

Department of Civil Engineering

**Catch Basin Insert: Characterization and Modelling of Stormwater
Treatment at Source**

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**This thesis is presented for the Degree of
Doctor of Philosophy
of
Curtin University**

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: 

Date: 15/03/18

DEDICATION

This dissertation is dedicated to my loving mother Mrs. Aklima Khatun, a very beautiful, pious, and self-learned woman, who had a limited academic study but tried to educate her children for highest academic education and practiced self-sacrifice throughout her sterling life.

This dissertation is dedicated to my affectionate father late Md. Mozammel Haque, an upright and honest man, who dedicated his entire life for the good of his family. Unfortunately, he passed away just after nine days of commencement of my PhD study and left us with his memories to pearl.

The dissertation is dedicated to my beloved and beautiful daughter Zarin Subhah, five and a half now, and never stops amusing me.

The dissertation is dedicated to my ever loving and caring wife Nowrin Zahan. A very good-looking woman (I do not usually say this in front of her for obvious reasons) and a woman of charm.

For me, not a full practitioner yet, a great believer in the wisdoms of the holy Quran and a follower of Muhammad (peace be upon him).

ABSTRACT

Nonpoint source pollution from stormwater is increasing with increasing urbanization which is becoming a major environmental concern both in Australia and internationally. Stormwater runoff carries pollutants such as trash, metals, nutrients, hydrocarbon and suspended solids to nearby receiving waterbodies. Various best management practices (BMPs) have been introduced for removing these pollutants including gross pollutant traps, constructed wetlands, retention ponds, detention basins, grass swales, vegetated filter strips, biofilters, sand filters and catch basin inserts (CBIs). Most of these technologies can effectively reduce the concentration of pollutants but require significant land area. Among these technologies, CBIs are a promising tool for pollutant removal from stormwater because they are typically mounted within catch basins (e.g. side entry pits) that do not require any extra land. Current research on CBIs is inadequate in providing detailed understanding of pollutant removal mechanisms. Existing CBIs are also not capable of removing dissolved pollutants from stormwater. This Thesis investigates the pollutant removal characteristics of CBIs using geotextile and proposes a modified CBI for removing dissolved pollutants using low-cost adsorbent materials.

Studies in this Thesis were conducted in two phases: field and laboratory investigations. For the field study phase, three locations in Western Australia were selected based on three different land uses: i) mixed land use; ii) residential area and iii) coastal cum recreational area. In these locations, industry partner, Urban Stormwater Technologies Pty Ltd (UST) installed CBIs that use a special type of synthetic non-woven needle punched polypropylene geotextile to capture the gross pollutants and several of these locations were selected for field investigations. CBIs at all sites were sampled monthly for gross pollutants (GPs), sediments and water over the course of one year. The collected materials were separated, and their detailed chemical and physical characteristics were determined. The results showed that the UST CBI can capture pollutants down to 150 microns while retaining its shape and pollutant capturing capacity for at least one year, performing better in these respects than comparable devices reported in the literature. The main component of GPs was vegetation (93%); the accumulation of which showed a strong relationship ($r^2=0.9$) with rainfall especially during the wet season. Improvements in water quality were

found to be 90%, 88%, 88% and 26% in terms of BOD, COD, TSS & PO₄-P, respectively: the heavy metal content in water samples was found negligible. Analysis of particle size distribution, specific surface area of solids and heavy metal content (Cu, Fe, Ni, Pb, Zn and Cd) in solids showed that sites in the residential area generally contained finer particles, and hence had greater surface area, than those in the commercial area but that solids in the commercial area contained greater concentrations of heavy metals than those from the residential area.

Investigations in phase two of the Thesis comprised a series of laboratory scale column experiments to determine the hydraulic and solids removal characteristics of CBIs using three types of geotextiles. A plexiglass column was constructed to model the CBI for capturing solids from the storm drainage system and three different geotextiles were compared, including that used in the UST CBI (nonwoven geotextile-NWG1) and two other commercially available versions (NWG2, NWG3). The results of solids removal trials showed that the desired stormwater TSS concentration (<30 mg/L; ANZECC, 2000) could be achieved with a short ripening process (e.g., 1-2 kg/m² of suspended solids loading) in the case of the larger particle size distribution (P2). Larger particle sizes (P2) were captured 36% more effectively than the smaller particle sizes (P1). The type of geotextile fibre used significantly impacted the solids removal capacity of the CBI. Geotextile NWG1 had higher permittivity than NWG3 but similar to NWG2. NWG1 could capture more TSS than NWG2 and NWG3 because of its special fibre pattern. The overall hydraulic performances showed higher potential of NWG1 for use in CBIs because of its greater strength and multiple reuse capability.

In order to develop a modified CBI to remove dissolved pollutants simultaneously with solids, low-cost adsorbent media to remove nutrients (nitrogen and phosphorous species) from stormwater was trailed. Biochar from *Eucalyptus wandoo* (EW), a by-product of a pyrolysis was used to remove nitrogen (NO₃-N, NO₂-N, NH₃-N,). Alum sludge, a by-product of water treatment processing, was used for phosphorous (PO₄-P) removal. Surface characterisation showed EW biochar to be a good adsorbent because of its H4 hysteresis type mesoporous structure with amorphous materials. Batch adsorption tests using EW biochar with varying nitrogen concentrations, dosage, pH and contact time were conducted to determine adsorption kinetics and isotherms. The maximum removal of NO₂-N and NH₃-N was found to be 100% at lower

concentrations (0.5-1 mg/L) but the removal of $\text{NO}_3\text{-N}$ was found negligible (<1%). The adsorption capacity was inversely related to dosage at the optimal pH of 4-5. Adsorption kinetics followed the pseudo-second-order model for both $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ and the Langmuir model fitted better than Freundlich model in the isotherm study. In order to remove both nitrogen ($\text{NO}_2\text{-N}$, $\text{NH}_3\text{-N}$) and phosphorous ($\text{PO}_4\text{-P}$) simultaneously, a mixture of *EW* biochar and alum sludge (4:1) was tested in another series of batch experiments. The results confirmed that more than 90% of $\text{PO}_4\text{-P}$ was removed within 5 minutes for all concentrations while >90% $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ removal was achieved within 2 and 4 hours respectively for a concentration of 1 mg/L. Adsorption kinetics followed the pseudo-second-order model for all species and adsorption isotherms showed that $\text{NH}_3\text{-N}$ adsorption followed both Langmuir and Freundlich models while $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ adsorption followed the Freundlich model.

In order to test the adsorbent materials under dynamic conditions, a laboratory scale column experiment was conducted using the same mixture of adsorbents (*EW* biochar and alum sludge) in layers to determine the extent of nutrient ($\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{PO}_4\text{-P}$) removal. This test was designed to replicate CBI field conditions: synthetic stormwater was pumped into the column at a constant flow rate with varying initial nutrient concentrations (1-5 mg/L) and time (i.e., until saturation of the adsorbent bed). The trials showed that the adsorbent bed saturated quickly leading to steeper and earlier breakthrough with a larger mass transfer zone at higher initial concentration. Considering the average yearly rainfall of 1 m in Western Australia, scaling up by 50 (runoff area to drainage area ratio) and runoff coefficient of 0.9, the maintenance days of the adsorbents varied between 73 to 166 days depending on nutrient types and their initial concentrations.

Based on the column results, a modified CBI with two chambers is proposed in this study which is capable of removing sediments (and gross pollutants) and dissolved nutrients from stormwater simultaneously. Both of these chambers have geotextile (e.g. NWG1) baskets but the bottom chamber is filled with the combined adsorbent media of biochar and alum sludge. The principle of this modified CBI would be to capture the gross pollutants in the top chamber, release the stormwater to the bottom chamber to remove the dissolved nutrients by adsorption and finally pass the cleaner water to the storm drainage system.

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This thesis would not have been possible without the direction and the support of several individuals who contributed their valuable assistance in the groundwork and accomplishment of this study.

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LIST OF PUBLICATIONS

Out of this research, two journal papers (impact factor: 4.9) and a conference papers are published, two journals papers are submitted and few more papers (journal, conference and book chapter) will be submitted soon. The copy right permission of published papers are attached in Appendix A. In all of these papers, I am the first author and the main contribution is made by me. Associate Professor Faisal Anwar and Anna Heitz are my PhD supervisor and co-supervisors respectively and hence they are the co-authors in all papers. Dr. Dipok C. Sarker was invited to be a co-author of two papers because of his contributions in field and laboratory experiments and reviewing the first draft of the manuscripts. Mr. Craig Rothleitner was invited to be a co-author of one paper because of his critical feedback on the first draft of this manuscript. However, separate written statement from each author are also included in Appendix B.

