environments with high dissolved oxygen conditions; otherwise, sorption would be the main mechanism for the removal, since most of the bacteria capable of biodegrading chemicals are aerobic species (Onesios et al., 2009). The results of batch experiments in a submerged membrane bioreactor conducted by Fan et al. (2014) demonstrated that the removal of ACE was achieved primarily by biodegradation, with a total removal rate of 83.4% through combination of biodegradation and sludge adsorption, where adsorption in the sludge phase was only 1.8%.

1.5.3.1 Activated Sludge Treatment

One of the most commonly applied biological treatment technologies is activated sludge treatment, often used as a secondary treatment, and it can lead to the efficient removal of organic pollutants. For instance, DEET concentration was reduced after activated sludge treatment, although it appeared to be relatively resistant to activated carbon adsorption and ozonation (Yang et al., 2011). Using this process, more than 99% of ACE and CAF was removed, followed by a median removal percentage of 58% for TRI (see Table 1.4). The high removals of these chemicals was observed in activated sludge process indicated that they are likely readily biodegradable (Yang et al., 2011).

Activated sludge treatment may effectively remove most of the organic contaminants from waters. Yu et al. (2006) conducted a biodegradability study of selected emerging contaminants in sewage effluent. The results observed in their study showed more than 80% elimination rate for most of the tested compounds after 50 days incubation. It indicated the high removal efficiency of activated sludge treatment. The average removal efficiency for chemicals varied, ranging from 38% to 100% in a full-scale WWTP study by Behera et al. (2011). Excellent removal rates were obtained for ACE (99 ± 1%) and CAF (98 ± 3%) during secondary treatment by activated sludge (see Table 1.4). A further study by Gao et al. (2012) achieved a similar removal efficiencies for both ACE and CAF (>99%). BPA was almost completely removed during the activated sludge treatment, with a removal rate of >92% in a study by Nakada et al. (2006). An early field study by Johnson and Sumpter (2001) suggested that the activated sludge treatment process could remove more than 85% of EE2. Nevertheless, TRI was confirmed to be very recalcitrant to degradation by the bacteria in activated sludge by Lindberg et al. (2006) and Chen et al. (2012).

However, compared with fixed-bed biofilm processes (e.g. trickling filters), activated sludge processes have some disadvantages. The disadvantages include higher operational costs (e.g. intensive energy for aeration), larger plant size, more space required and longer hydraulic retention time needed in order to obtain high removal efficiency (Guo et al., 2012, Luo et al., 2014b).

1.5.3.2 Membrane bioreactors

Membrane bioreactors (MBRs) have been introduced in many water treatment plants due to the high water quality and lower chemical emissions of effluent compared to conventional water treatment systems (Clara et al., 2005b). The results obtained by Trinh et al. (2011) showed a relatively high removal efficiency (>90%) for most of the investigated organic contaminants (e.g. CAF, BPA, DEET) through MBR, with the exception of some resistant chemicals (see Table 1.4). TRI were only partially removed, with a decreased percentage removal of 24%–68% (see Table 1.4). A similar relatively low removal efficiency for TRI was obtained by Reif et al. (2008). In a study by Radjenović et al. (2009), ACE was almost completely removed in both a pilot-scale MBR and a conventional activated sludge (CAS) plant. The removal efficiency for other chemicals was enhanced in MBR compared with the incomplete removal in CAS. Another study showed significantly better BEZ removal efficiency (61%) using MBR treatment than CAS, which removed only 37% (Weiss et al., 2006) (see Table 1.4). Fan et al. (2014) obtained a removal efficiency of 92.2% for ACE in a submerged MBR, and an additional batch experiment showed 7.9% sludge adsorption for ACE.

1.5.3.3 Constructed wetlands

Wetlands are a popular treatment tool for water treatment, as they were considered to be reliable and robust for the removal of nutrients and organic pollutants (Conkle et al., 2012, Matamoros et al., 2009). High removal efficiency has been observed for caffeine on both horizontal (97 ± 3%) and vertical flow (99 ± 1%) constructed wetlands with total solid suspends (TSS) and biological oxygen demands (BODs) removal of >95% (Matamoros et al., 2009). Although wetlands might appear promising for the removal of some classes of pharmaceutically active contaminants, they are mainly designed to remove nutrients (White et al., 2006).

1.5.3.4 Attached growth bioreactors

Fixed bed bioreactors and moving bed bioreactors are two major forms of attached growth bioreactors. Zearley and Summers (2012) conducted an experiment using biologically active sand media filters (fixed bed) to remove organic pollutants in laboratory scale. High removal was obtained for CAF (80%) and TRI (92%), followed by a medium removal for BPA (64%) and low removal for EE2 (22%) and ATZ (3%)

(Table 1.4). The removal efficiency of the sponge-based moving bed bioreactor ranged from 25.9% to 96.8% (Luo et al., 2014a). Most of the investigated pollutants were effectively eliminated, such as ACE (71.4%), BPA (77.8%) and EE2 (85.2%) (Table 1.4).

Comparing with the moving bed bioreactors, the fixed bed cross-flow material NTF has a large surface to volume ratio. This large ratio allow more degradation microorganisms to settle (Lydmark et al., 2006). Abundant microorganisms are important to get better removal efficiency of CoC. Thus, the NTF has the potential ability to effectively remove CoC.

1.5.4 Nitrifying trickling filters (NTFs)

One of the most attractive fixed bed biological trickling filters is the cross-flow nitrifying trickling filter, which has a large surface area to column volume ratio, providing sufficient area for microorganisms to attach to. Nowadays, NTF has attracted increasing interest to environmental researcher for biological treatment of wastewater and/or drinking water (van den Akker et al., 2008). Some optimising strategies have been put forward to improve the performance of NTFs, such as shift the high and low ammonium concentrations (Almstrand et al., 2011), change other potential affecting parameters (e.g temperature, pH and filter design) (Antoniou et al., 1990, Boller et al., 1994) and other strategies (Wik, 2000).

Because of the energy demand for aeration, nitrification is an energy consuming process in wastewater treatment. Thus, the natural versus forced aerating NTF can save massive energy and cost (Pearce, 2004), compared with the conventional nitrifying activated sludge process. NTF process is a cost-effective and low maintenance required biological water treatment technology, with minimal plant area usage and simple construction parts (Pearce, 2004, Wik and Lindeborg, 1994). The only energy consumption is pumping water to the top of NTF for distribution. Maintaining other parameters (e.g. ammonium hydraulic loading, specific surface area and ammonium influent concentration) the same, the aspect ratio (height : diameter) will be an important parameter for NTF to save energy. However, little is known about the effect of NTF aspect ratio on the nitrification performance. Nitrification performance in the NTF also plays a significant important role in CoC removal (see Section 1.6.2).

The application of NTF in WWTPs can efficiently remove ammonium, resulting in chlorine demand reduction in water treatment process (see Chapter 1, Section 1.2.1). The nitrifying bacteria in NTF also have a potential to remove some organic pollutants (van den Akker, 2008). A study undertook by Kasprzyk-Hordern et al. (2009) utilized activated sludge and trickling filter beds in the WWTP. The results showed <70% removal efficiency of investigated chemicals by trickling filter beds. Whereas using activated sludge, the removal efficiency was >85%. However, in another low-cost trickling filter bed experiment, some chemicals (e.g. caffeine) were efficiently removed, with a removal rate up to 99% (Camacho-Muñoz et al., 2012). Therefore, it is worth investigating the removal efficiency of NTF for variety of chemicals with different characteristics (see chapter 1, Section 1.3.1).

However, there are many factors that may affect the efficiency of the removal of CoC, such as hydraulic/solid retention time, dissolved oxygen concentration, initial nitrification rate, initial concentration of CoC, and exogenous organic carbon. Thus, it is possible to improve the efficiency of NTF for the removal of CoC.

1.6 Possible factors influencing the biodegradation efficiency

Since most of the CoC are biodegradable, except some relatively resistant chemicals, biological treatment is a feasible and effective way to removal CoC from water bodies. However, the removal efficiency is influenced by process operation conditions. Some possible environmental factors may affect the biodegradation rate; these include dissolved oxygen level, initial nitrification rate, hydraulic/solid retention time and chemicals' concentration.

1.6.1 Dissolve oxygen level

Dissolved oxygen (DO) is one of the important factors that affect bacterial activity in the biological treatment process. Ying et al. (2003) compared the biodegradation rates of selected organic contaminants in aquifer material under different conditions (aerobic and anaerobic). The results demonstrated that slower biodegradation was observed under aerobic conditions than under anaerobic conditions. A series of aerobic and anaerobic experiments were conducted by Liu et al. (2009). The results revealed relatively higher degradation efficiency under aerobic conditions. BPA was degraded by 72%–99% in 72 hours under aerobic conditions, while only 9%–22% in 30 days under anaerobic conditions (Ogawa et al., 2005). Thus, a higher DO levels have the potential to improve the removal efficiency of organic pollutants.

1.6.2 Initial nitrification rate in the bioreactors

The removal of CoC may be caused by various microorganisms, but the high removal under nitrification is mostly owing to the presence of nitrifying bacteria (Kim et al., 2007a). Thus, nitrification rate may have some relationship to the chemical removal efficiency. Vader et al. (2000) studied the degradation of EE2 by nitrifying activated sludge. No degradation of EE2 was observed within an insignificant nitrifying environment, but oxidation of EE2 was observed when using nitrifying activated sludge. Tran et al. (2009), who investigated the effects of an enriched culture of nitrifiers on the biodegradation of chemicals, showed that almost no degradation of selected chemicals was observed when nitrification was inhibited. Their study suggested that higher nitrification rate could enhance the biodegradation of pharmaceutical compounds (e.g. caffeine), and the biotransformation efficiency increased with an increase in ammonium concentration.

Furthermore, the removal percentage of trimethoprim reduced from 70% to 25% when the activity of nitrifying bacteria was limited in a laboratory-scale study by Batt et al. (2006). Another study by Yi and Harper (2007) investigated the link between nitrification performance and biodegradation of EE2, revealing the existence of a linear relationship between nitrification performance and the removal percentage of EE2 when operating under enriched nitrifying culture conditions. While a contrary result was obtained by Zielińska et al. (2014), who reported a strong negative correlation between BPA degradation rate and nitrification rate, indicating that ammonium-oxidising bacteria (AOB) contributed little to BPA elimination.

1.6.3 Hydraulic/Solid Retention Time

Solid retention time (SRT) was considered to be one of the important design parameters of WWTPs, which was related to the growth of biofilm and effluent concentrations of organic pollutants, low concentrations of organic pollutants in the effluent of WWTPs when operating at SRTs longer than 10 days (Clara et al., 2005a). A study undertaken by Petrie et al. (2014b) confirmed that optimised hydraulic retention time (HRT) and SRT enhanced the removal percentage of organic pollutants; for example, the removal of the recalcitrant synthetic estrogen EE2 increased from 30% when operated at SRT of 3 days and HRT of 8 h to a removal of 65% when operated at the highest SRT (27 days) and an extended HRT of 24 h. A further study by Petrie et al. (2014a) found that when operated at an constant HRT of 8 h, the removal of EE2 at SRT of 3, 10 and 27 days was 30%, 29% and 41% respectively, which implied that the influence of SRT was not significant when SRT extended from 3 days to 10 days, while the removal of EE2 was enhanced when SRT extended to 27 days. Additionally, in a MBR system, a notable elimination rate of up to 90% at 60–80 days SRT was observed for TRI, compared with the relatively lower removal rate of up to 50% at a SRT of 16-33 days (Göbel et al., 2005).

1.6.4 Initial concentration of chemicals of concern

An aerobic batch experiment with diluted activated sludge was conducted by Yu et al. (Yu et al., 2006), who spiked wastewater with different initial concentrations (1, 10 and 50 µg L^{-1}) of target chemicals (e.g. ACE). The similar biodegradation efficiency results showed that the biodegradation treNds did not change much with the broad concentration range. Additionally, Zearley and Summers (2012) demonstrated that the removal percentage of chemicals was independent of the influent concentration. Contrarily, the removal efficiency of BPA increased from 87.1% to 92.9% with increased BPA initial concentration (from 2.5 to 10.0 mg L^{-1}), indicating a slightly higher degradation rate at the higher initial concentration of BPA (Zielińska et al., 2014).

1.6.5 Exogenous Organic carbon

The addition of exogenous organic carbon source may affect the biofilm species composition including making heterotrophic bacteria more dominant, which would have different effects on chemical removal, compared with the more nitrifier dominant biofilm. Bagnall et al. (2012) demonstrated that the heterotropic microorganisms also had the ability to biodegrade some estrogenic chemicals, thus, organic carbon loads showed no significant impact on the biodegradation of estrogens. BPA also can be degraded by both heterotrophic microorganisms and ammonium-oxidising bacteria in the activated sludge (Roh et al., 2009). Furthermore, a study conducted by Koh et al. (2009) indicated that the EDC degradation was more likely to occur in organisms that utilised a wide range of carbon sources (organic carbon or inorganic carbon), the evidence obtained by Gaulke et al. (2008) have previously revealed that the degradation of EE2 was more likely to be caused by the heterotrophic microorganisms than nitrifying bacteria. Therefore, the addition of exogenous organic carbon is an important factor for the removal of CoC and is worthy of investigation.

1.7 Project aims

The removal of ammonium using NTFs has been investigated by researchers during past years, with very good nitrification rates achieved and the ammonium-driven chlorine demand reduced in water treatment process. However, considering the worldwide energy crisis, it is necessary to seek an energy saving and highly efficient water treatment system. This study provides a unique insight into the comparative nitrification performances of NTFs with different aspect ratios (height: diameter) and the same specific surface area under various ammonium-N loading rates. Because the low aspect ratio NTF requires more plant space area, while the high aspect ratio NTF requires more energy to pump water to the top for distribution.

Furthermore, because of the potential of NTF to remove CoC and the constructive and operational advantages comparing with other biological water treatment processes, this project also investigated the feasibility of high-rate NTF in removing CoC from synthetic wastewater. Studies have been conducted to reduce the environmental concentration of CoC by biodegradation — using for example activated sludge, membrane bioreactors (reviewed in Chapter 1, Section 1.5). Little is known about the biodegradation of chemicals within the higher concentration range in NTF, especially in high-rate recirculating NTF system with high aeration and low initial ammonium-N concentration. Several factors require investigation, and the related factors are nitrification rate of the NTF, the initial concentration of CoC and the exogenous organic carbon substrate.

This project aims to:

1. Compare the nitrification performance of high-rate NTF with different height-to-diameter aspect ratios and same specific surface area;

2. Determine the possibility of applying high-rate NTF to the removal of CoC from low ammonium-N concentration synthetic wastewater and the effect of the initial concentration of CoC on the removal of CoC in NTF;

3. Determine the effect of initial nitrification rate on the removal of CoC and the effect of CoC addition on the nitrification performance of NTF;

4. Determine the effects of additional organic carbon substrate on the removal efficiency of CoC.

2 GENERAL METHODOLOGY

2.1 Introduction

The general methodology applied in this study is described in this chapter. Methods for the construction and operation of two experimental systems, water sampling, sample analysis and statistical analysis are presented in this Chapter.

2.2 Nitrifying trickling filters with different aspect ratios

Two nitrifying trickling filters (NTFs) with different aspect ratios (height: diameter) and same effective filter packing medium surface area were constructed in the laboratory at Flinders University. Plate 2.1 presents some major components and structure of this system. More details are provided below.

2.2.1 NTF columns

The NTF columns were built by using two PVC pipes of different aspect ratios. One was 0.5 m high and 0.3 m in diameter, packed with a 0.3 m high medium (Plate 2.1 left), and the other one was 1.5 m high, 0.15 m in diameter, packed with a 1.2 m high medium (Plate 2.1 right). The overall packing medium volume was approximately 0.02 m^3 for both NTFs. A collar was added to the top of the 0.5 m column (the short NTF) to reduce overspray, with four distribution sprinklers installed on the cross-plastic (polyethylene) tube 0.1 m from the collar top, making the total column height 0.7 m. The distribution sprinklers for the 1.5 m column (the tall NTF) were also housed on the cross-plastic (polyethylene) tube 0.1 m from the top of column to decrease overspray.

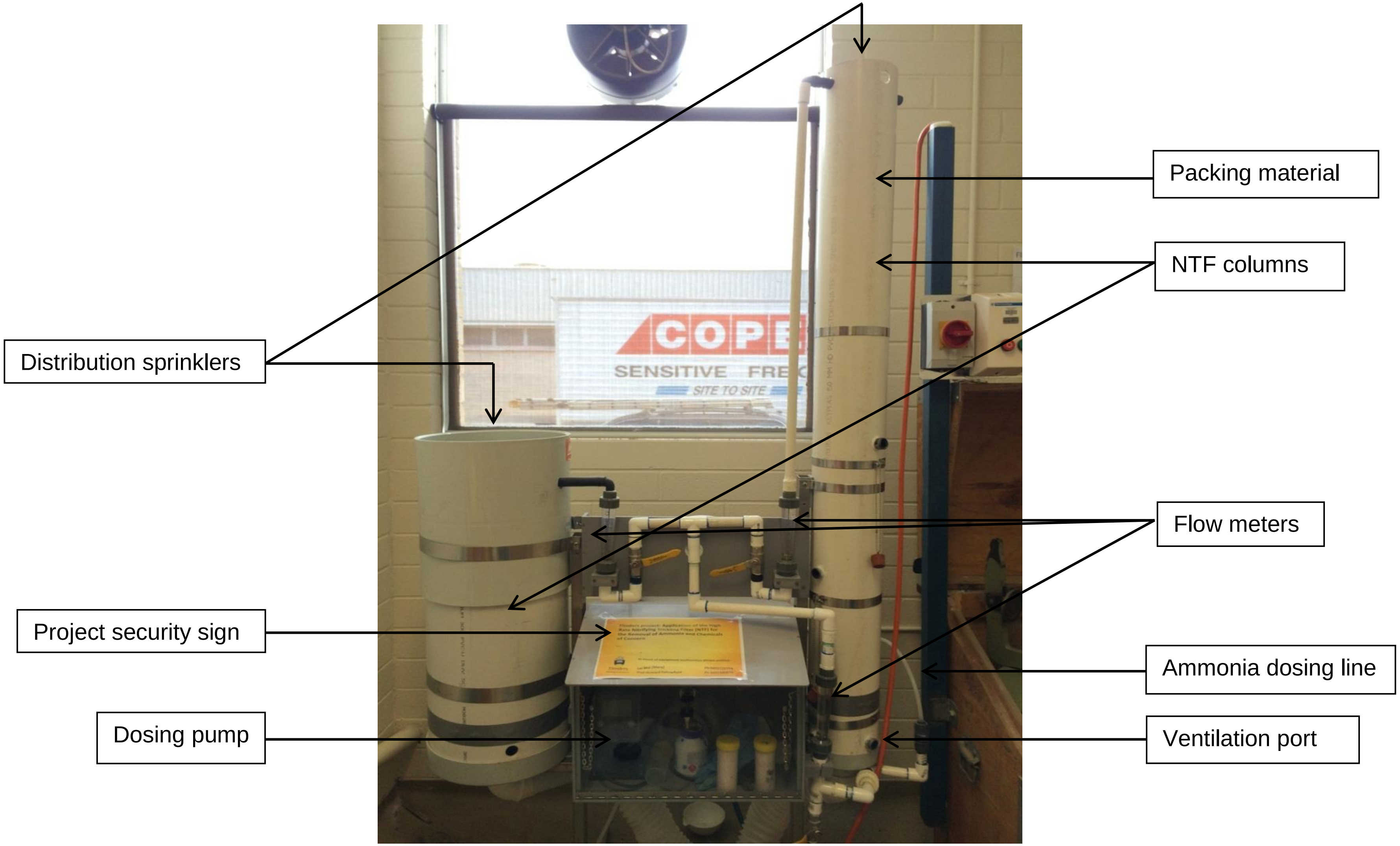


Plate 2.1 Two laboratory-scale NTFs of different aspect ratios and containing the same filter packing medium specific surface area.

2.2.2 Filter and media support stand and frames

All the internal and exogenous filters and the media stands and frames were constructed and fabricated by the Biomedical Engineering Department, Flinders Medical Centre.

2.2.2.1 Filter support stand

A steel stand to support two filter columns was fabricated by an engineer from the Biomedical Engineering Department. The stand (see Plate 2.2a) was designed to support the two columns 0.5 m above the ground to give space to install the drainage pipe for the filters' effluent. On the bottom of the filter support stand, four fabricated steel struts lay on the floor to form a stable support for the whole system. Plate 2.2b shows a long support strut horizontally extended across the stand, and was fabricated with the two vertical struts. This horizontal strut was used to support the two columns and the cabin.

2.2.2.2 Filter support frames

Two long steel struts fabricated with the ground struts extended vertically beside the columns. In order to hold the filter columns on the support strut, two ring shackles were fixed on the vertical struts with screws for each column (see Plate 2.3). The fabricated support stand struts were designed to be tough enough to support a great load and prevent the columns from collapsing.

2.2.2.3 Media support stand

Although the polypropylene media packed inside the columns was very light, a support stand was still needed to prevent the media base of the NTF column from sagging. The stand consisted of seven parallel struts, which were made of rigid plastic tubes (see Plate 2.4). Each struts extended the entire width of each NTF column to fully support all of the media. The slots between struts were large enough to allow the filtration from the media to drainage and also enable the air to circulate through the whole column.

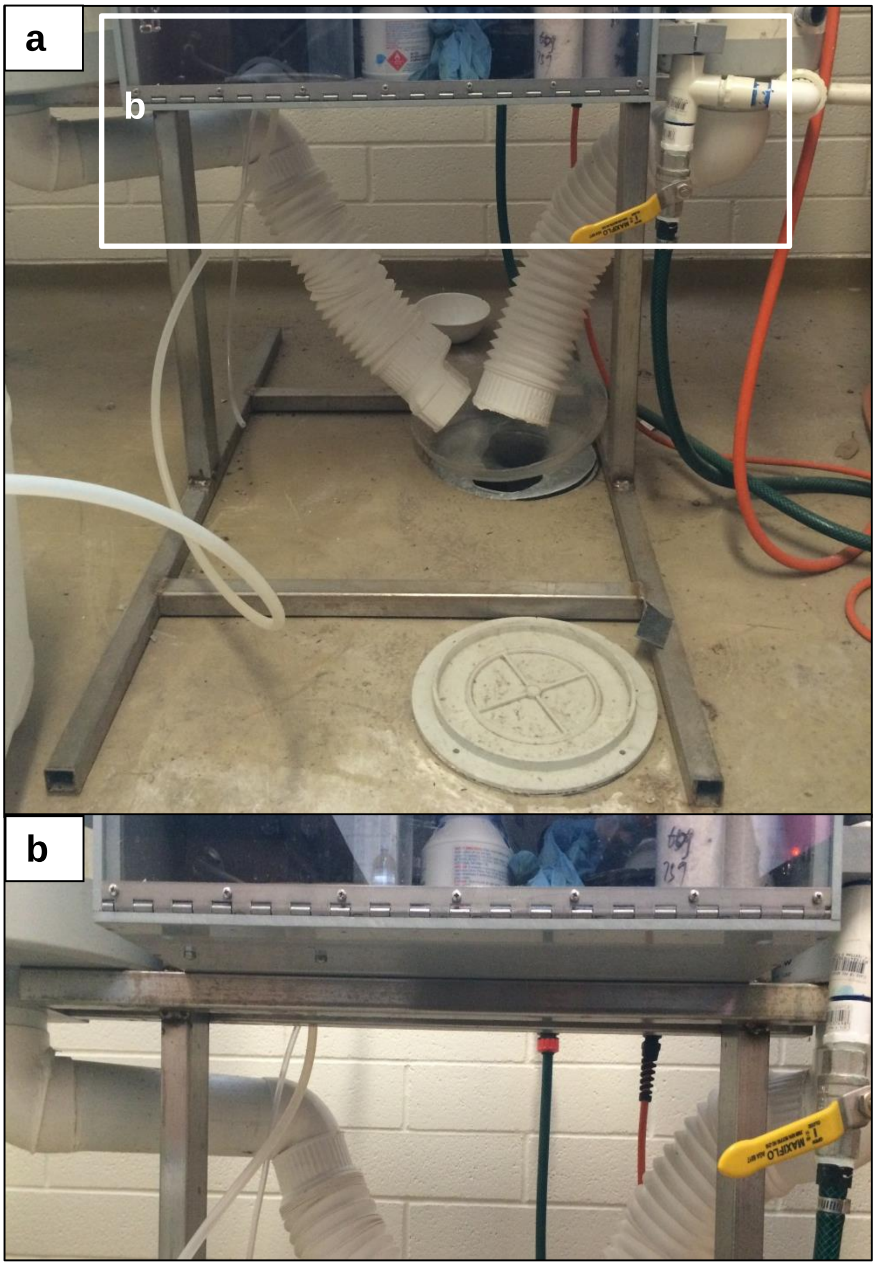


Plate 2.2 Support stand for NTFs: (a) Overview of the NTFs support stand structure; (b) The cross-strut, on which the filters sit.

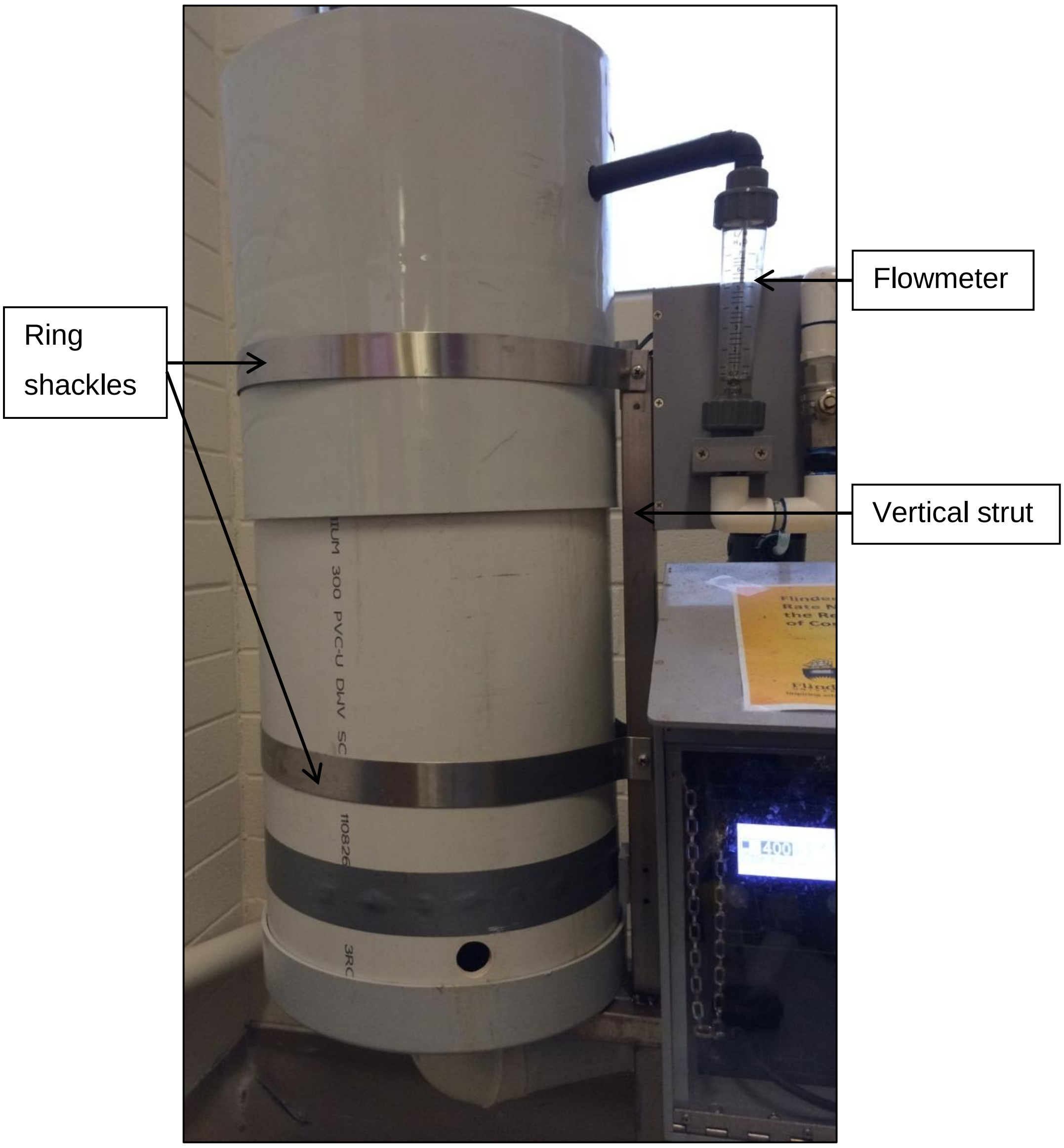


Plate 2.3 The support frames for NTFs.

Plate 2.4 The media support stand positioned inside the NTF.

2.2.3 Packing material

The biofilm support media, which was used in the previous study by van den Akker (2008), was packed in the NTF columns to provide a 0.3 m bed (1 layer) and a 1.2 m (4 layers) bed for the 0.5 m NTF and 1.5 m NTF respectively. The TKP 312 polypropylene packing material (2H Plastics, Victoria Australia) had a specific area-to-volume ratio of 240 $m^2 m^{-3}$, which provided a total surface area of 5.09 m^2 for both NTFs. The media is manufactured by welding the polypropylene sheets together to form a strong block, resulting in a much stronger and longer lasting welding than polypropylene blocks that are only glued. It would retain its shape both during the installation phase and during its operation life. The 60° channel to vertical angle and high void space (95%) benefits water filtration and aeration (Plate 2.5a). The original polypropylene block was cut into a round shape to tightly fit the filter columns, minimising hydraulic short circuiting adjacent to the pipe walls (Plate 2.5b).

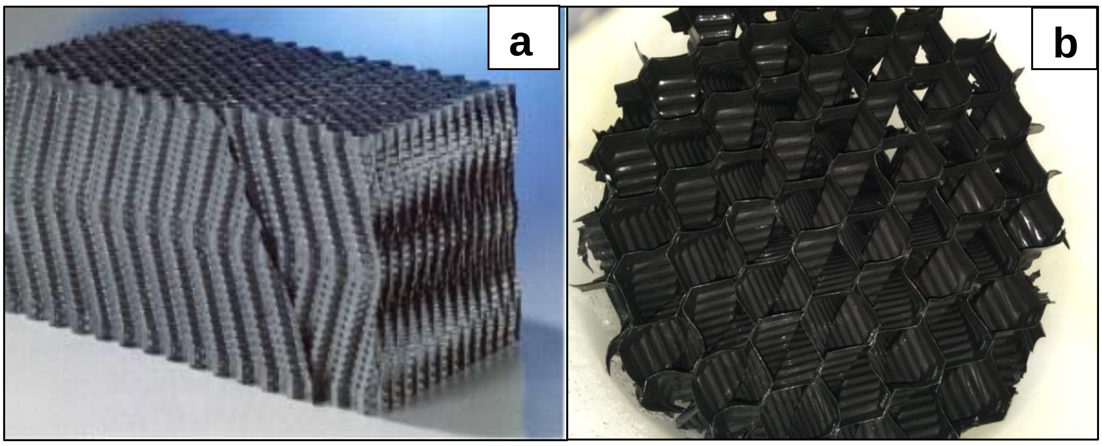


Plate 2.5 (a) Photograph of polypropylene media (2H Plastics, Australia); (b) the polypropylene media positioned in NTF column.

2.2.4 PVC pipes

The 20 mm (OD) PVC pipes were used for most of the water reticulation in the NTF system. Ammonium solution was dosed into the main tap water flow before going through a flowmeter (see below), which was used to measure the water flow rate and was controlled by a brass gate valve (Plate 2.8b). A 20 mm PVC pipe was installed to mix ammonium with tap water after the main flowmeter, before separating into two branches to supply each NTF. In Plate 2.6a, it can be seen that the flow rates of the two branches were measured by two flowmeters, which were controlled by two separate brass gate valves. This was designed to provide equal flow rate for the two NTFs. Immediately after getting through the flowmeter of the short filter, water was subsequently distributed through the sprinklers on the cross-plastic (polyethylene) pipes. However, for the tall filter, after the flowmeter, water was first delivered through a long PVC pipe to the filter top before being distributed by the sprinklers (Plate 2.6c).

2.2.5 Distribution system

Water was applied using a fixed distribution system for each NTF. A cross-rigid plastic pipe was installed and extended across the top of the short NTF, and four sprinklers were housed in the centre of each arm of the cross pipe (see Plate 2.7a). Water was discharged evenly from the sprinklers, which were driven by the water pressure from the tap. For the tall NTF, a single rigid plastic pipe was extended across the NTF top and two sprinklers were installed evenly on the pipe (see Plate 2.7b).This fixed distribution system was designed to wet the surface area evenly.

2.2.6 Hydraulic flow

The influent hydraulic flow rates for both NTFs were constant throughout this comparison study, and the flow rates were calibrated using the flowmeter for each NTF. The influent hydraulic flow rates were set at 1 L min^{-1}, which resulted in a hydraulic surface load (per unit of the total packing media surface area) of 283 L m^{-2} for both NTFs. Both NTFs were operated under single pass.

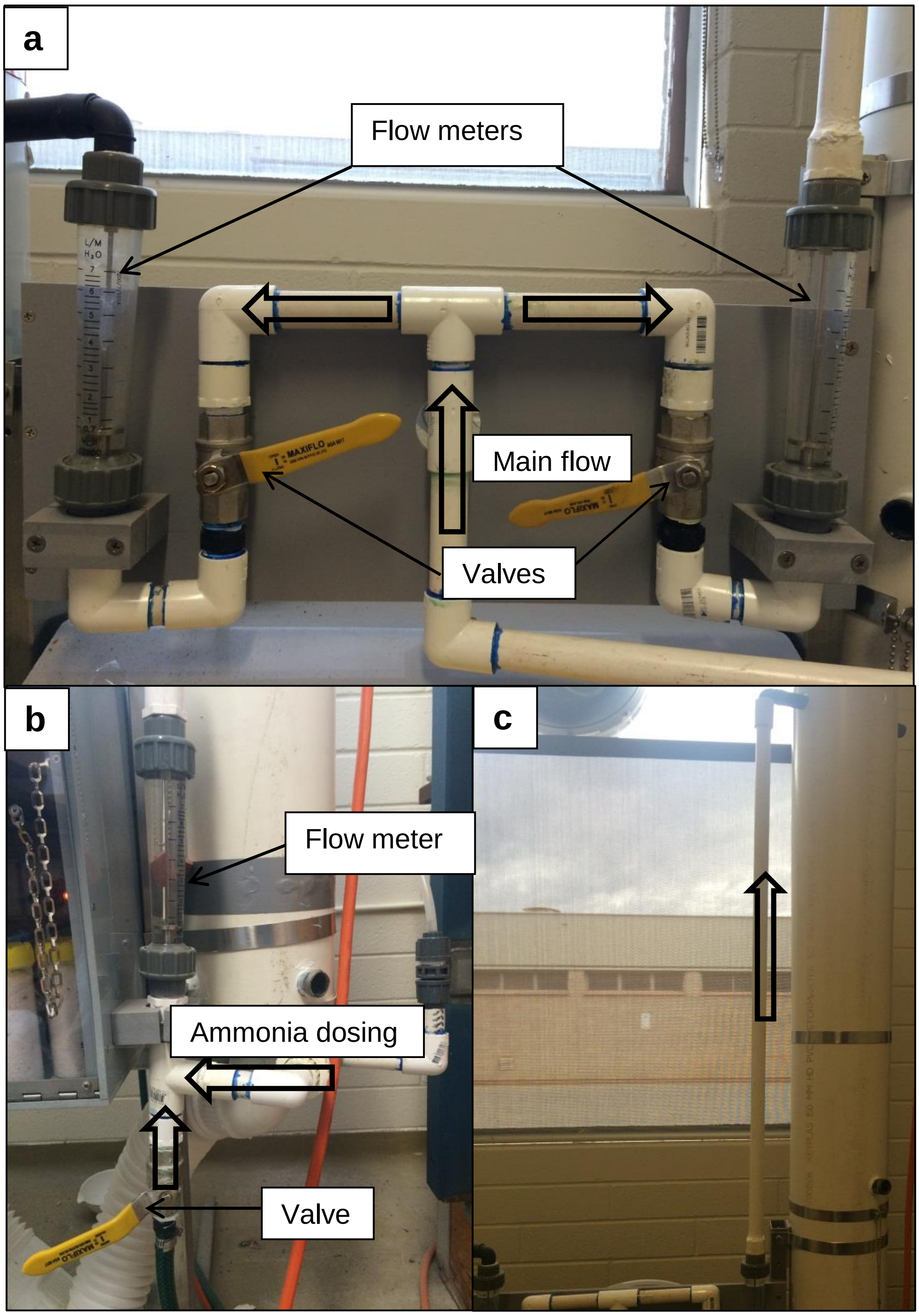


Plate 2.6 PVC manifold: (a) the main flow and two branches; (b) the main flow and the ammonium dosing line; (c) influent line for one of the filters.