Journals

- (1) **Alam, M. Z.**, Anwar, F., Sarker, D.C., Heitz, A. and Rothleitner, C., 2017. Characterising stormwater gross pollutants captured in catch basin inserts. *Science of The Total Environment*, 586, pp.76-86, <https://doi.org/10.1016/j.scitotenv.2017.01.210>
- (2) **Alam, M. Z.**, Anwar F., and Heitz, A., 2017. Stormwater solids removal characteristics of a catch basin insert using geotextile, *Science of The Total Environment*, 618, pp. 1054-1063, <https://doi.org/10.1016/j.scitotenv.2017.09.091>
- (3) **Alam, M. Z.**, Anwar, F., Heitz, A. and Sarker, D.C., 2018. Improving stormwater quality at source using catch basin inserts. *Journal of environmental management*. (submitted, under review)
- (4) **Alam, M. Z.**, Anwar, F., and Heitz, A., 2018. Removal of inorganic nitrogen species from water using *Eucalyptus wandoo* biochar. *Journal of environmental management* (to be submitted)

- (5) **Alam, M. Z.**, Anwar, F., and Heitz, A., 2018. Removal of nitrogen and phosphorous species from water using a mixed adsorbent of *Eucalyptus wandoo* biochar and alum sludge. *Journal of Environmental Management*. (to be submitted)
- (6) **Alam, M. Z.**, Anwar, F., and Heitz, A., 2018. Removing nitrogen and phosphorous from water and developing a modified catch basin insert. *Environment Pollution*. (to be submitted)

Book Chapter

- (7) **Alam, M. Z.**, Anwar, F., and Heitz, A., 2018. Feasibility study of dewatered alum sludge for removing phosphorous from stormwater. *Managing Stormwater: Practices and Challenges for Reuse and Recycling*. New York, USA: Nova Science Publications Inc. (abstract accepted, to be submitted)

Conference Papers

- (8) **Alam, M. Z.**, Anwar, F., and Heitz, A., 2018. Removal of nutrients from stormwater using a mixed biochar-alum sludge adsorbent. Creating water sensitives communities, WSUD 2018 & HYDROPOLIS 2018 12th-15th February 2018, Perth, Western Australia. https://wsud2018.org.au/wp-content/uploads/2018/02/Alam_Removal-of-Nutrients.pdf.
- (9) **Alam, M. Z.**, Anwar, F., and Heitz, A., 2018. Characteristics of stormwater pollutants captured in catch basin inserts. The 13th International Conference on Hydrosience & Engineering (ICHE), June 18-22, 2018, Chongqing, China. (abstract accepted, to be submitted)

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LIST OF NOTATIONS

<u>Notation</u>	<u>unit</u>
A :	catchment area (chapter 1, 2) m²
A :	loaded/captured area of geotextile (chapter 3) m²
a :	mean of pollutant concentration mg/L
a_{inf} :	average influent concentration mg/L
a_{eff} :	average effluent concentration mg/L
a_m :	theoretical specific surface area m²/g
C :	runoff coefficient dimensionless
C_m :	cumulative captured solid mass onto geotextile at the time clogging gm
C_U :	coefficient of uniformity dimensionless
C_c :	coefficient of curvature dimensionless
C_i :	influent EMC mg/L
C_e :	effluent EMC mg/L
C_0 :	initial concentration mg/L
C_{eq} :	equilibrium concentration mg/L
C_t :	concentration at specific time t mg/L
D :	particle sizes μm
D_m :	mean diameter μm
d_c :	the diameter of the spherical collector dimensionless
$D_{10}, D_{30}, D_{50}, D_{60}$:	the grain diameter at 10%, 30%, 50% and 60% passing respectively μm
I :	rainfall intensity mm/hr
K :	hydraulic conductivity m/sec
K_L :	Langmuir constant dimensionless
k_{TH} :	Thomas rate constant L/mg.hr
K_F :	Freundlich constant mg/g
K_1 :	first order adsorption reaction constant 1/min
K_2 :	second order adsorption reaction constant g/mg hr
L_m :	cumulative loaded solid mass onto geotextile at the time clogging gm
L :	adsorbent length in the column cm

M_m	:	cumulative loaded or captured mass of solid onto geotextile	gm
n_F	:	Freundlich constant for adsorption intensity	dimensionless
n	:	the filter bed porosity	dimensionless
N	:	Total number of data	
O_{95}	:	apparent opening size	μm
O	:	geotextile pore sizes	μm
pH_{PZC}	:	point of zero charge	dimensionless
Q	:	flow rate (chapter 1,2)	m^3/sec
Q	:	Unit flow rate (chapter 3)	$\text{L}/\text{min}/\text{m}^2$
Q_i	:	unit flow rate in a given amount of time (chapter 3)	$\text{L}/\text{min}/\text{m}^2$
R_L	:	adsorption intensity	dimensionless
q_0	:	column equilibrium adsorption capacity	mg/g
q_t	:	amount of adsorption at specific time t	$\mu\text{g}/\text{g}$
q_e	:	equilibrium adsorption	$\mu\text{g}/\text{g}$
q_{exp}	:	experimental values of adsorption capacity	$\mu\text{g}/\text{g}$
q_{cal}	:	calculated values of adsorption capacity	$\mu\text{g}/\text{g}$
q_m	:	maximum capacity constant of adsorbent for adsorbate	$\mu\text{g}/\text{g}$
T	:	thickness of filter	mm
t_b	:	breakthrough time	hr
t_e	:	exhaustion time	hr
u	:	unit flow velocity	m/day
V	:	volume of solution	L
V_f	:	linear flow velocity	mL/min
W	:	weight of biochar	gm
x	:	amount of adsorbent in column	gm
X	:	flow through constant	dimensionless
y	:	exponential constant	dimensionless
Z	:	transformed constant	dimensionless
Δt_i	:	the time interval between the samples	s
Ψ	:	permittivity	s^{-1}
α	:	The striking coefficient	dimensionless
η	:	the single collector contact efficiency	dimensionless

ρ_s	:	solid density	g/cm^3
Δq	:	normalized standard deviation	%
ΔpH	:	difference between the initial and final pH value	dimensionless
σ	:	standard deviation	
i	:	number of data points	

LIST OF ABBREVIATIONS

ANOVA	analysis of variance
ANZECC	Australian And New Zealand Environment and Conservation Council
AOS	apparent opening sizes
APHA	American Public Health Association
ARI	average recurrences interval
AS	Australian Standard
AWWA	American Water Works Association
ASPT	at source pit traps
ASTM	American Society for Testing and Materials
BMP	best management practice
BS	British Standard
BOD	biochemical oxygen demand
COD	chemical oxygen demand
BoM	Bureau of Meteorology
CBD	central business district
CBI	catch basin insert
CBR	California bearing ratio
CDS	continuous deflective system
CIM	Cook Industrial Minerals
CF	continuous filament
CIWMB	California Integrated Waste Management Board
COD	chemical oxygen demand
CSIRO	Commonwealth Scientific and Industrial Research Organization
DO	dissolved oxygen
DoEH	Department of Environment and Heritage
DoW	Department of Water
EMC	event mean concentration
Geo	geotextile
GP	gross pollutant
GPT	gross pollutant trap
GS	grain size

HLR	hydraulic loading rate
HM	heavy metals
ISO	International Organization for Standardization
MARV	manufacturer's minimum average roll value
MTZ	mass transfer zone
NET	in line netting system
NP	needle punched
NSW	New South Wales
NWG	nonwoven geotextile
PP	polypropylene
PSD	particle size distributions
RPM	radiation per minute
SEM	scanning electron microscope
SEPT	side entry pit trap
SS	suspended solids
SSA	specific surface area
STF	staple fibre
TN	total nitrogen
TP	total phosphorous
TPH	total petroleum hydrocarbon
TSS	total suspended solids
UCLA	University of California, Los Angeles
UST	Urban Stormwater Technologies Pty Ltd
WA	Western Australia

CHAPTER 1

INTRODUCTION

1.1 Overview

One of the unique and precious sources of life is water. It plays a vital role in the life of humanity and other species living on the planet. It was observed from the history of mankind that civilisations were always built where the rivers and water resources were found. The water usages for different purposes such as domestic, farming and industrial are increasing continuously due to increasing population but the resources are remaining fixed. Therefore, considering the limited resources, unpolluted water demand is a great concern. Unfortunately, the water quality is declining uninterruptedly due to misuse of this resource and polluted by different types and sources of pollution. The effluent from domestic and industrial sources generally produces deteriorations in water quality and generates wastewater. This should be treated effectively before being discharged into the nearby waters and other receiving bodies. Stormwater is one of the major sources of fresh and unpolluted water before flowing as runoff. Stormwater pollution reduction is a key intention for managing stormwater runoff from low intensity storm events and ‘first flush’ storm events. On the other hand, safety of buildings, infrastructure and other assets from flooding is the prime objective of stormwater flows from high intensity rainfall events. ‘First flush’ describes circumstances when pollutants that have gathered on impervious surfaces are transported at the commencement of a storm event. This shows high pollutant concentrations at the start of the runoff hydrograph and reduced gradually to lower levels before the peak flow occurs (Argue, 2004).

1.2 Sources of stormwater pollution

There are two types of pollutants are responsible for stormwater pollution which includes point sources and non-point sources of pollutants (Fig. 1.1). Point sources of stormwater pollution can be identified and shown to be directly liable for a source of pollution. The examples of point source pollution include industries or intensive farming where the effluent can be traced back to the particular zone

(Kidcaff, 2006). Point sources pollution is assumed as a medium of surface water pollution. Due to stricter regulations of these point sources pollution, the impact of these sources to water pollution has dramatically reduced (Peluso et al., 2002).

Another type of key source of the pollution which is difficult to control in the watercourses is termed as ‘non-point source’ pollution and opposite to ‘point source’ pollution. The example includes the pollution from large parking areas or agricultural land. It is noted that non-point sources of pollution are more unsafe and contribute more pollution in comparison to point source pollution (Peluso et al., 2002). According to Kidcaff (2006) “NPS of stormwater pollution are those which can possibly come from the large number of areas being non-specific”. “It results from the accumulation of contaminants from land surface, erosion of soils, debris, increased volumes of stormwater runoff, atmospheric deposition, suspended sediments, dissolved contaminants and other anthropomorphic contaminants. It is sometimes difficult to differentiate between a non-point source and a collection of many smaller point sources”, (Peluso et al., 2002). According to Environment Australia 2002, stormwater can be considered as a resource that could bring environmental, economic and social welfares for the sustainability to built-up regions. Rather than going to waste and causing pollution, stormwater can be used as a major alternative source of water supply through capture, treatment and reuse. The approaches and techniques of this potential resource mainly emphasis on the sources of runoff and pollutants and developing tools to manage and reuse this water within residential, commercial and industrialised regions.



(a) Point source pollution



(b) Nonpoint source pollution

Fig. 1.1 Source of stormwater pollution

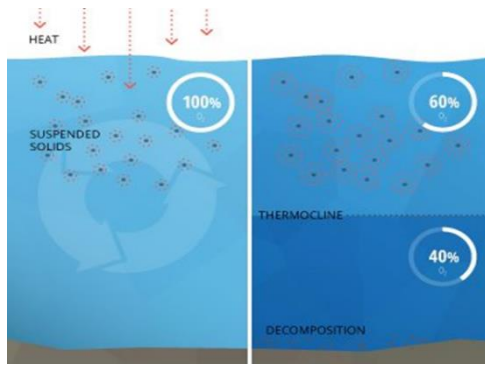
1.3 Background and problem statement

Urban stormwater runoff can contain varieties of pollutants such as gross pollutants (GPs), heavy metals, suspended solids (SS) or particulates, nutrients (nitrogen and phosphorous), polycyclic aromatic hydrocarbons (PAHs), oxygen consuming constituents (BOD and COD) and oil & grease (Durand et al., 2005; Graney and Eriksen, 2004; Lee et al., 1997; Marsalek and Marsalek, 1997; Nightingale, 1987; Pagotto et al., 2001; Robien et al., 1997; Root, 2000; Sansalone and Buchberger, 1997; Yousef et al., 1990). The large amounts of urban debris that are flushed from the catchment into the stormwater drainage system during storm events is often referred to as gross pollutants and includes all forms of solids such as urban-derived litter, vegetation and coarse sediment (Fig. 1.2). As indicated by the manual of ASCE (2007) and other literatures, pollutants more than 5 mm was categorized as gross pollutants (ASCE, 2007; Kim et al., 2006; Sidek et al., 2014; Wong et al., 2006). Gross pollutant pollution is generally the most visible indicator of water pollution to the community. Apart from the visual impact of gross pollutants, they can also reduce the capacity of a stormwater drainage systems. When dumped these pollutants into the nearby waterbodies, they become a hazard to the aquatic ecosystem. This impact can cause through a blend of physical impacts on aquatic biota and contamination of receiving water quality in corporation with other contaminants such as oxygen demanding substantial, PAHs and metals allied with gross pollutants (Khabbaz, 2009). Allison et al. (1997) has reported that the organic materials (such as branches, grass trimmings and leaves) create the major amount of gross pollutants transported by stormwater. This was found to be the case for all land use types (Alam et al., 2017a). Allison et al. (1997) also claimed that human-derived litter builds up approximately 25–30% of the total gross pollutant load. They also indicated that vegetation, litter, paper was the dominant pollutant type. The similar findings were observed by Alam et al. (2017a).

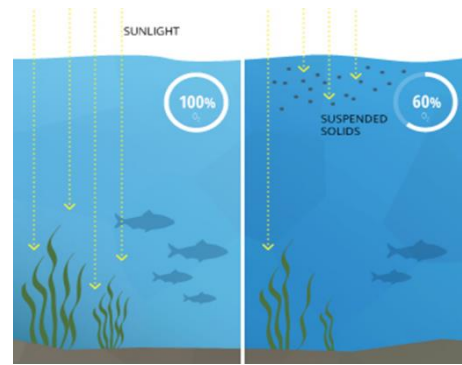


Fig. 1.2 Stormwater gross pollutants

Particulate matters are also dominant pollutants for stormwater pollution. Urban runoff is becoming a major concern in Australia and beyond because of its conveying particulate matters and other pollutants from impervious surfaces to aquatic biota (Alam et al., 2017a). The particulate matters are also found as suspended solid (SS) in stormwater runoff. These fine SS particles remain suspended in flowing waters which can carry the harmful pollutants. The U.S. environmental protection agency (1998) identified suspended solids and sediment as the most common cause of pollution of the nation's rivers, lagoons, basins, pools and bays. Suspended solids can increase the temperature of stream water as they absorb additional heat from the sun and impose a negative hydrological impact. This increase in temperature assists in evaporation of stream water which is a hydrological parameter. This can cause dissolved oxygen levels to drop below the thermocline, creating hypoxic conditions (Alam et al., 2017a; Fig. 1.3a). Suspended solids can block sunlight from reaching submerged plants. Therefore, the dissolved oxygen levels to drop, as the plants rely on respiration (consuming oxygen) instead of photosynthesis (Fig. 1.3b). The center for streamside studies (1991) stated that TSS concentrations of 300–400 mg/L may reduce the visibility of fish and hamper their food searching. Constant high concentrations of TSS could lessen primary production of aquatic animal (Khabbaz, 2009). Furthermore, coarse sediments from urban areas has physical impacts on receiving aquatic biota due to choking marine environments and clogging-up watercourses, causing a decrease in channel discharge capacity (Fig. 1.3c and d).



(a) Hypoxic conditions



(b) Sunlight blockage



(c) Side entry pit blockage



(d) Stormwater drainage blockage

Fig. 1.3 Effect of stormwater sediment pollution

Heavy metals (Fig. 1.4a), oil & grease, and PAHs (Fig. 1.4b) add toxicity to receiving aquatic environments. Urban runoff may contain sufficient heavy metals such as iron, arsenic, cadmium, chromium, copper, lead, nickel and zinc. There are various sources of heavy metals such as construction materials (e.g. guttering, flashings and walls) and traffic-related elements (e.g. brake linings, tyre wear, and auto catalyst) (Adachi and Tainosho, 2004, McKenzie et al., 2009, Gunawardana et al., 2012). Apart from copper and cadmium, most of the metals are obtainable in particulate form.



(a) Heavy metals pollution



(b) Oil & grease/PAHs pollution

Fig 1.4 Heavy metals and Oil & grease/PAHs pollution

The other types of pollutants namely nutrients are liable for eutrophication process, where excess aquatic plant growth is reason for blockage of sunlight. An excess of nitrogen (N) or phosphorus (P) can stimulate marine life to the extent that plant growth converts a major problem for a waterbody. Excessive plant growing can congest watercourses and lead to large instabilities in dissolved oxygen levels, which threaten fish and other creatures in the aquatic body. A number of natural compounds such as nitrogen and phosphorous species are the core element of plant and animal life released into waterbodies when the organic wastes are decomposed. Australian soils and waterways are usually low in nutrient content (Khabbaz, 2009). Thus, the existing living creatures in these waterways are survived with low nutrient environments. Australian aquatic biota is therefore remarkably vulnerable to superfluous nutrients in waterways. The excess of threshold of nitrogen (in marine systems) or phosphorus (in freshwater systems) can fuel aquatic being to the extent that plant progression becomes a major problem for a water body. This unnecessary plant growth can lead to huge instabilities in dissolve oxygen levels and warn the fish and other beings in water bodies. This can also be a cause of choking of waterways. Fig. 1.5 shows a sequence of this situation. The production of oxygen throughout day time in the presence of sunlight more than compensates for the oxygen consumed by organisms including beneficial microbes. However, the oxygen consumed by aquatic plant and animal during night time can deplete oxygen to a level that can be destructive to fish and other living organisms. Consequently, an enormous amount of plants can die off which promote further drop in oxygen level due to their decay. Humans, many organic substances and human used materials are the main sources of nutrients. The key sources of nutrients as mentioned by Khabbaz (2009) are:

- human or other animal wastes
- plant substance (twigs, leaves, whole plants)
- organic wastes
- manures, fertilizers
- detergents, shampoos, soaps
- kitchenette garbage
- nitrous oxides coming from car exhaust and lightning

- ashes from bush fires
- landfill leachate

Composts for example, blood and bone, super phosphate, sea weed, and animal manure are generally used for private enclosures, public parks and golf courses. Runoff from these regions contributes phosphorus and nitrogen to waterways. Commercial fertilizers such as super phosphates are widely used in rural areas for intensive farming which includes market gardens, feedlots, crops and orchards. The other sources of bulky phosphorous are washing cars and boats on pavements and driveways with detergents which contain phosphates. Soil erosion from rural and urban areas are also a further source of nutrients especially phosphorous.