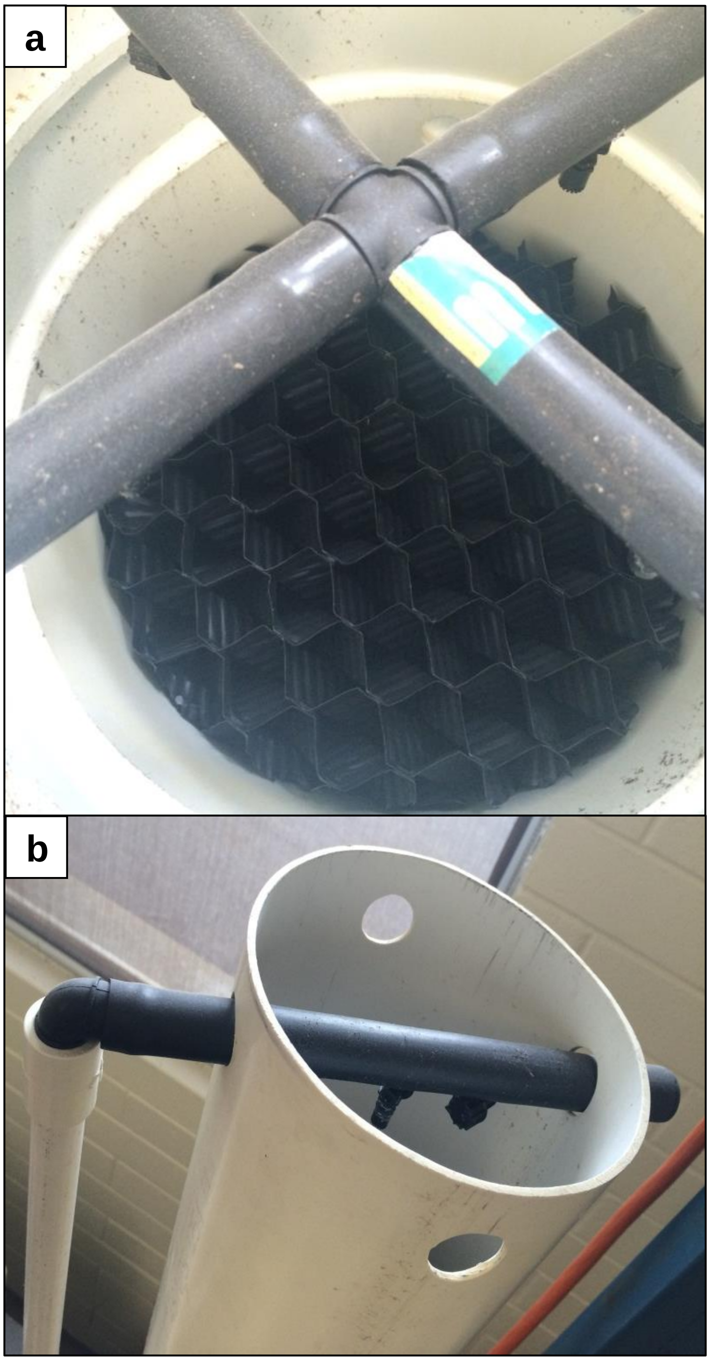


Plate 2.7 Distribution system for NTFs: (a) Cross sprinklers distribution for the short NTF, (b) two sprinklers for the tall NTF distribution.

2.2.7 Dosing

An ammonium stock solution was made by dissolving into 20 L tap water 80g–120 g fertiliser containing 21% ammonium sulphate. Different influent ammonium concentrations (1.0–4.0 mg NH_4-N L^{-1}) were obtained by changing the amount of fertiliser that dissolved in 20 L tap water. The tap water was provided by SA Water, with negligible concentrations of ammonium and NOx and no other contaminants were detected. In order to make sure the fertiliser dissolved completely in water, the ammonium stock solution was prepared one day prior to use. The ammonium stock solution was dosed into the main water flow by a digital pump (Grundfos, model DDA 7.5-16AR, Australia). The digital pump, which was connected with a non-return valve (food valve) to prevent the backflow of water into the ammonium stock solution reservoir, was installed and housed in a cabinet in this system (see Plate 2.7). The dosing pump was set at a fixed dosing rate of 400 mL per hour, which resulted in influent ammonium-N concentrations generally between 1.0 and 4.0 mg NH_4-N L^{-1}. Another pressure loading valve was installed with two PVC flanges on each side. One side connected to the pump with a 20 mm outer diameter (OD) rigid PVC pipe, and the other side was connected with a 6/9 (OD=9 mm) tubing for the dosing pump outlet. The ammonium stock solution from the dosing pump outlet line then joined the main flow via a T-pipe.

2.2.8 Ventilation ports and drainage

Four ventilation ports with diameter of 20 mm for each NTF were distributed evenly around the NTF column 50 mm from the base. To minimise water loss from the ports, 20 mm of rigid plastic tubing was inserted into each ventilation port. Two PVC pipes were used for the NTFs, each 70 mm in diameter and installed at the bottom of the NTF for water drainage to sewer (Plate 2.8).

2.2.9 Sampling sites

The influent samples (100 mL) were taken directly from the underneath the sprinklers in each NTF and collected in 120 mL caped sample bottle. The effluent samples were grabbed from the ventilation ports by inserting a half silicone tube into the ventilation ports, and the filtrate water samples (100 mL) were collected in a 120 mL caped bottle. All the samples were immediately transported to the laboratory within one hour, and the parameter values of DO, pH and alkalinity were analysed immediately. After being filtered through a 0.45µm filtration (Pall Corporation), all the samples were stored 3.0 ± 2.0 °C and analysed within 2 days.

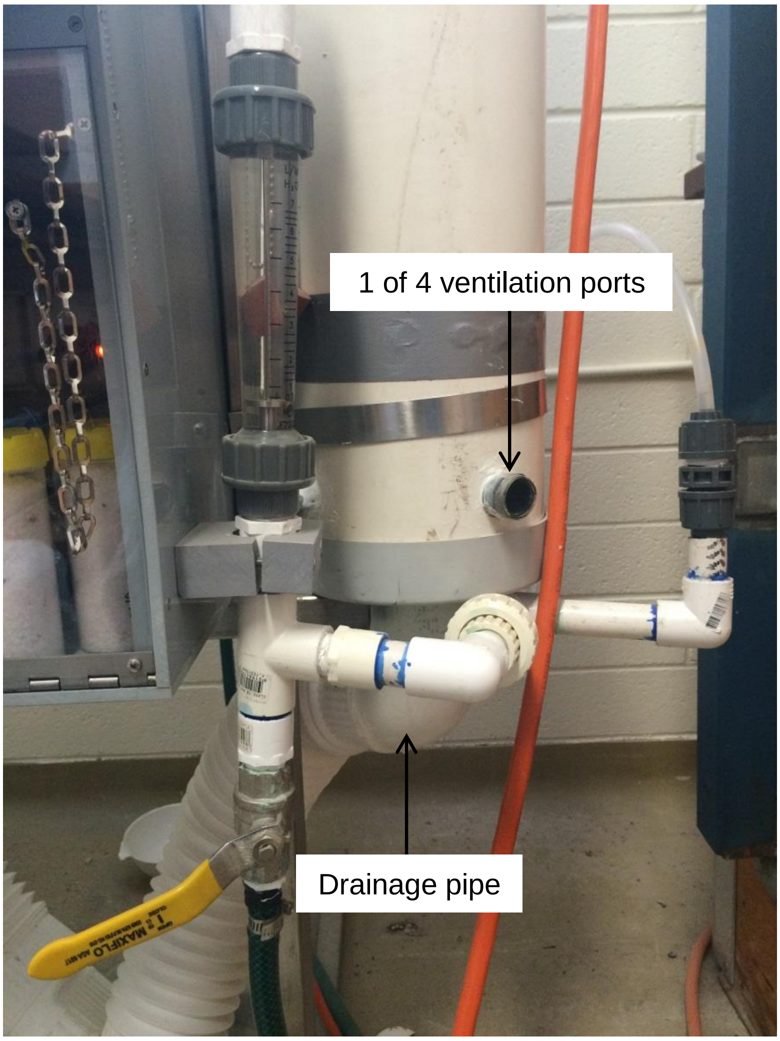


Plate 2.8 The drainage pipe and ventilation ports of NTFs.

2.3 Parallel NTFs for chemicals of concern removal

A small laboratory-scale NTF system was constructed from four parallel biofilters. Some key components of this system are presented in Plate 2.9.

2.3.1 NTF construction

The NTF columns were constructed using four PVC pipes (wall thickness 0.02 m). Each of the columns was 0.8 m high, with an inner diameter (ID) of 0.09 m and a total volume of 0.0051 m^3. The distribution sprinklers were installed on the centre of the cross-plastic tube, which was 0.5 m from the top of each column. The steel stand was used to support columns and fixed with screws. Each column was bedded with 0.6 m of polypropylene packing material (specific surface area of 240 m^2 m^{-3}), the same as that used in the two comparison NTFs presented in Section 2.2.3. The total specific media surface area was 0.916 m^2 for each column. Four 1 L volume reservoirs were used for the water circulation, and the reservoirs were wrapped with aluminium foil to block direct sunlight from the water, to avoid algae growth. Each reservoir contained 1 L of 5 mg NH_4-N L^{-1} ammonium solution and respective chemicals of concern (CoC), more details about the synthetic wastewater preparation for each reservoir is presented in Section 2.3.3.

More details of the NTF construction are presented in Plate 2.10 for one of the parallel NTFs. Two sprinklers were installed on centre of the extended rigid plastic pipe, which was located at the 0.05 m from the top of each NTF, to obtain even water distribution through the column and to avoid the edge effects and overspray. Four ventilation ports (10 mm in diameter) were evenly distributed on each column, 50 mm from the base, to provide sufficient aeration.

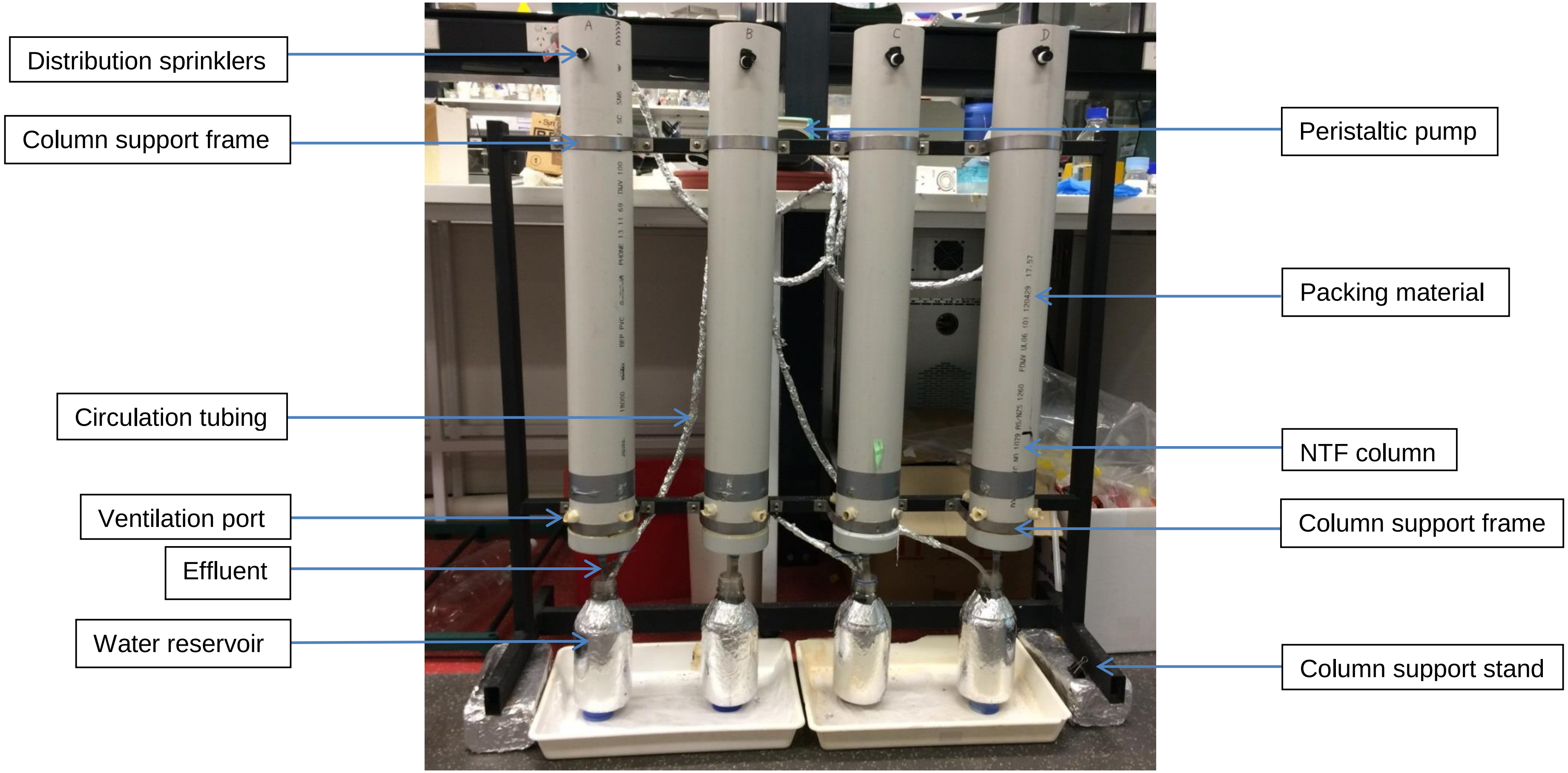


Plate 2.9 Four parallel NTFs in the laboratory.

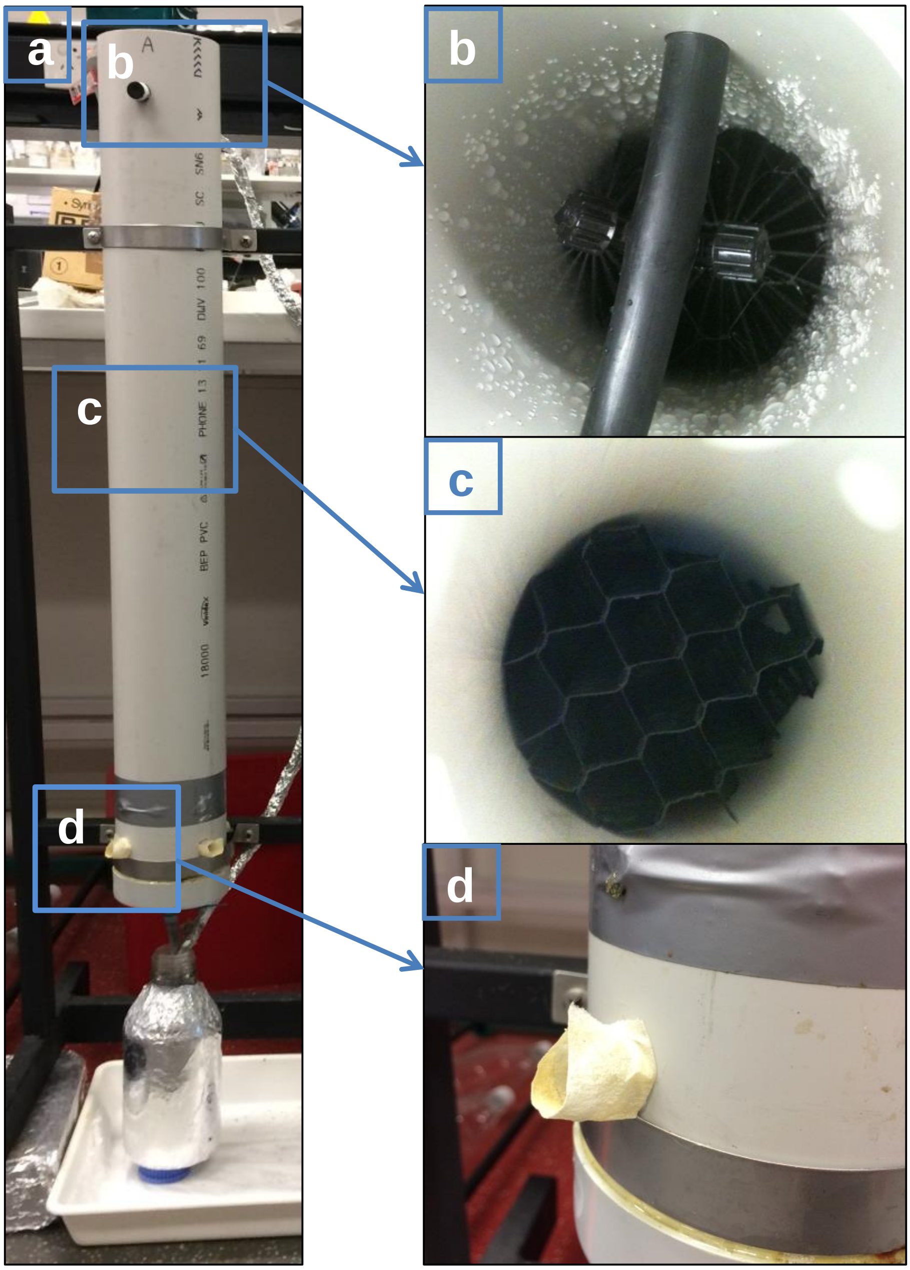


Plate 2.10 Detailed NTF construction: (a) one of the four parallel NTF columns; (b) water distribution; (c) packing material; (d) one of the four ventilation ports for each column.

2.3.2 Peristaltic pump

In this circulation system, a peristaltic pump (Watson-Marlow, model sci-q 323s, Germany) was used to pump the synthetic water from reservoirs to the filters distribution sprinklers. The manual speed control for this pump was 3 to 400 revolutions per minute (rpm). Because four filter columns were used in this study, four pump heads were installed (each with a roller), and precision soft silicone tubing (Watson-Marlow, South Australia) was used to transport water through the pump (Plate 2.11). The silicone tubing thickness was 1.6 mm and the ID was 4.8 mm. Inlet and outlet lines of the pump were connected to two sections of 8 mm ID silicone tubing. The water from the reservoir was pumped to the top of the filter along 1.2 m (reservoir to pump) and 0.8 m (pump to sprinklers) of 8 mm ID silicone tube, which was wrapped with Aluminium foil to prevent algae growth in the tubing.

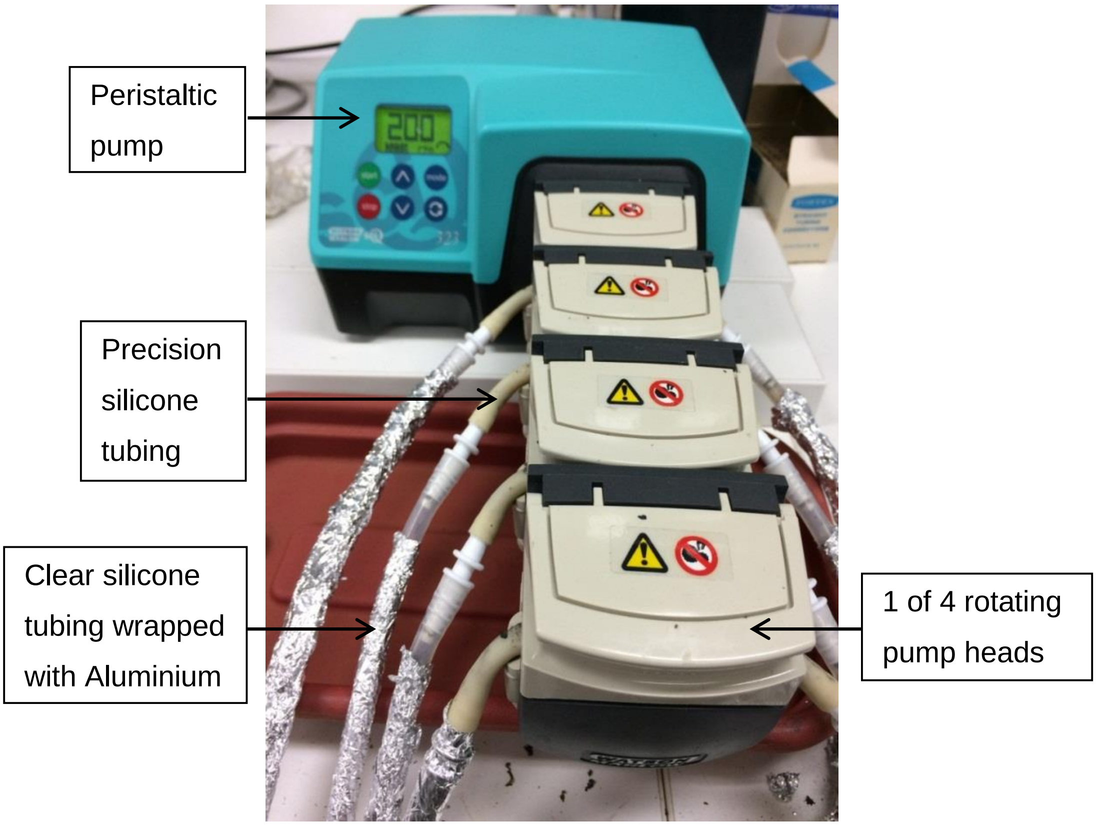


Plate 2.11 The peristaltic pump used for water circulation.

2.3.3 Recirculating water preparation

The synthetic wastewater used in this study was prepared by adding the components into 1 L tap water. Table 2.1 presents the components and their concentrations of the synthetic wastewater used in this study.

2.3.3.1 Ammonium-N solution

An ammonium stock solution was prepared at a concentration of 1 g L^{-1} by dissolving 3.189 g of analytical reagent grade Ammonium Chloride (provided by Fisher Scientific) into 1 L Milli-Q water. 5 mL of the ammonium stock solution was added into 1 L tap water to form a basic ammonium solution. Four bottles of the 1 L ammonium solution were prepared in this study.

2.3.3.2 Chemicals of concern preparation

For the chemicals of concern preparation, each chemical stock solution was prepared at a concentration of 1 g L^{-1} by dissolving 0.1 g of each chemical (purchased from Sigma Aldrich) separately into 100 mL high performance liquid chromatograph (HPLC) standard methanol. A known amount of chemical stock solution was added into the ammonium solution that was prepared above.

2.3.3.3 Organic carbon source preparation

A sucrose stock solution was prepared by dissolving 15 g sucrose (from sugar cane) (AnalaR, MERCK Pty. Limited) into 1 L Milli-Q water. During the investigation of the impact of the organic carbon stage, 5 mL of the sucrose stock solution was added into the solution containing ammonium and the chemicals of concern.

Table 2.1 The primary components in the synthetic wastewater.

Composition of the synthetic wastewater in each reservoir (based on tap water)	**Ammonium concentration (5 mg NH_4-N L^{-1}) (5 mL of the ammonium stock solution)**			
	Exogenous organic carbon concentration (75 mg L^{-1}) (5 mL of sucrose stock solution) (if applicable)			
	Abbreviations	**Concentrations of chemical stock solution in methanol (g L^{-1})**	**Volumes of chemicals (mL)**	**Chemical concentrations in reservoir (mg L^{-1})**
Caffeine	CAF	1	1	1
Acetaminophen	ACE	1	1	1
Trimethoprim	TRI	1	1	1
Benzotriazole	BEZ	1	1	1
Bisphenol A	BPA	1	1	1
Atrazine	ATZ	1	2	2
17α-ethynylestradiol	EE2	1	5	5
N, N-diethyl-m-toluamide	DEET	1	10	10

2.3.4 Hydraulic flow

Throughout this parallel NTF study the peristaltic pump was set at 200 rpm, resulting in an influent hydraulic flow rate of 20.1 L per hour. This high flow rate provided a hydraulic surface load per unit of media surface area of 21.9 L m^{-2} h^{-1}. With the initial ammonium concentration of 5 mg NH_4-N L^{-1}, an ammonium surface loading rate of 109.5 mg NH_4-N m^{-2} h^{-1} was achieved. The ammonium-N was compensated every two hours to maintain the nitrification in NTFs. The filters were operated under recirculation.

2.3.5 Sampling

Because the parallel NTFs were in recirculation, all the samples (10 mL) were collected directly from the effluent tubing at the bottom of each column, except for the initial samples, which were taken from the initial water solution in the 1 L reservoir prior to commencement of filtration. Sampling was performed every two hours. The reduced volume of treated water was compensated via adding diluted ammonia stock solution after each sample collection. The samples were filtered through 0.45 µm mixed cellulose ester membrane filtration (Pall Corporation), and 1 mL of each sample was stored in a 1.5 mL caped vial at -18°C before processing the determination of chemical concentration. The remainder of the samples were stored at 3.0 ± 2.0°C and analysed for inorganic nitrogen content within 2 days.

2.4 Water sample analysis

2.4.1 Ammonium-N

Ammonium nitrogen (NH_4-N) was determined using the American Public Health Association (APHA) (1992) standard method for ammonium-N concentration analysis. To manage a large quantity of samples analysis, a FIAStar 5000 analyser (Foss, Sweden) was used. Analysis was performed in duplicate, together with an internal standard.

2.4.2 Nitrite-nitrogen and nitrate-nitrogen

The oxidised nitrite-nitrogen (NO_2-N) and nitrate-nitrogen (NO_3-N) were determined by using the APHA (1992) standard method. Analysis was performed in duplicate using the FIAStar 5000 analyser (Foss, Sweden), together with an internal standard.

2.4.3 Total Alkalinity

The measurement of total alkalinity was performed in the laboratory using the APHA (1992) standard titrimetric method. Each sample was transferred into a 250 mL conical flask before adding 2 drops of sodium thiosulphate (0.1 N). After adding 2 drops of methyl orange indicator, the alkalinity value was determined by titrating the sample against 0.02 N sulphuric-acid until a faint pink colour appeared. The volume of titrant was recorded and alkalinity was calculated as mg $CaCO_3$/L. Titration was performed in duplicate.

2.4.4 Total organic carbon

Total organic carbon was determined using a TOC-L total organic carbon analyser (Shimadzu Corporation).

2.4.5 pH

The pH was measured by using a handheld Jenway 370 pH meter (Crown Scientific PTY. LTD, New South Wales).

2.4.6 Dissolved oxygen

Dissolved oxygen was measured by using a hand held Jenway 970 DO_2 meter (Crown Scientific PTY. LTD, New South Wales).

2.4.7 Chemicals of concern concentration analysis

The concentrations of chemicals of concern (CoCs) were determined by applying reverse-phase HPLC (Agilent 1100 with DAD detector; Agilent, CA, USA). 50 µL of each sample was injected into the Alltima C18-column (250 × 4.5 mm; 5 µm, Grace Davison Discovery Scientific, MD, USA) by auto-sampler. The mobile phases, at a constant flow rate of 1.2 µL per minute, comprised 0.15% (v/v) formic acid in Milli-Q water and 100% acetonitrile. The gradient elution of the mobile phase presented as 0.15% formic acid solution as follows: 90% at 0 min, 65% at 4 min, 45% at 10 min, 30% at 12 min, 90% at 16 min and 4 minutes post-time, with a total analysis time of 20 minutes. The retention time (RT), limit of detection (LOD) and chemical concentration standard line for each CoC were determined by analysis of authentic standard using the method described above.

2.5 Statistical analysis

The mean value was presented as arithmetic mean ± SD except otherwise indicated. Statistical significance was accepted at >95% confidence ($p<0.05$) level. Graphical data was analysed using Microsoft Excel 2010 (Microsoft Corporation, USA). Other statistical analyses were produced by using SPSS (PASW Statistics 18, USA) and R (R i386 3.1.1, USA).

3 COMPARISON OF NITRIFICATION PERFORMANCE OF TWO HIGH RATE NITRIFYING TRICKLING FILTERS WITH DIFFERENT ASPECT RATIO

3.1 Introduction

As a part of the current research project, observations were made of the ammonium-nitrogen removal performance of two high-rate nitrifying trickling filters (NTFs) with the same specific media surface area but different aspect ratios (height : diameter), at low ammonium concentrations.

Generally, NTFs are applied to the treatment of nitrogen abundant wastewater, and studies have been based on the wastewater concentrations of ammonium-N (Mofokeng et al., 2009). Few studies have been conducted on the low concentrations of ammonium experienced in drinking water treatment. In particular, a study was conducted by van den Akker et al. (2008) on a passively ventilated, pilot-scale high-rate NTF operated with a 3 metre bed of polypropylene filling media under single-stage filtration. The results revealed that the high-rate NTF could efficiently remove low concentrations of ammonium for potable water treatment.

However, the nitrification rate has been considered to be affected by some operating parameters, such as mass transportation, oxygen diffusion, filter depth (van den Akker, 2008), ammonium feeding concentration, and hydraulic flow rate (Tekerlekopoulou and Vayenas, 2003). The results obtained by van den Akker et al. (2008) revealed that at low ammonium concentrations, ammonium loading rate based on the packing media specific surface area (g NH_4-N m^{-2} d^{-1}) was one of the most important design parameters influencing nitrification rate. The increased hydraulic loading rate was able to effectively change ammonium mass loading on the filter, further enhancing the nitrification performance, while the percentage ammonium removal reduced (van den Akker et al., 2008). Thus, in the study reported here, the mass loading rates and the influent ammonium concentrations of the two NTFs were kept the same.

The two principal genera in NTF are *Nitrosomonas* and *Nitrobacter*, which are responsible for oxidising ammonium nitrogen to nitrite nitrogen and nitrite nitrogen to nitrate nitrogen, respectively. The two bacteria species are both autotrophic organisms (Antoniou et al., 1990). Thus, gaseous diffusion of CO_2 and oxygen, into the biofilm was an important filter design parameter for ammonium removal (van den Akker et al., 2011), especially under high organic carbon loading, which would result in the nitrifiers competing with heterotrophic bacteria for the available oxygen. The structured cross-flow plastic media incorporated in the trickling filter design is able to provide sufficient oxygen to satisfy both heterotrophic and autotrophic bacteria simultaneously (Pearce and Edwards, 2011). Therefore, the high flow rate was applied in the current study to provide sufficient oxygen for the microorganisms in the biofilm. van den Akker et al. (2008) reported that the high flow rates might induce biomass sloughing, resulted in better oxygen transfer in a thinner biofilm, and further cause a better oxygen exposure throughout the entire filter depth. Therefore, oxygen diffusion was not a critical consideration in this study.

The NTFs were used to remove ammonium from water as an alternative to pre-chlorination to reduce ammonium-driven chlorine consumption. van den Akker et al. (2008) had reported that the high-rate NTF was able to efficiently remove low concentrations of ammonium (0.5–5.0 mg NH_4-N L^{-1}) for potable water treatment. Thus, the ammonium concentrations used in this study ranged from 1.0 to 4.0 mg NH_4-N L^{-1}. In van den Akker's (2008) study, the measurement of ammonium oxidation decreased with increasing filter depth, and most oxidation occurred within the top 0.3 metres of the 3-metre filter bed. A potential nitrifying capacity was assumed to occur at the lower bed depths of the high-rate NTF (van den Akker et al., 2008). The additional nitrifying capacity at the lower bed depths may prevent high ammonium concentrations in the effluent of NTF (van den Akker et al., 2008), especially when operated under high organic loads, which may have negative effects on nitrification (van den Akker et al., 2010). Pearce (2004), who studied a cross-flow plastic media filter, observed that the majority of nitrification occurred at the top of the filter, with an insignificant nitrification rate at the bottom. If additional filter depth is required to enable heterotrophic oxidation of carbon in the upper filter bed followed by nitrification in the lower depths of the filter bed, aspect ratio (height : diameter) may have an important influence on filter performance and the additional bed depth may be warranted. These findings have important implications for filter operation and design.

Furthermore, a high aspect ratio NTF can reduce plant area space than a low aspect ratio NTF, but may suffer from heavy vertical mass loading, causing filter-bed clogging. Increased energy costs are associated with loading a 3-metre high filter bed (high aspect ratio) compared to a 1 metre filter bed (low aspect ratio), especially for the waste water treatment plants (WWTPs) in those low-income developing countries. Thus, it is worth considering the aspect ratio of the NTF in WWTPs.

This chapter provides the findings from a series of laboratory-scale experiments that were designed to compare the nitrification performances of two high-rate NTFs with different aspect ratios. The nitrifying population had been reported to be able to establish itself on the media surface when fed with low concentrations of ammonium (van den Akker et al., 2011). The aims of this study were firstly to investigate the nitrification performance difference between the two NTFs at low influent ammonium-nitrogen concentrations over the short-term and the long-term; secondly, to determine the effect of influent ammonium concentration or ammonium hydraulic loading rate on the nitrification performance of the two NTFs; and third, to investigate the effects of some typical operational parameters on nitrification rates in both NTFs.

3.2 Methods

The experiments were conducted on a laboratory-scale NTF system. In this system, two NTFs with different aspect ratios and the same packing material surface area (m^2) were operated under controlled conditions. The hydraulic surface loading rates ($L\ m^{-2}\ d^{-1}$) of two NTFs were kept consistent (283 $L\ m^{-2}\ d^{-1}$), and the influent ammonium concentrations were kept low (1.0–4.0 mg NH_4-N L^{-1}) (see Table 3.1). The construction details of the NTFs were presented in Chapter 2, Section 2.2. Some operational parameters of each NTF, including media surface area, hydraulic loading, influent ammonium concentration and influent ammonium surface loading rate, are shown in Table 3.1.

Table 3.1 Some operational parameters of the two NTFs.

NTFs	**Tall NTF**	**Short NTF**
Aspect ratio	8:1	1:1
Bed depth (m)	1.2	0.3
Filter diameter (m)	0.15	0.3
Media surface area (m^{-2})	5.09	5.09
Flow rate (L min^{-1})	1.0	1.0
Influent ammonium-N concentration (mg NH_4-N L^{-1})	1.0–4.0	1.0–4.0
Hydraulic surface loading rate ($L\ m^{-2}\ d^{-1}$)	283	283
Influent ammonium-N surface loading rates (mg NH_4-N $m^{-2}\ d^{-1}$)	396 ± 57 566 ± 57 849 ± 85	396 ± 57 566 ± 57 849 ± 85

3.2.1 NTFs start up

As described in Chapter 2, Section 2.2, two NTFs were constructed. In order to obtain sufficient nitrifying bacteria, the polypropylene packing materials of both NTFs were immersed in diluted activated sludge for three days. The activated sludge was collected from the Bolivar WWTP in Adelaide, South Australia. This step was necessary to inoculate the polypropylene packing media with nitrifying bacteria in the activated sludge and to further initiate ammonium oxidation (Chen et al., 2005). After three days' immersion the polypropylene media, with some nitrifying bacteria attached, were packed into the NTFs. During the commissioning phase (about one month period), the influent ammonium was maintained at very low concentrations of 1.4 ± 0.2 mg NH_4-N L^{-1}. The concentration was then increased to 2.0 ± 0.2 mg NH_4-N L^{-1}, then 3.0 ± 0.3 mg NH_4-N L^{-1} by increasing the concentration of ammonium stock solution. Influent and effluent data were collected over a three-month study period.

3.2.2 Ammonium surface loading rate

In the experiments presented in this section, the ammonium surface loads were supplemented by dosing ammonium sulphate fertiliser stock solution (see Chapter 2, Section 2.2.7) into the flow. All the experiments were conducted on both the short and tall NTFs under the same environmental conditions (e.g. temperature). For both NTFs, which had the same flow rate (1.0 L min^{-1}) and similar packing material surface area (5.09 m^{-2}), the hydraulic surface loading (per specific media surface area) was also relatively consistent, maintained at approximately 282.9 L m^{-2} d^{-1}. Hence, in order to achieve a high ammonium surface loading rate (mg NH_4-N m^{-2} d^{-1}), the concentration of influent ammonium (mg L^{-1}) was increased. Both NTFs were operated under a range of ammonium surface loads per specific media surface area: 396 ± 57, 566 ± 57 and 849 ± 85 mg NH_4-N m^{-2} d^{-1} (Table 3.1). The ammonium surface loads of both NTFs were recorded and compared.

3.2.3 Sampling and chemical analysis

For each influent and effluent grab, 100 mL sampling was performed every-day at 11:00 am (± 1 h). Samples were stored in 120 mL caped containers and transported to the laboratory within 1 hour. Immediately on reaching the laboratory, samples were analysed for dissolved oxygen (DO), pH and total alkalinity. Within two days after sampling, analyses were performed for ammonium-N, nitrite-N and nitrate-N using the procedures described in Chapter 2, Section 2.4. Ammonium-N, nitrate-N and nitrite-N concentrations were recorded to compare the nitrification performance of short and tall NTFs during short- and long-term monitoring. DO, pH and total alkalinity were also recorded to evaluate the parameter variation of both NTFs and the effects of these operational parameters on NTF nitrification performance. Statistical significance was accepted at the $p < 0.05$ level.

3.3 Results

3.3.1 Nitrification of NTFs during start-up

During the start-up stage (short-term investigation), the influent ammonium concentrations of NTFs were maintained at 1.4 ± 0.2 mg L^{-1}. The inorganic nitrogen changes in both tall and short NTFs, which were monitored in a one-month period, are shown in Figure 3.1 and Figure 3.2, respectively. The concentrations of inorganic nitrogen were measured daily to profile the process of nitrification performance.

As can be seen in Figure 3.1 and Figure 3.2, the effluent ammonium-N concentrations were lower than influent in the first 20 days, with some fluctuations after Day 20. Nevertheless, the presence of nitrate-N and minimal nitrite-N in the effluent showed the occurrence of nitrification in the NTFs, revealing the presence of nitrifying bacteria species in both short and tall NTFs.

In the tall NTF (shown in Figure 3.1), nitrification was not observed until day 5, with a small decrease in effluent ammonium concentration and the generation of nitrate. By Day 16, effluent ammonium concentration continued to decrease and reached a minimum of approximately 0.8 mg NH_4-N L^{-1}. The continued generation of nitrate revealed ongoing nitrification until Day 21, whereas nitrate-N concentration remained at approximately 0.2 mg NO_3-N L^{-1} with little fluctuation. The decreased nitrate-N concentration from Day 21, coupled with the similar influent and effluent ammonium-N concentration, indicated that the nitrification was weakening.

In the short NTF (shown in Figure 3.2), nitrification was observed from Day 1 until Day 21. During the first 21 days, nitrate was produced continuously with little fluctuation, staying at around 0.2 mg NO_3-N L^{-1}, and was accompanied by the lower effluent ammonium-N concentrations than influent ammonium-N concentrations. After 21 days, the nitrate-N concentration began to decrease steadily, with almost no difference in the ammonium-N concentration of influents and effluents, evidence of a decrease in the nitrification rate.

The statistical analysis of the nitrification performance (nitrate-N producing rate) of the two NTFs revealed insignificant difference between the NTFs ($F = 2.279$, $p > 0.05$, ANOVA), suggesting that the aspect ratio did not influence the nitrification performance in the NTF.

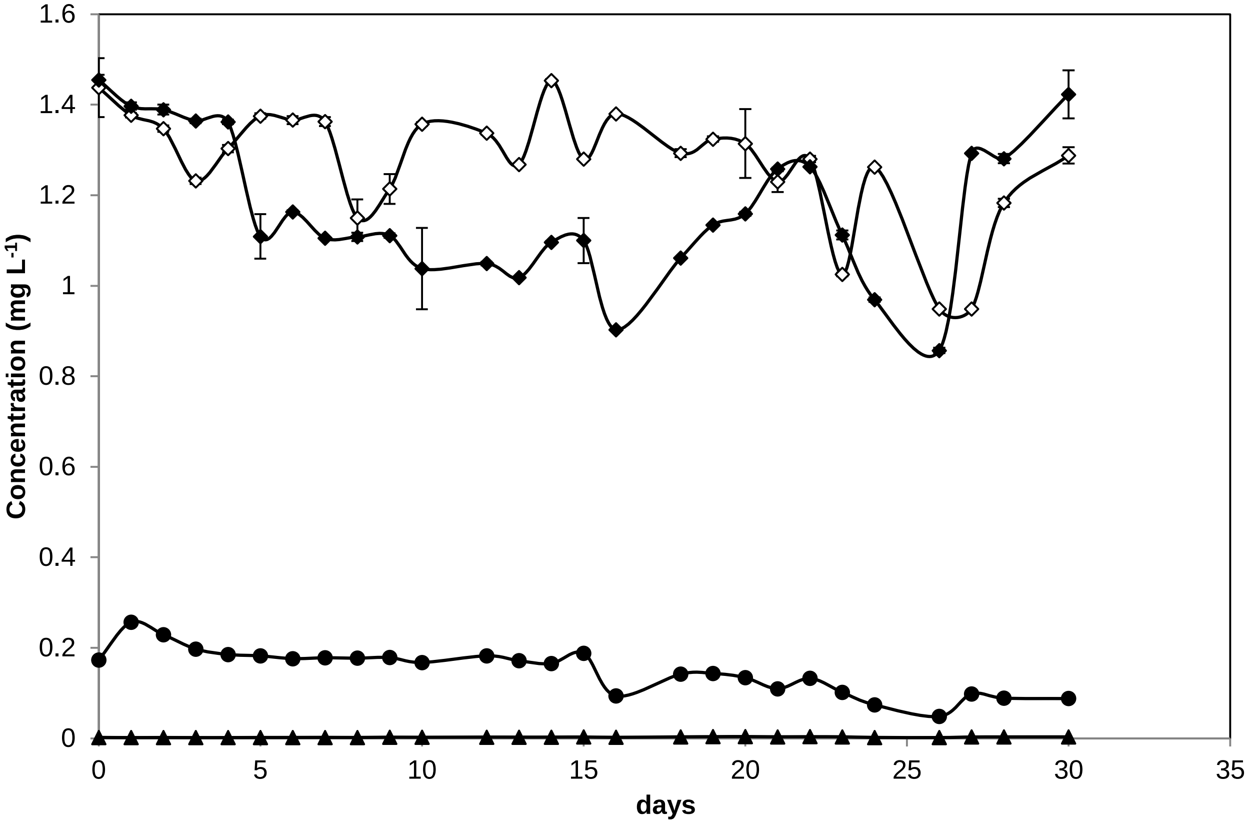


Figure 3.1 Nitrification performance in the tall filter during start-up fed with low concentrations (1.4 ± 0.2 mg NH_4-N L^{-1}) of ammonium. Data points show average concentrations ± SD of influent ammonium-N (◇), effluent ammonium-N (◆), nitrite-N (▲) and nitrate-N (●).

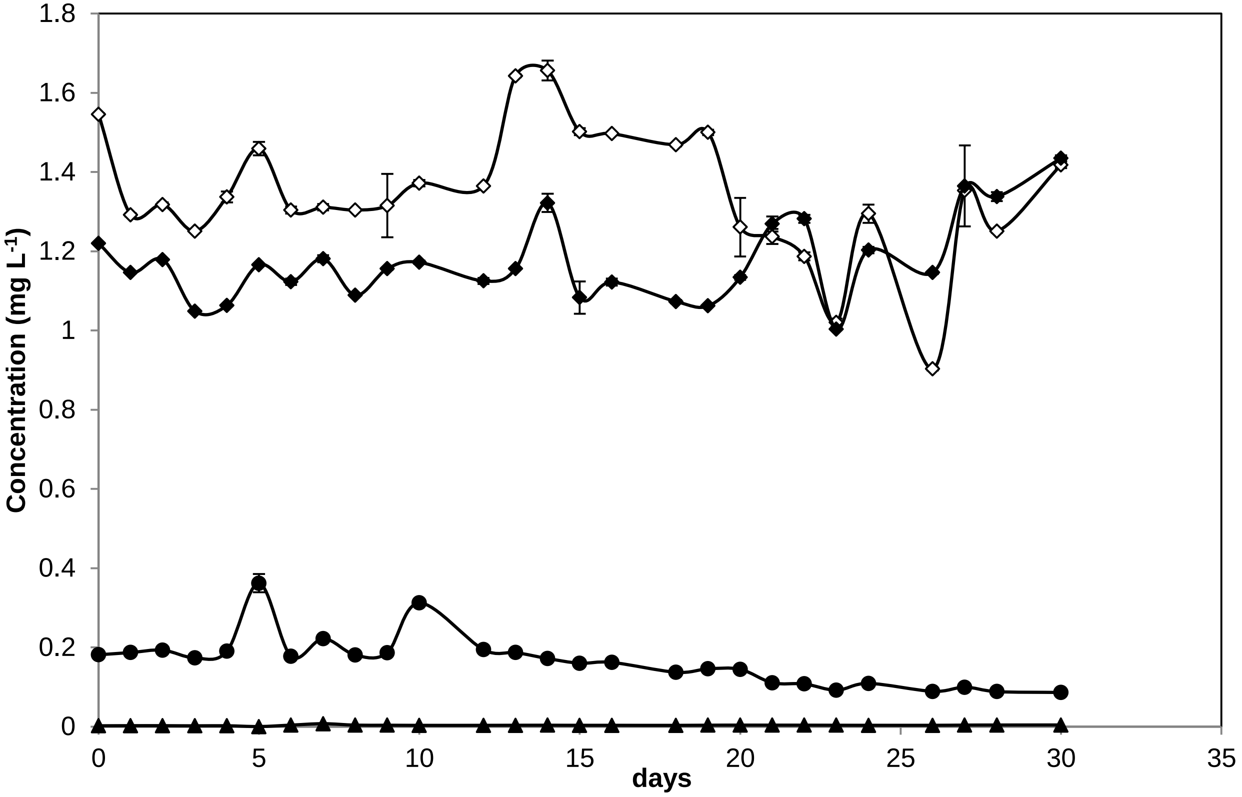


Figure 3.2 Nitrification in the short filter during start-up, fed with low concentrations (1.4 ± 0.2 mg NH_4-N L^{-1}) of ammonium. Data points show average concentration ± SD of influent ammonium-N (◇), effluent ammonium-N (◆), nitrite-N (▲) and nitrate-N (●).

3.3.2 Long-term nitrification of NTFs

During the 3-month long-term monitoring period, the concentrations of influent ammonium-N were maintained at <5 mg NH_4-N L^{-1}, and the concentration changes of inorganic nitrogen species in both tall and short NTFs were recorded. Figure 3.3 and Figure 3.4 (tall and short filter, respectively) show the nitrogen concentration tendencies of the two NTFs under different ammonium loading rate ranges (Table 3.1) were similar.

Figure 3.3 shows almost no ammonium-N difference between influents and effluents in the tall NTF from Day 30 to Day 59, and the nitrate-N concentrations disappeared altogether (influent ammonium surface loading rates 566 ± 57mg NH_4-N m^{-2} d^{-1}). From Day 62, the nitrate-N concentrations increased continuously except for a few fluctuations, reaching a maximum value of approximately 1 mg NO_3-N L^{-1} on Day 84 (influent ammonium surface loading rates 849 ± 85mg NH_4-N m^{-2} d^{-1}), coupled with a fall in effluent ammonium-N concentration compared to influent ammonium-N concentration. The extremely low concentrations of nitrite-N indicated that the ammonium had oxidised to nitrate completely.

From Figure 3.4, it can be seen that after Day 30, the effluent nitrate-N concentrations in the short NTF were unstable, with two high peaks before Day 59 (influent ammonium surface loading rates 566 ± 57mg NH_4-N m^{-2} d^{-1}). From day 62, the concentration of nitrate-N increased steadily until Day 84, achieving a maximum concentration of 1 mg NO_3-N L^{-1} on Day 87 (influent ammonium surface loading rates 849 ± 85mg NH_4-N m^{-2} d^{-1}). Effluent ammonium-N concentrations also stayed lower than influent ammonium-N concentrations, pointing clearly to ammonium-N removal through the short NTF. Nitrite-N concentrations remained extremely low through the long-term operating period, indicating that the reduced ammonium-N oxidised to nitrate-N before discharging from the effluent.

During the long-term observation under different ammonium surface loading ranges, the nitrification performances of the two NTFs with different aspect ratios were relatively similar, no statistical difference was observed between the NTFs (ANOVA, $p>0.05$). The results revealed that the aspect ratio of NTF has no significant impact on nitrification performance during long-term observation.

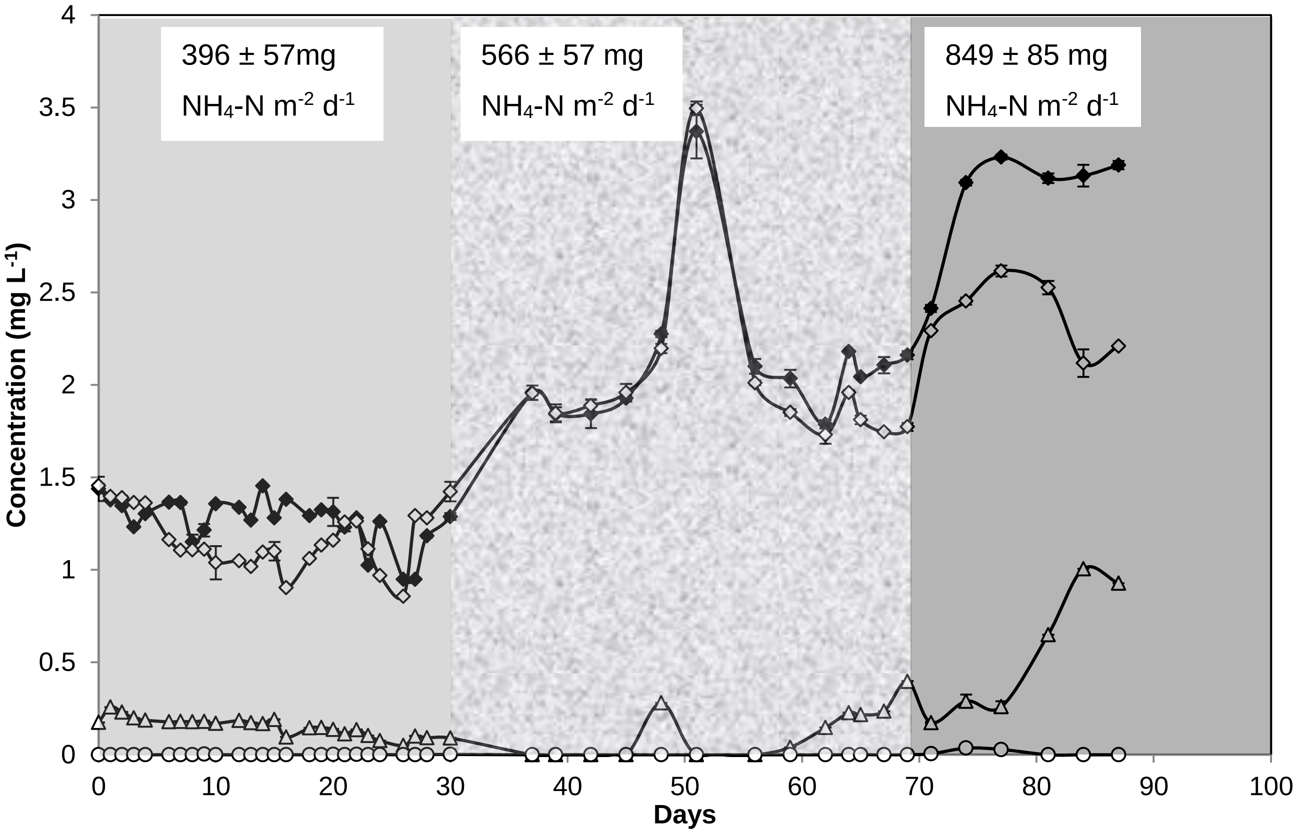


Figure 3.3 Long term nitrification monitoring in the tall filter with feeding low concentrations of ammonium (1.0–4.0 mg NH_4-N L^{-1}). Data points show average concentration ± SD of influent ammonium-N (◆), effluent ammonium-N (◇), nitrate-N (△) and nitrite-N (○). Shade areas indicate different ammonium surface loading rate ranges.

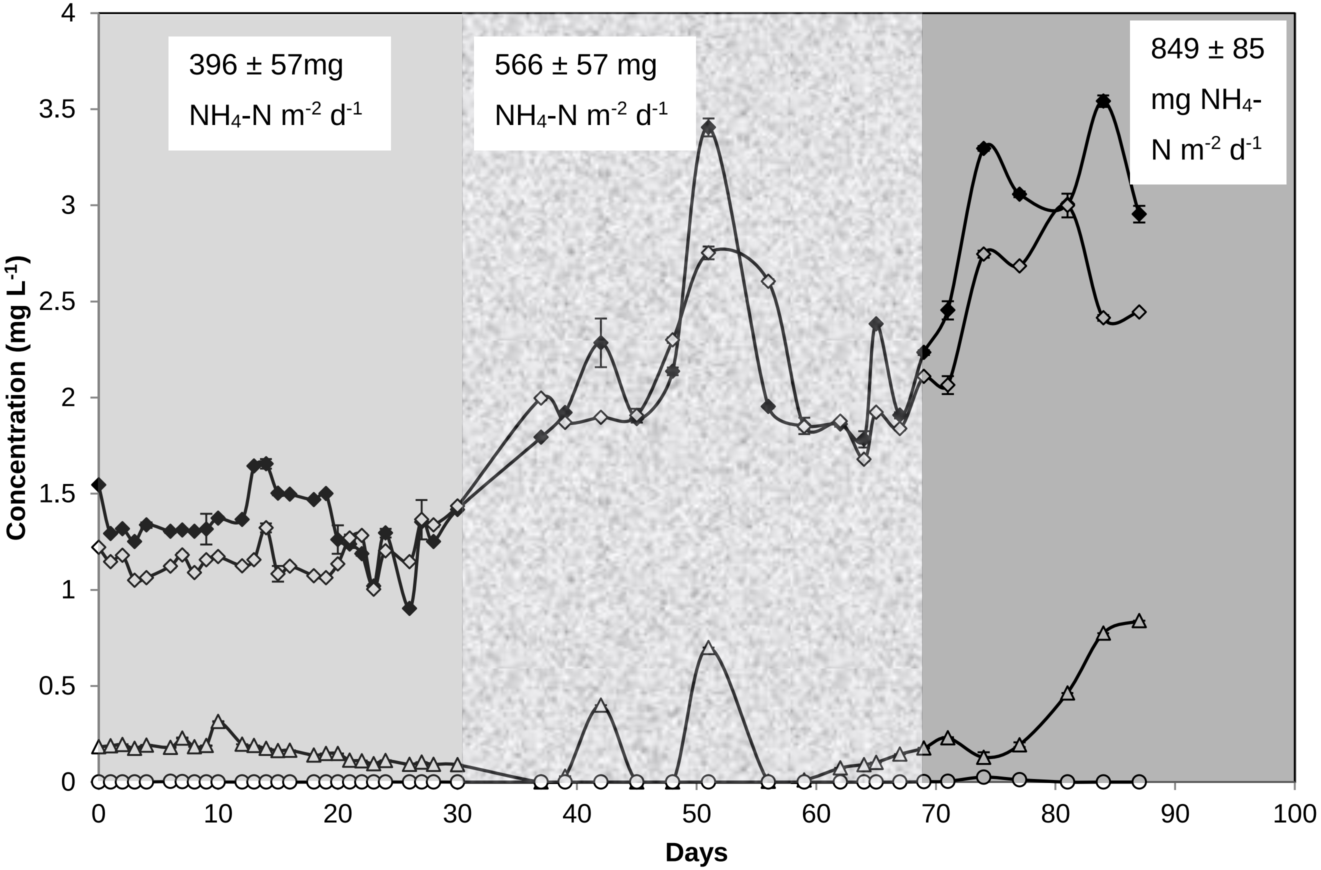


Figure 3.4 Long term nitrification monitoring in the short filter with feeding low concentrations of ammonium (1.0–4.0 mg NH_4-N L^{-1}). Data points show average concentration ± SD of influent ammonium-N (◆), effluent ammonium-N (◇), nitrate-N (△) and nitrite-N (○). Shade areas indicate different ammonium surface loading rate ranges.

3.3.3 Long-term nitrification performance comparison of the tall and short NTFs

As described in Chapter 2, Section 2.2, the tall and short NTFs had different aspect ratios and the same packing material surface area. Both NTFs were operated under a range of low ammonium-N concentrations and surface loads (Table 3.1). The inorganic nitrogen profiles showed in Section 3.3.2 revealed that the influent ammonium surface loading rate range would not affect the nitrification performance comparison of the two NTFs. Thus, the average nitrification rates of tall and short NTFs were compared.

The difference between the overall nitrification rates measured from the tall and short NTFs at both influent ammonium-N concentrations (1.0 mg NH_4-N L^{-1} to 4.0 mg NH_4-N L^{-1}) were statistically insignificant (*t*-test; $p>0.05$). Additionally, the boxplot (Figure 3.5) of the nitrification rate, which is presented as ammonium-N removal rate (mg NH_4-N m^{-2} d^{-1}), confirmed that insignificant statistical differences between the two NTFs ($n=34$; $p>0.05$). The ammonium-N hydraulic loadings for both NTFs were statistically similar, with a variance ratio of 1.066 (two variances F test; $p>0.05$). To determine nitrification activity (because ammonium-N was finally oxidised to nitrate-N), the differences in nitrification performance were based on comparing the nitrate-N-producing rate throughout the NTFs, and were evaluated by *t*-test. The long-term nitrate-N profile data were collected from both the tall and short NTFs and were used to measure nitrate-producing rates throughout the NTFs. Each NTF was observed operating under three influent ammonium-N concentrations (1.4 ± 0.2, 2.0 ± 0.2 and 3.0 ± 0.3 mg NH_4-N L^{-1}), resulting in different ammonium surface loading rate ranges (396 ± 57, 566 ± 57 and 849 ± 85 mg NH_4-N m^{-2} d^{-1}) in this study (Figure 3.3 and 3.4). The results demonstrated that the nitrification performances obtained from the tall and short NTFs were very similar (ANOVA; $p>0.05$). Furthermore, the boxplot in Figure 3.6 shows the difference in nitrate-N generation rates (mg NO_3-N m^{-2} d^{-1}) between the tall and short NTFs, were also confirmed as statistically insignificant ($p>0.05$).

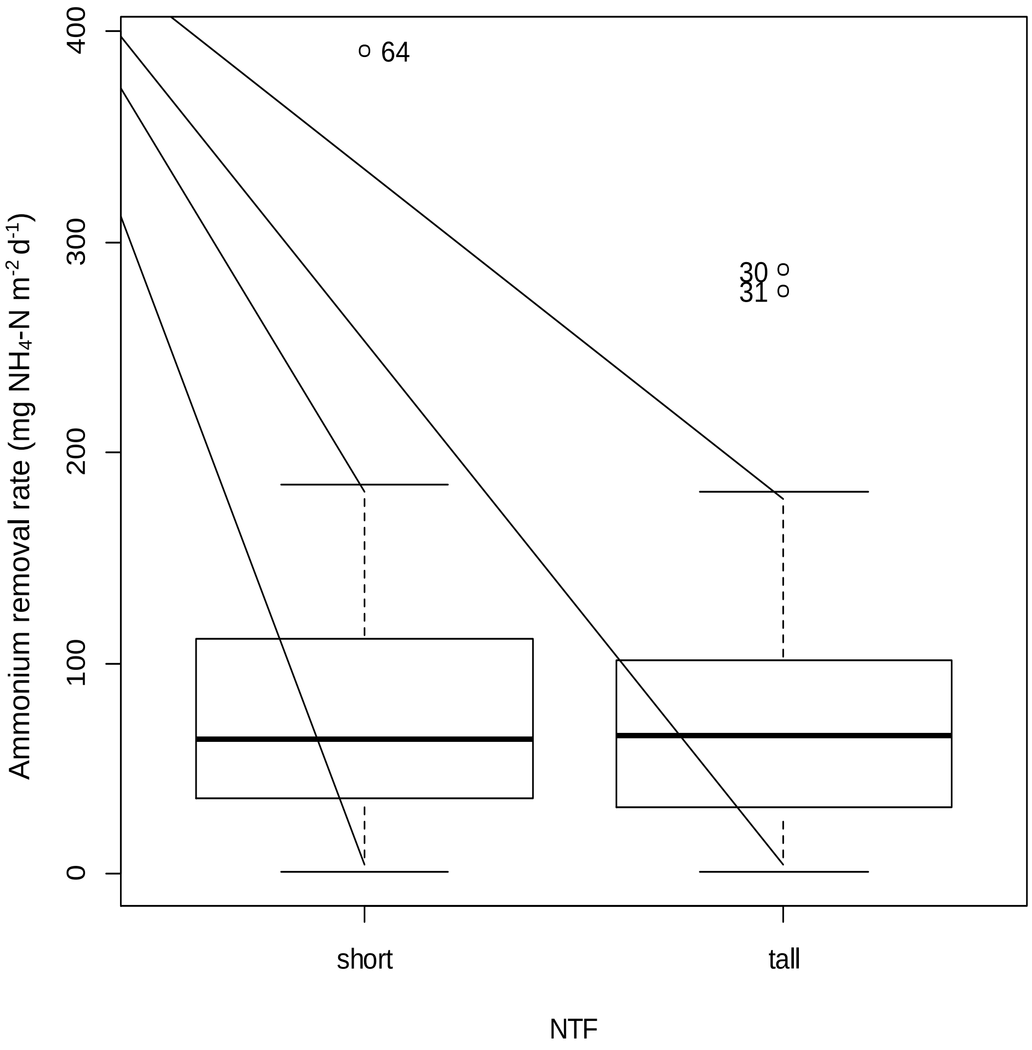


Figure 3.5 Nitrification performances, presented as ammonium-N removal rate (mg NH_4-N m^{-2} d^{-1}) for the tall and short NTFs. The bold lines present mean values of ammonium-N removal rates for the NTFs.

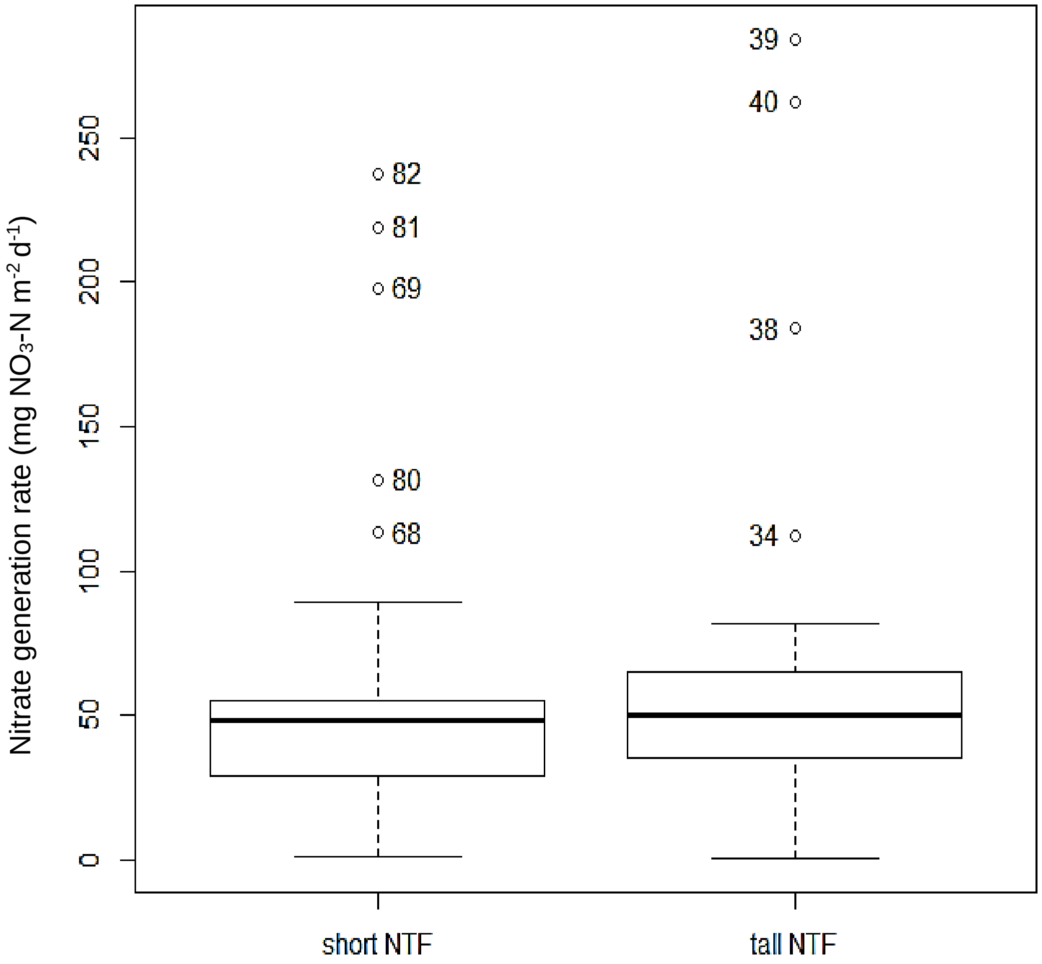


Figure 3.6 Nitrification performances, presented as nitrate-N generation rate (mg NO_3-N m^{-2} d^{-1}), of the tall and short NTFs. The bold lines present mean values of nitrate-N generation rates for both NTFs.

3.3.4 Effect of ammonium hydraulic surface loading on nitrification performance of both short and tall NTFs

During the long-term investigation of the nitrification performance in both NTFs, the nitrification performance varied with the different ammonium surface loading rate ranges (see Table 3.1). Figure 3.7 presents a linear relationship between the ammonium surface loading rate and the nitrification rate in the tall NTF, obtained from the long-term experiments (Pearson's $r = 0.869$; $p<0.001$), with correlation significant at the 0.01 level (2-tailed). The mean nitrification rate was 103.8 ± 70.6 mg NH_4-N m^{-2} d^{-1} and had ranged between 26.0 mg NH_4-N m^{-2} d^{-1} and 286.6 mg NH_4-N m^{-2} d^{-1}. The increase in the nitrification rate in the tall NTF correlated well with the increase of ammonium surface loading rate.

Figure 3.8 shows a linear relationship between the ammonium surface loading rate and the nitrification rate in the short NTF, which was also obtained from the long-term nitrification experiments (Pearson's $r = 0.742$; $p<0.001$), with correlation significant at the 0.01 level (2-tailed). Similar positive correlations were obtained for both the short NTF and the tall NTF. The mean nitrification rate in the short NTF was 104.4 ± 65.7 mg NH_4-N m^{-2} d^{-1} and had ranged between 4.8 mg NH_4-N m^{-2} d^{-1} and 319.1 mg NH_4-N m^{-2} d^{-1}. The nitrification rate in the short NTF increased with the increase in the ammonium surface loading rate.

The correlation coefficients of ammonium surface loading rate and nitrification performance were very similar between the two NTFs with different aspect ratios, and no statistically significant difference was observed (ANOVA, $p>0.05$). The mean nitrification rates (either presented as ammonium removal rate or showed as nitrate-N generating rate) in the two NTFs also showed very similar values (ANOVA, $p>0.05$).

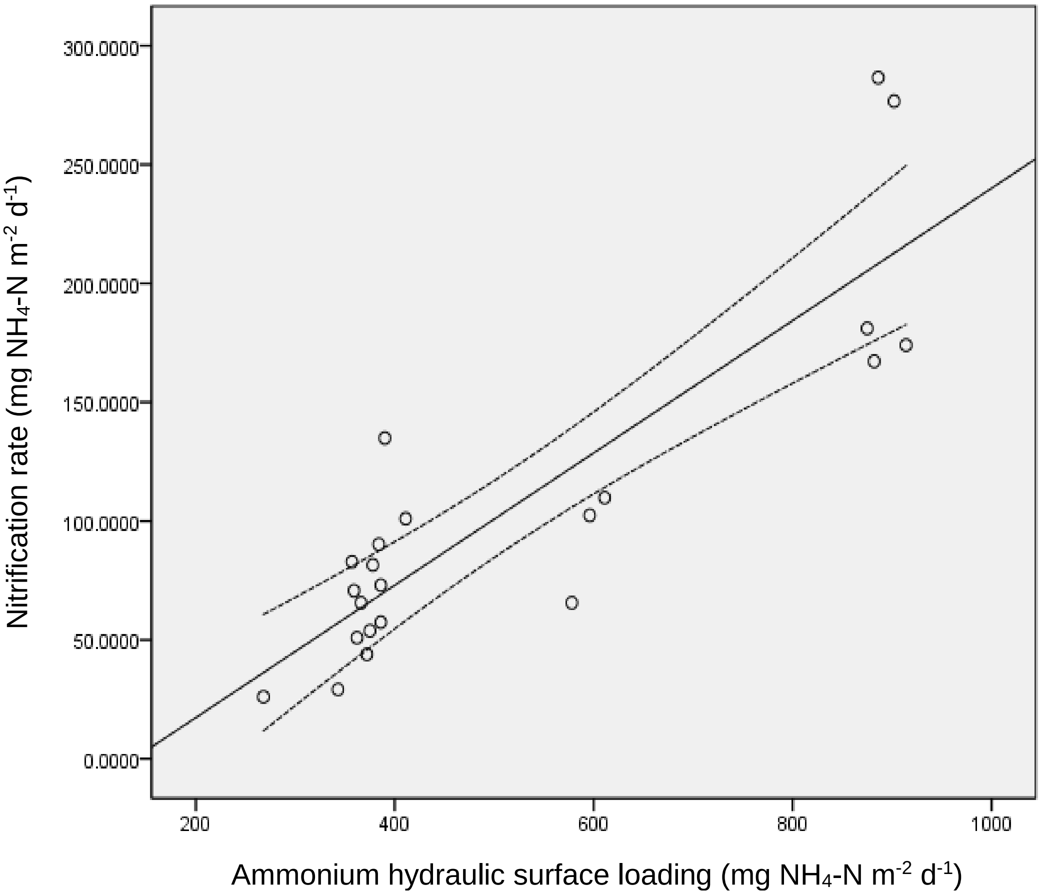


Figure 3.7 The linear relationship between the nitrification rate (mg NH_4-N m^{-2} d^{-1}) and the ammonium hydraulic surface loading rate (mg NH_4-N m^{-2} d^{-1}) in the tall NTF. Dash lines present the 95% confidence interval.

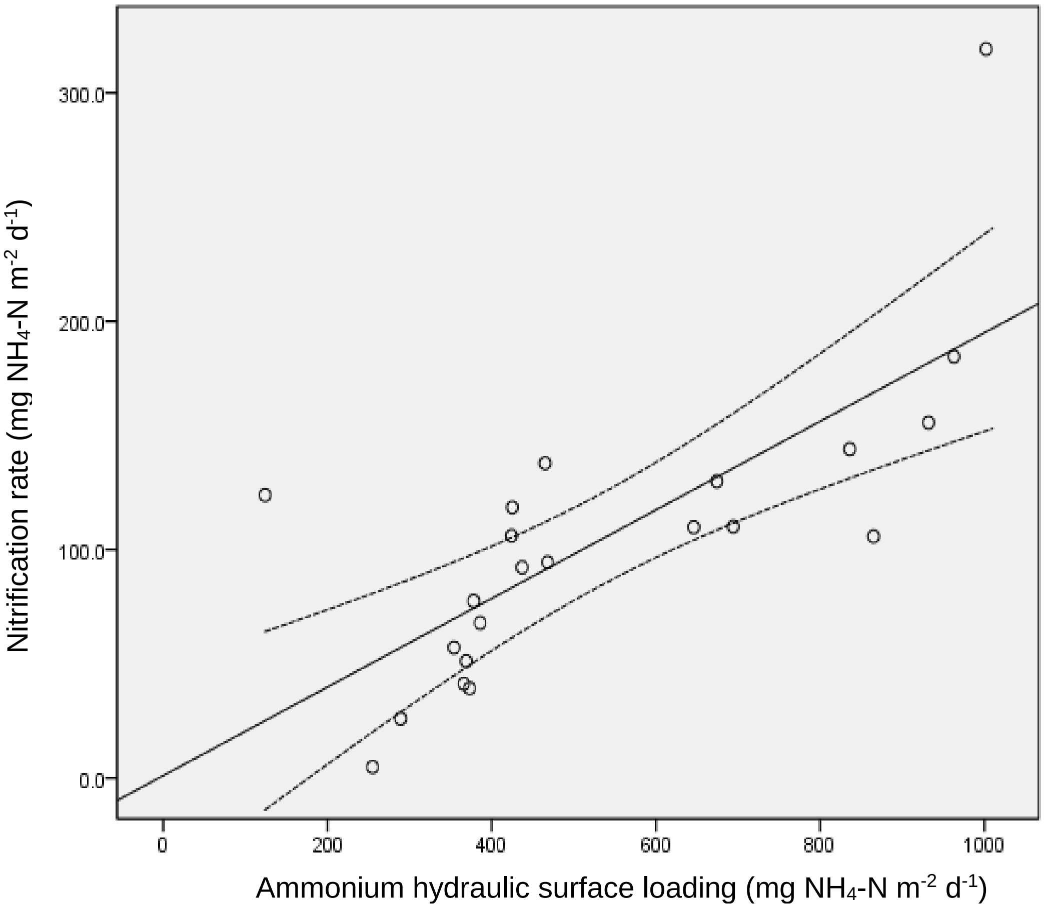


Figure 3.8 The linear relationship between the nitrification rate (mg NH_4-N m^{-2} d^{-1}) and the ammonium hydraulic surface loading rate (mg NH_4-N m^{-2} d^{-1}) in the short NTF. Dash lines present the 95% confidence interval.

3.3.5 Effect of water quality parameters on the short and tall NTFs

The effects of the water quality parameters (influent DO, influent total alkalinity and effluent pH) on nitrification performance were investigated. The variation of these parameters throughout the experiment period was not significant, such as DO (8.25–9.58 mg L^{-1}), pH (7.96–8.55), total alkalinity (75–109 mg $CaCO_3$ L^{-1}). The effects of these parameters on the short and tall NTFs were compared.

In this study, the environmental temperature for both NTFs was controlled at 20 ± 2 °C. A negative correlation was obtained between the ammonium-N removal and effluent pH for both short and tall NTFs ($r_s = -0.733, -0.814$; $p<0.01$; Table 3.2). The results indicated that the increased ammonium-N removal could cause decrease in the pH value in the NTFs. This result can be explained by the nitrification reaction equation:

Equation 3.1 $\boldsymbol{NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+}$ (Antoniou et al., 1990).

The produced hydrogen iron (H^+) during nitrification process led to the lowered pH values in the effluents. In both short and tall NTFs, the total alkalinity in the influent showed a positive correlation with the effluent pH ($r_s= 0.794$; $p<0.05$; $r_s= 0.810$; $p<0.01$; Table 3.2). The findings suggested that the higher influent total alkalinity can lead to the higher pH value in the effluent. Pearce and Edwards (2011) reported that alkalinity was consumed in the biological nitrification process as the oxidation of ammonium produced hydrogen ions, and the total alkalinity consumption equation was:

Equation 3.2 $\boldsymbol{NH_4^+ + 2O_2 + CaCO_3 = NO_3^- + 2H_2O + Ca^{2+} + CO_2}$

However, there was no significant correlation between ammonium-N removal and the influent DO or influent total alkalinity for both short and tall NTFs (Spearman's; $p>0.05$; Table 3.2).

In summary, the effects of the water quality parameters on ammonium-N removal performed similarly for both short and tall NTFs, and no statistically difference of these effects between the short and tall NTFs was observed (ANOVA, $p>0.05$).

3.3.6 Comparison of the ammonium-N removal and nitrate/nitrite-N generation on the tall and short NTFs

From Table 3.2, it can be observed that the water quality parameters were correlated between the two NTFs, including influent DO ($r_s = 0.782$; $p < 0.05$), influent total alkalinity ($r_s = 0.912$; $p < 0.05$) and effluent pH ($r_s = 0.945$; $p < 0.05$). The correlation coefficient of ammonium-N removal between the short and tall NTFs was also highly positive related ($r_s = 0.411$; $p < 0.01$). As to the generated nitrate/nitrite-N concentrations, the correlation between the two NTFs was achieved ($r_s = 0.464$; $p < 0.01$).

In the ANOVA analysis of the nitrification performance (ammonium-N removal and nitrate/nitrite-N generation) between the two NTFs, no statistically significant difference was observed for both ammonium-N removal and nitrate/nitrite-N generation (one-way ANOVA, $p > 0.05$). This result indicates that the nitrification performance of the two NTFs with different aspect ratio was similar. The aspect ratio of the NTF cannot significantly affect the nitrification performance of the NTF.

Table 3.2 The Spearman’s correlation coefficients pointing to relationships between the water quality parameters in the short and tall NTFs.

Parameters	**Short NTF Ammonium-N removal (mg NH_4-N L^{-1})**	**Short NTF effluent pH**	**Short NTF influent DO (mg L^{-1})**	**Short NTF influent Total Alkalinity (mg $CaCO_3$ L^{-1})**	**Tall NTF Ammonium-N removal (mg NH_4-N L^{-1})**	**Tall NTF effluent pH**	**Tall NTF influent DO (mg L^{-1})**
Short NTF Ammonium-N removal (mg NH_4-N L^{-1})							
n	14						
Short NTF effluent pH	-0.733**						
n	14						
Short NTF influent DO (mg L^{-1})	0.282	-0.223					
n	11	11					
Short NTF influent Total Alkalinity (mg $CaCO_3$ L^{-1})	-0.201	0.794*	-0.285				
n	9	9	9				
Tall NTF Ammonium-N removal (mg NH_4-N L^{-1})	0.411**	-0.832*	0.036	-0.285			
n	45	14	11	9			
Tall NTF effluent pH	-0.760*	0.945*	0.247	0.675*	-0.814**		
n	14	14	11	9	14		
Tall NTF influent DO (mg L^{-1})	0.173	-0.023	0.782*	-0.134	-0.027	-0.211	
n	11	11	11	9	11	11	
Tall NTF influent Total Alkalinity (mg $CaCO_3$ L^{-1})	-0.310	0.895*	-0.410	0.912*	-0.527	0.810**	-0.276
n	9	9	9	9	9	9	9

**Correlation is significant at $p<0.01$ level (2-tailed); *Correlation is significant at $p<0.05$ level (2-tailed).

3.4 Discussion

This chapter presents the findings from a series of experiments that investigated the short-term and long-term nitrification performance difference between two NTFs with different aspect ratio (height : diameter) and the same specific media surface area at low influent ammonium concentrations. The relationship between ammonium hydraulic surface loading and nitrification rate was observed for both NTFs. The comparison of this relationship observed in the short and tall NTFs was made. Furthermore, the correlation coefficients between the environmental parameters and ammonium removal in both NTFs were investigated.