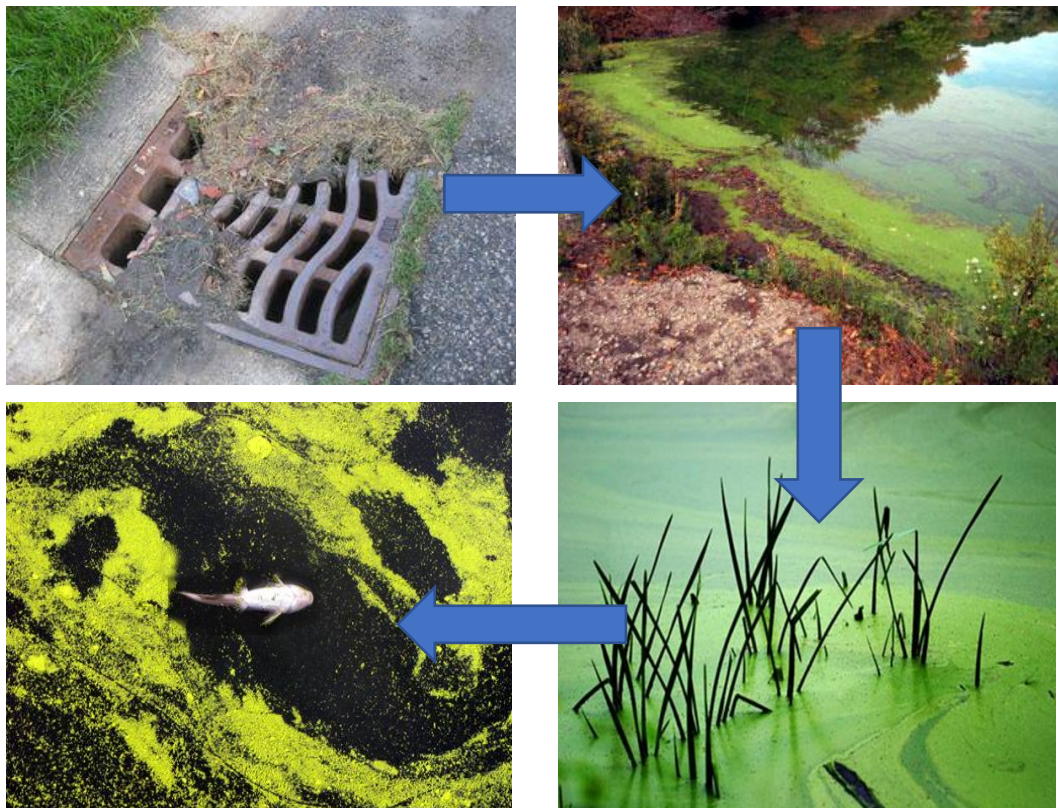


Fig. 1.5 Effect of stormwater nutrient in aquatic life

An effective, low-cost remediation system is therefore needed to reduce the impact of these pollutants particularly gross pollutants, sediments and nutrients (Boxall and Maltby, 1997; Makepeace et al., 1995). Thus, the core interest of this research to capture these pollutants at source before entering into stormwater drainage systems. It was assumed that if an intercept can construct on the flow by building a trap containing

a substrate it will reduce the pollutant concentration (Pandey et al., 2003). There are several researches on the application of gross pollutant trap (GPT) to capture litter and debris and placed at outlets of piped drainage system (Ab Ghani et al., 2011; Allison et al., 1997; Madhani and Brown, 2011 & 2015; Madhani et al., 2009; Saberi et al., 2008; Sidek et al., 2014). However, the GPT are end of pipe solution and more applicable for gross pollutants.

Total suspended solids (TSS) load can be reduced up to 85 - 90% by properly designed, implemented and maintained erosion controls on land development and construction areas (Taylor and Wong, 2002; Schueler and Holland, 2000; Lehner et al., 1999). Again, well-planned, designed, executed and upheld sediment controls can usually remove the TSS up to 60 - 70% (DoW, 2004, US EPA, 1997 and 2001; Schueler and Holland, 2000). A construction site with best management practices and with a combination of erosion and sediment controls may have a TSS removal efficiency of 60%. All of these technologies are effective to reduce stormwater TSS concentration but necessitate significant land area. Hence, difficult to retrofit in highly urbanized area and regular maintenance. Bio filter and sand filters are common stormwater runoff treatment systems used in urban areas (Hatt et al., 2009, Barret, 2003). Large subsurface of these filters can effectively capture the particulate matter from stormwater runoff (Franks et al, 2012). However, upstream pre-treatment of litter and coarse sediments is essential to minimize filter clogging. Hence, its trapping efficiency for GP is nil and fine to coarse sediments is 30-80% (<http://www.wsud.org/wp-content/uploads/2012/08/part1.pdf>). Moreover, all or a portion of sand must be replaced to ensure adequate drainage through the filtration system when it clogs (SEMCOG, 2008). Replace of filter media is highly labor intensive.

Recently the drain basket is used as a trap for gross pollutants and suspended solids which is also known as catch basin insert-CBI (Allison et al., 1997; Brian Currier et al., 2005; GeoSyntec and UCLA, 2005; ICBIC, 1995; MacLure, 2009; Woodward-Clyde, 1998). This CBI is possible to integrate with 'low impact development' (LID), 'water-sensitive urban design' WSUD, or 'sustainable urban drainage systems' a management philosophy that emerged to lessen, detain, infiltrate, clean or use stormwater at its source. Some field experiments of CBIs have also been carried out (Brian Currier et al., 2005; GeoSyntec and UCLA, 2005; ICBIC, 1995; MacLure,

2009; Woodward-Clyde, 1998) but most of these tests involved capturing influent and effluent samples during storm events or leaving the inserts in typical installations for a specific duration and evaluating the captured material. ICBIC (1995) and Woodward-Clyde (1998) evaluate the TSS and oil & grease removal efficiency of different types of CBIs. In contrast, a few reports have focused on capturing other micro pollutants (GeoSyntec and UCLA, 2005; Kostarelos and Khan, 2007) and nutrients (Balakrishnan, 2012) before entering into drainage system. Kostarelos and Khan (2007) focused on evaluating pollutant removal efficiency of 6 CBIs in USA on the removal of total suspended solids (TSS), total nitrogen (TN), total phosphorus (TP), total petroleum hydrocarbon (TPH) and BOD. Similar type of study was performed by GeoSyntec and UCLA (2005) but main aim of this research was oil and grease removal efficiency of four CBIs. Saberi et al. (2008) determined the hydraulic characteristics of GPT. Recently Urban Stormwater Technologies Pty Ltd. (UST, formerly known as Templug International Pty Ltd.) has installed CBIs with a special type of geotextile fabrics in several city councils of Western Australia. But there was no scientific study on UST CBI for removing solids from stormwater and improve the stormwater quality. This study is the first to use UST CBI for field investigation and modified the CBI for dissolved pollutants also. The geotextile used in UST CBI is a non-woven special type geotextile. The consequence of fine particles build-up in the CBIs is a progressive decrease of infiltration in filter materials. This increase must not reach a critical value which will make difficult to flow water through the filter (corresponding to geotextile clogging). Predicting such critical value from infiltration characteristics (corresponding to a critical quantity of retained particles in the filter materials) is also needed for determining its servicing frequency. Franks et al. (2012-14) studied efficiency of three types of geotextile filter for removing suspended solids from stormwater. They also developed a semi-theoretical model for hydraulic conductivity of geotextile filter during suspended solids accumulation and determined the maintenance frequency due to the suspended particles build up in geotextile. However, they did not consider any dissolve pollutants removal from stormwater which is a key concern for urban runoff. At present the UST CBI can only remove the pollutants down to 150 μm . Hence a modified CBI will be developed by integrating a novel mixed adsorbent medium to remove gross and dissolve pollutants simultaneously. Although recently different types of trapping devices are available due to the increasing concern of gross pollutant traps in urban water ways but there is little

information on their performance, clogging criteria and servicing time. Therefore, the current research will be focusing on these issues of newly modified CBI to remove both suspended and dissolved pollutants at source.

1.4 Objectives of this research

The main goal of this research is to determine the hydraulic and solid removal characteristics of catch basin inserts (CBIs) such as drain basket and its further improvement to remove suspended solids and dissolve pollutants from stormwater by integrating new adsorbent materials with geotextiles. Low cost and available adsorbent materials in Australia will be chosen for this purpose to check their optimum performances for pollutant removals. The specific objectives to this task are as follows:

- 1) To characterize the stormwater gross pollutants captured in CBI in field condition.
- 2) To investigate the stormwater quality improvement using CBI in field condition.
- 3) To determine the hydraulic and solid removal characteristics of CBI using different types of geotextile filters in a laboratory condition.
- 4) To study the adsorption characteristics of selected green medium such as *Eucalyptus wandoo* (EW) biochar to remove inorganic nitrogen from stormwater/wastewater.
- 5) To study the adsorption characteristics of a mixed adsorbent (EW biochar and dewatered alum sludge) to remove nitrogen and phosphorous simultaneously from stormwater/wastewater.
- 6) To develop a modified CBI integrating geotextile (3) and mixed adsorbent (5) to remove sediments and nutrients simultaneously to treat stormwater at source.