During the short-term (start-up stage) investigation, the influent ammonium concentrations were maintained at 1.4 ± 0.2 mg NH_4-N L^{-1}, which can provide ammonium hydraulic surface loading of 396 ± 57mg NH_4-N m^{-2} d^{-1}. The results showed that nitrification occurred in both tall and short NTFs, indicating the presence of nitrifying bacteria. Because the two NTFs shared the same specific surface area and the flow rate was set the same, the ammonium hydraulic surface loading rate for both NTFs was almost the same. The inorganic nitrogen profiles in both NTFs presented very similar tendencies. The low nitrite-N and the higher nitrate-N concentrations in the NTF effluents characterised the development of nitrifying biofilm within the NTF, and indicated the complete nitrification in both NTFs. These observations in this study revealed that the presence of ammonium-oxidising bacteria (AOB) and nitrite-oxidising bacteria (NOB) in the NTFs, with similar nitrification performance in both NTFs. Although the nitrification rates in both NTFs were low, the two NTFs showed similar ammonium-removal rates and nitrate-producing rates.

A three-month, long-term observation of the NTF system was conducted. The influent ammonium concentrations were increased to 2.0 ± 0.2 mg NH_4-N L^{-1} and then to 3.0 ± 0.3 mg NH_4-N L^{-1}, and the ammonium hydraulic surface loading were 566 ± 57 mg NH_4-N m^{-2} d^{-1} and 849 ± 85 mg NH_4-N m^{-2} d^{-1}.The inorganic nitrogen profiles showed the nitrification performance in both NTFs. From Day 30 to Day 60, the nitrification activity, as seen in the fluctuation on the inorganic nitrogen profiles, was unstable in both NTFs. After day 60, with the increased influent ammonium concentration, the produced nitrate-N concentration steadily increased. The nitrification performance tendency of both NTFs was similar, showing only slight difference. Statistically, the two NTFs achieved almost the same average nitrification rate (either as ammonium-N removal or produced nitrate-N). Although the aspect ratio for the two NTFs was different, the nitrification performances were similar when they received similar influent ammonium concentrations (resulting in similar ammonium hydraulic surface loading rates).

A linear relationship between ammonium hydraulic surface loading and nitrification rate (ammonium removal rate) was observed in both NTFs. This finding indicated that the nitrification rate increased with the increase in ammonium hydraulic surface loading. The result was consistent with the finding in a study using high-rate NTF for drinking water treatment (van den Akker et al., 2008). Eding et al. (2006) also reported a positive effect of the increased ammonium hydraulic surface loading on the nitrification rate, which may have been caused by the increased availability of ammonium or biocarbonate in the lower depth of the trickling filter. A slight difference (ANOVA, $p>0.05$) was observed in the Pearson's correlation coefficients of the tall (r = 0.869) and short (r = 0.742) NTFs. The positive effect of increased ammonium hydraulic surface loading performed better in the tall NTF than the short NTF. This can be explained by the filter construction design: the filter bed depth of the tall NTF was four times that of the short NTF bed depth. The bottom depth bed of the tall NTF might be able to take the full advantage of ammonium residues from the top. Nevertheless, Eding et al. (2006) suggested that there might be a limit to the impact of hydraulic surface loading on the nitrification rate in trickling filters, because there were more parameters influencing the design and performance of NTF, such as pH, DO and total alkalinity.

In this study, the environmental parameters of the tall and short NTF were compared, with the objective to confirm two NTFs operating under similar conditions. Furthermore, the effects of environmental parameters (influent DO, influent total alkalinity and effluent pH) on the nitrification performance were investigated and compared between the tall and short NTFs. The results showed that the correlation coefficients between the short and tall NTFs for the three investigated parameters were statistically significant (see Table 3.2). These findings revealed that the tall and short NTFs operated under similar environmental conditions. The only difference between the tall and short NTFs in this study was the aspect ratio.

Among the three investigated environmental parameters, effluent pH showed a significant negative correlation coefficient to the nitrification performance (ammonium-N removal rate) for both of the tall and short NTFs. The results revealed that the increased ammonium-N removal rate decreased the pH value in the NTF. Equation 3.1 explained the likely reason for pH decline. The relationship between influent total alkalinity and effluent pH was determined using Equation 3.2. This finding was consistent with the conclusion by Pearce and Edwards (2011). Whilst the impacts of influent DO and influent total alkalinity on the nitrification performance of both NTFs were not significant in this study.

The results of this study confirmed that nitrifying bacteria were growing in the high-rate NTF (both tall and short NTFs). In addition to the aspect ratio, the two NTFs operated under almost the same environmental conditions and received nearly the same ammonium-N hydraulic media surface loading rate. The nitrification performance in both NTFs remained consistent. These findings revealed that the aspect ratio of NTF has no significant impact on nitrification performance in the high rate NTF.

The findings in this study are valuable to water treatment industry, which can design and build the water treatment plant depending on the conditions of location. In the design and construction of large scale trickling filter plant, a high aspect ratio NTF (tall and slim) can make full use of the vertical space of the plant and further save plant area. However, more energy will be consumed to pump water to the top of a tall NTF. A low aspect ratio NTF (short and wide) can save energy for water delivery to the NTF, and also achieve the same nitrification performance as the tall NTF. While a short and wide NTF will require a large plant area to build. Overall, a tall NTF is more suitable to be constructed at the location which has limited area availability, while a short NTF is better to be built at the location which has sufficient field area. A short NTF is also a good alternative for the water treatment plants in developing countries, because the short NTF can save money for water delivery.

The high rate NTF is not only effective for ammonium removal, but also for organic contaminants removal from wastewater. The nitrifying bacteria in NTF were considered to have the potential to biodegrade organic contaminants in wastewater (Roh et al., 2009). The persistence of these contaminants in the environment is an emerging issue that faced by most of the countries (either developing or developed countries) in the world. The application of NTF to remove the organic pollutants is likely to save plant space, compared with the large plant area required for activated sludge treatment. In addition, the cheap and easy maintenance of a passively aerated NTF can greatly reduce the operating cost. All those benefits motivated the application of high-rate NTF to the removal of CoC, which are some emerging organic pollutants, in a laboratory study. The feasibility, removal efficiency and some impact factors are investigated in Chapter 4, 5 and 6.

4 APPLICATION OF HIGH RATE NITRIFYING TRICKLING FILTER TO REMOVE CHEMICALS OF CONCERN FROM WASTEWATER

4.1 Introduction

The occurrence, toxicity and fate of the CoC were summarised in Chapter 1, Section 1.3. It is important to develop an efficient and cost-saving technology for CoC removal from waters. Since the bacteria (e.g. ammonium-oxidising bacteria) in NTF have the ability to biodegrade some CoC (Roh et al., 2009), investigations were conducted on the feasibility of removing CoC by applying a high-rate NTF. In addition to biodegradation, sorption of CoC by the biomass and the possible contacting materials is also a potential pathway for chemicals removal. Sorption by biomass was widely studied and the results showed negligible removal through biomass sorption. Thus, in the current study, the sorption of CoC by the surface of pure materials in the NTFs was taken into account.

Generally, NTFs are primarily used for the removal of nitrogen from wastewaters. Most of the previous studies were focused on using low rate NTFs to remove the ammonium-nitrogen at concentration level in wastewater. While uniquely, van den Akker et al. (2008) carried out research on the application of high-rate NTFs to remove nitrogen from potable water, in which the ammonium concentration was 10- to 50- fold lower than in wastewater. The completed nitrification demonstrated that nitrifiers were abundant in this high-rate NTF system (van den Akker et al., 2008).

Because most of the organic contaminants have bioactive characteristics, there has been growing interest in removal of these chemicals using biological treatment technologies. Among these chemicals, caffeine has been shown by many researchers to be one of the most efficiently removed, with removal of 80% to 100% (Camacho-Muñoz et al., 2012, Kim et al., 2007b, Sui et al., 2010, Trinh et al., 2011). The removal efficiencies of chemicals vary across different treatment technologies. Typically, acetaminophen was removed (96%) by activated sludge treatment (Yamamoto et al., 2009), whereas lower removal efficiency (71.4 ± 10.6%) was obtained in a moving bed bioreactor (Luo et al., 2014a). Trinh et al. (2011) reported that both bisphenol A and DEET were removed in a full-scale membrane bioreactor, where removals of more than 90% were achieved. Lower removal figures have been reported for benzotriazole (Reemtsma et al., 2010), atrazine (ATZ) and trimethprim (Zearley and Summers, 2012). A batch study by Shi et al. (2004) confirmed that

17α-ethynyestradiol (EE2) could be efficiently degraded by nitrifying bacteria, and the degradation rate constant was 0.035 h^{-1} at initial concentration of 1 mg L^{-1}. Therefore, biological treatment has been shown to be a feasible approach for removing CoCs.

Much of the previous work has concentrated on suspended growth biological treatment systems, such as activated sludge treatment (Shi et al., 2004, Urase and Kikuta, 2005, Yang et al., 2011), moving bed bioreactor (Luo et al., 2014a), and membrane bioreactor (De Gusseme et al., 2009, Trinh et al., 2011). However, the performance of attached growth biofilm systems for the removal of organic contaminants has received less attention. Zearley and Summers (2012) constructed a bio-filter system with sand media and reported removal efficiencies ranging from <15% to nearly complete removal. The laboratory- and pilot-scale experiments conducted by Ho et al. (2011) revealed that biologically active sand filtration was ineffective in removing these chemicals from wastewater, with no ATZ removal and 41 ± 21% removal for EE2; however, bacteria that existed in the biofilm had the potential to degrade ATZ or EE2. Furthermore, the enhanced biodegradation of some CoCs in the nitrifying enriched biological treatment systems (Batt et al., 2006, Shi et al., 2004, Tran et al., 2009) illustrated that the bacteria in nitrifying system have the biodegradation ability to remove CoCs. The genera (*Nitrosomonas europaea*) associated with biodegradation have been detected in many NTF systems (van den Akker et al., 2008). Considerably higher removal efficiencies of some chemicals were obtained in a batch study for the attached biofilm compared to the suspended activated sludge (Falås et al., 2013).

Many of the previous studies that have characterised the removal of CoCs were undertaken at very low initial concentrations, resulting in extremely low or undetectable concentrations in the treated effluent. This makes it difficult to determine the effect of operating conditions on removal. The problem was overcome in this study by employing high challenge doses of CoCs in the order of 100 to 1000-fold higher than other studies. Furthermore, because the bacteria which are responsible for biodegrading the organic contaminants are aerobic species, and also because Johnson and Sumpter (2001) concluded that the chemicals degradation should increase with an increase in hydraulic retention time, a recirculating aerobic NTF system was selected for the research reported here. The goals of this study were to determine the feasibility of applying high-rate NTF utilising cross-flow plastic packing to the removal of CoCs; and to evaluate the removal rates of the selected

CoCs in NTFs.

4.2 Methods

4.2.1 Chemicals

All the selected CoCs including caffeine (CAF), acetaminophen (ACE), N, N-diethyl-m-toluamide (DEET), benzotriazole (BEZ), 17α-ethynylestradiol (EE2), trimethoprim (TRI), atrazine (ATZ) and bisphenol A (BPA) were purchased from Sigma-Aldrich (Sigma-Aldrich, Australia). Some important characteristics of these CoCs are listed in Table 1.1 (see Chapter 1, Section 1.3). The HPLC-grade acetonitrile and methanol were purchased from Sigma-Aldrich. A stock solution (1 g L^{-1}) of each authentic standard was prepared in HPLC-grade methanol.

4.2.2 Generation of standard lines of CoCs for HPLC analysis

In order to obtain the retention time (RT), limit of detection (LOD) and the standard line of each CoC, several concentrations of authentic standards (5000 µg L^{-1}, 2000 µg L^{-1}, 1000 µg L^{-1}, 500 µg L^{-1}, 200 µg L^{-1}, 100 µg L^{-1} and 20 µg L^{-1}) were prepared from the 1 g L^{-1} stock solution of the respective CoCs in Reverse Osmersis (RO) water in HPLC vials. The HPLC analyses were started from a blank sample (containing RO water only), which was followed by the standard samples, using the method described in Chapter 2, Section 2.4.7. Calibration generation was performed in duplicate. Statistical analysis using Spearman's correlation coefficient (r_s) was used to identify the statistical significance of calibration curves. Statistical significance was accepted at the $p<0.05$ level.

4.2.3 Sorption of CoCs to the surface of pure materials in NTF system

The sorption of the eight selected CoCs (CAF, ACE, EE2, ATZ, BPA, BEZ, DEET and TRI) by pure contacting materials (filter PVC walls, packing materials and silicon tubing) was measured by immersing samples of material of known surface area individually in the respective CoC solution, which was prepared by adding 1 mL of the CoC stock solution into 100 mL tap water. Each solution, in which the test material was immersed, was sterilised and stored in a 250 mL sealed bottle, and incubated in the dark at 20 ± 2 °C for 24 h. A control solution of each CoC was used in absence of the test materials. The initial and final concentration of the respective

CoC was determined by HPLC and the amount of CoC adsorption calculated by difference and expressed as mg m^{-2} of contacting material.

4.2.4 NTFs for removal of CoCs

As described in Chapter 2, Section 2.3, the laboratory recirculating, aerobic NTFs system, which consisted of four parallel filters, was used for the removal of CoC. One column was used as a control nitrifying column in the absence of any CoC, and the remaining three columns were challenged with CoC individually to avoid potential interaction. The development of a nitrifying biofilm on the surface of the packing material was aided by flooding and incubating the packing media with wastewater activated sludge for one week prior to the commencement of the experiments.

Following incubation over one week, the activated sludge was drained from the filters. The recirculating NTFs were then continuously fed at a hydraulic flow rate of 20.1 L h^{-1} with a 5 mg NH_4-N L^{-1} ammonium chloride solution which was used as the nitrogen source to support continuous nitrification for 2 months to develop a mature nitrifier-dominated biofilm within the filters. The nitrification rate was determined from the reduction of NH_4-N concentration and the increase of NO_3-N concentration throughout the time operated, in either the absence or presence of CoC.

The initial concentration setting of the CoC applied to the NTF depended on the LOD of the respective CoC. The initial concentration, in a 5 mg NH_4-N L^{-1} solution in tap water, was CAF, ACE, BEZ, TRI and BPA 1 mg L^{-1}, ATZ 2 mg L^{-1}, EE2 5 mg L^{-1} and DEET 10 mg L^{-1}. Three of the four filters, each received a solution of one of the respective CoCs in a solution containing 5 mg NH_4-N L^{-1}, and were run parallel, to the fourth column operating as a control column that received the 5 mg NH_4-N L^{-1} solution but was not exposed to any CoC. Ammonium-N was compensated every 4 hours to maintain the nitrification rate throughout the experiments. All the experiments were performed in duplicate. The CoC degradation rate was expressed as a relative concentration C_t/C_0, where C_t was the concentration at t time and C_0 was the initial concentration of each chemical.

4.2.5 Effect of the initial concentration of CoC on removal efficiency in NTF

In order to investigate the effect of CoC initial concentration on the removal performance of CoCs by NTF, another series of experiments were conducted. During these experiments, the concentration of CoC was cut to half of the previous experiments. The initial concentration, in a 5 mg NH_4-N L^{-1} solution in tap water, was CAF, ACE, BEZ, TRI and BPA 0.5 mg L^{-1}, ATZ 1 mg L^{-1}, EE2 2.5 mg L^{-1} and DEET 5 mg L^{-1}. The other operation parameters were kept the same. Furthermore, in order to explore more removal potential, the recirculation time was prolonged to 48 h for each operation. Ammonium-N was compensated (as above) to maintain the nitrification throughout the experiments. All of the experiments were performed in duplicate.

4.2.6 Sampling and analysis

The water samples were taken directly from the effluent tubing on the bottom of each filter. The 10 mL grab sample was obtained every 2 hours for the first 12 hours, and then after 24 hours, and 27 hours. For the half concentration experiments, sampling was performed until 48 hours, before analysing the concentrations of CoC by using procedures described in Chapter 2, Section 2.4.7, 1 mL of each of the samples was transported to the HPLC vial and stored in the freezer at -18°C. The rest of samples were stored in the cold room at 3 ± 2 °C and analysed within 2 days for ammonium-N, nitrite-N and nitrate-N concentrations by using procedures that described in Chapter 2, Section 2.4.

4.3 Results

4.3.1 Calibration generation

The calibration curve of each CoC was obtained by analysing the authentic standards. Table 4.1 presents the RT and LOD of the respective standard. The RT was identified when a clear peak appeared. The LOD was determined by the lowest concentration which was able to be detected using the method in this study.

Figure 4.1 and 4.2 show the calibration curve of each standard. The calibration curve was created by showing the relationship between chemical concentration (*x*-axis) and the peak area (*y*-axis). The Spearman statistical analysis results showed that the calibration curves of all selected CoCs were statistically reliable (r_s=0.999, p<0.01).

Table 4.1 The retention time (RT) and limit of detection (LOD) for CoCs.

chemicals	**Abbreviation**	**RT* (min)**	**LOD** (µg L^{-1})**
Caffeine	CAF	8.46	20
Acetaminophen	ACE	5.35	100
N, N-diethyl-m-toluamide	DEET	13.98	1000
benzotriazole	BEZ	9.26	100
17α-ethynylestradiol	EE2	15.25	500
Trimethoprim	TRI	8.69	100
Bisphenol A	BPA	14.18	100
Atrazine	ATZ	13.80	200

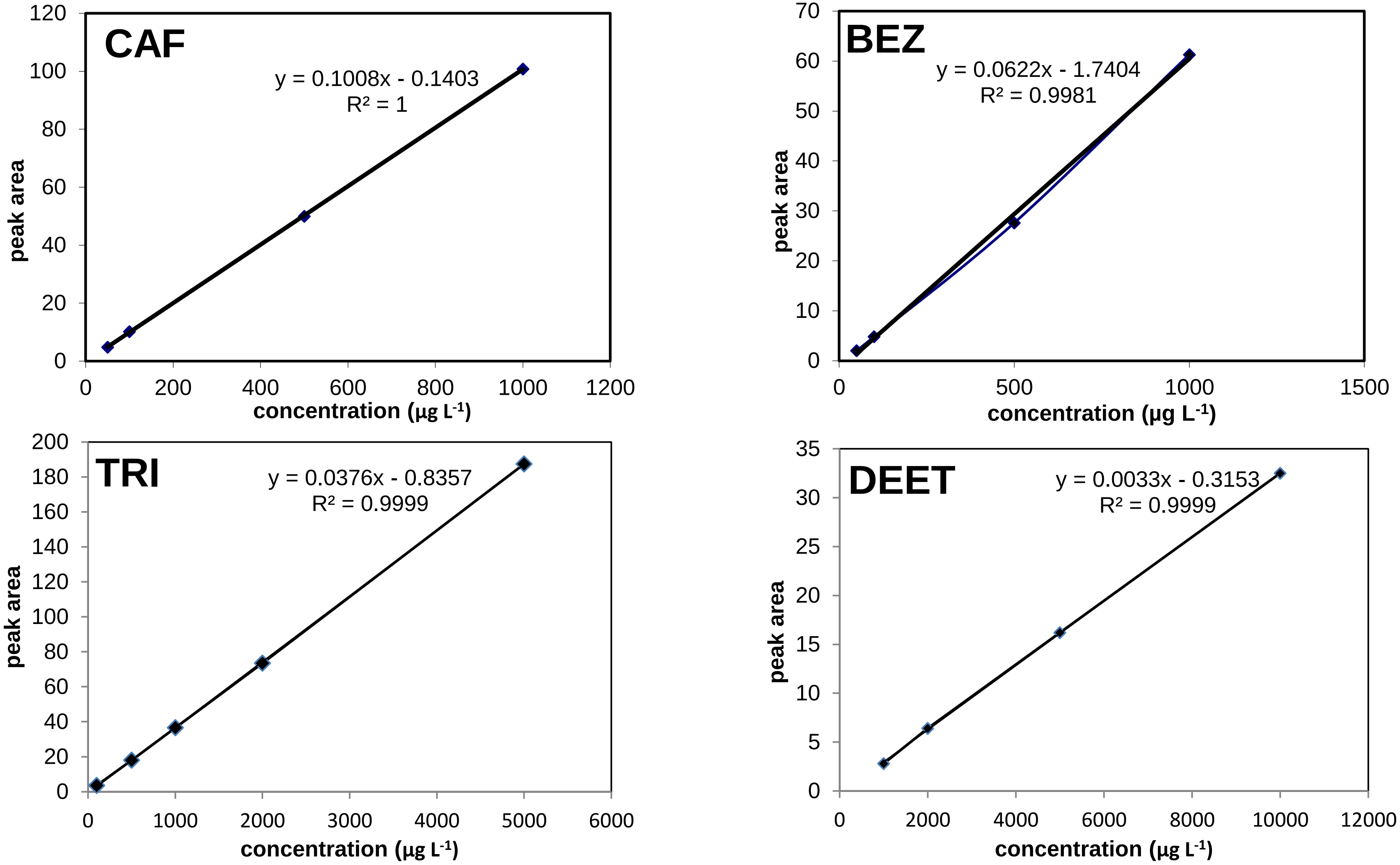


Figure 4.1 Standard lines of caffeine (CAF), N, N-diethyl-m-toluamide (DEET), trimethoprim (TRI) and benzotriazole (BEZ). All the points present the mean value (± 1 SD).

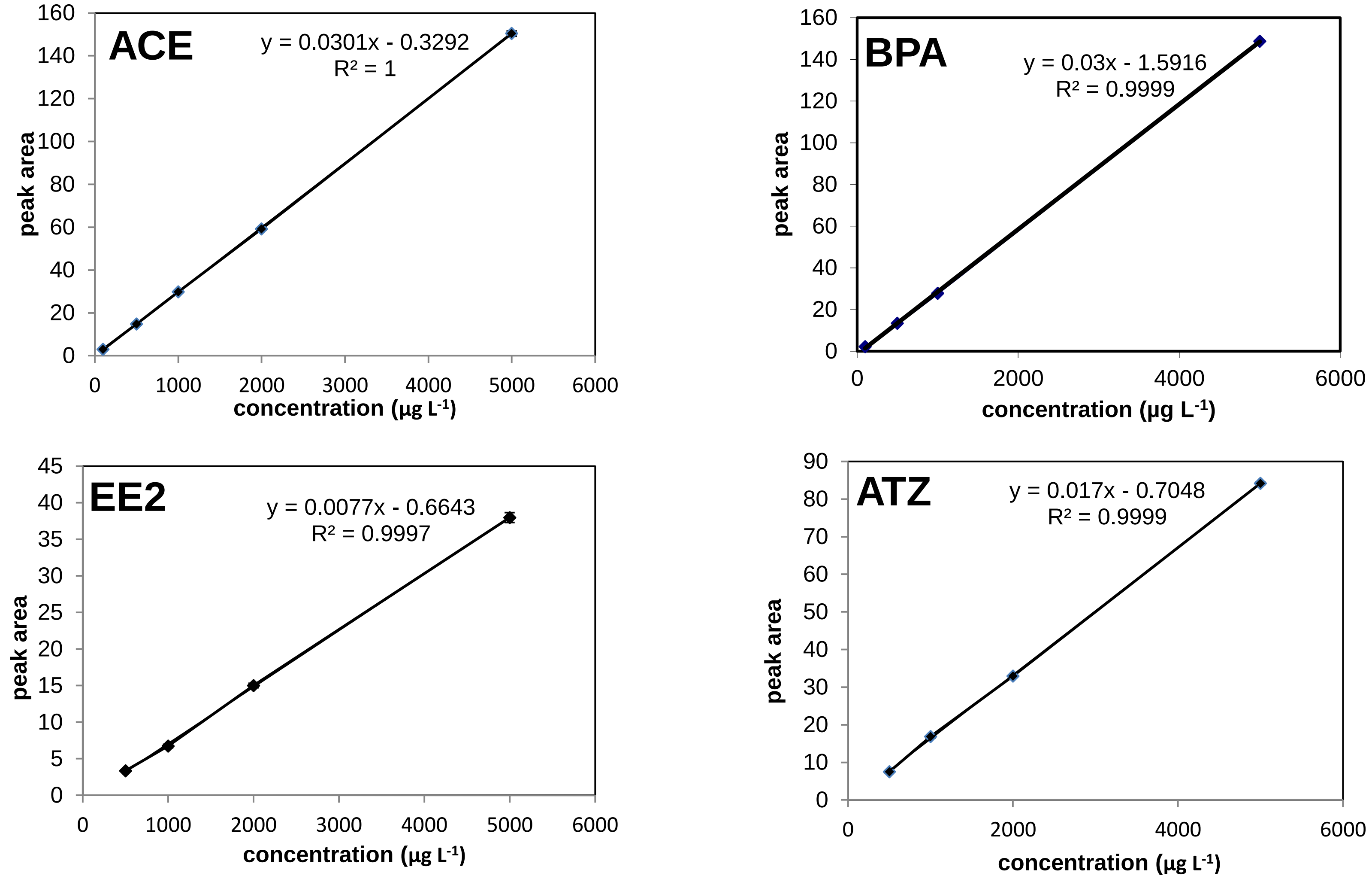


Figure 4.2 Standard lines of acetaminophen (ACE), bisphenol A (BPA), 17α-ethynylestradiol (EE2) and atrazine (ATZ). All the points present the mean value (± 1 SD).

4.3.2 Removal of CoC by sorption

In the sorption experiments, because all the materials and solutions were sterilised and stored in capped bottles, the amount of chemicals loss could be considered to be sorption onto the material surface, including polypropylene packing material, the silicon tubing and the polyvinyl chloride (PVC) pipe column wall.

During the 24 hours of incubation, a minimal amount of CoC was adsorbed on the surface of the polypropylene packing material (Table 4.2), whereas for most of the CoCs, there was higher sorption by the PVC wall of the filter. The highest value recorded for sorption by the PVC pipe wall was 5 mg m^{-2} for ATZ. Amongst the other construction materials, the surface of the connecting silicon tubing adsorbed significant quantities of EE2 (~14 mg m^{-2}) and ATZ (~27 mg m^{-2}). The highest recorded sorption by silicon tubing was for DEET (~37 mg m^{-2}), whereas its sorption by the pipe wall and packing material was negligible. In contrast, minimal amounts of CAF, BAP, BEZ, ACE and TRI were adsorbed by all three construction materials. Furthermore, the estimated sorption amount of CoCs by the total wetted surface area of the respective construction material in NTF, which was calculated from the sorption rate displayed in Table 4.2, was minimal (0.002 mg to 1.108 mg). The results presented here were for sorption in the absence of biofilm.

4.3.3 Nitrification performance of NTF before adding individual CoC

After the first two months of operation, a stable NH_4-N concentration decrease and continuous NO_3-N increase with time were obtained. Figure 4.3 shows that at an initial concentration of 5 mg NH_4-N L^{-1}, ammonium-N concentration dropped to about 0.2 mg L-1, coupled with the steady increase of nitrate-N concentration and a minimal nitrite-N concentration in the NTFs. The inorganic nitrogen profiles in the NTFs indicate that nitrification was almost completely achieved after 9 hours of recirculation through the biofilters, and this was equivalent to a nitrification rate of 0.52 ± 0.15 mg NH_4-N L^{-1} h^{-1}.

Table 4.2 Sorption of CoC (mg d^{-1}) in the recirculating NTF system in 24 h was calculated from the sorption rate (mg m^{-2} d^{-1}) of the batch sorption test and the contact surface area (m^2) of the component materials of the NTF.

	Wetted surface area of material used in Batch sorption test (m^2)			**Total wetted surface area of the respective material in the NTF system (m^2)**		
Materials	Polypropylene filter material	Silicon tube	PVC pipe	Polypropylene filter material	Silicon tube	PVC pipe
Wetted surface area (m^2)	0.0096	0.002	0.003	1.06	0.03	0.24
Compounds	**Areal batch sorption rate (mg m^{-2} d^{-1})**			**Estimated daily total sorption in NTF (mg d^{-1})**		
CAF	0.019	0.491	0.153	0.021	0.015	0.024
BPA	0.055	0.591	0.008	0.064	0.018	0.002
BEZ	0.445	2.519	0.082	0.466	0.076	0.012
ACE	0.174	0.171	0.144	0.184	0.005	0.024
ATZ	0.201	26.85	4.546	0.212	0.806	1.092
EE2	0.158	14.48	1.564	0.167	0.434	0.374
TRI	0.055	2.176	0.019	0.064	0.065	0.005
DEET	0.046	36.94	0.216	0.049	1.108	0.052

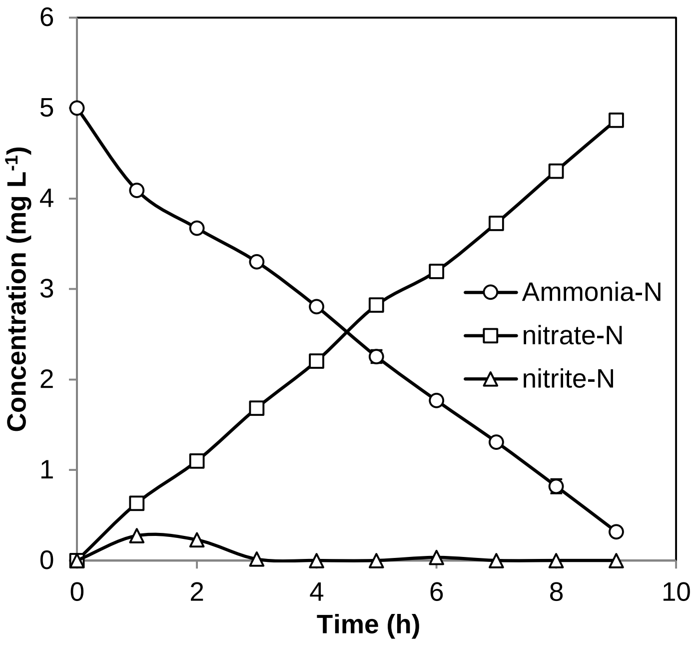


Figure 4.3 Representative ammonium-N (mg NH_4-N L^{-1}) removal against time in a recirculating NTF fed a solution of 5 mg NH_4-N L^{-1} in the absence of CoC, and the removal rate was 0.52 ± 0.15 mg NH_4-N L^{-1} h^{-1}. All data points present parameter means ± 1 SD.

4.3.4 Nitrification performance in the NTFs in the presence of individual CoC

In the presence of individual CoC, the removed ammonium concentrations and the generated sum nitrite-N and nitrate-N was recorded. The nitrification performance of the NTF following challenge with CoC (CAF, BEZ, BPA, ATZ, EE2, TRI, ACE and DEET) is presented in Figure 4.4a (ammonium removal) and Figure 4.4b (sum nitrite-N and nitrate-N generation). It can be seen that in the presence of CoC, the ammonium removal and nitrite-N/nitrate-N generation in the NTFs were both severely depressed, compared with the control NTF (without CoC challenge).

In the presence of individual CoC, ammonium removal over time was minimal during the first 8 hours (Figure 4.4a). After 8 hours recirculation in the columns, the ammonium removal started to increase, and achieved about 2 mg NH_4-N L^{-1} ammonium removal after 12 hours recirculation (Figure 4.4a). No statistically significant difference of ammonium removal between the NTFs challenged with different CoCs was observed (ANOVA, p>0.05). Nevertheless, in the control NTF, ammonium removal increased steadily and showed statistically significant difference with that challenged with individual CoC (ANOVA, p<0.05).

Similarly, as shown in Figure 4.4b, in the presence of CoC, generated nitrite-N and nitrate-N concentration over time maintained much lower than that in the control NTF without CoC challenge. The difference between nitrite-N/nitrate-N concentrations generated in the control NTF and the NTFs challenged with individual CoC was statistically significant (ANOVA, p<0.05). However, the nitrification behaviour in the NTFs challenged with different CoC was quite similar, no statistically significant difference was observed (ANOVA, p>0.05).

Overall, nitrification performance was depressed by the challenge of individual CoC in the NTFs.

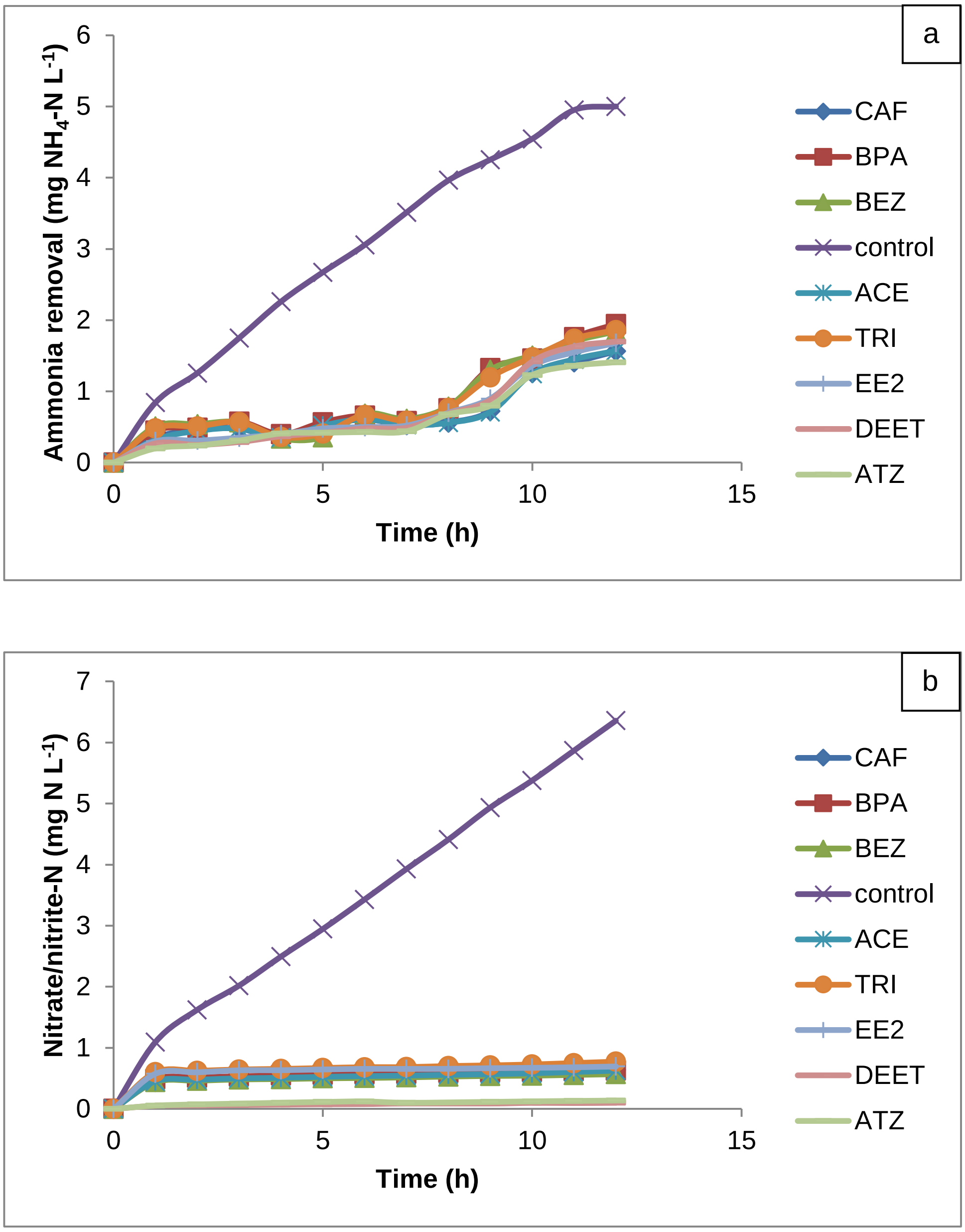


Figure 4.4 Nitrification performance that shown as ammonium removal (a) and nitrate/nitrite-N generation (b) in the control NTF and the NTFs in the presence of individual CoC.

4.3.5 Removal of CoC in NTF

Figure 4.5 presents the removal rates of CoCs as relative concentration C_t/C_0, which was determined by dividing the concentration amount at *t* time by the initial concentration of each chemical. The CoCs showed different removal rates within the NTFs, which maintained a nitrification rate of 0.52 ± 0.15 mg NH_4-N $L^{-1}h^{-1}$.

CAF degraded rapidly within 12 hour and ended with a C_t/C_0 value of 0.02, equal to a removal percentage of 98%. BPA and BEZ degraded much more slowly, where C_t/C_0 was 0.73 and 0.57 (equal to removal percentage of 27% and 43%), respectively. ATR and DEET demonstrated very similar levels of removal in this study, where the C_t/C_0 values were 0.51 and 0.41 respectively after 21 hour of recirculation. ACE was removed gradually, reaching a C_t/C_0 value of 0.41, and showed a linear decrease with time (Figure 4.5), suggesting that there was potential for further removal in NTF. The relative concentration of EE2 after 24 hours recirculation through the NTF was 0.52. TRI was poorly removed by the NTF, reaching a steady C_t/C_0 value of 0.82 after 24 hours.

The susceptibility of CoC to removal by the recirculating NTF was in the order of CAF>ACE>EE2>ATR>DEET>BEN>BPA>TRI. CAF and TRI were the most and least susceptible respectively to treatment in the NTF.

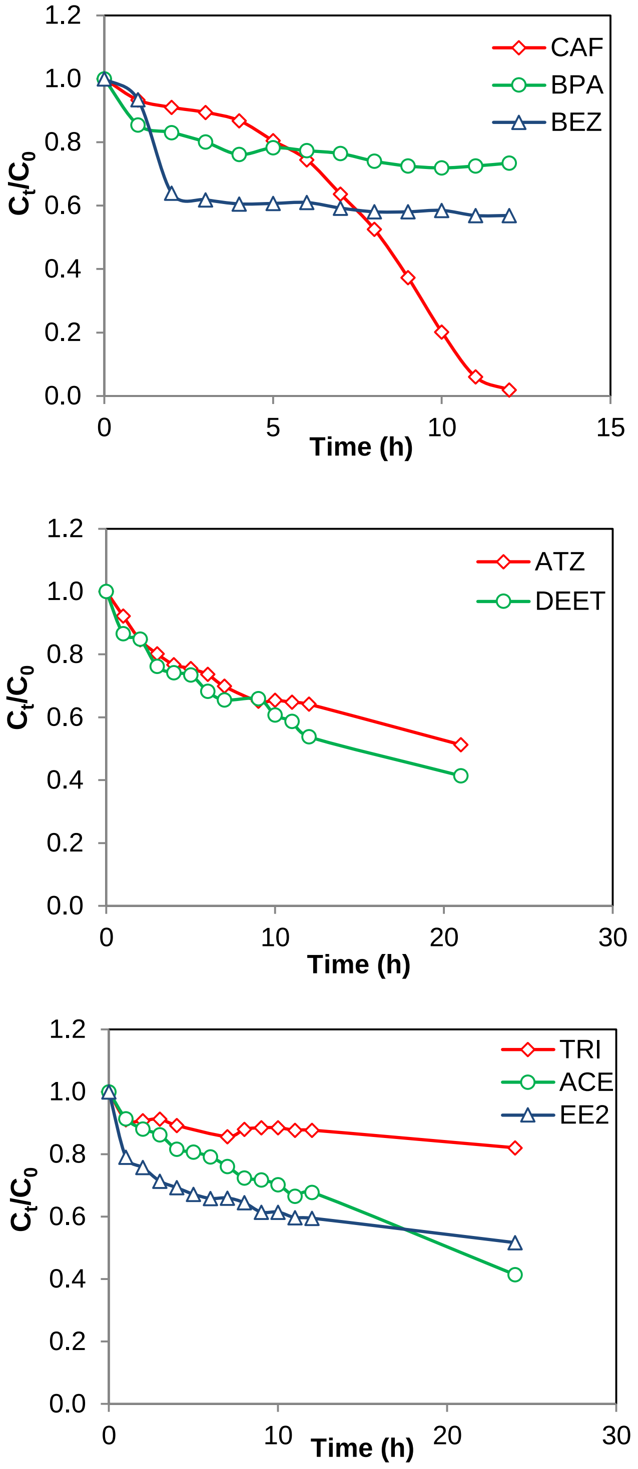


Figure 4.5 The removal of chemicals of concern at a NH_4-N removal rate of 0.52 ± 0.15 mg NH_4-N L^{-1} h^{-1}, CAF, BPA, BEZ, ATZ, DEET, TRI, ACE and EE2 following recirculation through a nitrifying trickling filter. C_t/C_0 is the relative concentration which was obtained by dividing the concentration (C_t) at *t* time by the initial concentration (C_0) of each chemical of concern.

4.3.6 Contribution of sorption by the pure contact materials and degradation by the bacteria in NTF on the total removal percentage of CoC

From Figure 4.6, it can be observed that the contributions of sorption and degradation to the total removal percentage vary for the different investigated chemicals. Sorption contributed the least to the total removal of CAF and the most to the total removal of ATZ in NTF.

For CAF, BPA, ACE and TRI, more than 90% of the total removal was caused by degradation by bacteria on the packing material surface of the NTF. For CAF especially, a large portion (99.39%) of total removal was the contribution of degradation. For BEZ, DEET and EE2, the sorption accounted for about 13% to 20% of the gross removal. The dominant sorption pathway for DEET removal was onto the surface of the silicone tube (18.9% of the total removal), and most of the BEZ sorption occurred on the surface of polypropylene packing material (10.89% of the total removal). The largest portion of sorption in the total removal (42.3%) was observed for ATZ. The two primary sorption pathways for ATZ were onto the surface of the silicone tube and the PVC pipe wall, with portions of the total removal of 16.54% and 22.4%, respectively.

Overall, degradation by the bacteria in NTF could be considered to be the primary removal mechanism for all investigated chemicals in this study.

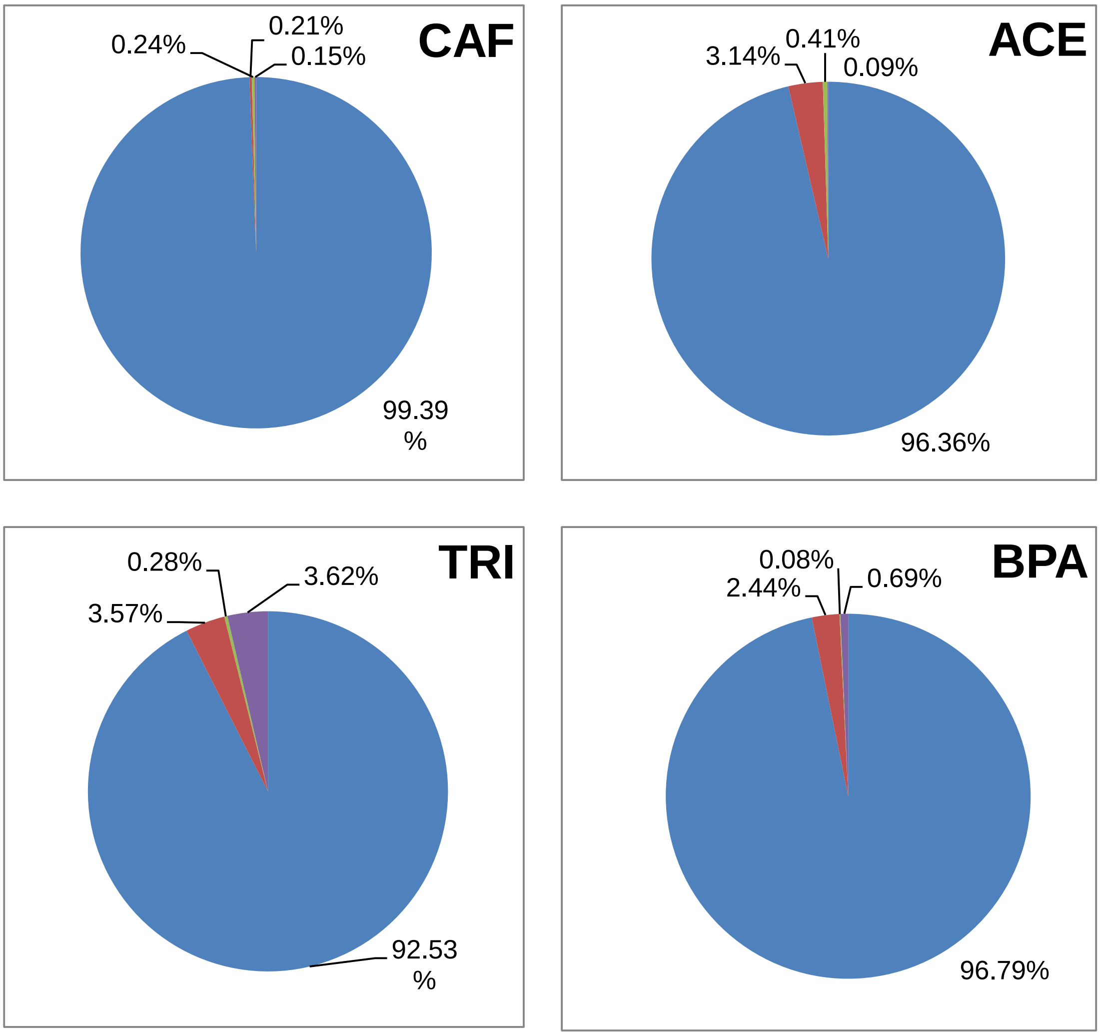
Figure 4.6 Contribution of sorption by construction materials (polypropylene packing material, PVC pipe wall and silicone tubing) and degradation by bacteria in biofilm, as percentage of total removal percentage of respective chemical: CAF, BPA, BEZ, ATZ, DEET, TRI, ACE and EE2 in NTF, with higher initial CoC concentrations of 1 mg L^{-1}, 1 mg L^{-1}, 1 mg L^{-1}, 2 mg L^{-1}, 10 mg L^{-1}, 1 mg L^{-1}, 1 mg L^{-1} and 5 mg L^{-1}, respectively.

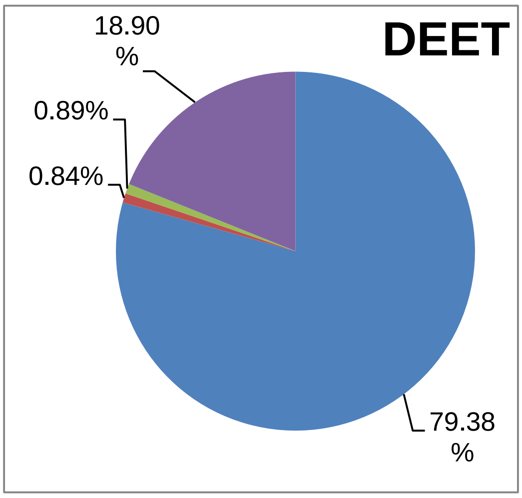
🟦 Degradation by bacteria in biofilm

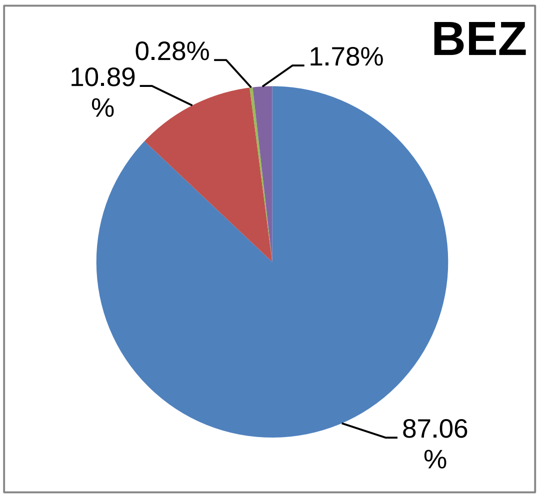
🟥 Sorption by polypropylene packing material

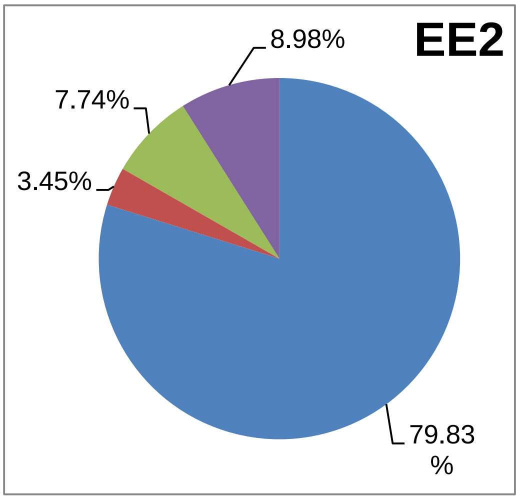
🟩 Sorption by PVC pipe wall

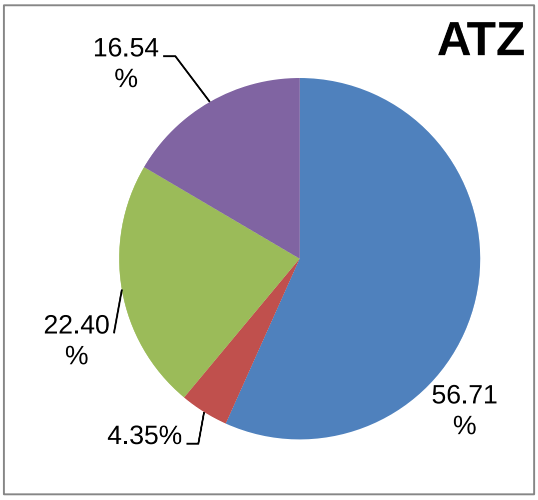
🟪 Sorption by silicone tubing




DEET
18.90 %
0.89%
0.84%
79.38 %


BEZ
0.28%
1.78%
10.89 %
87.06 %


EE2
8.98%
7.74%
3.45%
79.83 %


ATZ
16.54 %
22.40 %
4.35%
56.71 %

4.3.7 Impact of the initial concentration of CoCs on NTF performance

When the initial concentration of CoCs was reduced to a value of 0.5 mg L^{-1} for CAF, BPA, BEZ, ACE and TRI; 1 mg L^{-1} for ATZ; 2.5 mg L^{-1} for EE2 and 5 mg L^{-1} for DEET, the recorded removal percentage changes were variable.

From Figure 4.7, it can be observed that the removal percentages of DEET, TRI, BPA and ATZ changed little when operated under the lower initial concentration, with the removal percentage differences less than 10%. However, with reduced initial concentration, the removal efficiency for ACE decreased from 58.59% to 44.3%, and the removal percentage of EE2 decreased more than 25%. Noticeably, very low removal percentages were observed for CAF and BEZ, with removal efficiency of 12.3% and 3.45% respectively, which indicated a statistically significant (ANOVA, $p<0.05$) reduction in removal percentage when operating under lower initial concentration.

4.3.8 Contribution of sorption by the pure contact materials and degradation by the bacteria in NTF on the total removal percentage of CoC at lower CoC initial concentrations

Figure 4.8 shows that the contributions of sorption and degradation to the total removal percentage vary for the different investigated compounds. Sorption contributed the least to the total removal of BPA and the most to the total removal of ATZ in NTF.

For CAF, BPA, ACE and TRI, more than 90% of the total removal was contributed by degradation by bacteria on the packing material surface of the NTF. For DEET, the sorption accounted for about 18% of the gross removal. The dominant sorption pathway for DEET removal was onto the surface of the silicone tube (16.01% of the total removal). The portion of sorption for BEZ, ATZ and EE2 ranged from 30% to 40%, and most of the BEZ sorption occurred on the surface of polypropylene packing material (29.68% of the total removal). The largest portion of total sorption in the total removal (37.61%) was observed for ATZ. The two primary sorption pathways for ATZ were onto the surface of the silicone tube and the PVC pipe wall, with portions of the total removal of 14.37% and 19.47%, respectively.

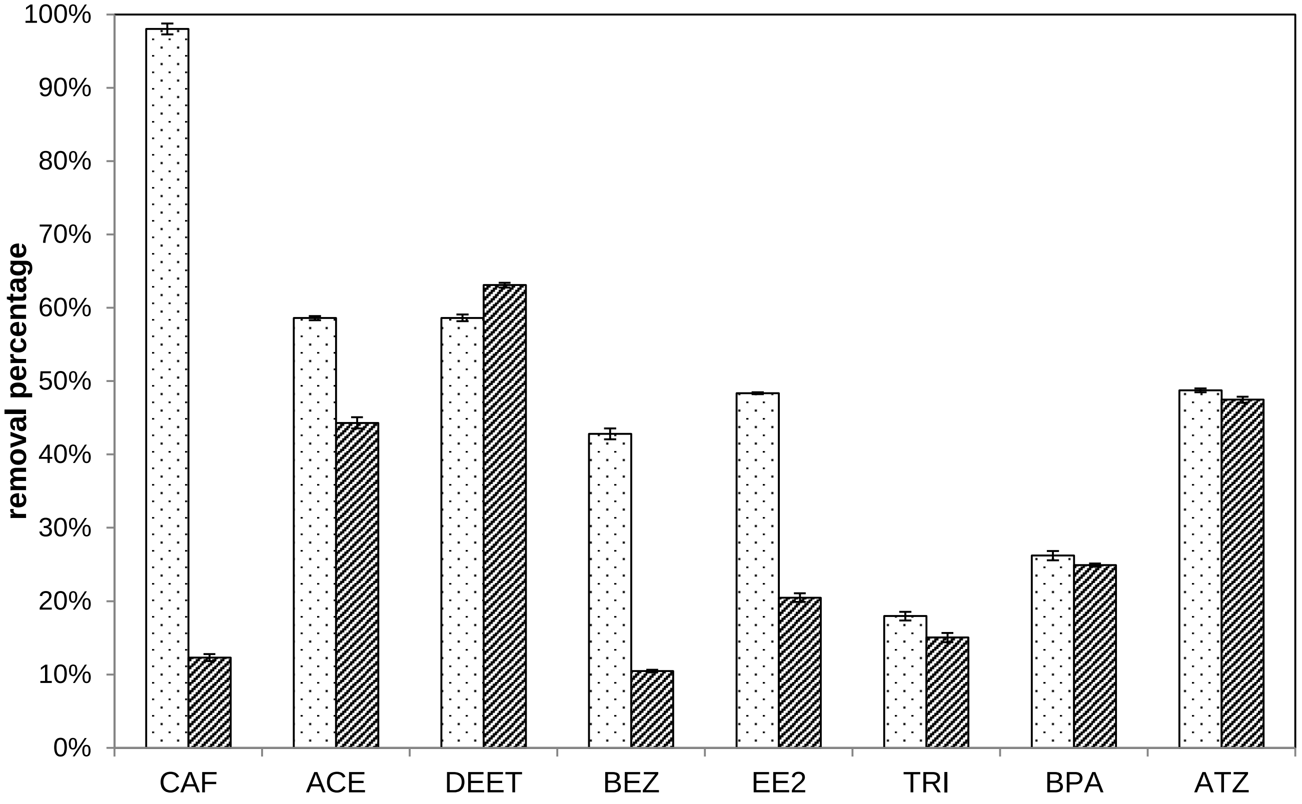
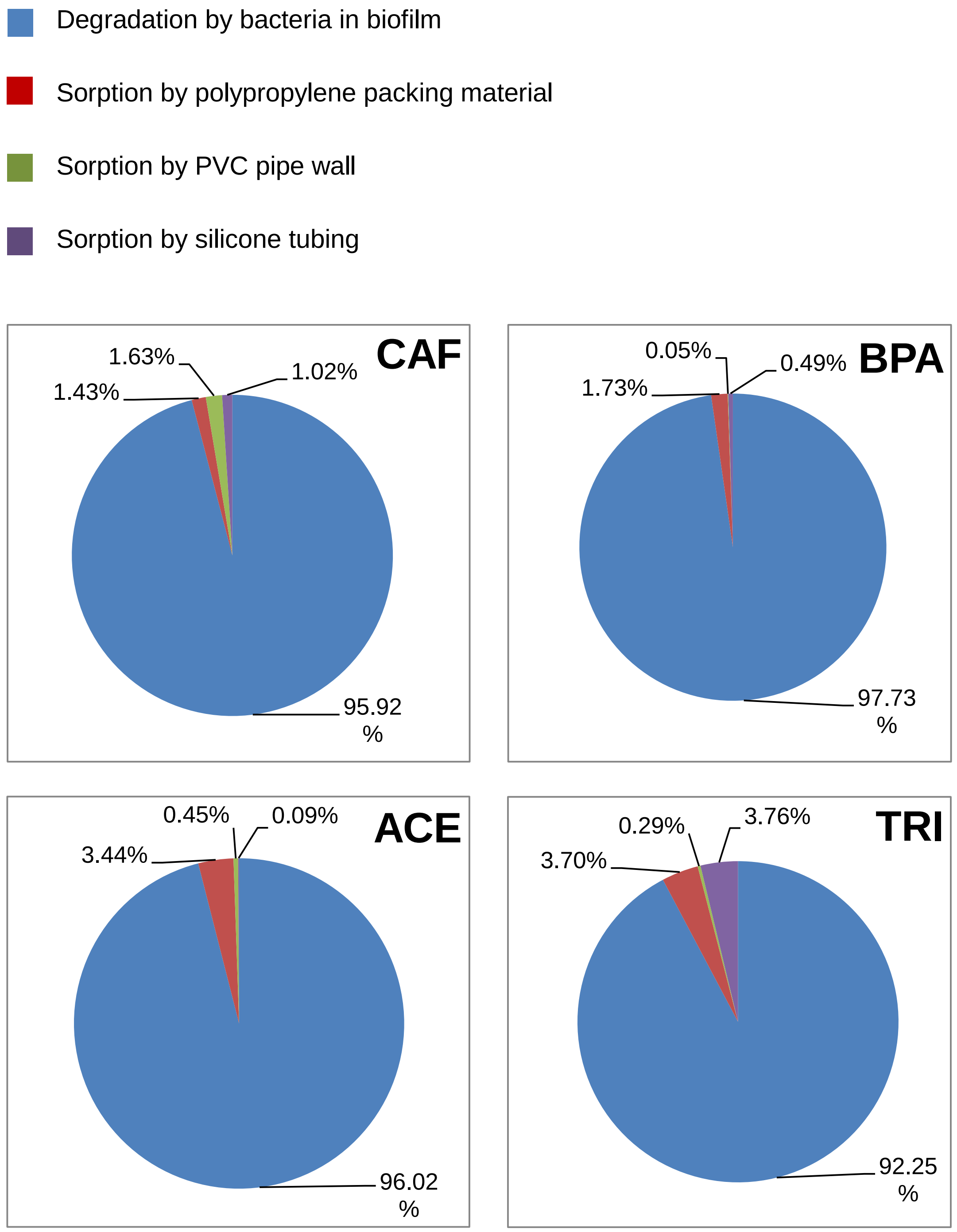
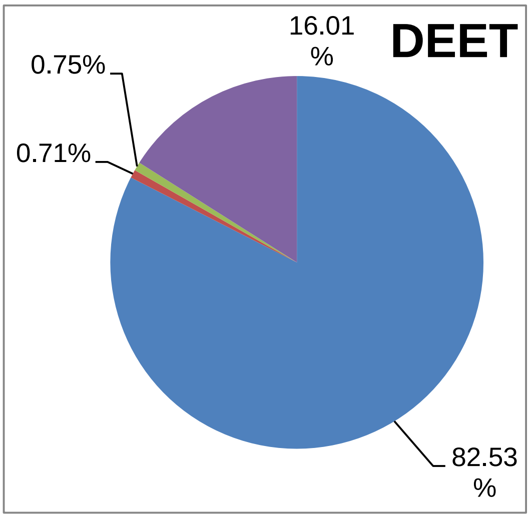
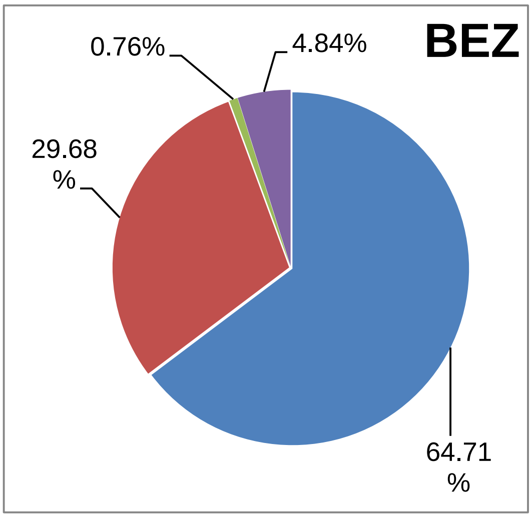


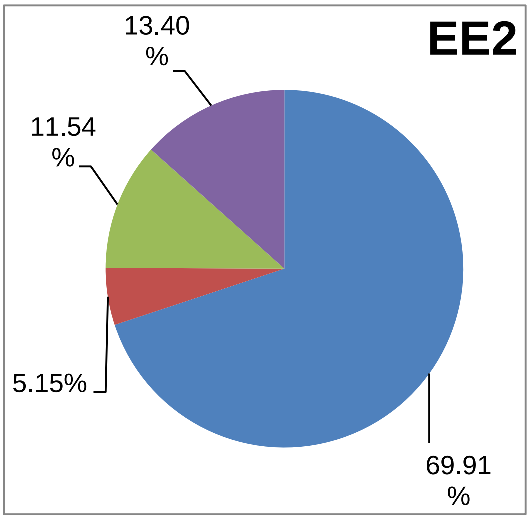
Figure 4.7 Comparison of removal percentages of CAF, ACE, DEET, BEZ, EE2, TRI, BPA and ATZ under different initial concentrations: (⬚) removal % under respective initial concentrations of 1 mg L^{-1}, 1 mg L^{-1}, 10 mg L^{-1}, 1 mg L^{-1}, 5 mg L^{-1}, 1 mg L^{-1}, 1 mg L^{-1} and 2 mg L^{-1}; (▨) removal % under respective initial concentrations of 0.5 mg L^{-1}, 0.5 mg L^{-1}, 5 mg L^{-1}, 0.5 mg L^{-1}, 2.5 mg L^{-1}, 0.5 mg L^{-1}, 0.5 mg L^{-1} and 1 mg L^{-1}. All data points show mean values ± 1 SD.

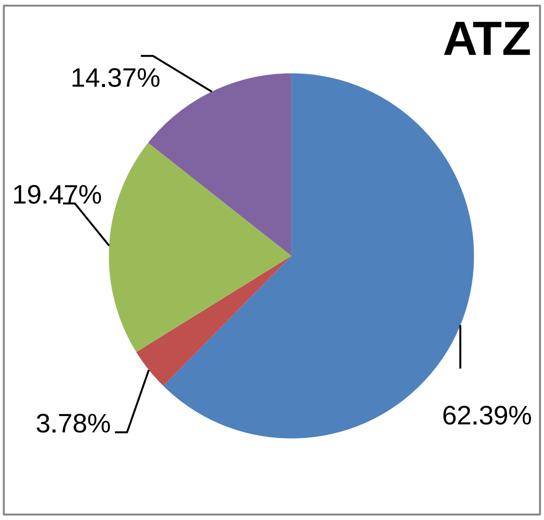
Figure 4.8 Contribution of sorption by construction materials (polypropylene packing material, PVC pipe wall and silicone tubing) and degradation by bacteria in biofilm, as percentage of total removal percentage of respective chemical: CAF, BPA, BEZ, ATZ, DEET, TRI, ACE and EE2 in NTF, with higher initial CoC concentrations of 0.5 mg L^{-1}, 0.5 mg L^{-1}, 0.5 mg L^{-1}, 1 mg L^{-1}, 5 mg L^{-1}, 0.5 mg L^{-1}, 0.5 mg L^{-1} and 2.5 mg L^{-1}, respectively.




DEET
16.01 %
0.75%
0.71%
82.53 %


BEZ
0.76%
4.84%
29.68 %
64.71 %


EE2
13.40 %
11.54 %
5.15%
69.91 %


ATZ
14.37%
19.47%
3.78%
62.39%

4.3.9 Further removal with prolonged operation time

Figure 4.4 shows the removal tendencies of CoCs with time, which indicates the potential for further removal. From Figure 4.9, it can be seen that when the operation time was prolonged to 48 hours, further removal percentages were observed for all selected CoCs.

The largest improvement in removal percentage was achieved for EE2, with a further removal of 37.68%, reaching 58.14% after 48 hours. The removal efficiency improvement for EE2 was statistical significant (p>0.05). CAF, BEZ and TRI obtained only a small increase in removal percentage, with less than 5% improvement in removal efficiency. For the remainder of the chemicals (ACE, DEET, BPA and ATZ), the removal efficiencies were enhanced with additional operation time, with improvements ranging from 10% to 15%. These findings indicated that the prolonged operation time increased the contacting time between chemicals and the nitrifying bacteria in the NTF. The longer contacting time resulted in a long hydraulic retention time (HRT), which is significantly important in the biological treatment of chemicals of concern (Zorita et al., 2009).

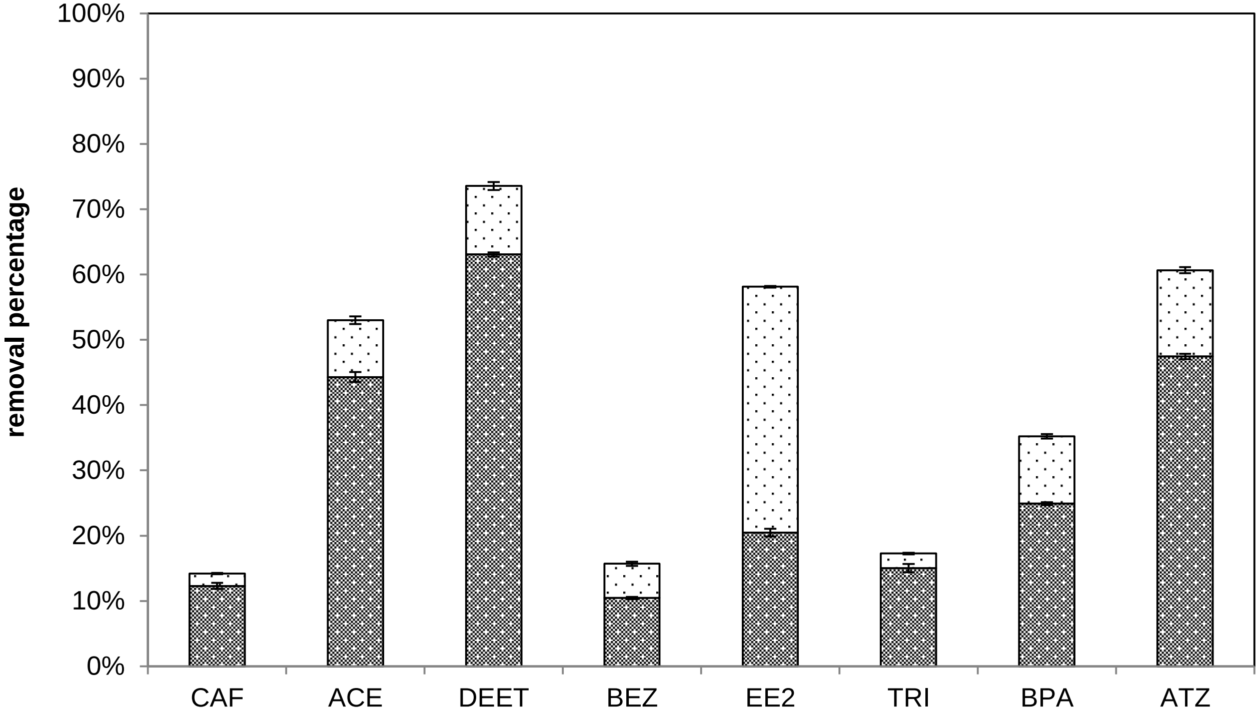


Figure 4.9 The removal percentages of CAF, ACE, DEET, BEZ, EE2, TRI, BPA and ATZ under initial concentrations of 0.5 mg L^{-1}, 0.5 mg L^{-1}, 5 mg L^{-1}, 0.5 mg L^{-1}, 2.5 mg L^{-1}, 0.5 mg L^{-1}, 0.5 mg L^{-1} and 1 mg L^{-1}, respectively: (▩) removal percentage within 24 h; (⬚) the further removal percentage after 48 hours recirculation. All data points present mean values ± 1 SD.

4.4 Nitrification recovery in the NTFs

After ceasing the CoC challenge in the NTF, the NTFs were fed with 5 mg NH_4-N L^{-1} every 5 hours and then 12 hours feeding at night. Nitrification performance was determined after two days recirculation with ammonium. Figure 4.10 shows the representative inorganic profiles in the NTFs during the recovery time. It can be observed that the ammonium removal rate returned to about 0.5 mg NH_4-N L^{-1} h^{-1}. The increased nitrate-N concentration and initial increase followed by a decrease nitrite-N indicated that nitrification occurred and completed nitrification was achieved after ceasing the addition of CoC. Nitrification performance has completely recovered from the depression of CoC challenge.

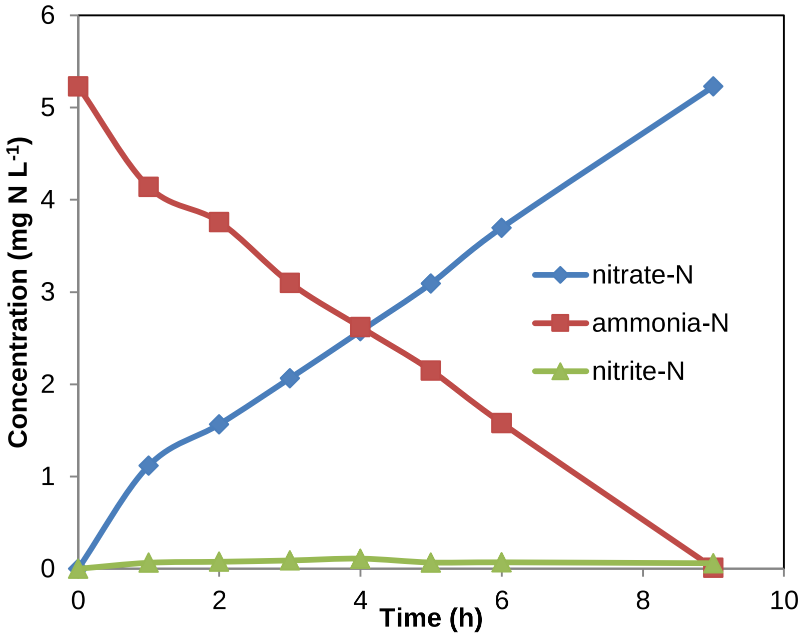


Figure 4.10 Representative nitrification performance in the NTFs after ceasing the CoC challenge. Data present mean values ± 1 SD.

4.5 Discussion

This chapter reports the observations from a series of laboratory-scale experiments that explored the feasibility of using high-rate NTFs for the removal of CoCs under low ammonium-N concentration. The effect of chemicals' initial concentration was investigated. The potential of additional chemical removal percentage with prolonged operation time was also taken into account.

Generally, the CoCs may be removed from waters by many different technologies, such as membrane bioreactors (Clara et al., 2005b, Trinh et al., 2012b), advanced oxidation (Bahnmüller et al., 2015, Esplugas et al., 2007), activated sludge treatment (Göbel et al., 2005, Johnson and Sumpter, 2001) and low-cost trickling biofilters (Camacho-Muñoz et al., 2012). Because most CoCs have been observed to have bioactive characteristics, biological treatment has been considered to be one of the most efficient approaches for their removal. Thus, in this study, the NTFs were chosen for CoC removal. The results revealed that high-rate NTFs could effectively remove CoC from wastewater.

During biological treatment, CoCs could be removed through degradation and sorption (onto biomass or the surface of the pure contacting materials). In this open NTF system, only biodegradation and sorption by pure contacting materials was considered. Because the chemicals sorption by biomass was negligible in literatures. Previous studies have demonstrated that the contribution to CoC removal of sorption onto biomass is insignificant (Gao et al., 2012). In a moving bed bioreactor system, the contribution of sorption has been shown to be limited, contributing only minimally to the total removal of EE2 and BPA (Luo et al., 2014a). A sterile control activated sludge batch study found that sorption to the biomass in sludge was insignificant under all testing conditions (Yu et al., 2006). Fan et al. (2014) illustrated that 83.4% of ACE was removed during activated sludge treatment, of which only 1.8% was removed by sorption onto biomass. In another study, a positive correlation was found between sludge biomass sorption and chemicals octanol-water partition coefficients (Log K_{ow}) (Fan et al., 2014). The dominant microorganisms in these reactors or plants were nitrifying microorganisms. The comparison of biomass types of studies in the literature and the study in this thesis is presented below (Table 4.3). As presented in Table 1.1 in Chapter 1, Section 1.3, the Log K_{ow} values of the chemicals selected for this study were relatively low, therefore sorption onto NTF biofilm could be considered to be insignificant.

Table 4.3 Sorption of some exampled CoCs onto biomass in the literatures.

References	Chemicals used	Biomass	Sorption rate
(Luo et al., 2014a)	EE2 and BPA	Nitrifying bacteria colonies	Very low sorption shown in Figure 3 in Luo et al.'s paper.
(Gao et al., 2012)	ACE and CAF	Activated sludge	Less than 7%
(Fan et al., 2014)	ACE	Sludge	1.8%
(Vasiliadou et al., 2013)	CAF	Activated sludge	6.8%
(Fernandez-Fontaina et al., 2012)	TRI	Nitrifying activated sludge	Negligible sorption shown in Figure 1 in the cited paper
(Yu et al., 2006)	ACE	Activated sludge	Sorption was negligible
This study	As listed in Table 1.1	Nitrifying microorganisms from activated sludge, which was obtained from the Bolivar WWTP, SA	The sorption was assumed to be low.

However, little is known about the sorption of CoC onto the surface of contact construction materials. In this study, a 24-hour batch experiment of material sorption was conducted. The results suggested that the packing material, polypropylene plastic, showed the lowest and most negligible sorption for all studied chemicals. A similar sorption result was observed in a previous study by Topp and Smith (1992), which demonstrated that polyethylene, which had quite similar characteristics to polypropylene, showed little sorption of the studied chemicals. The pipe wall (inner surface area of the NTF column), which was made of the PVC material, had minimal sorption for majority of the studied chemicals, except for ATZ, of which a relatively high amount was adsorbed by the pipe wall. The low sorption effect of PVC pipe was also reported by Bruning et al. (1981). A noticeable amount of DEET, ATZ and EE2 was adsorbed by the silicone tube inner surface, whereas there was little sorption for other chemicals (CAF, BEZ, ACE, BPA and TRI). Topp and Smith (1992) demonstrated that ATZ was adsorbed rapidly to silicone rubber materials, which was consistent with the result obtained in this study. Bruning et al. (1981) also demonstrated that less polar chemicals could be easily adsorbed by silicon rubber materials.

The low sorption results suggested that the dominant contribution to the chemicals removal was biodegradation by the bacteria in NTF. The nitrification rate obtained before chemical challenge indicated that the dominant bacteria in NTF were nitrifiers, such as ammonium oxidising bacteria (AOB) (e.g. *Nitrosomonas europaea*) and nitrite oxidising bacteria (NOB). As mentioned in Chapter 1, these nitrifiers have the potential to biodegrade some organic chemicals. Much less and slower EE2 degradation has been observed with AOB inhibitor (degradation rate constant: 0.059 h^{-1}) compared with no inhibitor (degradation rate constant: 0.0085 h^{-1}), suggesting that nitrifiers make the major contribution to degradation (Shi et al., 2004).

The results showed the capability of the high-rate NTF system for CoC removal, with removal efficiencies ranging from 18% to 98%. Among these chemicals, the most readily removed was CAF, which was almost completely removed within 12 hours. This outcome was consistent with previous studies, which demonstrated that CAF was one of the most degradable chemicals using either conventional wastewater treatment plants (WWTPs), activated sludge treatment, or low-cost trickling filter treatment, with high removal percentages up to 99% (Camacho-Muñoz et al., 2012, Yang et al., 2011). The lowest removal efficiency was observed for TRI, with a minimal removal percentage of approximately 18% (See Figure 4.4). This result was not a surprise. In some early studies, TRI has been reported to be resistant to biodegradation, with no degradation over 21 days during the primary treatment and activated sludge treatment stage (Pérez et al., 2005). TRI was detected in the effluent at almost the same concentration as in the untreated wastewater in a sewage treatment plant, which used the conventional activated sludge method (Lindberg et al., 2006). In a membrane bioreactor, TRI was only partially removed, with a removal percentage range of 24% to 68% (Trinh et al., 2012b). Nevertheless, Pérez et al. (2005) observed that this compound degraded completely within 3 days in the nitrification process stage, indicating that the microorganisms from the nitrification process are highly capable of degrading TRI.

A linear decrease with time was observed for ACE removal, and 59% of ACE was removed after 24 hours. This phenomenon indicated that the NTF had the potential to further remove ACE from wastewater. Yamamoto et al. (2009) and Yang et al. (2011) reported that the removal of ACE during activated sludge treatment was greater than 90%. Yu et al. (2006) observed >99% removal efficiency in a sewage treatment plant that was designed to obtain biological nutrient removal, with high ACE concentration (960 ng L^{-1}) in influent and extremely low ACE concentration in effluent. In another study, almost complete removal of ACE from wastewater was observed either by conventional activated sludge treatment or advanced membrane bioreactor (Radjenović et al., 2009). These findings suggest that ACE is a compound that could be readily degraded in biological wastewater treatment system.