1.5 Significance and novelty of this research

The volume of urban stormwater runoff is increasing because of increased impervious areas. The surface runoff together with gross pollutants are accumulated in side entry pit from where it is meant to be either infiltrated to the groundwater or transmit to the receiving water (e.g. lakes, stream or sea) through underground stormwater drainage network. In many occasions, the gross pollutants can clog the underground pipe network system. Gross pollutant traps may be used to capture the gross pollutants, but it does not have the opportunity to clean the system time to time as it is embedded with

the system permanently. Currently, there are no other devices available that can be used as a part of stormwater treatment capturing the pollutants at source and at the same time, it can be serviced. Drain basket as CBIs can be used for this purpose. The special type of CBI introduced in few city councils in Western Australia by UST used in this research to investigate the working capability of stormwater treatment of CBI. However, the current CBI cannot remove any dissolved pollutants. This research will make an effort to develop a cheap locally available adsorbent medium and integrate with this CBI to remove nutrients from stormwater. This research will quantify the adsorption capacity of biochar and dewatered alum sludge in the removal of nutrients specifically: nitrate-nitrogen ($\text{NO}_3\text{-N}$), nitrite-nitrogen ($\text{NO}_2\text{-N}$), dissolved ammonium-nitrogen ($\text{NH}_3\text{-N}$) and phosphate-phosphorus ($\text{PO}_4\text{-P}$). The quantification of the adsorption capacity of the biochar and dewatered alum sludge will assist the urban water way engineer to design and execution of stormwater treatment practices. Urban water way manager may able to predict and evaluate the stormwater treatment practices which includes alum sludge and biochar. Biochar is produced by pyrolysis of wood waste and alum sludge is obtained from the waste formed by coagulation method in water treatment plants (Sohi et al., 2010; Adhikari et al., 2016). Wood waste and alum sludge are considered as waste and are ended up in landfill sites (Boving and Neary, 2004; Yang et al., 2006). Hence, the use of these two materials will decrease the disposal cost and reduce soil and water pollution and secure our valuable water store. Therefore, the use of biochar and alum sludge in stormwater management strategies would act as an approach to satisfies the economics, ecological and social aspects of sustainability. The outcome of this research will have significant effect on stormwater management industry in Australia and beyond. As pollution problem from stormwater is becoming worse due to increased population and urbanization, there is a great need for developing a sustainable approach for stormwater treatment. This research was undertaken to develop such a sustainable approach for stormwater treatment. It will provide guideline for reusing the stormwater in an efficient manner by releasing clean water to the environment. The long-term aim of the integrated CBI is to provide local government, developers and construction companies with a cost-effective solution that will protect drainage infrastructure and receiving environments from stormwater pollutants. This information can be used as a guide for city councils for using CBI in the storm drainage system. Finally, this research will contribute to improve the economic development of the country and protect the environments.

1.6 Organization of the thesis

This thesis has been formatted with published and unpublished materials. Three papers have been published (two in journal and one in conference proceedings), two papers are in review and few more will be submitted soon. All of the chapters are formatted as research papers and the sequence of chapters are arranged to reflect the objectives of the whole thesis (Fig 1.6). The status of papers are given in a footnote on the first page of each chapter.

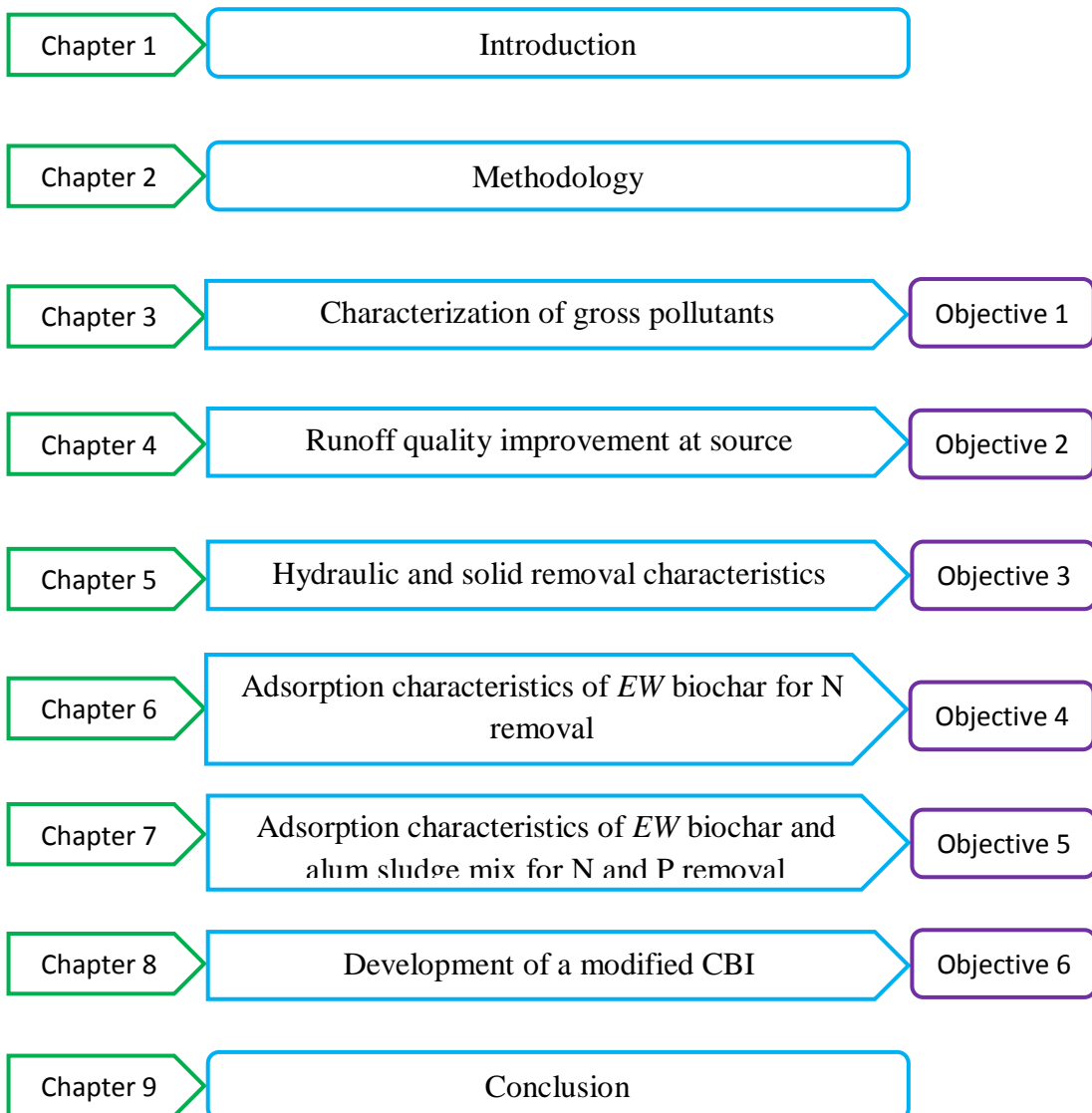


Fig. 1.6 Organization of the thesis

Chapter one provides the background of the study, identifies the problem and outlines the objectives. This also provides the significance and the novelty of this research. Finally, it represents the organization of the thesis.

Chapter two provides an overall methodology of this work. This includes the field and laboratory investigation for sediment and nutrients removal from stormwater using CBI and modified CBI.

Chapter three characterizes the stormwater gross pollutants captured in CBI in field conditions for one year. This was done by collecting monthly data of gross pollutants captured in CBI in a selected location of Western Australia. The effects of catchment characteristics on GPs load, moisture contents, and particle size distribution were evaluated.

Chapter four presents how CBI can improve the stormwater quality at source. To do this, several locations at residential and a commercial-marine-recreational area were selected, and water and soil samples were collected for analysis. The results on water quality parameters are presented and discussed in this chapter. A detail comparison of CBIs used across the world is also presented in this chapter.

Chapter five presents a laboratory results of three types of geotextiles used in CBI and provides their suitability for using them to remove sediments from stormwater. The hydraulics of solid removal in geotextiles were studied for different particle size distributions and their clogging criteria were determined.

Chapter six uses a green medium - *Eucalyptus wandoo* (EW) biochar to remove inorganic nitrogen from stormwater by adsorption. In addition to the batch adsorption tests, the results from Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), nitrogen adsorption-desorption isotherm and SEM imaging are also presented.

In chapter seven, a mixed novel adsorbent (EW biochar and dewatered alum sludge) was chosen to remove nitrogen and phosphorous simultaneously from stormwater. The morphology and surface characteristics of alum sludge was presented in this chapter using SEM, EDS and nitrogen adsorption-desorption isotherm.