The removal of BPA observed in this study (27%) was less than that reported in a sponge-based moving bed bioreactor, which achieved removal of 77.8% ± 8.8% (Luo et al., 2014a). Deblonde et al. (2011) stated that the removal efficiency of about 71% for BPA in activated sludge treatment, resulting in WWTP effluent concentrations ranging from 0.006 to 4.09 μg per litre. Guerra et al. (2015) illustrated that the removal efficiency of BPA varied in different treatment technologies, ranging from 1 to 77%, and the membrane bioreactor and biological aerated filter treatments showed better performance than primary treatment. Few studies have investigated biological removal of BEZ, and those reported removal efficiencies ranging from 30% to 55% (Reemtsma et al., 2010), which were close to the results reported in this study. The removal efficiency for BEZ in conventional activated sludge municipal wastewater treatment has been found to be 37% (Weiss et al., 2006), lower than the removal in NTF applied in this study.

The studies relating to the biological treatment of ATZ have reported variable outcomes. The removal efficiency for ATZ by NTF in this study (49%) was greater than the 3 ± 3.6% reported for a sand biofilter (Zearley and Summers, 2012) but less than that achieved by applying biological granulated activated carbon treatment (Herzberg et al., 2004). However, this study showed the potential of NTF to further remove ATZ by prolonging the contact time. DEET (59%) levels of removal were very similar to ATZ in this study. Similar removal efficiency (69 ± 21%) was observed in the full scale municipal WWTP in China (Sui et al., 2010). Better removal of DEET was detected in an advanced wastewater reclamation plant, where the concentration of DEET had decreased by more than 90% after activated sludge treatment and membrane filtration (Yang et al., 2011). DEET has also been effectively removed through the membrane bioreactor with 90% to 100% removal (Trinh et al., 2012b).

The concentration of EE2 decreased 48% after 24 hours recirculation in NTF. A much higher EE2 removal efficiency (99%) was obtained in a nitrifier enriched membrane bioreactor (De Gusseme et al., 2009). One of the estrogenic hormones, EE2, was considered to be efficiently degraded under a nitrifying environment, and a removal percentage of 85.2 ± 4.5% was achieved in moving bed bioreactor (Luo et al., 2014a). The data from a field study of an activated sludge treatment process demonstrated that over 85% of EE2 could be consistently removed (Johnson and

Sumpter, 2001).

The removal of CoC in this study was influenced by sorption onto the surface of pure construction material and the degradation by bacteria in NTF, but it is necessary to know the contribution of sorption and degradation to the total removal percentage of CoC. The results revealed that degradation was the dominant removal pathway for all of the investigated chemicals. Amongst them, sorption contributed least to the removal of CAF, but most to the removal of ATZ. Nevertheless, the ratio might change with different gross removal percentages under different operating conditions.

The effect of initial concentration of CoC on the removal performance in NTF was also investigated in this chapter. The results from this study showed that the removal percentage was independent of the initial concentration for most of the CoC. This presented as minimal changes on removal percentage for some of CoC (DEET, TRI, BPA, ATZ), which was consistent with the statement by Zearley and Summers (2012). A previous finding demonstrated that the removal efficiency for BPA increased slightly from 87.1 ± 5.5% to 92.9 ± 2.9% with increasing influent BPA concentration (Zielińska et al., 2014). Nevertheless, in this study the removal of CoC increased when operating with higher initial concentration of some chemicals (CAF, BEZ, ACE and EE2).

In the total removal percentage of CoC at lower initial concentrations, the contributions of sorption onto the contacting materials and degradation varied for different CoC. Comparing with the relative contributions of sorption and degradation at higher initial CoC concentrations, no apparent difference was observed between high and low initial CoC concentrations. Degradation by the nitrifying bacteria in NTFs was still the dominant removal mechanism for CoC. Overall, the initial concentrations of CoC might not affect the relative contribution of sorption and degradation to the total removal. These findings confirmed that it was reasonable to apply higher CoC concentrations (comparing with environmental concentrations) to investigate the potential impact factors (e.g. nitrification rate and exogenous organic carbon) of CoC removal in the high-rate NTFs, which will be presented in the following Chapters.

As mentioned above, some of the CoC still might have the potential for further removal in NTF. The additional removal percentage in prolonged operation time supported this hypothesis. According to the results, the improved removal percentages for all investigated chemicals ranged from 2% to 40% after an additional 24 hours recirculation. Bolong et al. (2009) had suggested that the biological treatment process with longer hydraulic/solid retention time could increase the removal extent of organic compounds. Especially in advanced biological treatment at low temperature, longer solid retention time (SRT) (>9 d) and hydraulic retention time (HRT) (>21 d) were essential to optimise the removal percentage (>76%) of BPA (Guerra et al., 2015). The elimination behaviour of TRI was enhanced from 30% at SRT of 16 ± 2 – 33 ± 3 d, to 85% at SRT of 60–80 d in membrane bioreactor treatment (Göbel et al., 2007). The CoC removal efficiency in membrane bioreactor and conventional WWTPs also depend on the SRT, BPA and other compounds were effectively removed (>90%) with SRT >10 days (Clara et al., 2005b). The results obtained in this study had a good agreement with these previous findings, which indicated that longer HRT/SRT could optimise the efficiency of removing CoC. Thus, the HRT/SRT is a vital parameter on NTF design and operation to achieve effective removal of CoC.

The feasibility of using a high-rate NTF system to biologically remove CoCs at relatively high concentration levels (mg L^{-1}) with initial ammonium-N concentration of 5 mg NH_4-N L^{-1} was confirmed in laboratory-scale experiments. The minimal sorption indicated that biodegradation was the primary mechanism for CoC removal. For most of the investigated CoCs, the initial concentration of CoCs was independent of removal efficiency. Prolonged operation time could improve the removal performance of CoCs in NTF.

The completed nitrification in the NTFs indicated that some nitrifying microorganisms existed in the biofilm and these microorganisms were capable of degrading CoC. Therefore, increasing the initial nitrification rate before adding CoC may increase the CoC removal efficiency in the high rate NTFs. However, in the presence of CoC, the nitrification performance in the NTF was severely depressed, after ceasing the addition of CoC, the nitrification performance recovered after two days incubation with ammonium. It is important to investigate the relationship between initial nitrification rate in the NTFs before adding CoC and the behaviour of chemical removal, and it will be discussed in next chapter.

5 RELATIONSHIP BETWEEN NITRIFICATION RATE AND REMOVAL EFFICIENCY OF CHEMICALS OF CONCERN

5.1 Introduction

In Chapter 4, the possibility of applying high rate NTF to remove chemicals of concern (CoC) was demonstrated. In this nitrifying environment, most of the chemicals were effectively removed, indicating that an NTF could potentially enhance the removal of CoC. The objective of this chapter is to develop a relationship between the nitrification rate and removal efficiency of CoC by increasing the initial nitrification rate in the NTF before challenged by CoC and compare the nitrification rates before and after challenging the CoC.

Most previous studies on chemical removal in a nitrifying environment were conducted with relatively high initial concentrations of ammonium (20 mg L^{-1} to 300 mg L^{-1}), which were 10- to 50- times higher than the concentration used in this study (Shi et al., 2004, Tran et al., 2009). In Chapter 4, the feasibility of using NTF with a low initial concentration of ammonium (5 mg L^{-1}) for chemical removal was investigated and confirmed. However, Tran et al. (2009) reported that increased initial ammonium concentration could promote the efficiency of the removal of some pharmaceuticals by changing the amount of ammonium *monooxygenase* induced, which indicated that nitrification activity might have some effect on chemicals' removal. Although the effect and contribution of a nitrifying environment to the efficiency of the removal of some organic contaminants has been demonstrated (Fernandez-Fontaina et al., 2012, Shi et al., 2004), little is known about the removal efficiency of the NTFs with different initial nitrification rates before challenging with CoC or the effect of the chemicals' challenge on the nitrification rate in the NTFs.

The nitrification rate of NTFs shown in Chapter 4, Section 4.3.3 was approximately 0.5 mg NH_4-N L^{-1} h^{-1} with an initial NH_4-N of 5 mg L^{-1}. van den Akker (2008) reported that the nitrifiers in the NTFs that were responsible for nitrification activity were slow-growing bacteria, and the nitrification rate could be improved when continuing to feed the NTF with ammonium. Thus, it is possible to achieve a higher nitrification rate in the NTF, where more mature nitrifiers produced.

Yi and Harper (2007) investigated the relationship between nitrification performance and EE2 biodegradation, showing that with the increase of ammonium removal rate, the biotransformation of EE2 increased. The findings indicated that enrichment of nitrifiers can enhance chemicals' removal. Batt et al. (2006) and Fernandez-Fontaina et al. (2012) reported the higher removal efficiencies of some organic pollutants in the nitrifier-enriched nitrifying activated sludge than in conventional wastewater treatment systems (Maeng et al., 2013, Tran et al., 2009). It is clear that nitrification rate is an important factor to consider when optimising a NTF for CoC removal.

Most of the studies in the literature were conducted at low chemical concentrations ranging from 10 ng L^{-1} to 100 µg L^{-1} (Benotti et al., 2009, Radjenović et al., 2009). It is more problematical to investigate the effect of the presence of CoC to nitrifying activities at low CoC concentrations. Because the inhibitory effect of some organic contaminants to the growth and activity of nitrifying bacteria is hard to detect. For instance, Barra Caracciolo et al. (2015) reported that a significant inhibition on nitrification rate was observed when the acetaminophen concentrations ≥ 250 mg L^{-1}. The presence of BPA limited nitrification when the influent BPA concentrations were 2.5 to 10.0 mg L^{-1} (Zielińska et al., 2014). These findings suggested that the presence of organic pollutants might depress the activity of nitrifying bacteria, and subsequently affect nitrification performance.

In this study, a constant ammonium influent concentration of 5 mg L^{-1} was maintained for two months for the incubation of nitrifying bacteria in the NTFs. The aim of this chapter is to present data which interrogates the relationship between nitrification rate and the removal efficiency of CoC. This was achieved by increasing the initial nitrification rate in the NTF before challenging CoC, and comparing the nitrification rates before and after challenging the CoC. The chemicals removal efficiencies recorded in this study will be compared with the removal efficiencies presented in Chapter 4.

5.2 Methods

5.2.1 Experimental design

Laboratory-scale NTFs were operated under the conditions described in Chapter 4, Section 4.2.4. The influent ammonium-N concentration was maintained at a constant 5 mg NH_4-N L^{-1} and the NTF system was operated for another two months to further develop a nitrifying biofilm. A detailed description of the laboratory-scale NTF system can be found in Chapter 2, Section 2.3.

The results described in Chapter 4 revealed that better removal efficiency could be obtained when applying higher concentrations of CoC. Thus, in order to achieve better removal efficiency, the higher CoC concentrations described in Chapter 4, Section 4.2.4 were used. The nitrification rates of the NTF were measured before and after adding CoC, and the initial ammonium-N concentration was maintained at 5 mg NH_4-N L^{-1}. Each CoC was added into the 1 L ammonium solution reservoir independently. The NTFs were operated in parallel, with one as the control column, in which there was no chemical challenge. During the chemical challenge phase, 1 mL ammonium-N, as ammonium chloride (5 mg NH_4-N L^{-1}), was added hourly to the reservoir of each NTF to maintain ammonium-N concentration.

5.2.2 Sampling and chemical analysis

Before challenging with the respective CoC, samples were drawn once an hour directly from the effluent of the NTFs before it discharged into the 1 L reservoir for recirculation.

During the challenge period, sampling was performed seven times for the first 12 hours, and then at 21 hour, 24 hours and 27 hours. From each of the samples, 1 mL was transported to the HPLC vials and stored at -20°C before the concentrations of CoC were measured using the procedures described in Chapter 2, Section 2.4.7. The reminder of the samples were kept at 3 ± 2°C for ammonium-N, nitrite-N and nitrate-N analysis using procedures described in Chapter 2, Section 2.4.

5.3 Results

5.3.1 Nitrification performance before challenging with CoC

After a further incubation of two months, when the biofilm on the surface of NTF packing material was mature, the nitrification performance of the NTF was measured before challenging with CoC. The initial ammonium-N concentration was maintained at approximately 5 mg NH_4-N L^{-1}. Figure 5.1 shows the changes of ammonium-N, nitrite-N and nitrate-N concentrations with time, which suggested that nitrification rate (calculated as ammonium-N removal) in the NTF was 1.0 ± 0.1 mg NH_4-N $L^{-1}h^{-1}$. The nitrification rate was nearly double that obtained (0.52 ± 0.15 mg NH_4-N L^{-1} h^{-1}) before the two-month incubation period.

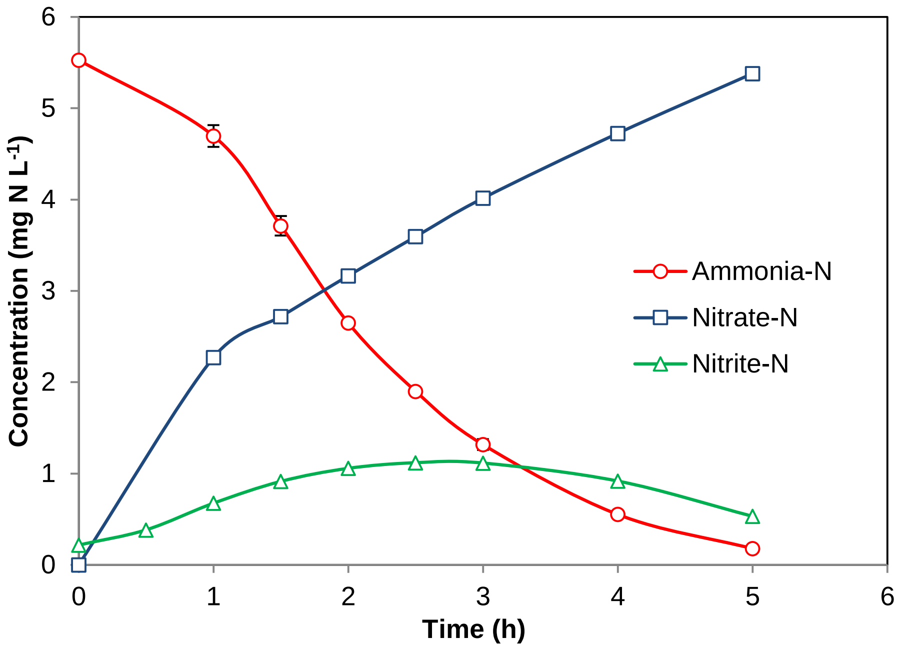


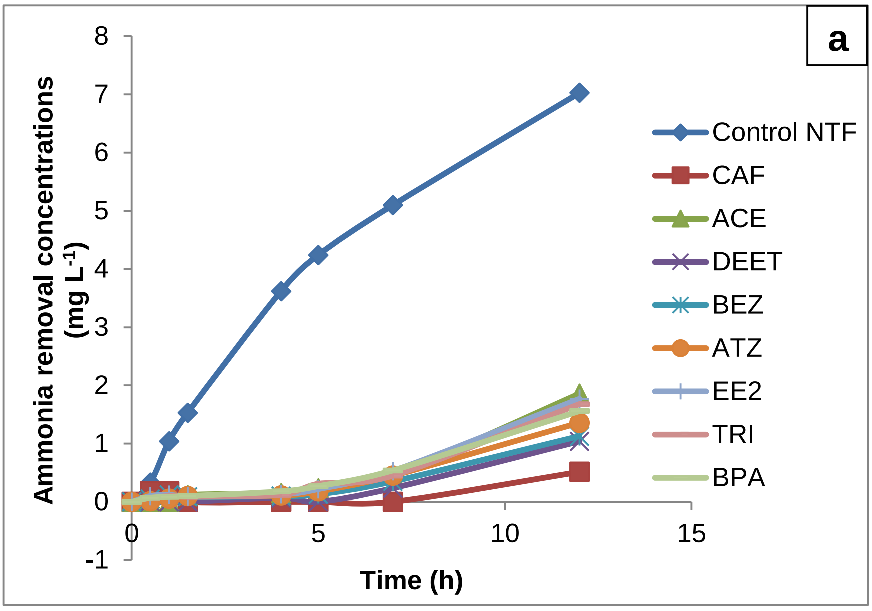
Figure 5.1 The typical nitrification performance, presented as the concentration changes of ammonia-N, nitrate-N and nitrite-N, in the four parallel NTFs before challenging with CoC. (All data points show means ± 1 SD)

5.3.2 Nitrification performance in NTFs when challenging CoC

After a higher nitrification rate was obtained, three of the NTFs were challenged with CoC individually. The nitrification performance of the NTFs was monitored when challenging three NTFs with CoC, with the fourth NTF operating as control. In order to maintain nitrification, ammonium-N was compensated hourly. Thus, the nitrification performance was presented as the production of nitrite-N and nitrate-N in NTFs.

From Figure 5.2a, it can be seen that in the control NTF the ammonium removal concentration increased steadily over time, whist the ammonium removal concentration in the NTFs challenged with individual CoC remained low during the first 7 hours, and started to increase over the following hours. Although the final ammonium removal concentrations in the NTFs challenged with different CoC varied, no statistically significant difference was observed among them (ANOVA, $p>0.05$). Although, comparing the ammonium removal concentration in the control NTF, statistically significant difference was observed between the ammonium removal in the NTFs challenged with individual CoC and the control NTF (ANOVA, $p<0.05$).

Figure 5.2b shows the generated nitrate/nitrite-N in the NTFs. In the presence of CoC, minimal nitrate/nitrite-N was produced throughout the operation period. There is no significantly statistical difference on generated nitrate/nitrite-N concentrations between the NTFs challenged difference CoCs (ANOVA, $p>0.05$). Similarly, as the ammonium removal in Figure 5.2a, a steady increase in nitrate/nitrite-N was observed in the control NTF without CoC challenge. The difference between generated nitrate/nitrite-N concentrations in the control NTF and the NTFs challenged with individual CoC was statistically significant (ANOVA, $p<0.05$), and the nitrification rate in the NTFs challenged with CoC was much lower than that in the control NTF.



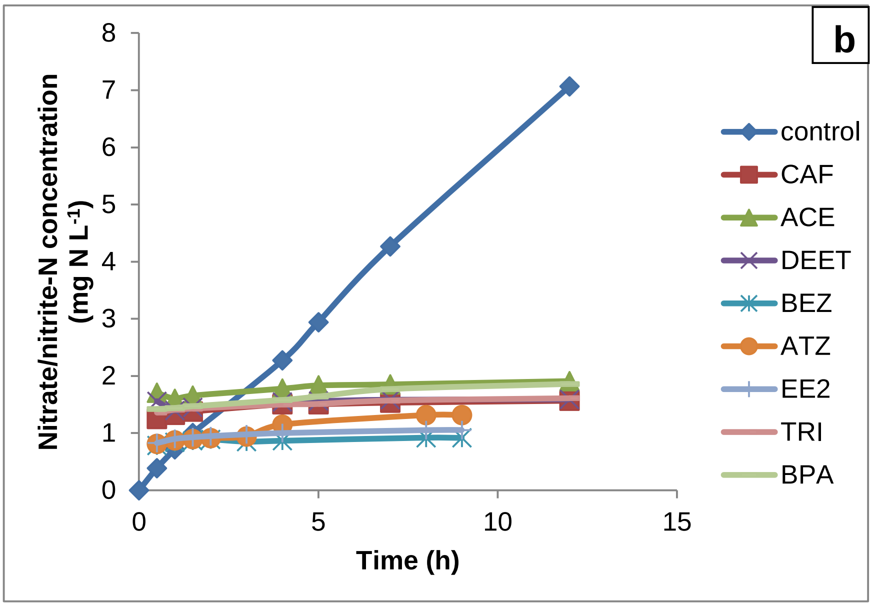


Figure 5.2 The nitrification performance that shown as ammonium removal (a) and nitrate/nitrite-N generation (b) in the control NTF without CoC challenge and the NTFs challenged with individual CoC.

5.3.3 Removal of CoC in the NTFs with higher initial nitrification rate

After achieving a high initial nitrification rate (ammonium-N removal rate) of 1.0 ± 0.1 mg NH_4-N L^{-1} h^{-1} in the NTFs, a series of laboratory-scale experiments for the removal of CoC were conducted. Three of the NTFs were challenged with respective CoC, while the fourth NTF as control. Figure 5.3 shows the relative concentration changes in C_t/C_0 throughout the operating period.

From Figure 5.3, it can be observed that CAF and BPA were largely removed after 27 hours recirculation in NTF, reaching relative concentrations of 0.101 and 0.294 respectively (equal to removal percentages of 89.9% and 70.6%). Meanwhile, the relative concentration of BEZ remained consistently high with a C_t/C_0 value of 0.892 after 27 hours. This value indicated that only a minimal percentage (10.75%) of BEZ was removed throughout the experiments. ATZ and DEET showed a similar removal tendency but achieved different relative concentrations after 27 hours, with respective C_t/C_0 values of 0.429 and 0.287 (equivalent to removal percentages of 57.1% and 71.3%). The most effective removal achieved in this study was for ACE, which was almost completely removed (>99%) after 27 hours recirculation in the NTF. For TRI and EE2, medium removal efficiency was obtained, with respective C_t/C_0 values of 0.499 and 0.374 (equivalent to removal percentages of 50.1% and 62.6%).

Most of the investigated chemicals were effectively removed in the NTFs system with high initial nitrification rate before CoC challenge. The removal percentages of CoC in this study were then compared with those obtained in Chapter 4, to investigate the effect of initial nitrification rate in the NTF to the efficiency for CoC removal.

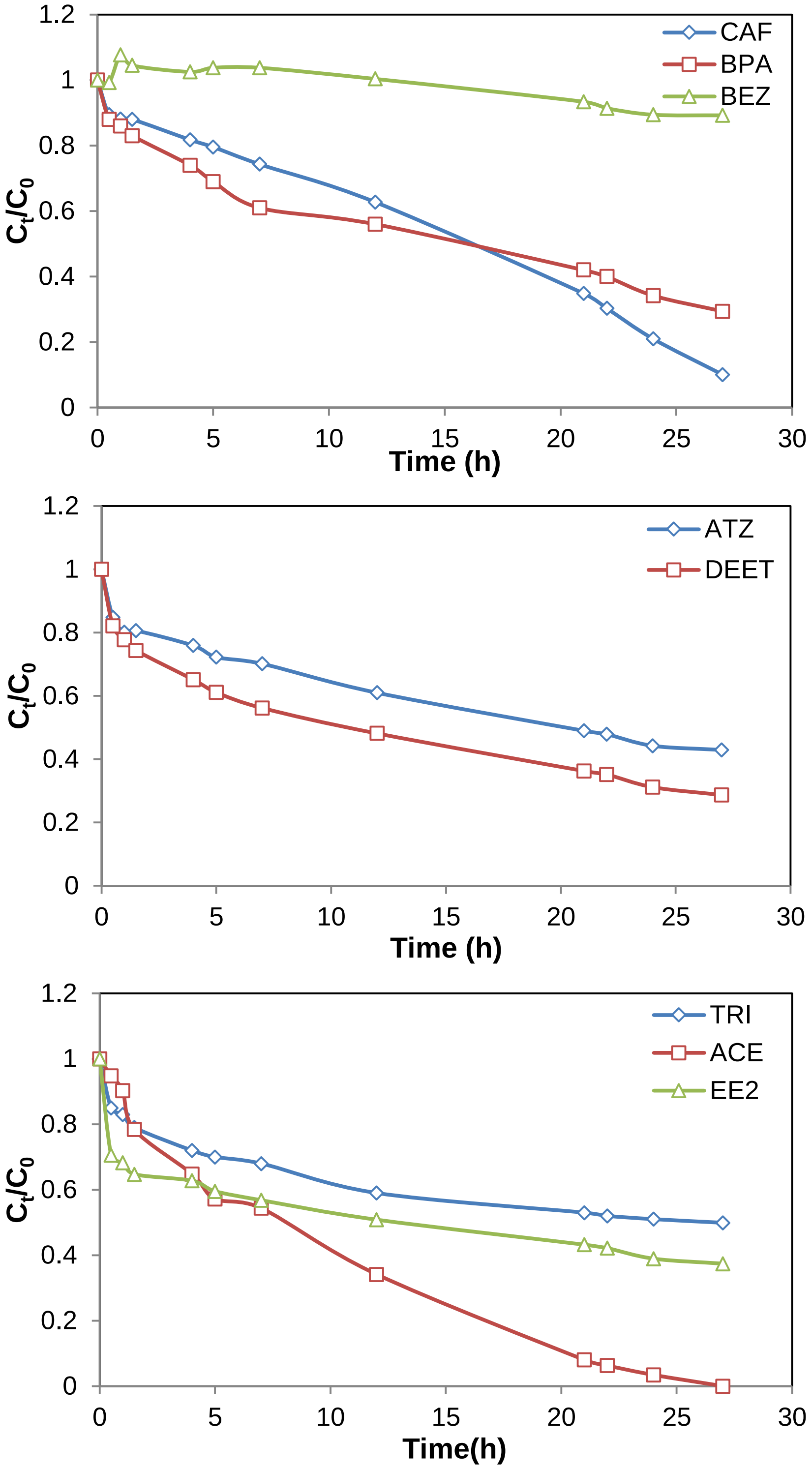


Figure 5.3 The removal of chemicals of concern at a NH_4-N removal rate of 1.0 ± 0.1 mg NH_4-N L^{-1} h^{-1}, caffeine (CAF), bisphenol A (BPA), benzotriazole (BEZ), atrazine (ATZ), N, N-diethyl-m-toluamide (DEET), trimethoprim (TRI), acetaminophen (ACE) and 17α-ethynylestradiol (EE2) following recirculation through a nitrifying trickling filter. C_t/C_0 is the relative concentration obtained by dividing the concentration at *t* (time) by the initial concentration of each CoC.

5.3.4 Effect of nitrification rate on the removal of CoC in NTF

Figure 5.4 presents the comparative removal percentages of CoC under higher nitrification rate (1.0 ± 0.1 mg NH_4-N L^{-1} h^{-1}) and lower nitrification rate (0.52 ± 0.15 mg NH_4-N L^{-1} h^{-1}). The removal efficiency for most of the investigated CoC increased with the increase of the initial nitrification rate in the NTFs before challenging CoC. The initial nitrification rate indirectly indicates the extent of nitrifier abundance within the biomass in the NTFs.

After the nitrification rates in all four NTFs reached a high of 1.0 ± 0.1 mg NH_4-N L^{-1} h^{-1}, the respective CoC was added into the three of the NTFs for recirculation. An improvement of removal efficiency was observed for ACE, BPA, TRI, DEET, EE2 and ATZ in the NTF with the higher initial nitrification rate. Additional removal of 30%–40% was recorded for ACE, BPA and TRI, and 10%–15% for DEET, EE2 and ATZ, comparing with the removal efficiency in the NTF with lower initial nitrification rate before challenged with CoC. This was enhanced by the increased initial nitrification rate in the NTFs, where more matured nitrifying biofilm was produced. Although the removal efficiency for CAF was reduced by approximately 10% when the initial nitrification rate in the NTF increased, its removal percentage was still relatively high. The removal efficiency variation for CAF in the NTFs with high and low initial nitrification rate was statistically insignificant (p<0.05). Surprisingly, only 11% BEZ was removed in this nitrifying-enhanced filter, 30% less than the result observed in the NTF with the lower initial nitrification rate.

The results revealed that the initial nitrification rate in NTFs before challenged with CoC could affect the removal efficiency of CoC, but the extent of the effect varied. For most of the investigated chemicals, the higher initial nitrification rate, obtained in the NTFs before challenged with CoC, showed a positive effect on their removal. These findings also indicate that although the nitrifiers were relatively inactive for nitrification when challenging the NTFs with individual CoC, they were still capable of degrading CoCs.

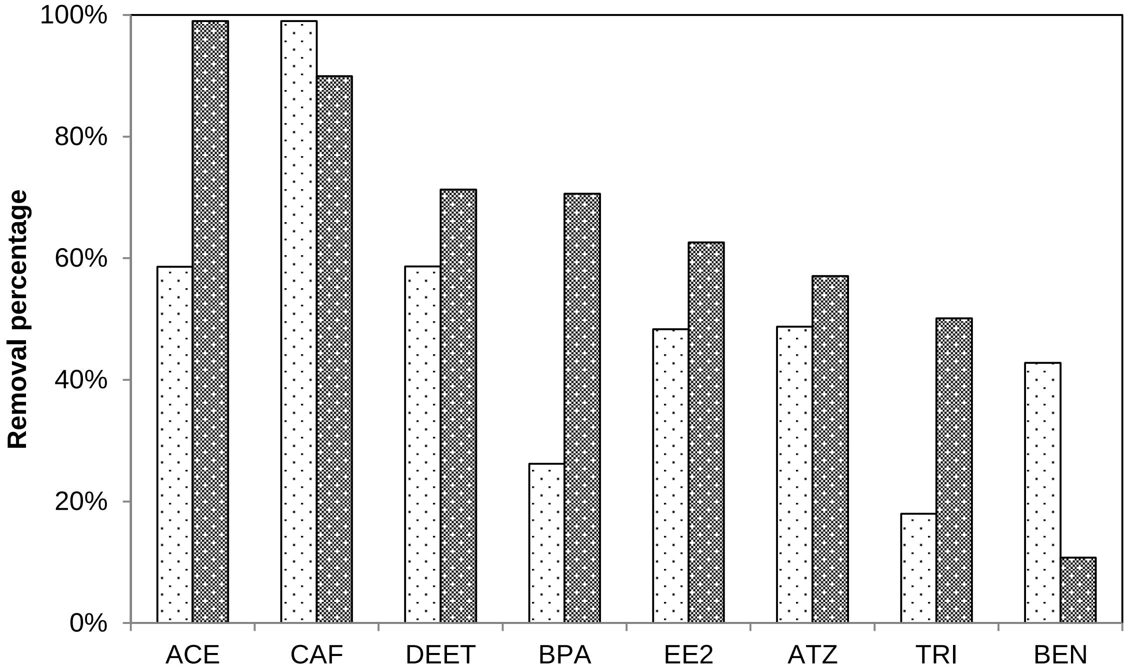


Figure 5.4 Comparison of removal percentages of caffeine (CAF), acetaminophen (ACE), N, N-diethyl-m-toluamide (DEET), benzotriazole (BEZ), 17α-ethynylestradiol (EE2), trimethoprim (TRI), bisphenol A (BPA), atrazine (ATZ) under different nitrification rates in NTF: (⬚) low nitrification rate of 0.52 ± 0.15 mg NH_4-N L^{-1} h^{-1}; (▩) high nitrification rate of 1.0 ± 0.1 mg NH_4-N L^{-1} h^{-1}.

5.3.5 Nitrification recovery in the NTFs after ceasing the addition of individual CoC

After cessation recirculation of CoC in the NTFs, the NTFs then restarted recirculating only with ammonium. The concentration of ammonium was maintained at about 5 mg NH_4-N L^{-1}. After two days recirculation, the nitrification performance was determined in 6 hours with initial ammonium concentration of 5 mg NH_4-N L^{-1}. Figure 5.5 shows the representative inorganic nitrogen profiles in the NTFs. The decreased ammonium concentration and increased nitrate-N revealed that nitrification performance readily recovered demonstrating the robustness of the NTF.

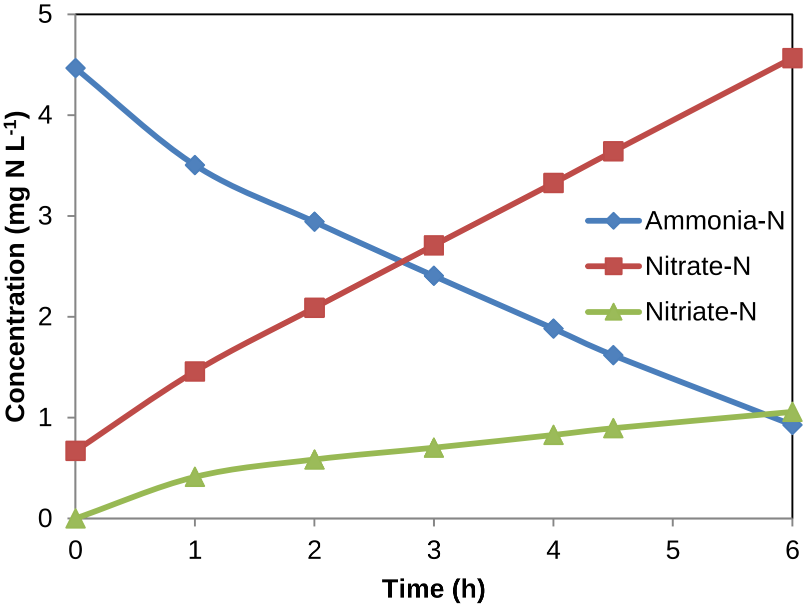


Figure 5.5 The representative nitrification performance in the NTFs after ceasing the challenge of individual CoC.

5.4 Discussion

The effect of nitrifying culture on the removal of some organic contaminants has been documented (De Gusseme et al., 2009). Little is known about the influence of the initial nitrification rate in the NTFs before challenged with CoC on the removal efficiency for a variety of CoC. Because the main purpose of the project was to remove ammonium and other CoC, it was necessary to consider the interaction between these two components. The experimental element reported in this chapter investigated the removal efficiency of CoC immediately after the relatively high nitrification rate was obtained in the laboratory-scale NTFs. The typical nitrification rate in the NTFs with CoC challenge was compared with that in the control NTF. Further, the removal efficiency of CoC observed in this chapter was compared with the removal efficiency observed in Chapter 4.

After two months' further incubation, the nitrifying activity of the biofilm on the surface of the packing material in the NTF was enhanced. An initial nitrification rate of 1.0 ± 0.1 mg NH_4-N L^{-1} h^{-1} was observed for all four NTFs before challenged with CoC, almost the double the nitrification rate previously obtained (Chapter 4, Section 4.3.3). This result indicated that the further incubation with ammonium-N feeding improved the population and activity of the nitrifying bacteria in the NTFs.

After a higher initial nitrification rate was observed in the NTF, individual CoC was added into the three NTFs for investigation of CoC removal. The NTFs achieved relatively high CoC removal efficiency. The highest removal was achieved for ACE, which was almost completely removed after 27 hours of recirculation in the NTF. This result was consistent with the findings observed by Okuda et al. (2008), who reported almost complete removal for ACE from the aqueous phase in the biological nutrient removal process. Yang et al. (2011) reported that 99% of ACE was removed after activated sludge treatment, and this was attributable primarily to microbial degradation. Blair et al. (2013) reported that only 22% of ACE was removed during the primary disinfection process, while high removal efficiency was achieved throughout the secondary treatment (e.g. activated sludge process).

High removal efficiency was observed for CAF, with a relative concentration of 0.1, which is equivalent to 90% removal. This was expected in the nitrifying-enhanced NTF. Because CAF is considered to be a readily biodegradable chemical and has been reported to be effectively removed in both conventional and low-cost wastewater treatment technologies (Hijosa-Valsero et al., 2010). When the initial nitrification rate in the NTFs before challenged with CoC was lower (0.52 ± 0.15 mg NH_4-N L^{-1} h^{-1}), CAF was almost completely removed, whereas a slight decrease in removal percentage was observed when the initial nitrification rate was higher (1.0 ± 0.1 mg NH_4-N L^{-1} h^{-1}). Overall, CAF was a readily biodegradable compound in the high-rate NTF.

The lowest removal efficiency was obtained for BEZ, which had a C_t/C_0 value of 0.89. BEZ has been consistently considered to be a poorly degradable chemical and less amenable to biological treatment, the elimination rates observed in 10 WWTPs in Switzerland ranged from 0% to 60% (Voutsa et al., 2006). The poor degradation of BEZ in the WWTPs resulted in relatively high concentration in WWTP effluents (7–18 µg L^{-1}) and frequent detection in surface waters (0.1–0.5 µg L^{-1}) in Germany (Reemtsma et al., 2010, Weiss et al., 2006). When the initial nitrification rate in the NTF increased to 1.0 ± 0.1 mg NH_4-N L^{-1} h^{-1}, the percentage removal for BEZ showed a significant decrease from 43% to 11%. This phenomenon indicated that there was decline in the bacteria responsible for BEZ degradation in the NTF.

As for other investigated chemicals (BPA, TRI, DEET, ATZ and EE2), over a test period of 27 hours, the removal percentage ranged from 50% to 72%, showing a notable improvement in the NTFs with higher initial nitrification rate before challenged with CoC. For BPA and TRI in particular, removal efficiency was largely enhanced in the more nitrified NTF.

Pérez et al. (2005) reported that no TRI degradation was observed during the conventional activated sludge treatment after 21 days, whereas it was almost completely eliminated after 3 d during the nitrification process. This finding indicated that the micro-organisms capable of degrading TRI were generated during the nitrification process. In the current study, the improved removal percentage of TRI in the NTF with higher initial nitrification rate also confirmed the importance of enhanced nitrification process to the removal of TRI. Batt et al. (2006) pointed out that when the nitrification activity was inhibited, the percentage removal of TRI decreased significantly, whereas the percentage removal of TRI increased from about 1% in the less nitrified conventional activated sludge to 50% in the more nitrified activated sludge, suggesting that the abundant nitrifying bacteria were important to the effective degradation of TRI. Miège et al. (2009) pointed out that activated sludge with nitrogen removal was one of the most efficient processes for the removal of most pharmaceuticals and personal care products (including TRI) in WWTPs.

In the nitrifying-enhanced NTF, the removal efficiency of BPA reached 70.6%, a large increase from the low removal percentage (26.2%) obtained under the lower initial nitrification rate (0.52 ± 0.15 mg NH_4-N L^{-1} h^{-1}). This finding was consistent with the results observed by other researchers in the biological wastewater treatment process. For example, the removal efficiency of the sewage treatment plant in Spain was about 72% (Gómez et al., 2007). Similar result (71%) was observed in WWTP (Deblonde et al., 2011). and 64±29% removal was obtained in the drinking water biological filters (Zearley and Summers, 2012). The increased removal efficiency in this study indicated that the higher initial nitrification rate in the NTF had a positive effect on BPA removal. In a decentralised membrane bioreactor, >97.8% of BPA was removed over a 5-day period (Trinh et al., 2012a). This high removal efficiency suggests that the biological system NTF might have the potential ability to further degrade BPA from wastewater.

Similar removal efficiency improvement was observed for DEET, EE2 and ATZ in the NTF with the higher initial nitrification rate (1.0 ± 0.1 mg NH_4-N L^{-1} h^{-1}). Yi and Harper (2007) investigated the relationship between nitrification performance and the removal of EE2, pointing out that the NH_3-N transformation rate and EE2 biotransformation rate showed a nearly linear relationship. This finding strongly suggests that nitrification could improve the removal of EE2. In the current study, the increased EE2 removal percentage in the NTF with higher initial nitrification rate confirmed this finding. DEET was also reported to be a readily biodegradable compound in activated sludge treatment (Yang et al., 2011). Thus, the increased removal percentage of DEET in this study indicated that the nitrifying-enhanced NTF could provide more sufficient bacteria responsible for biodegradation.