In chapter eight, EW biochar and alum sludge were tested in dynamic condition for

removing nitrogen and phosphorous from stormwater. Next, a modified CBI is proposed to treat stormwater by capturing gross pollutants/sediments and adsorbing dissolved nutrients. The green medium, a mixture of *EW* biochar and alum sludge, was integrated with geotextile to remove these pollutants simultaneously from stormwater at the beginning of storm drainage system. The servicing frequency (e.g., maintenance period) of geotextiles and adsorbent media were determined.

Chapter nine presents the overall conclusions of this research. These conclusions are mainly derived from the conclusions presented in different chapters (papers). The limitations of the study are also outlined here and recommendations for future studies are presented.

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CHAPTER 2

METHODOLOGY

2.1 Introduction

The accumulation of stormwater pollutants in waterbodies leads to decline in water quality, resulting in danger of public health and decrease in the life span of the aquatic biota. Therefore, pre-treatment of stormwater has been required to reduce the stormwater pollutant load on receiving waters. Catch basin inserts is a pre-treatment device of stormwater before entering to stormwater drainage system. The construction and maintenance of CBI for stormwater treatment processes are generally easier than the other methods currently available in the market (Alam et al., 2017a and 2017b). This lead to the investigation of CBI and its further development. This chapter presents the overall research steps carried out for characterizing and treating stormwater using CBI. The research steps are shown in Fig 2.1.

This study involves both field data collection and laboratory experiments. The field study involves data collection and characterising gross pollutants captured in CBIs and investigating stormwater quality improvement. Based on these data, laboratory experiments were designed and conducted. The laboratory experiments involve determining the suitability of using geotextile in CBI for capturing sediments, selecting green media for treating nutrients in stormwater and finally developing modified CBI that can treat stormwater for both sediments and nutrients simultaneously at source.

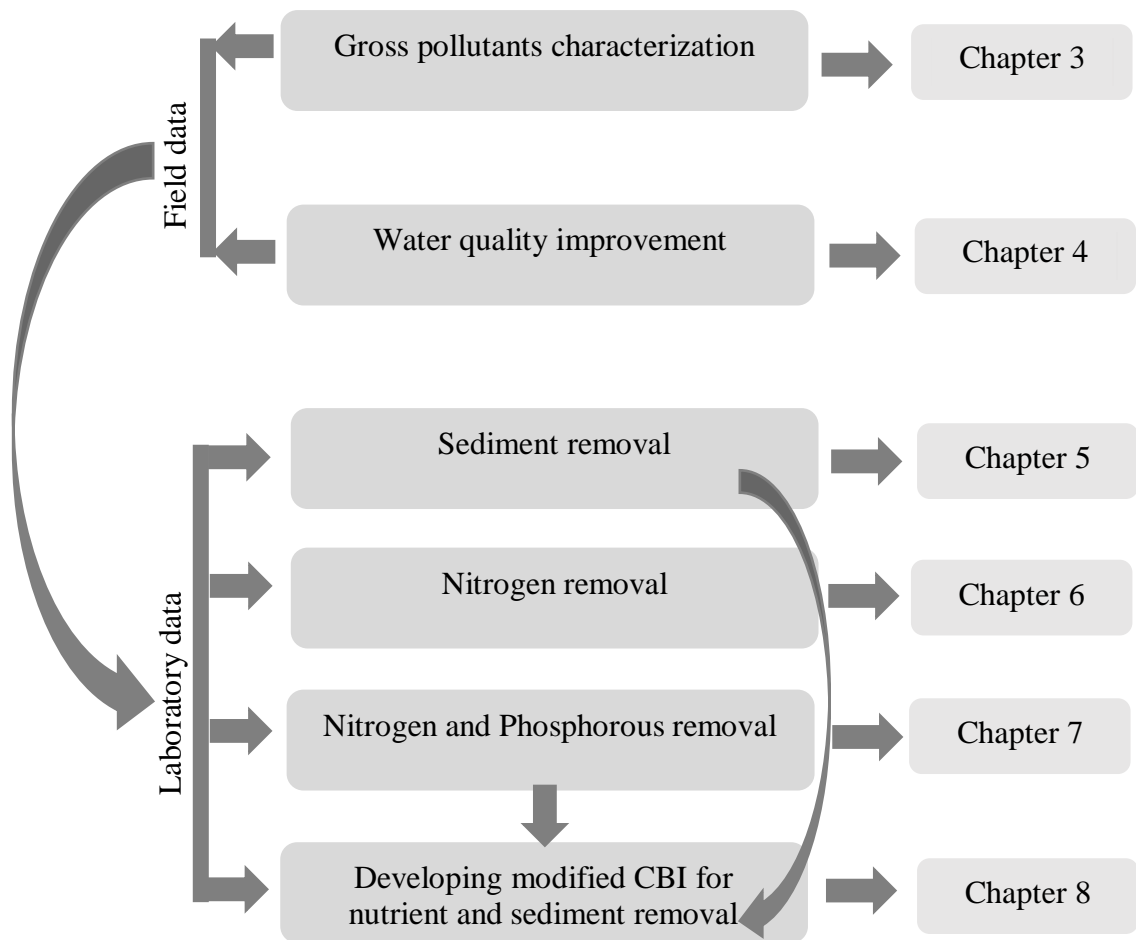


Fig. 2.1 Research steps

2.2 Field investigation

2.2.1 Study area

The study areas for field data collection were selected based on three different land-use patterns located in Western Australia: i) Gosnells: mixed land used area; ii) Subiaco: residential area and iii) Hillarys: coastal-marine-recreational area. The Federation Parade (2.83 ha) of City of Gosnells in Western Australia was selected for collecting gross pollutants captured in CBIs. It is a south-eastern suburb located 20 km southeast of Perth CBD and located near a commercial area consists of market and library and surrounded by a lot of vegetations. The other two different sites (i) Olive street at Subiaco and (ii) Southside drive at Hillarys in Western Australia were selected to observe the runoff water quality improvement due to CBI installation. These two

catchments (Subiaco: 25.5 ha; Hillarys catchment: 45.5 ha) are mixed land use types. The Subiaco catchment is mostly residential with high vegetation waste and located 3 km from Perth CBD. Hillarys is located on the coast approximately 18 km northwest of Perth CBD and consisting of more than 2700 car parking bays. These CBIs are installed by Urban Stormwater Technologies-UST (previously known as Templug International Pty Ltd). UST provided all the logistical supports to collect the field data.

2.2.2 Pollutant characterization

A total of 17 CBIs out of 30 drains in Federation Parade, Gosnells was installed by UST and maintained by them since 2013. Out of 17, four CBIs were selected for monthly data collection for 1 year. The gross pollutants (GP) collected from these CBIs were characterised for size and different types. For example, GP more than 5 mm was categorized for different types such as litters, organic debris and coarse sediments. GPs less than 5 mm were categorized by sieve analysis. The monthly load captured from each CBI was determined and the runoff for each inlet was calculated by rational formula (Subramanya, 2013). These data were used to calculate the loading rate coefficients of pollutant for unit runoff flow volume for different pollutant sizes (Kim et al., 2006). The meteorological data was collected from the Bureau of Meteorology, Australian Government. The water samples collected from the inside of pit were analysed for TP (total phosphorous), ammonia (NH_3), nitrite (NO_2^-), and nitrate (NO_3^-) using AQUAKEM 200 water analyser following standard methods (APHA, 1998)

2.2.3 Water quality improvement

The water samples collected from inside and outside of the CBIs in Subiaco and Hillarys were analysed for water quality parameters (TSS, phosphate ($\text{PO}_4\text{-P}$), BOD, COD and heavy metals (i.e., Cu, Fe, Ni, Pb, Zn and Cd)). Two and four CBIs (out of 17 and 14 respectively) from Olive street at Subiaco and Southside drive at Hillarys respectively were selected for this purpose. The soil samples were also collected from these sites and analysed for particle size distribution, density, specific surface area. The SEM image of soil samples was also analysed. The water and soil samples were analysed in CSIRO laboratory and Curtin Civil Engineering water laboratory

respectively. The efficiency of CBIs for water quality improvement was determined by efficiency ratio method based on log transformed influent and effluent pollutant concentrations (Barret, 2003).

2.3 Laboratory investigation

2.3.1 Use of geotextiles

A plexiglass column of 130 mm diameter and 350 mm length was constructed to simulate the CBI in laboratory condition. A series of column experiment was conducted to check the suitability of three geotextiles for using it in CBI for capturing sediments under different experimental conditions. The geotextiles chosen for these experiments are the one used in UST CBI and other two readily available in the market. All of these geotextiles were non-woven. The apparent opening sizes (AOS), thickness and G-rating were chosen as selection criteria for geotextile selection (Alam et al., 2017b). The prototype CBI model comprised of a pump, a stirrer, a plastic container, tubing, the geotextile filters, diffuser and a circular column. A uniform flow rate of 6 mL/sec and TSS concentration of 200 mg/L were used for entering the synthetic stormwater into the prototype CBI. The TSS concentration was measured for every 10 minutes of an 80 minutes test by following Standard Method 2540B and SSC B (Nordqvist et al., 2014, Eaton et al., 1995). A total of 15-92 tests were performed for two particle size distributions (P1:0-180 μm , d_{50} : 106 μm and P2: 0-300 μm , d_{50} : 150 μm). Particle capture and hydraulic conductivity changes were evaluated as a function of solids loading to the filter (Alam et al., 2017b, Franks et al., 2013, 2014). This data was also used to determine the maintenance period of the geotextile (Franks et al., 2013).

2.3.2 Nitrogen removal

Current CBI is able to remove GPs (including sediments down to 150 micron) from stormwater and cannot remove the dissolved pollutants such as nutrients. In this study, *Eucalyptus wandoo* (*EW*) biochar was tested for removing inorganic nitrogens ($\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$) from water. The biochar was chosen because they were found as one of the good adsorbent medium for removing nitrogenous pollutants from aqua phase (Reddy et al., 2014a, Sun et al., 2013). The *EW* biochar was collected from [‘Energy](#)

[Farmers Australia Pty Ltd](#) in Geraldton, Western Australia. Two-step sieve analysis method i.e., dry and wet sieving method (ISO 3310: BS 410-1:2000 sieve size 2.36 mm) was followed to remove the fine residue and separate the required particle size of 2.36 mm. The morphology and surface characteristics of biochar was observed by Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), nitrogen adsorption-desorption isotherm, energy dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) images. The synthetic stormwater containing NO₃-N, NO₂-N and NH₃-N was prepared from NaNO₃, NaNO₂ and NH₄Cl respectively. A series of batch experiments was conducted to check the nitrogen adsorption capacity of *EW* biochar with varying initial concentrations (0.5-5 mg/L), dosages (2-10 g), pH (4-9), and contact times (0-24 hr). Each biochar dosage of 2.36 mm diameter was mixed with 100 mL of nitrogen solution (0.5-5 mg/L) in a 250 mL Erlenmeyer flask in different pH levels. The flasks were placed on a 16-flask capacity shaking platform (Innova 2100, New Brunswick Scientific) and shaken at 100 rpm at room temperature (22±2°C). Then filtered water samples (filtered through 0.45 µm syringe) were collected at predetermined time interval 5 to 60 mins and analysed using AQUAKEM 200 water analyser following standard methods given in APHA (1998). The adsorption capacities and removal efficiencies were determined by using the equations given in Harmayani and Anwar (2016). The adsorption kinetic was analysed by pseudo first and second order kinetic models (Sun et al., 2013). The Langmuir and Freundlich isotherm models were applied to fit the experiment data (Foo and Hameed, 2010).

2.3.3 Nitrogen and Phosphorous removal

The *EW* biochar was found good to remove nitrogens but unable to remove phosphorous from water. Previous literatures show alum sludge a good adsorbent for phosphorous removal from liquid phase (Yang et al., 2006; Adhikari et al., 2016). Therefore, *EW* biochar and dewatered alum sludge was used further to remove nitrogen and phosphorous simultaneously. The synthetic stormwater containing NO₂-N, NH₃-N and PO₄-P was prepared from NaNO₂, NH₄Cl and NaH₂PO₄ respectively. Since stormwater contains both nutrients (nitrogen and phosphorous) together, biochar (8 gm) and alum sludge (2 gm) of same diameter (2.36 mm) was mixed and a series of

similar batch experiments was carried out with varying initial concentrations (0.5-5 mg/L), dosage (2-10 g), pH (4-9) and contact time (0-24 hr). The adsorption capacities, removal efficiencies, the adsorption kinetics and the isotherms were investigated for these mixed adsorbents (Harmayani and Anwar, 2016; Sun et al., 2013; Foo and Hameed, 2010).

2.3.4 Development of modified CBI

As current CBI using geotextile is able to capture GPs only, there is a need to modify the existing CBI to remove the dissolved pollutants from stormwater. In this research a green media of mixed adsorbents (biochar and alum sludge) are developed in previous sections in batches. Based on the optimum ratio of biochar and alum sludge (4:1) from the batch experiments, the adsorption capacity of these media is tested in dynamic conditions in laboratory column for different initial concentrations (1-5mg/L) and a uniform flow rate of 10 mL/min. Based on the results on geotextile filtration and adsorption capacity of biochar and alum sludge, a new modified CBI is developed which contains two chambers. The upper chamber is designed for removing GPs (including sediments down to 150 micron) and the lower chamber is designed for nutrient adsorption and thus clean the stormwater at source. Finally, the maintenance period for both upper chamber geotextile and lower chamber adsorbent materials are derived using the number of rain events, average yearly rainfall, runoff/drainage ratio and runoff coefficient (Franks et al., 2013; Alam et al., 2017a & b).

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CHAPTER 3

CHARACTERISING STORMWATER GROSS POLLUTANTS CAPTURED IN CATCH BASIN INSERTS

Abstract

The accumulation of wash-off solid waste, termed gross pollutants (GPs), in drainage systems has become a major constraint for best management practices (BMPs) of stormwater. GPs should be captured at source before the material clogs the drainage network, seals the infiltration capacity of side entry pits or affects the aquatic life in receiving waters. BMPs intended to reduce stormwater pollutants include oil and grit separators, grassed swales, vegetated filter strips, retention ponds, and catch basin inserts (CBIs) are used to remove GP at the source and have no extra land use requirement because they are typically mounted within a catch basin (e.g. side entry pits; grate or gully pits). In this study, a new type of CBI, recently developed by Urban Stormwater Technologies (UST) was studied for its performance at a site in Gosnells, Western Australia. This new type of CBI can capture pollutants down to particle sizes of 150 microns while retaining its shape and pollutant capturing capacity for at least 1 year. Data on GP and associated water samples were collected during monthly servicing of CBIs for one year. The main component of GPs was found to be vegetation (93%): its accumulation showed a strong relationship ($r^2=0.9$) with rainfall especially during the wet season. The average accumulation of total GP load for each CBI was 384 kg/ha/yr (dry mass) with the GP moisture content ranging from 24-52.5%. Analysis of grain sizes of GPs captured in each CBI showed similar distributions in the different CBIs. The loading rate coefficient (K) calculated from runoff and GP load showed higher K-values for CBI located near trees. The UST developed CBI in this study showed higher potential to capture GPs down to 150 microns in diameter than similar CBI devices described in previous studies.

Keywords: Stormwater, Catch Basin Insert, Pollutants, Treatment, Water Quality

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3.1 Introduction

In urban areas, natural vegetation has been replaced by paved surfaces, resulting in soil compaction, which renders the surfaces impervious and prevents the natural infiltration of rainwater, increasing surface runoff. This rapid urbanization with the construction of new urban assembly may drastically change the hydrologic, hydraulic and environmental characteristics of rural catchments (Sidek et al., 2016). Urbanization not only causes flooding as a physical impact but also increases pollution problems in urban rivers and other receiving waters (Wong et al., 2002). Stormwater pollutants may cause physical, chemical and/or biological damage to the environment.

Stormwater pollutants may be broadly classified into two categories: (i) gross pollutants (GP) such as vegetation (plant-based debris), litter (paper, plastic, cans and others) and sediments of different sizes and (ii) dissolved pollutants including nutrients, heavy metals, and hydrocarbons. The dissolved pollutants result mainly from automobile emissions, fluid leaks from vehicles, residential use fertilizers and pesticides, refuse, and animal faeces (Harmayani and Anwar, 2016). The pollutants such as trash, litter and vegetation with diameters larger than 5 mm are usually considered as GPs (ASCE, 2007). In this study, pollutants down to 150 μm diameter captured in catch basin inserts (CBI) were considered as GPs. These finer particles are classified as suspended solid (SS) in stormwater runoff and remain suspended in flowing waters which can carry harmful pollutants (Zhao and Li, 2013; Zhao et al., 2010).

The concentration of nutrients such as total phosphorous (TP) or total nitrogen (TN) may increase in urban waterways because of decomposition of vegetation. These pollutants are particularly problematic because they contribute to eutrophication in receiving water bodies (Meng Nan et al., 2011; Sansalone and Buchberger, 1997; Taylor et al., 2005; Seitzinger et al., 2002) hypoxia, and loss of biodiversity. While some data exists for TN and TP contribution to waterbodies from vegetation or leaf litter captured in continuous deflective systems (CDSs) and side entry pit traps (SEPTs) (Allison et al., 1998b) there is no data available for CBIs.

A critical review on urban catchments showed that a significant amount of street waste enters stormwater drainage systems due to rain and wind (Madhani et al., 2009) and that this waste also has important effects on the dissolved and total nutrient content being discharged to the environment by stormwater. Selbig (2016) studied the reduction of nutrient concentrations in road runoff by implementing municipal leaf collection and street cleaning programs. It was shown that the total and dissolved phosphorus could be reduced by 84 and 83% and total and dissolved nitrogen by 74 and 71%, respectively, by implementing these programs. However, the current Australian street sweeping practices are not effective for removing the growing street wastes (Walker and Wong, 1999). Similar findings were also found elsewhere in the USA (Lippner et al., 2000). This led to the development of stormwater quality improvement devices at the point of waste generation such as a drain basket/SEPT in order to protect the urban waterways from street borne pollution (Allison et al., 1998a). The other type of device used for the removal of GP is the GP Trap (GPT) but this is difficult to clean periodically and is not effective for removal of pollutants less than 5 mm. The GPT is not effective in treating stormwater at the source because it is placed at outlets of piped drainage system and mainly captures litter and debris (Ghani et al., 2011; Allison et al., 1998a; Madhani et al., 2009; Madhani and Brown, 2011; Madhani and Brown, 2015; Saberi et al., 2008).