Most of the studies on ATZ removal applied ozone treatment or chlorination, with variable removal efficiencies. For example, the removal efficiency for ATZ by chlorination or ozonation in drinking water treatment was in the range of 20% to 50% (Benotti et al., 2009). Whereas high removal percentage for ATZ after ozone treatment ranged from 66% to 96% (Hua et al., 2006). Little research has been carried out using biological treatment technology to remove ATZ. Zearley and Summers (2012) applied the biological active sand filters to remove ATZ, but the results showed that ATZ was recalcitrant to biological treatment with remove percentage of 3 ± 3.6%. Nevertheless, the medium removal efficiency (57%)

obtained in this study revealed that ATZ could be effectively removed in the nitrifying-enhanced filters, and the NTF with higher initial nitrification rate could further improve the removal efficiency for ATZ.

In the literature, most of the research concentrated on the factors that could affect the removal efficiency of CoC, whereas little is known about the effect of CoC on nitrification performance in NTFs. In order to better remove CoC and ammonium-nitrogen at the same time, this study also investigated the effect of CoC challenge to the nitrification rate in the NTF.

The comparison of nitrification performances before and after challenging the NTF with CoC was illustrated in this study. Almost no nitrification activity was observed when challenging the NTF with CoC. Thus, at the concentrations employed in this study the CoC challenge depressed nitrification activity in NTFs. A contrary finding was reported by Yi and Harper (2007), who demonstrated that the presence of EE2 (0.3 mg L^{-1}) might not affect ammonium removal efficiency during the biological treatment process. However, Zielińska et al. (2014) found that the when the biomass was exposed to BPA, the quantity and diversity of ammonium-oxidising bacteria (AOB) in the biomass might be altered. Their research also demonstrated that nitrification efficiency decreased when the investigated BPA concentration in wastewater was the high (2.5–10 mg L^{-1}). Thus, the high concentrations of introduced CoC might be a reason that caused the nitrification depression in the NTF. Wang and Gunsch (2011) reported that some pharmaceutically active compounds at higher concentration (10 μM) can inhibit microbial activity in the bioreactor, whereas no effect was observed at lower concentration (0.5 μM).

Overall, the results from this study showed that the initial nitrification rate in the NTFs exerted a positive influence on the removal of most of the investigated CoC in the high-rate NTFs, while there was, at the concentrations used here, a negative impact of CoC challenge on nitrification rate. Although the nitrifiers were inactive for nitrification process, they still showed the capability to degrade CoC. The nitrification performance recovered two days after ceasing CoC challenge and incubating with only ammonium in the NTFs. The depression mechanism of CoC challenge to nitrification activity in the high-rate NTF will be further illustrated in Chapter 6.

6 EFFECT OF EXOGENOUS ORGANIC CARBON SUBSTRATE ON REMOVAL EFFICIENCY OF CHEMICALS OF CONCERN

6.1 Introduction

The operational parameters of NTFs have become increasingly important to optimise for the performance of NTFs to the removal of nutrients, which have been widely studied in researches at pilot- or full- scale level for water treatment (Almstrand et al., 2011, Lekang and Kleppe, 2000, Pearce and Edwards, 2011, Tekerlekopoulou and Vayenas, 2003, ter Haseborg et al., 2010). Those researches provided various strategies to improve the nitrification performance in NTF. One of the most important operational parameters in NTF is the organic carbon loading, which was investigated by Pearce and Edwards (2011) and van den Akker et al. (2010), because the organic carbon loading may affect the biofilm structure and bacteria species in NTF. van den Akker et al. (2010) demonstrated that only when the organic carbon load was less than 4 mg soluble biochemical oxygen demand (sBOD$_5$) L^{-1} could the nitrification rate be maintained at 90 to 100%, otherwise the nitrification would decrease. The depression of nitrification by high organic carbon load might because the high concentration of organic carbon loading could promote the growth of heterotroph bacteria which compete with the slow growing nitrifiers for dissolved oxygen and biofilm space (van den Akker et al., 2010). Thus the exogenous organic carbon loading may have impact on the bacteria in NTF, which are responsible for degradation of CoC, and further affect the total removal of CoC. However, little study has been carried out to explore the effect of exogenous organic carbon substrate on the removal of CoC in the laboratory-scale high-rate attached growth NTF.

Although the operating parameters and factors affecting the removal of some organic contaminants during biological wastewater treatment processes have been widely reported, such as temperature (Hai et al., 2011), chemical properties, hydraulic retention time (HRT), solid retention time (SRT), pH and nitrification level (Cirja et al., 2008, Koh et al., 2009), little is known about the effect of exogenous organic carbon loading on the removal of CoC in biological treatment; where NTFs are expected to operate under lower ammonium-N concentrations and higher chemical concentrations. The addition of exogenous organic carbon substrate may change the dominate bacteria species from nitrifying bacteria to heterotrophic bacteria in NTF (van den Akker et al., 2010), which may affect the nitrification process and further affect the degradation of CoC.

As described in Chapter 2, Section 2.3.1, the bed depth of NTF was 0.6 m, and different microorganisms can develop throughout a gradient of changing conditions, including the availability of nitrogen source and carbon source (van den Akker, 2008). The effect of the mixed culture microorganism in NTF on the removal of CoC is not well understood. Nevertheless, Bagnall et al. (2012) investigated the role of ammonium oxidising and heterotrophic bacteria in the biodegradation of estrogens, and the authors demonstrated that heterotrophic bacteria had the ability to biodegrade estrogens, moreover, organic loading appeared to have no apparent effect on biodegradation of estrogens. Gaulke et al. (2008) also elucidated that the heterotrophic bacteria activity was more likely to be the primary mechanism for EE2 removal. These findings have led to the hypothesis that both of the nitrifying and heterotrophic bacteria can biodegrade a wide range of CoC, and the effects on different CoC may vary.

Findings presented in Chapter 5 showed that in the more nitrified NTF system, high nitrification rate was obtained and the removal efficiency of most CoC was improved, suggesting that the growth of nitrifying bacteria had positive effect on the CoC removal. Little study has been conducted to optimise the CoC removal efficiency in NTF by using exogenous organic carbon substrate, coupled with low ammonium concentration as the nitrogen substrate, and hence the impact of exogenous organic carbon loading on CoC removal was investigated during this study. Additional research was conducted in order to investigate the influence of organic carbon on nitrification rate in the applied NTF system in this study.

In the present study, the laboratory-scale recirculation NTF system was operated under low influent ammonium-N concentration (5 mg NH_4-N L^{-1}) and high flow rate (0.335 L min^{-1}) in the presence of exogenous organic carbon source (sucrose). The results from Chapter 5 demonstrated that the addition of CoC in the recirculation water negatively affected the nitrification performance in the NTFs. As the CoC were dissolved in methanol to prepare the stock solution, the first aim of this study was to investigate the effect of individual methanol and sucrose on nitrification performance in the absence of CoC to make the impact factors clearer. The second aim was to observe the influence of exogenous organic carbon on nitrification performance when challenging the NTFs with CoC. The third aim was to investigate the removal efficiency of CoC in the presence of exogenous organic carbon in NTFs, and subsequently to observe the removal difference between respective chemicals. This was achieved by adding an exogenous carbon source into the initial solution before recirculating. Finally, the removal efficiencies of CoC in the absence and presence of exogenous organic carbon substrate were compared when operating the NTFs under the same initial ammonium-N concentration and flow rate. Additionally, the high rate NTF was reported to have the ability to remove organic carbon from wastewater and/or drinking water (van den Akker et al., 2010), therefore, the total organic carbon (TOC) removal in the NTFs was also investigated.

6.2 Methods

Experiments were conducted on four parallel laboratory-scale NTFs (three of them were challenged with individual CoC and the fourth was operated as control filter). A detailed description of the construction of the parallel NTFs was presented in Chapter 2, Section 2.3. In this study, NTFs were operated under low initial ammonium concentration (5 mg NH_4-N L^{-1}), high flow rate (0.335 L min^{-1}) and in the presence of exogenous organic carbon. The exogenous organic carbon in this study was achieved by supplementing the NTF recirculation water with sucrose solution as an exogenous carbon source. The description of all the chemicals and reagents used in this study was presented in Chapter 2, Section 2.3.5.

6.2.1 Recirculating water preparation

Ammonia stock solution (1 g NH_4-N L^{-1}) was prepared by dissolving 3.819 g ammonium chloride in 1 L Milli-Q water. The exogenous organic carbon source was 15 g sucrose (Thermo Fisher Scientific, Australia) dissolved in 1 L Milli-Q water. 4 bottles (1 L for each) of recirculating water were prepared in tap water, which had a very low TOC concentration of 0.21 mg L^{-1}. Each bottle of prepared water was made by adding 5 mL ammonia stock solution and 5 mL sucrose stock solution. The initial concentration of ammonium and sucrose in the recirculating water was 5 mg NH_4-N L^{-1} and 30 mg TOC L^{-1}, respectively. Each CoC was added individually into three of the bottles, the fourth bottle was a control in the absence of CoC. In order to determine the effect of exogenous organic carbon on the efficiency of NTFs for CoC removal, high initial concentrations of these compounds were introduced in this study. CAF, ACE, TRI, BEZ and BPA were all individually added at an initial concentration of 1 mg L^{-1}. The initial concentrations for other CoC in water were 2 mg ATZ L^{-1}, 5 mg EE2 L^{-1} and 10 mg DEET L^{-1}.

6.2.2 The effect of individual sucrose and methanol on nitrification performance in the absence of CoC

The results obtained in Chapter 5 revealed that the nitrification performance was depressed when challenging NTFs with CoC. In order to clarify the depression factor, experiments were conducted to individually investigate the effect of methanol (CoC dissolving substrate) and sucrose (the exogenous organic carbon that introduced in this study) on the nitrification performance in the absence of CoCs. The NTF, which never had been challenged with CoC, was used in this study. The NTF was operated for 7 hours under each of three experimental conditions: first one with initial ammonium concentration of 5 mg NH_4-N L^{-1}, second one initiated with 5 mg NH_4-N L^{-1} ammonium and 5 mL of the sucrose stock solution (15 g L^{-1}), the third one with 5 mg NH_4-N L^{-1} ammonium and 1 mL L^{-1} of the HPLC standard methanol. Initial samples were taken directly from each reservoir, and subsequent samples were taken hourly from the effluent of the NTF. Nitrification performances in the NTF under these three experimental conditions were recorded and compared.

6.2.3 Experimental design for CoC removal in the NTFs in the presence of exogenous organic carbon

In order to obtain high nitrification rate, the packing media (Chapter 2, Section 2.2.3) were immersed in the diluted activated sludge for a week to encourage the rapid development of nitrifying microorganisms, before it was reinserted into the NTF columns. The activated sludge conditioned packing media were reinstalled in the NTF columns, and the NTFs were then fed with ammonia (5 mg NH_4-N L^{-1}) for one month. In order to maintain this feeding concentration in the recirculating NTFs, 1 mL of ammonia stock solution (1 g NH_4-N L^{-1}) was added every 5 h during the day and after 12 h overnight.

Firstly, the representative nitrification rate of the NTFs operated in this mode was determined over 5 h. Secondly, to investigate the effect of exogenous organic carbon on nitrification performance, the NTFs were again fed ammonia (5 mg NH_4-N L^{-1}) but with the addition of sucrose (30 mg TOC L^{-1}) as an exogenous organic carbon source, which is a readily biodegradable carbon source, for one month. The representative nitrification rate of the NTFs operated in the presence of sucrose was also determined over 5 h. Finally, in the presence of ammonia (5 mg NH_4-N L^{-1}) and sucrose (30 mg TOC L^{-1}), three of the NTFs were challenged with individual CoC. The fourth NTF was operated as a control column with initial ammonia concentration of 5 mg NH_4-N L^{-1} and sucrose concentration of 30 mg TOC L^{-1} in the absence of CoCs. The NTFs were operated in recirculation mode for 27 h. In order to avoid the depletion of nitrogen source during the 27-h operation, each recirculation reservoir was supplemented with ammonia after the collection of each sample via adding 1 mL of ammonia stock solution (1 g NH_4-N L^{-1}). Because sucrose is a readily degradable organic carbon source, 5 mL sucrose stock solution was also added into the recirculation reservoirs of the NTFs every 12 h to compensate for the organic carbon removed over time. In the 27-h experiments, the concentration changes of CoCs were determined to evaluate the CoC removal efficiency. The TOC concentration changes after 12 hours recirculation were also determined to investigate the correlation between TOC loadings and removals. The concentration of ammonium removed by the NTFs was calculated. All experiments were conducted in duplicate.

6.2.4 Sampling and chemical analysis

The water samples were taken directly from the tubing returning the effluent to the reservoir after passage through each NTF. A 10 mL sample was collected hourly for 5 hours to determine nitrification rate. The samples were stored at 3°C ± 2°C and analysed within 2 days for ammonia-N, nitrite-N and nitrate-N using the method described in Chapter 2, Section 2.4.1 and 2.4.2. To determine the removal of CoC, a 10 mL sample was collected every 2 hours for the first 12 hours, and then after 24 hours, and 27 hours. 1 mL of the sample was stored in a vial at -18°C for subsequent HPLC analysis of CoC concentrations using the method described in Chapter 2, Section 2.4.7. The remainder of the 10 mL sample was stored at 3°C ± 2°C for subsequent ammonia-N, nitrite-N, nitrate-N and TOC analysis using the method described in Chapter 2, Section 2.4.4.

6.3 Results

6.3.1 Impact of methanol and sucrose on nitrification performance in the NTF in the absence of CoC

Figure 6.1 shows the nitrification performance in the NTF under three experimental conditions in the absence of CoC.

From Figure 6.1a, it can be seen that when the NTF was operated with ammonium only, the ammonia removal concentrations (mg NH_4-N L^{-1}) increased steadily over time. Similar ammonia removal was obtained in the NTF when operated with ammonia and sucrose, and no statistically significant difference was observed between them (ANOVA, $p>0.05$). However, in the presence of methanol, only minimal ammonia removal concentration was observed, and the ammonia removal was statistically significantly lower than that obtained under the other two conditions (ANOVA, $p<0.05$). The results indicate that the addition of methanol can depress ammonia removal, while the addition of sucrose has no influence on ammonia removal.

Similarly, from Figure 6.1b, it can be seen that when the NTF was operated with ammonium only, the produced nitrite/nitrate-N concentration increased steadily over time. Almost the same nitrite/nitrate-N concentrations were achieved in the NTF when operated with ammonia and sucrose, and there was no statistically significant difference between them (ANOVA, $p>0.05$). However, when operating the NTF with ammonia and methanol, low nitrite/nitrate-N concentrations were observed, and statistically significantly lower than those obtained under the other two conditions (ANOVA, $p<0.05$). The results indicate that in the presence of sucrose, nitrification rate was not affected, while in the presence of methanol, nitrification rate was depressed.

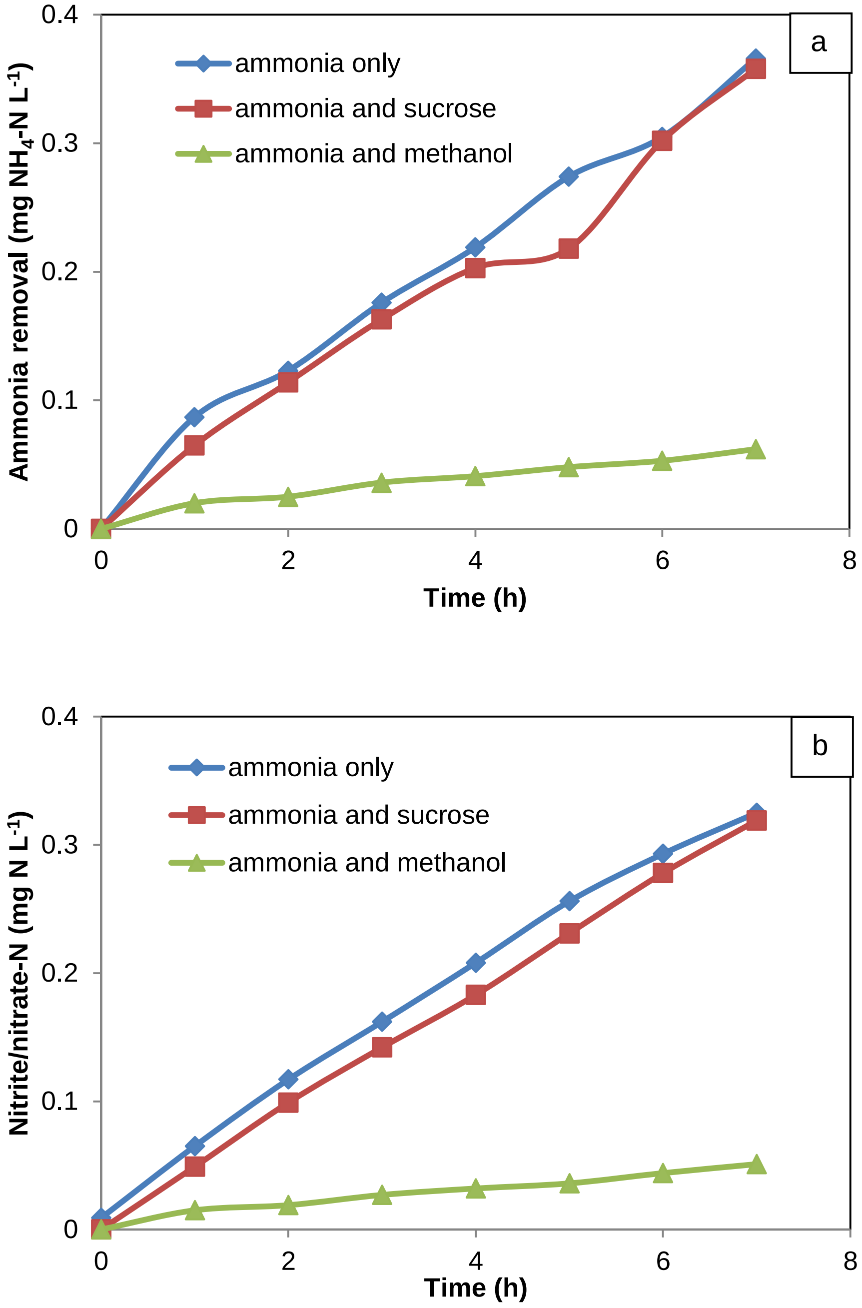


Figure 6.1 Nitrification performance shown as ammonium removal (a) and nitrite/nitrate-N generation (b) after 7 hours recirculation in the NTF under three experimental conditions: ammonia only (5 mg NH_4-N L^{-1}), ammonia (5 mg NH_4-N L^{-1}) with sucrose (75 mg L^{-1}) and ammonia (5 mg NH_4-N L^{-1}) with methanol (1 mL in 1 L recirculating water).

6.3.2 Nitrification performance before challenging CoC

The NTFs were operated at an initial ammonia concentration of 5 mg NH_4-N L^{-1} throughout the experiments. The representative inorganic nitrogen profiles in the NTFs in the absence of CoC are shown in Figure 6.2.

After feeding the NTFs with ammonia (5 mg NH_4-N L^{-1}) for one month, the representative nitrification performance in the NTFs is shown in Figure 6.2a. It can be seen that in the absence of sucrose, the ammonia removal rate was about 0.46 ± 0.07 mg NH_4-N L^{-1} h^{-1}. In order to better understand the influence of the addition of sucrose on nitrification performance, the microorganisms in NTFs were incubated with ammonia (5 mg NH_4-N L^{-1}) and sucrose (30 mg TOC L^{-1}). After feeding the NTFs for one month, a steady nitrification performance was observed in the NTFs (Figure 6.2b). The regression analysis showed that ammonia removal rates, following 1 month of conditioning, measured over 5 h between ammonia additions in the presence of sucrose were 0.44 ± 0.27 mg NH_4-N L^{-1} h^{-1}. There was no statistically significant difference between the two ammonia removal rates (ANOVA, p>0.05). This finding indicated that the ammonia removal rate was not affected by the addition of sucrose in the NTF.

However, the nitrate-N and nitrite-N concentrations in the NTF in the presence of sucrose were slightly lower (ANOVA, p>0.05) than that in the absence of sucrose. Clearly, the lower production of nitrate indicated that the nitrifying process was slightly impeded by the one month incubation with the addition of an exogenous carbon source (sucrose) compared with the results of the short term incubation shown in Figure 6.1.

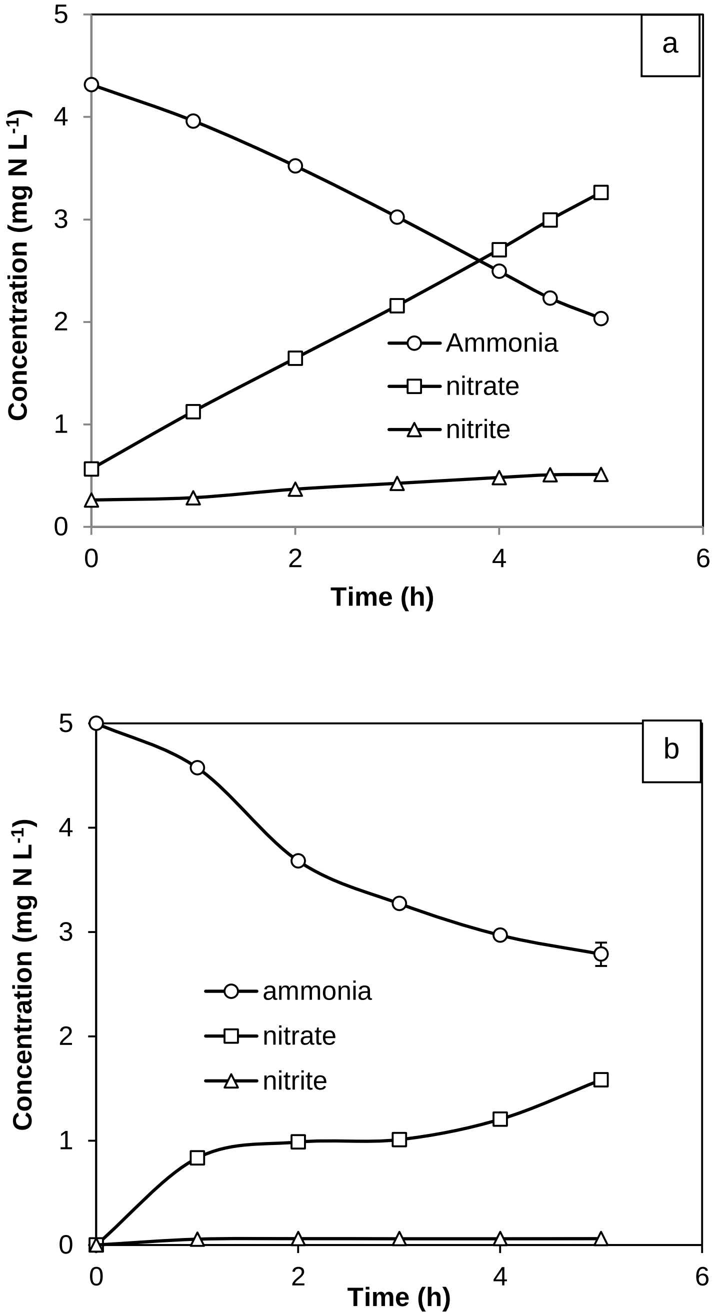


Figure 6.2 Nitrification performance in the NTFs fed 5 mg NH_4-N L^{-1} and operated under different experimental conditions: (a) representative inorganic nitrogen profiles in the NTFs over 5 h following ammonia addition in the absence of exogenous organic carbon; (b) representative inorganic nitrogen profiles in the NTFs over 5 h in the presence of ammonium (5 mg NH_4-N L^{-1}) and sucrose (75 mg L^{-1})

6.3.3 Nitrification performance in the NTFs in the presence of CoC and sucrose

Subsequently, when the nitrification performance in carbon (sucrose) augmented NTFs reached steady-state, the target CoC was added into the NTFs. The mass of ammonia-N removed nitrite/nitrate-N produced over time (27 hours) by the carbon (sucrose) augmented control NTF and the NTFs also fed sucrose (a readily available organic carbon source for the microorganisms) in the presence of each CoC is shown in Figure 6.3.

Figure 6.3a shows the ammonium removal in the control NTF in the presence of sucrose (without CoC) and the NTFs in the presence of CoC and sucrose. Regression analysis showed that the ammonia removal rates (mg NH_4-N L^{-1} h^{-1}) in the NTFs in the presence of sucrose and the different CoCs were 0.53 ± 0.32 (control NTF), 0.51 ± 0.12 (CAF), 0.39 ± 0.18 (TRI), 0.56 ± 0.16 (BPA), 0.40 ± 0.17 (BEZ), 0.43 ± 0.19 (ATZ), 0.40 ± 0.25 (EE2), 0.52 ± 0.16 (ACE) and 0.47 ± 0.20 (DEET) mg NH_4-N L^{-1} h^{-1}. No statistically significant difference was observed between these ammonia removal rates (one-way ANOVA, $p>0.05$). The results indicated that in the presence of exogenous organic carbon, ammonia removal rate (mg NH_4-N $L^{-1}h^{-1}$) was not affected by the challenge of CoCs.

As to the produced nitrite/nitrate-N in the NTFs, Figure 6.3b shows that although no statistically significant difference between the nitrite/nitrate-N concentrations in the NTFs challenged with individual CoCs (ANOVA, $p>0.05$), the produced nitrite/nitrate-N concentrations in the presence of CoC were much lower than that in the control NTF (ANOVA, $p<0.05$).

In summary, in the presence of sucrose and CoC, the ammonium removal in the NTFs maintained the same as the control NTF, which was operated in the presence of sucrose without CoC challenge. Significantly, the depression in ammonia removal (mg NH_4-N L^{-1}) in the presence of methanol alone (Figure 6.3a) was not evident in NTFs fed sucrose in the presence of CoC and methanol (Figure 6.3b) However, the nitrification process was negatively affected by the addition of sucrose and CoC.

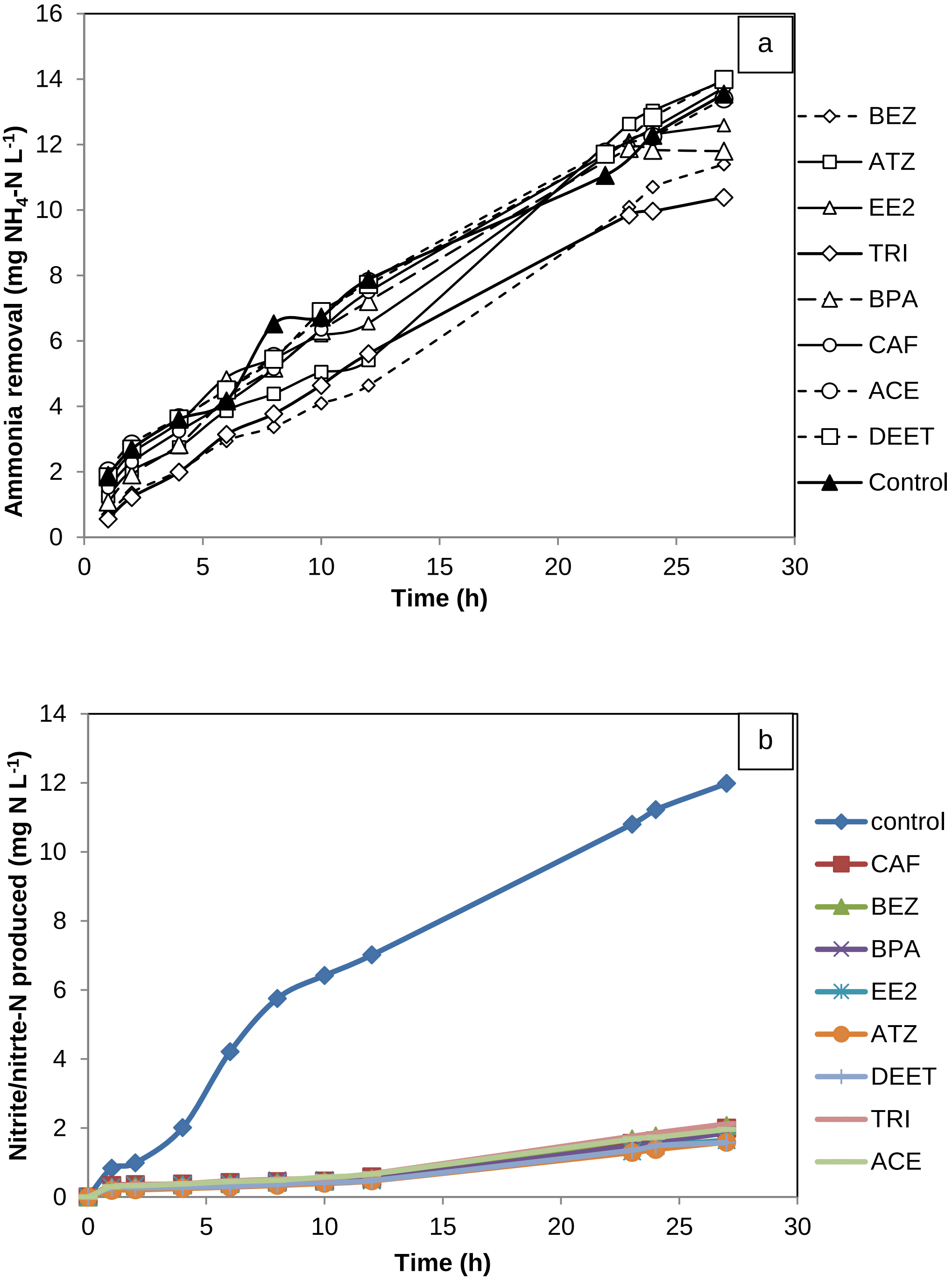


Figure 6.3 The ammonium-N concentration removal (a) and nitrite/nitrate-N produced (b) measured throughout the recirculation NTF during 27 h in the presence of sucrose and respective CoC. The investigated CoCs were benzotriazole (BEZ), atrazine (ATZ), 17α-ethynylestradiol (EE2), trimethoprim (TRI), bisphenol A (BPA), caffeine (CAF), acetaminophen (ACE) and N, N-diethyl-m-toluamide (DEET).

6.3.4 The removal of CoC in the presence of exogenous organic carbon in NTF

In the presence of exogenous organic carbon (sucrose), within 27 hours of the addition of the respective eight CoCs, all the investigated compounds showed varied removal efficiencies in the NTFs.

Figure 6.4 shows that the removal efficiency of the investigated CoCs can be divided into three groups: low removal (BEZ and CAF), medium removal (ATZ and DEET) and high removal (ACE, BPA, EE2 and TRI), according to the C_t/C_0 values and change tendency over time. The low removal group only obtained a removal efficiency of 20% and 30% with a C_t/C_0 value of about 0.8 and 0.7 for BEZ and CAF respectively after 27 h recirculation in NTF. The relative concentration C_t/C_0 values of medium removal group chemicals ATZ and DEET were decreasing gradually, and reached a C_t/C_0 value of 0.43 and 0.38 respectively after 27 h. In the high removal group, C_t/C_0 of ACE maintained a stable decline throughout the operation time, and achieved a C_t/C_0 value of 0.12 (equivalent to a removal percentage of 88%) after 27 hours recirculation in the NTF. For the other three chemicals (BPA, EE2 and TRI) in this group, the C_t/C_0 value dropped sharply within the first one hour, and then gradually decreased to lower than 0.2 at 27 h, which equals to the removal percentage greater than 80%.

The microbial structure in the biofilm may have been changed when the NTFs were operated in the presence of sucrose, which is a readily available exogenous organic carbon source for microorganisms. The high removal efficiency of ACE, BPA, EE2 and TRI may be attributed to the degradation of diverse microorganisms in the NTFs.

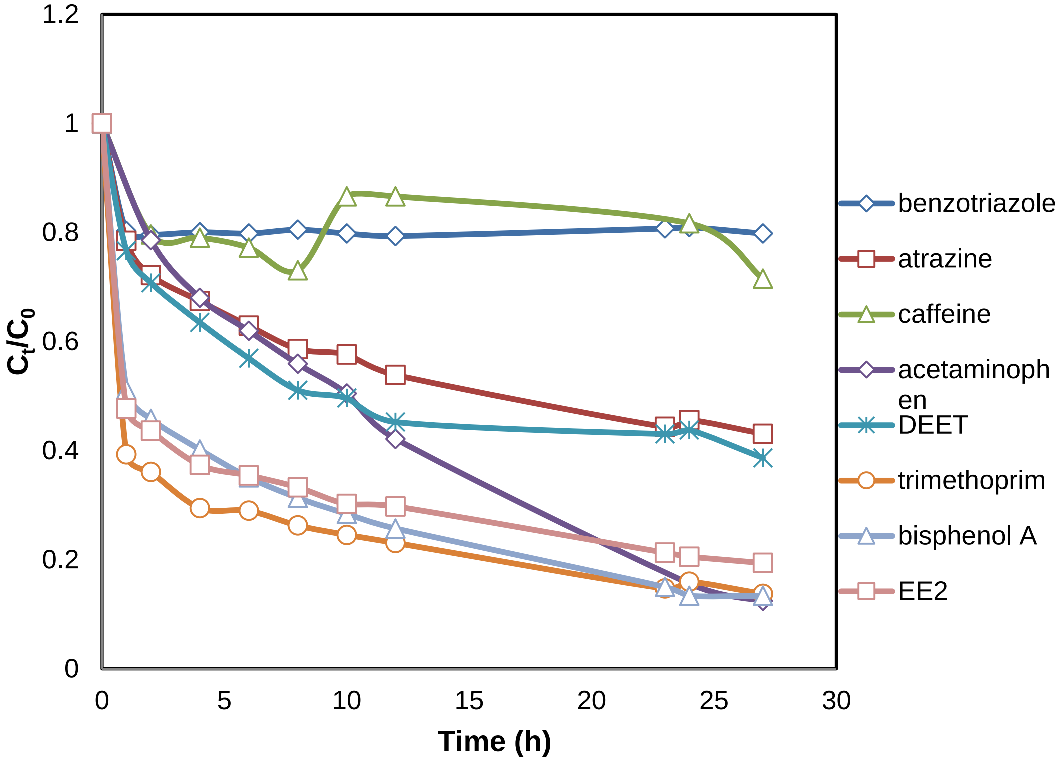


Figure 6.4 The relative concentrations of the respective chemicals of concern over the 27 hous recirculation period in the NTFs in the presence of sucrose (75 mg L^{-1}) as an exogenous organic carbon source. C_t/C_0 is the relative concentration which was obtained by dividing the concentration at time *t* by the initial concentration of each CoC**.**

6.3.5 Comparison of CoC removal in the presence and absence of sucrose

After recirculating the exogenous organic carbon (sucrose) in the NTFs, the nitrification rates were 0.48 ± 0.05 mg NH_4-N L^{-1} h^{-1}, which were statistically similar (ANOVA, $p>0.05$) to the nitrification rate (0.52 ± 0.15 mg NH_4-N L^{-1} h^{-1}) that obtained in previous experiments (see Chapter 4, Section 4.3.3). In order to investigate the impact of exogenous organic carbon on the removal of CoC, the removal percentages under similar initial nitrification performances in the presence and absence of exogenous organic carbon were compared. From Figure 6.5, it can be seen that higher removal efficiencies were generally recorded for most of the compounds (except for CAF and BEZ) in the presence of sucrose.

A notable improvement in removal was observed in the presence of sucrose from 17.95% to 86.3% and 26.2% to 86.6% for TRI and BPA respectively. The improvement in the removal of ACE and EE2 in the presence of sucrose was also worth noting, with a removal percentage of 87.5% and 80.6% respectively. The removal improvement for ACE and EE2 was obvious when comparing with the removal percentage in the absence of exogenous organic carbon (58.59% and 48.34% respectively). Nevertheless, the removal efficiency for DEET and ATZ did not change much, only a slight increase (ANOVA, $p>0.05$) was observed in the presence of exogenous organic carbon. Contrarily, the removal activity of CAF and BEZ was depressed by the addition of exogenous organic carbon in NTFs. The removal efficiency of CAF incredibly decreased from 99% to 28.4%, and a notable decrease in the removal percentage of BEZ was also observed, from 42.8% to 20.2%.

In summary, the addition of exogenous organic carbon sucrose showed a positive effect on the removal efficiency of most CoC, except for CAF and BEZ. The might be attributed by the cooperation of the microbial communities in the NTFs for CoC removal, and the new generated microorganisms may not capable of effectively removing CAF and BEZ. The readily degradable sucrose may be an easier available carbon source for those microorganisms than CAF and BEZ.

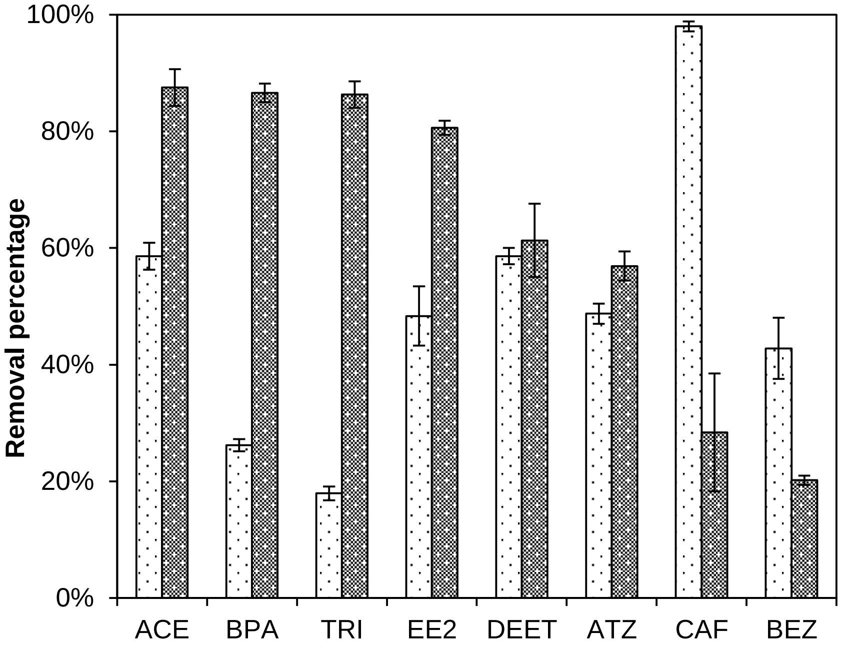


Figure 6.5 Comparison of removal percentages of caffeine (CAF), acetaminophen (ACE), N, N-diethyl-m-toluamide (DEET), benzotriazole (BEZ), 17α-ethynylestradiol (EE2), trimethoprim (TRI), bisphenol A (BPA), atrazine (ATZ) under similar nitrification rates in NTF with the absence and presence of exogenous organic carbon: (⬚) absence of exogenous organic carbon when nitrification rate was 0.52 ± 0.15 mg NH_4-N L^{-1} h^{-1} before CoC challenge; (▩) presence of additional organic carbon when the nitrification rate was 0.48 ± 0.05 mg NH_4-N L^{-1} h^{-1} before CoC challenge. Data present mean values ± 1 SD.

6.3.6 The total organic carbon loading and removal in NTF in the presence of sucrose and respective CoC

Table 6.1 displays the initial total organic carbon (TOC) loadings and the TOC removal after recirculation over 12 h in the NTFs. The TOC load in the NTFs challenged with individual CoC includes the contribution from the addition of exogenous organic carbon (sucrose), the CoC and the methanol in which they were dissolved. The TOC concentration in the control NTF only includes the exogenous organic carbon (sucrose), which is a readily available carbon source for microorganisms. The TOC concentrations reported in the influent of a municipal WWTP in Barcelona, Spain was 67.67 ± 24.29 mg TOC L^{-1} (Radjenovic et al., 2007), while in the surface water in Seminole County, FL, USA, the TOC concentration was 15–32 mg TOC L^{-1} (Boyer et al., 2011). The TOC concentration contributed by exogenous organic carbon (sucrose) in this study (29.7 mg TOC L^{-1}, Table 6.1) was comparable to the TOC concentrations found in the literature. However, the total TOC in this study was higher than that found in the environment, predominantly because the organic carbon within the added CoC.

The high rate NTFs showed the ability to remove these high concentrations of TOC. After 12 hour recirculation in the NTFs, the TOC percentage removals varied between NTFs in the presence of individual CoC and ranged from 45.68% to 84.43% (Table 6.1). Similar TOC removal efficiencies were found in the conventional activated sludge treatment (60%) and membrane bioreactor (84%) (Radjenovic et al., 2007). Figure 6.6 presents a linear relationship between initial TOC concentration loading and TOC concentration removal, which was obtained from the NTFs with the respective compound and the control NTF (without CoC challenge) in the presence of ammonia and sucrose ($r = 0.984$; $p<0.0001$). This result is consistent with the findings reported by van den Akker et al. (2010) in a high rate NTF. Overall, the findings obtained in this study indicated that the addition of CoCs has no significant influence on the TOC removal in the NTFs.

Table 6.1 The initial TOC loading and the TOC removal percentage after 12 hours recirculation in each NTF.

Chemicals	Initial TOC concentration (mg L^{-1})	TOC removal percentage
CAF	299.6	63.15%
ACE	157.6	60.25%
DEET	685.8	48.70%
ATZ	579.0	49.90%
EE2	1451.0	45.68%
BEZ	155.7	56.44%
TRI	301.9	73.32%
BPA	297.1	84.43%
No chemical	29.7	80.77%

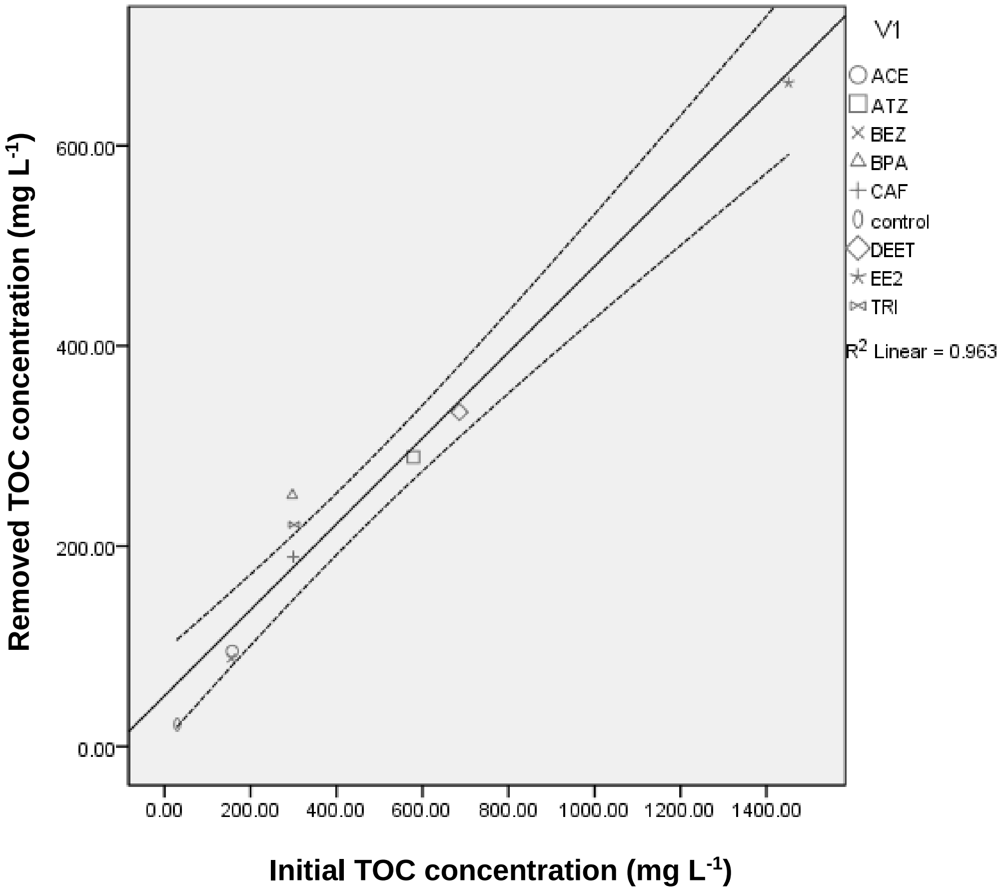


Figure 6.6 Relationship between TOC initial loading and removal concentrations after 12 hours recirculation in the control NTF (in the presence of ammonium and sucrose without CoC challenge) and the NTFs in the presence of ammonium, sucrose and individual CoCs, caffeine (CAF), bisphenol A (BPA), benzotriazole (BEZ), atrazine (ATZ), N, N-diethyl-m-toluamide (DEET), trimethoprim (TRI), acetaminophen (ACE) and 17α-ethynylestradiol (EE2). Dash lines represent 95% confidence interval.

6.4 Discussion

The effect of exogenous organic carbon on nitrification in biological processes for wastewater treatment is commonly reported (Ling and Chen, 2005, van den Akker et al., 2010). Racz et al. (2012) investigated the impact of different organic carbon sources on estrogen removal in the suspended growth nitrifying bioreactors. They suggested that the different population of microorganisms were generated in the bioreactors, fed with different organic carbon sources, which might affect the degradation of estrogen in the bioreactors. Little is known about its effect in the high-rate attached growth NTF for the removal of CoC from wastewater, especially where the influent ammonium-N concentrations are low. Although the influent concentrations of CoC introduced in this study were higher than those detected in the surface water (Benotti et al., 2009) and the WWTPs (Behera et al., 2011), the higher CoC concentrations can clarify the effect of exogenous organic carbon source to the elimination of CoC in the NTF.

The results obtained in Chapter 5, Section 5.3.2 demonstrated that nitrification rate was depressed in the presence of CoC. Roh et al. (2009) reported that the BPA and triclosan mixture caused the inactivation of the *Nitrosomonas europaea* (nitrifying bacteria) in the nitrifying activated sludge. The results obtained by Wang and Gunsch also demonstrated that the presence of some pharmaceutical active compounds might influence the activity of nitrifying bacteria, and further affect the nitrogen removal in the treatment process in the WWTPs (Wang and Gunsch, 2011). Nevertheless, the presence of methanol might inhibit the nitrification activity of nitrifying bacteria (Zhang et al., 2007). Because the growth of methanol degraders consumed a large amount of nutrients and oxygen in the biofilter, and resulted in the poor oxygen and nutrients availability for nitrifying bacteria (Zhang et al., 2007).

In order to clarify the depression factor, additional experiments were carried out to investigate the effect of individual methanol (CoC dissolvent) and sucrose on the nitrification rate in the absence of CoC. The results presented in Section 6.3.1 indicated that the presence of methanol alone showed a severely negative impact on the nitrification performance in the NTF. Although the nitrification rate was slightly depressed by the addition of sucrose, effective ammonia removal was still observed in the presence of sucrose, but not in the presence of methanol alone. In contrast, ammonium removal in the presence of sucrose, CoC and methanol was similar to that in the presence of sucrose alone and not statistically different from the control

NTFs. This suggests that methanol in the presence of sucrose had little impact on ammonium removal.

A readily biodegradable organic carbon source—sucrose was introduced in this study. The high biodegradability of sucrose was easily available for microorganisms, and then produced effect on the population or activity of microorganisms, which further affected the nitrification performance (van den Akker, 2008) and the removal of some CoC (Racz et al., 2012) in the NTF.

In this study, before CoC challenge, the inorganic nitrogen profiles in the NTFs revealed that nitrification rate was slightly affected by the addition of exogenous organic carbon (TOC = 29.7 ± 1.0 mg L^{-1}), while the ammonium removal rate maintained unaffected. Ammonium removal rate of 0.44 ± 0.27 mg NH_4 L^{-1} h^{-1} was observed in the NTFs with the presence of sucrose. Before adding sucrose as exogenous organic carbon, the ammonium removal rate achieved 0.46 ± 0.07 NH_4-N $L^{-1}h^{-1}$. For nitrite-N and nitrate-N, the addition of sucrose slightly affected the ammonium oxidising to nitrate/nitrite-N process. The inorganic nitrogen balance was achieved in the NTF in the absence of the sucrose. However, in the presence of sucrose, the generated nitrite/nitrate-N concentration was lower than removed ammonium concentration. The imbalance in the nitrogen mass balance due to loss of ammonium-N might because of the assimilation for the growth of a variety of bacteria in NTFs. Denitrification in the inner biofilm might be one of the reasons accounting for the unbalance of inorganic nitrogen.

These findings demonstrated that the addition of exogenous organic carbon can boost ammonium removal rather than nitrification rate. van den Akker et al. (2010) reported that a depression was observed on nitrification rate throughout the NTF filter bed with high organic carbon loads. They also suggested that the nitrification inhibition might because of the increase of heterotrophic activity in the presence of exogenous organic carbon.

When challenges with CoC, the typical ammonium-N removal rate obtained in the NTF was 0.44 ± 0.27 NH_4 L^{-1} h^{-1}. No significant difference on ammonium removal rate was observed before and when challenge with CoC, with the presence of exogenous organic carbon. The results obtained in Chapter 5, Section 5.3.2 demonstrated that nitrification performance might be suppressed in the presence of CoC. The findings obtained in this Chapter further suggested that the presence of exogenous organic carbon together with CoC showed no significant influence on ammonium-N removal in the NTF. The higher ammonium removal was observed during the first 4 hours with CoC presence than before CoC challenge. This phenomenon implied that the increased microorganism population in the NTF resulted in the more ammonium-N consumption. Overall, the presence of exogenous organic carbon together with the CoC showed a minimal negative influence on ammonium-N removal in the NTF.

The removal efficiency in the presence of sucrose ranged from 20% to 88%. High removal efficiency was obtained for most of the CoC, in particular, for ACE, EE2, TRI and BPA, the removal efficiency was >80%. With the presence of exogenous organic carbon, the population or activity of microorganisms in the NTF might change (e.g. the growth of heterotrophic microorganisms) (Racz et al., 2012, van den Akker et al., 2010). From the CoC removal result in this study, it can be observed that concentrations of CoC sharply decreased during first one to two hours of recirculation. This might be explained as the abundant biomass on the surface of packing material absorbed more CoC than that before the addition of exogenous organic carbon. Katsoyiannis and Samara (2007) reported that the presence of dissolved organic carbon was able to change the partition of dissolved and adsorbed phase of the organic pollutants in wastewater. The decreased of CoC concentration might also be because the heterotrophic bacteria utilised the CoC for the metabolic activity (Koh et al., 2009). Overall, after 27 hours recirculation in the NTF, high removal efficiency was achieved for most of the investigated CoC.

The high-rate NTF with the presence of exogenous organic carbon also showed the ability to remove the total organic carbon. The high total organic carbon removal percentage was observed for the NTF with and without CoC presence, ranging from 70% to 99%. The result in this study showed a linear relationship between total organic carbon loading and removal. This finding was consistent with the result reported by van den Akker et al. (2010), in which study a linear relationship between carbon loading and removal was observed.

With the presence of exogenous organic carbon, the improvement of removal efficiency was observed for most of the CoC, except for CAF and BEZ. The heterotrophic organisms, derived by the addition of exogenous organic carbon, also can degrade most of the organic contaminant via cometabolism and/or metabolism (Tran et al., 2013).

Compared with CAF, the exogenous organic carbon source might be an easier available carbon source for the changed bacteria population or activity in the NTF, which resulted in the low removal efficiency for CAF (approximately 30%). BEZ was a biodegradation recalcitrant compound, with low elimination of 30% to 55% in the WWTPs in Berlin (Reemtsma et al., 2010), the abundant microorganisms in the NTF showed negative effect on the removal efficiency for BEZ. The suggested effective removal technology for BEZ was advanced oxidation process (UV/H_2O_2) or UV irradiation (Bahnmüller et al., 2015). The motivation to optimise the NTF for BEZ in this study is the poor removal efficiency obtained in the NTF and the high treatment cost or energy consumption in other process mentioned above. Further study is still need to improve BEZ removal in the high-rate NTF.

Significant improvement of the removal efficiency for BPA, TRI, EE2 and ACE was observed with the presence of exogenous organic carbon. Among them, the largest improvement was observed for TRI removal. TRI showed a recalcitrant behaviour in the conventional activated sludge treatment, with a minimal removal of up to 20% (Göbel et al., 2007), and a lower removal of 14% was observed in a conventional activated sludge reactor under nitrifying condition by Suarez et al. (2010). Fernandez-Fontaina et al. (2012) reported that 78% of TRI was eliminated in a nitrifying reactor. The similar high elimination efficiency (70%) for TRI was obtained in the batch study with nitrifying activated sludge (Batt et al., 2006). In the current research, the improved removal efficiency for TRI might be because of the mixed bacteria species (nitrifying bacteria and heterotrophs), derived by adding the exogenous organic carbon, in the NTF. Khunjar et al. (2011) reported that the cooperation of ammonium oxidising bacteria and heterotrophs enhanced the degradation of TRI in the nitrifying activated sludge (NAS). Their study also demonstrated that heterotrophs showed principal contribution to TRI removal in NAS.

The removal efficiency for BPA significantly improved after adding the exogenous organic carbon. The diversity of microorganisms (nitrifying microorganisms and heterotrophs) in the NTF might be one of the important reasons for the BPA removal efficiency improvement. The nitrifying water treatment system (e.g. nitrifying activated sludge) is capable of eliminating BPA, and the primary removal mechanism is biological activity rather than sorption (Kim et al., 2007a). Further study by Roh et al. (2009) reported that both nitrifying microorganisms and heterotrophs showed the ability to degrade BPA. In the current study, the growth of heterotrophic microorganisms after adding exogenous organic carbon was responsible for a large fraction of the improved BPA removal efficiency.

EE2, a synthetic estrogen, which can cause fish population collapse in aquatic environment (Kidd et al., 2007), the biodegradation of EE2 has been widely studied (Bagnall et al., 2012, Bautista-Patacsil et al., 2014, Gaulke et al., 2008, Khunjar et al., 2011). Khunjar et al. (2011) reported that the high removal efficiency for EE2 is expected when ammonium oxidising bacteria cooperate with heterotrophs during the EE2 biotransformation in the NAS. Further study by Racz et al. (2012) confirmed the ability of heterotrophs to degrade EE2, showing a removal of 76.9% when the nitrifying activity was inhibited. Complete removal was achieved for EE2 removal when combined heterotrophs and nitrifying cultures together (Bautista-Patacsil et al., 2014). Thus, both nitrifying bacteria and heterotrophs played an important role on the elimination of EE2 during the biological treatment process (Larcher and Yargeau, 2013). The current study also obtained a significant improvement for EE2 removal when the exogenous organic carbon added into the NTF, in conditions where the growth of heterotrophs was encouraged.

The importance of nitrifying bacteria in the biotransformation of ACE has been demonstrated by Chiron et al. (2010). Little is known about the effect of heterotrophs to the removal of ACE in a nitrifying biological system. In this study, the removal efficiency improvement for ACE in the NTF, after adding exogenous organic carbon, revealed that the contribution of heterotrophs to the ACE removal was significant.

For DEET and ATZ, a minimal improvement on removal efficiency was observed when added sucrose as exogenous organic carbon in the NTF. Sharif et al. reported that the high carbon loading rate slowed the degradation of ATZ in a constructed wetland (Sharif et al., 2014). Slight improvement on ATZ removal in the current study revealed that the addition of exogenous organic carbon showed no significant effect on ATZ removal in the NTF. DEET is a biodegradable compound in the secondary treatment in WWTP, with a removal percentage of 70% (Sui et al., 2010). The comparative removal efficiency was obtained in the current study. The slight improvement after added exogenous organic carbon suggested that, the growth of heterotrophs in the NTF showed no apparent influence on the removal efficiency of DEET in the nitrifying treatment system.

The exogenous organic carbon augmented NTFs showed the ability to remove TOC, and the TOC concentration removal showed linear relationship with TOC concentration loading. The results revealed that the NTFs were capable of removing high concentrations of TOC, and the TOC removal increased with the increase of the initial TOC concentration.

Overall, in the presence of sucrose, effective ammonium removal rate was observed, despite the slightly depressed nitrification rate. The nitrogen was likely removed through assimilation by the diverse microorganism communities in the NTFs. After incubating the NTFs with sucrose, the sucrose augmented NTFs showed better removal efficiencies for most of the investigated CoC. This might be attributed to the effective cooperation of nitrifying and heterotrophic microorganisms in the biofilm. Therefore, native or additional exogenous organic carbon may be considered as a means of optimising the performance of NTFs for CoC removal. The high rate NTFs can effectively remove ammonium-nitrogen, TOC and CoC.

7 GENERAL DISCUSSION

The application of treated wastewater for agricultural irrigation, industrial usage, domestic usage and recreational activity usage has increased, because of the clean water shortage in most areas around the world, especially those arid or semi-arid areas. The poor protection of some natural water catchments also contributes to poor water quality. One of the keynotes to solve this problem is to improve the efficiency of wastewater treatment processes and ensure the quality of the WWTP effluent for reuse.

Chlorination is an important and traditional pathway to disinfect the wastewater. The presence of ammonium in the wastewater increased the chlorine demand for pre-chlorination during the treatment (van den Akker et al., 2005). The pre-chlorination by-products are harmful to human health, and the extra cost and corrosion will be caused by the overdosing of chlorine (van den Akker, 2008). In order to protect human health and optimise the water treatment process, it is essential to remove ammonium before the chlorination process to reduce the chlorine demand. van den Akker et al. (2008) successfully employed a 3 m high NTF to remove ammonium at low concentrations. This 3 m high NTF effectively transformed ammonium-N to nitrate-N, which is a less chlorine-demanding form of nitrogen. Considering the world-wide energy crisis and greenhouse gas (GHG) emissions, energy saving is now an important consideration for the design of WWTP. Compared to the 3 m high NTF, a shorter NTF with the same specific packing media area will save energy for water delivery to the shorter NTF.

This study compared two NTFs with different aspect ratios and the same specific packing media surface area. The concept was to explore the effect of filter aspect ratio to the ammonium removal efficiency in the high-rate NTF at low ammonium concentrations. van den Akker (2008) demonstrated that the specific ammonium loading rate (mg NH_4-N m^2 d^{-1}) was a key design parameter (van den Akker et al., 2011) and the hypothesis was that NTFs with the same specific surface area would yield the same nitrification performance independent of aspect ratio. The effect of some of the water quality parameters, such as DO, pH and total alkalinity on the ammonium removal efficiencies of the two NTFs was also compared.

This study was the first to take filter aspect ratio into account to assess the nitrification performance of the polypropylene-packed high-rate NTF. The influent ammonium concentrations for both NTFs were maintained low (1.0–4.0 mg NH_4-N L^{-1}). The variation of other parameters throughout the experiment period was not significant, such as DO (8.25–9.58 mg L^{-1}), pH (7.96–8.55), total alkalinity (75–109 mg $CaCO_3$ L^{-1}). The nitrification performance (ammonium removal rate or nitrate producing rate) observed in both NTFs were relatively similar either in short-term or long-term operation. The result further demonstrated that the aspect ratio of the filter design was not a significantly important factor that will affect the ammonium removal efficiency in the NTF.

The result analysis of the water quality parameters (Chapter 3, Section 3.3.5; Table 3.1) showed that both NTFs received similar influent DO and total alkalinity concentrations. The correlation between ammonium removal and the effluent pH was almost the same (ANOVA, $p>0.05$) in both tall and short NTFs. These findings also confirmed that the effect of filter aspect ratio on the nitrification performance in the high-rate NTF was insignificant.

The significance of this study is that it provided more filter design options for the NTF construction under different conditions. For example, the WWTPs with large available construction area and restrictions on the cost of filter operation and management may choose the short design with a larger 'footprint'. Whereas for WWTPs where space is at a premium, the tall and slim filter design may be a better alternative to make full use of the vertical space, however, operational costs will be higher since more energy will be required for pumping effluent onto an elevated NTF.

Nutrients (e.g. nitrogen and phosphate) contamination is prevalent and commonly detected in many polluted fresh waters (Dodds et al., 2008). In recent decades, emerging biologically active organic contaminants have also been detected in many water sources, such as surface water (Loos et al., 2007), drinking water (Benotti et al., 2009), influent and effluent water from WWTPs (Behera et al., 2011). This might be caused by the increased usage of new technology chemicals and the ineffective treatment in the conventional WWTPs. The direct and acute toxicity effects are uncertain for human health, however, potential for bioaccumulation or bio-concentration of these organic pollutants will have indirect negative effect to the environment and public health (Geyer et al., 2000). The chemicals of concern (CoC) evaluated in this thesis are organic contaminants, including endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs).

The most efficient candidate technologies to remove CoC from waters are the biological treatment processes. Effective elimination of CoC has been achieved in the activated sludge treatment (Nakada et al., 2006), membrane bioreactors (Trinh et al., 2012b) and low-cost trickling filters (Camacho-Muñoz et al., 2012). Tran et al.

(2013) reported that both autotrophic nitrifying bacteria and heterotrophic microorganisms are capable of degrading some organic pollutants. These microorganisms are found in the high-rate NTF (van den Akker et al., 2011). Considering the energy consumption for aeration in the activated sludge WWTP and the high-cost for operation and maintenance for the membrane bioreactors, a low-cost, easily-operated and low maintenance NTF might be a better alternative for the CoC removal.

This study applied the high-rate NTF to remove the CoC from wastewater. Eight compounds from a variety of classifications were investigated in this study. In order to better understand the effect factors of the NTF for the CoC removal, high concentrations of the CoC were employed to enable better identification of the effect of operational configuration of CoC removal. The batch CoC adsorption experiments using sterile NTF construction materials were performed. The results demonstrated minimal sorption of the tested materials. Considering these results together with the biomass sorption results obtained by other researchers (Fan et al., 2014), degradation is considered the dominant mechanism for CoC removal in the NTF.

Operating the NTF in recirculation mode showed that the high-rate NTF had the ability to remove CoC from wastewater, and the removal efficiency ranged from 18% to 98%. The efficiency varied for different CoCs because of the different characteristics of each CoC. The highest removal efficiency was achieved for caffeine (98%), which is recognised by many researchers as a readily biodegradable compound in the biological treatment process (Camacho-Muñoz et al., 2012). The least removed compound was trimethoprim (18%), which showed high resistance to the biological treatment. Similar results were observed by Lindberg et al. (2006) in the Swedish WWTPs. Benzotriazole is also a biodegradation resistant compound, the removal efficiencies ranged from 30% to 55% (Reemtsma et al., 2010). In the current study, low removal efficiency was also observed for BPA (27%), compared with 77.8% removal in a sponge-based moving bed bioreactor (Luo et al., 2014a). Guerra et al. (2015) reported that the removal efficiency of BPA ranged from 1% to 77% in different treatment process. EE2 was removed 48% in the NTF, whereas a higher efficiency was achieved in a nitrifying enriched membrane bioreactor (De Gusseme et al., 2009). Acetaminophen, DEET and atrazine all showed similar removal efficiency (approximately 60%) in this study, whereas higher removal efficiencies were obtained in the biological activated carbon treatment for atrazine (Herzberg et al., 2004), in the membrane bioreactor for DEET (Trinh et al., 2012b) and in the activated sludge treatment for acetaminophen (Yang et al., 2011). These findings indicated the potential for additional removal for the CoC.

Servos et al. (2005) noted that a longer hydraulic retention time (HRT) or solid retention time (SRT) could increase the removal of the CoCs. The finding suggested that the efficiency of the NTF in this study can be optimised to achieve higher removal efficiency for CoC. Thus, the efficiencies of the NTF for CoC removal were recorded under prolonged recirculation time. The results showed that removal improvement was observed for most of the investigated chemicals after prolonged recirculation time, the enhancement of CoC removal efficiency ranged from 2% to 40%. The removal efficiency improvement in this study confirmed the importance of HRT/SRT in the biological treatment process for the removal of some emerging organic contaminants, and prolonging the operation time might be one of the optimisation approaches.

Prolonged incubation of the NTF in the presence of ammonia enhanced the nitrifying microorganism population. This study investigated the effect of nitrification rate on the efficiency of the NTF for CoC removal. When a high nitrification rate (almost double the nitrification rate before enrichment) was achieved, the removal efficiencies for CoC showed notable improvement for most of the target CoC. The largest improvement was observed for ACE, with an additional 40% percentage removal in the more nitrified NTF. Batt et al. (2006) also reported the higher percentage removal of TRI in the more nitrified activated sludge. The current study reported here confirmed that an increased nitrification rate can improve the efficiency of the NTF for the CoC removal, supported the results of Yi and Harper (2007).

This study also provided a new insight into the effect of the CoC challenge to the nitrification performance in the NTF. From the results of the inorganic nitrogen profiles before and after challenging CoC, it was shown that the CoC challenge severely suppressed the nitrification performance in the NTF. Since the CoC used in this study were dissolved in the HPLC-grade methanol (1 mL) prior to add to water (1 L). Additional experiments were carried out to explore the toxicity of methanol to nitrification performance. The response of the NTF to challenge with exogenous carbon sources was complex. Initial results confirmed that water/methanol alone could depress both the nitrifying and ammonia removal activity in the NTF. However, sucrose alone depressed neither nitrification nor ammonia removal compared with a control NTF fed only ammonia. Conversely, the CoC challenge mixture containing sucrose, methanol and CoC suppressed nitrification but not ammonia removal. The effect of the CoC-methanol-sucrose solution on ammonia removal was the similar to that in the presence of sucrose alone suggesting that the influence of methanol on ammonia removal was minimal. Furthermore, from the TOC analysis of the mixtures it can be inferred that the methanol contributed little to the TOC, likely volatilising from solution. The challenge concentrations of CoC were higher that reported environmental concentrations, the effects on nitrification may therefore be more pronounced and the effect of CoC on nitrification requires further investigation at environmental concentrations.

Zhang et al. (2007) showed that the mechanism for the inhibition of nitrification was most likely via the limited availability of oxygen and nutrients for nitrifying bacteria caused by metabolism of the methanol. Wang and Gunsch (2011) reported that the presence of some pharmaceutically active compounds might have negative effect on nitrogen removal by affecting the activity of nitrifying bacteria. Zielińska et al. (2014) found that the presence of high concentration of BPA decreased the nitrification rate in a nitrifying system with immobilized biomass.

In the high-rate NTF that developed by van den Akker et al. (2011), the biofilm structure changed when exogenous organic carbon was dosed into the water delivery line, a more complex microbial biofilm (including nitrifying bacteria and heterotrophic bacteria) was produced. Khunjar et al. (2011) elucidated the contribution of heterotrophs and nitrifying bacteria in the removal of some emerging pollutants, demonstrated that both of the microorganism species showed ability to remove some of the emerging contaminants (e.g. EE2 and TRI). In the current study, the effect of exogenous organic carbon on the efficiency of the NTF for CoC removal was explored. Sucrose was introduced as a simple exogenous organic carbon source.

After incubating the NTF with an addition of exogenous organic carbon, the nitrification rate in the NTF slightly decreased, but effective ammonium removal was still observed in the presence of sucrose. Greater suppression of nitrification was observed by van den Akker et al. (2010) when the NTF was fed with high carbon loads. In the study present here, the removed ammonium concentration was slightly higher than generated nitrite/nitrate-N. The nitrogen mass imbalance, indicative of a removal pathway other than nitrification, might be caused by the nitrogen assimilation in the NTFs (van den Akker, 2008).

The efficiency of the sucrose fed NTF for CoC removal was investigated. After 27 hours recirculation, high removal efficiency was achieved for most of the target CoC, ranging from 20% to 88%. Especially for acetaminophen, EE2, trimethoprim and BPA, the removal efficiency for which was >80%. In the presence of sucrose, the population and activity of the microorganisms (nitrifying bacteria and heterotrophs) in the NTF increased, and the improvement of removal efficiency was observed for most of the target CoC. For example, the removal efficiency for BPA was significantly improved after adding the exogenous organic carbon source. Roh et al. (2009) found that both heterotrophs and nitrifying bacteria were able to degrade BPA. With the growth of heterotrophs in the NTF, the removal of EE2 was enhanced. Larcher and Yargeau (2013) demonstrated the importance of both heterotrophs and nitrifying bacteria on the EE2 removal in biological treatment process. Racz et al. emphasized the ability of heterotrophs to the removal of EE2 by showing 76.9% removal efficiency for EE2 at the absence of nitrifying activity. Overall, the contribution of heterotrophs to the removal of CoC was significant. Thus, the presence of exogenous organic carbon sucrose displayed positive influence to the efficiency of the NTF for the removal of most of the investigated compounds.

This study also explored the TOC removal in the high-rate NTF. Results showed that the NTF could effectively remove the TOC, with the percentage removal up to 85%. A linear relationship between TOC initial concentrations and the total removed TOC concentrations was observed. This finding was consistent with the results reported by van den Akker et al. (2010). In addition, the TOC removal was independent of the classification of the challenged CoCs, showing no significant difference on percentage removal when the NTF was challenged with different compounds.

Throughout the entire project, the efficiency of the NTF for CoC removal was comparatively high. Combining the results from all the NTF recirculation studies under different operational conditions, the highest removal was selected for each investigated compound. Figure 7.1 shows the highest percentage removal of each chemical obtained in the entire study. CAF and ACE (99%) were the most effectively removed compounds under the nitrifying condition, which followed by BPA, TRI and EE2 (>80%) under the exogenous organic carbon augmented condition. Approximate 70% removal was observed for DEET. Lower removal efficiency of <60% was obtained for ATZ. No significant difference was found for the removal efficiencies of DEET and ATZ between different operational conditions. The least removed compound was BEZ, which demonstrated resistance to biological degradation throughout this study. An advanced UV/H_2O_2 oxidation process might be a better alternative for the removal of BEZ (Bahnmüller et al., 2015).

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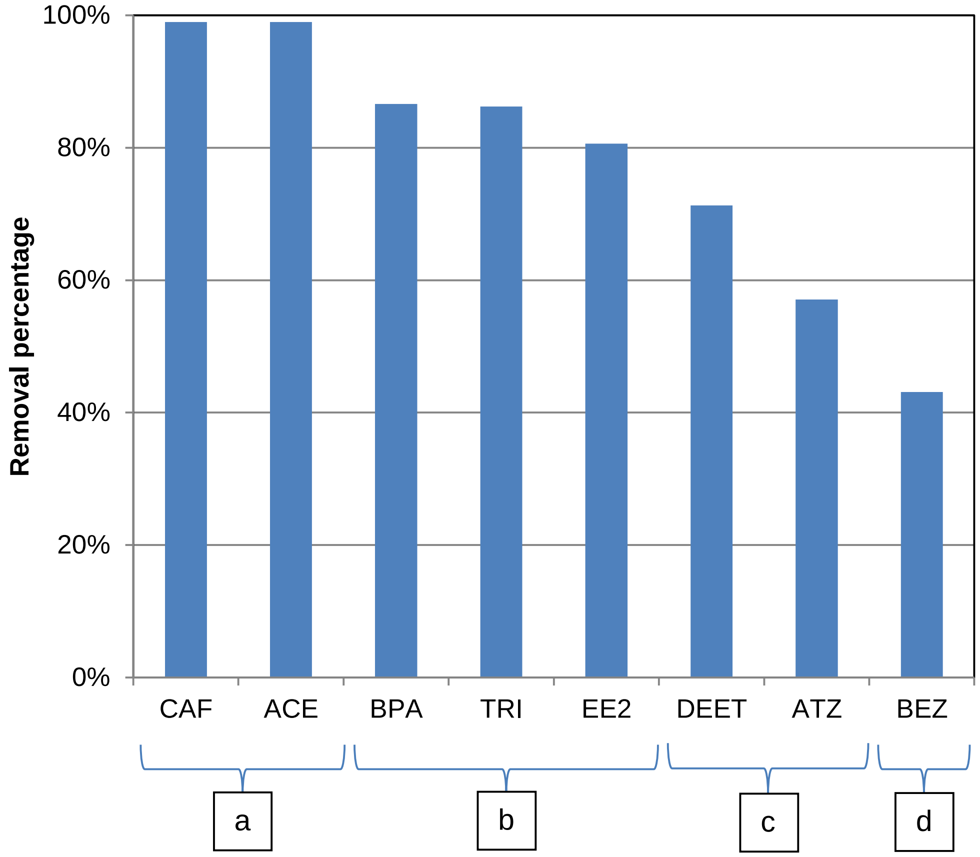


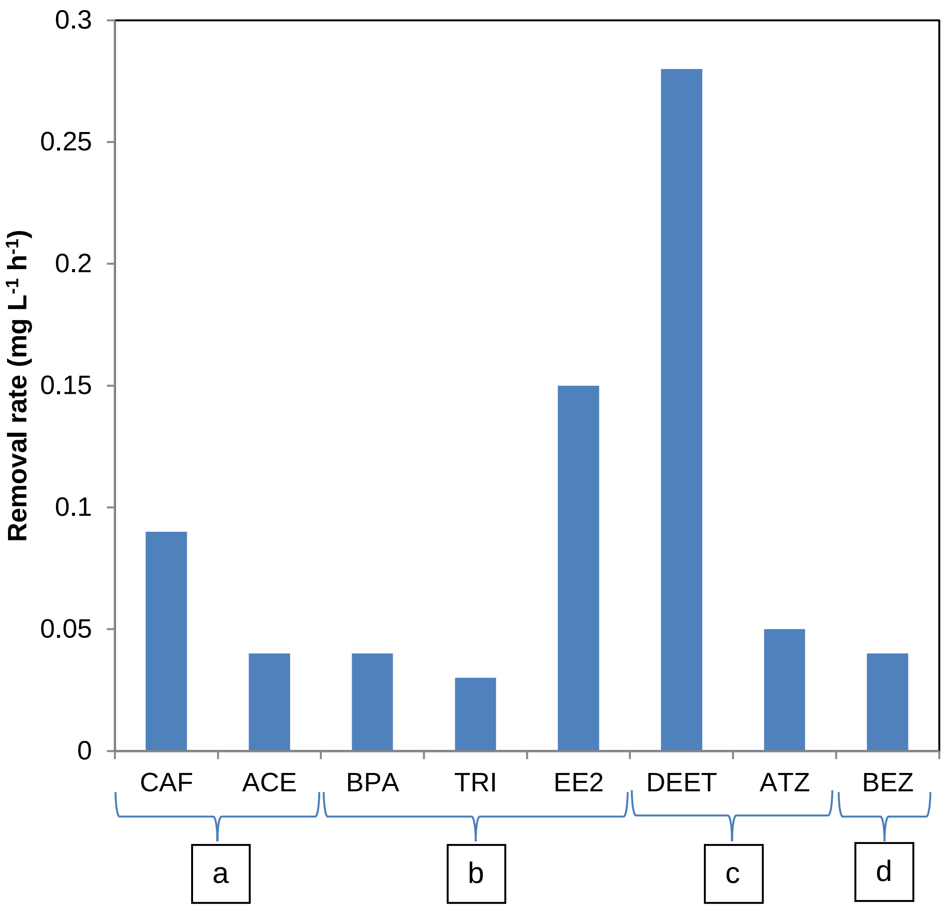
(a) High removal efficiencies were observed in the nitrifying environment;

(b) High removal efficiencies were observed in the presence of exogenous organic carbon;

(c) No significant difference on removal efficiencies in nitrifying environment or in the presence of exogenous organic carbon;

(d) Low removal efficiencies were observed under all studied conditions.

Figure 7.1 The highest removal efficiencies (%) under different conditions for all the investigated CoCs throughout the entire project.



(a) High removal rates were observed in the nitrifying environment;

(b) High removal rates were observed in the presence of exogenous organic carbon;

(c) High removal rates were observed in both nitrifying environment and the presence of exogenous organic carbon;

(d) Low removal rates were observed under all studied conditions.

Figure 7.2 The highest removal rate (mg L^{-1} h^{-1}) of each investigated chemical in the NTFs under different operational conditions, with initial concentrations of 1 mg L^{-1} for CAF, ACE, BPA, TRI and BEZ, 2 mg L^{-1} for ATZ, 5 mg L^{-1} for EE2 and 10 mg L^{-1} for DEET.

Figure 7.2 shows the highest removal rate (mg L^{-1} h^{-1}) of each chemical under different operational conditions. The high removal rates of all the investigated chemicals indicate that the high rate NTF has the potential to effectively remove the CoC when recirculating under certain conditions.

In conclusion, the application of a high-rate NTF could effectively remove ammonium, CoC and TOC from wastewater. The NTFs with different aspect ratios and the same specific packing media surface area showed very similar nitrification performance. For the CoC removal, the efficiency could be enhanced by increasing the operation time, improving the nitrification rate and adding exogenous organic carbon source (sucrose) to increase the population and activity of bacteria (nitrifying bacteria and heterotrophs) in the high-rate NTF. The CoC at the challenged concentrations might inhibit the microorganism activity in the NTF, thus, recovery time for the microorganisms may be needed between challenges. TOC also can be effectively removed simultaneously with CoCs in the high-rate NTF. The results of this study demonstrated that NTF technology offers significant opportunities for energy efficient, sustainable wastewater treatment.

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