A few studies have focused on capturing pollutants using drain baskets (also termed as catch basin insert-CBI) in side entry pits before they enter the drainage system (CIWMB, 2005; GeoSyntec and UCLA, 2005; Kostarelos and Khan, 2007; MacLure, 2009; Kostarelos et al., 2011). Kostarelos and Khan (2007) and Kostarelos et al. (2011) evaluated pollutant removal efficiency of six CBIs under laboratory and field conditions. They studied the removal of five water quality parameters (TSS, TN, TP, TPH and BOD₅) at three different flow rates (50, 150 and 300 L/min) with three contaminant concentrations (low, medium, high). The study also focused on the installation characteristics, durability and maintenance of CBIs, as well as whether the inserts can be conveniently, safely, and economically installed and maintained. A similar study was performed by GeoSyntec and UCLA (2005) to remove oil and grease in four CBIs. Chrispijn (2004) did a field survey for three different ASPT namely Enviropod Filter, Ecosol RSF 100 and SEPTs (designed by Hobart City Council). A small number of traps from each type were installed in comparable locations in and

around Sullivans Cove, Hobart, Tasmania, Australia to monitor the retention of pollutant materials (e.g., GP) including heavy metals for 6 months 22 days. Lau et al. (2001) performed field and laboratory tests on CBI in the City of Santa Monica, USA, collecting the GP from CBI twice during their testing period to determine the pollutant size distribution. Although different types of trapping devices are now available, there is a dearth of information on pollutant characteristics captured in CBIs. The characteristics of pollutants captured in CBIs has not been fully tested in practical field conditions under the influence of seasonal variations for a Mediterranean climate such as occurs in Perth, Western Australia where high rainfall intensity in short duration prevails.

A new form of CBIs has recently been introduced by Urban Stormwater Technologies Pty Ltd (UST; previously known as Tempplug) to remove stormwater pollutants at source in the drainage systems and installed by a few city councils in Western Australia (Rothleitner, 2011). In this study, gross pollutants (GPs) and water quality data were collected from the new UST CBIs during their monthly servicing over one year. The data are presented to understand the types, quantities, physical and chemical properties of urban stormwater pollutants captured at source in the CBIs and the contribution of nutrients from these pollutants to the aquatic environment.

3.2 Study area, materials and methods

3.2.1 Study site

The study site was Federation Parade (City of Gosnells, Western Australia) (Fig. 3.1), which is located in the vicinity of a market and library and surrounded by trees, primarily *Eucalyptus salubris*. The catchment contributing the road runoff has an area of 2.83 ha. Only the runoff from this catchment, as shown by the boundary lines in Fig. 3.1 enters the pits. The site is classified as a commercial land use type. The city of Gosnells is within the Perth metropolitan area (32.0481°S 115.9844°E) located 20 km southeast of Perth CBD and is 10 m above average mean sea level. The city maintains an extensive drainage network designed to prevent flooding of roads and properties. As part of this maintenance, sweeping of roads and cleaning of gullies is undertaken on a regular basis to reduce build-up of leaf litter and other detritus in drains. Although a considerable level of effort is undertaken, leaves and debris washed

from private property can still block the drainage network. Due to the high water table and the nature of the soil types across the city, on site stormwater disposal for new real estate developments is becoming increasingly complex.



Fig. 3.1 The study site showing Federation parade, city of Gosnells, Western Australia

3.2.2 The UST Catch Basin Insert (CBI)

The CBIs used in this study were designed and developed by UST (formerly Templug) which can capture pollutants down to 150 μm . None of the previously discussed CBIs can capture pollutants down to these small particle sizes. The UST CBI has a bypass flow section for high flows of heavy rain to avoid flooding; a diffuser (a small perforated section) into the basket to dissipate the energy of incoming water flow; a special type of geotextile which is reusable (>12 times) that does not deform with time and heavy load (Fig. 3.2). CBIs reported in the literature comprise either only framed structures or only geotextile bags or both, without the above features (Kostarelos et al., 2011; MacLure, 2009; GeoSyntec and UCLA, 2005; CIWMB, 2005; Chrispijn, 2004; Lau et al., 2001). The UST device is designed to insert into each individual side-

entry pit, which can be easily retrofitted to existing drainage infrastructure. The geotextile drain basket material is a special type of synthetic non-woven needle punched polypropylene geotextile, which can be re-used, and is cleanable by reverse flushing. UST was the first to integrate this material into a CBI for the purposes of stormwater management with the aim of capturing GP at the source. After significant research, the material originally designed for marine purposes, has been further developed to produce a highly effective filter system. The shape of the basket supports the glue holding the material sections together, forming a frame. The basket is angled (α) specifically to allow optimal water flow through the material. If the inserts fill up and water passes over the sides, the water will flow down the side of the basket and into a tray under the basket (not shown in Fig. 3.2) which can contain adsorbents (e.g. Mycelex) to remove hydrocarbons and other dissolved pollutants.

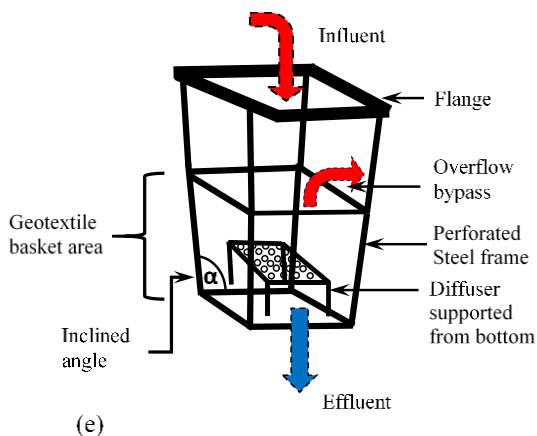
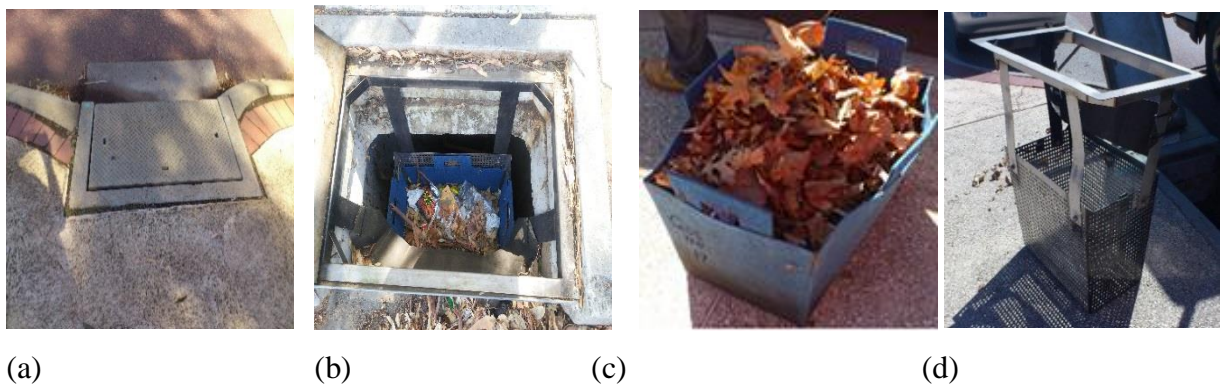


Fig. 3.2 The UST CBI used at the study site (a) External view of a side-entry pit; (b) UST CBI showing the blue geotextile basket; (c) Geotextile basket filled with typical plant detritus during our servicing; (d) Perforated steel frame to support the geotextile with bypass section (e) Schematic diagram of UST CBI (green colour indicates filtered water).

The UST CBIs were installed into 17 side entry pits within the stormwater drainage system in Federation Parade and the site has been maintained by monthly servicing since 2013. Out of these 17 CBIs, four were selected for this study (CBIs 6,7,8 and 13). CBIs 6-8 were selected based on their location and slopes considering the maximum runoff and vegetative waste entering the CBIs. CBI 13 was selected because it is on the other side of the road and is also located near a car park, so it is more likely to collect contaminants derived from motor vehicles. The stormwater runoff that passes through the CBIs enters the drainage system and ultimately drains into the Canning River.

3.2.3 Sampling and methodology

In order to collect samples from the selected CBIs, twelve site visits were made during the monthly servicing of CBIs between May 2015-April 2016. The monthly servicing intervals varied from 14 to 38 days depending on the availability of industry personnel and weather conditions.

The monthly load captured in each CBI was manually collected and stored in a plastic bag for further analysis. Each bag was weighed immediately upon return to the lab for gross wet mass. The samples were then oven dried at 60⁰C for at least 48 hrs. Higher temperature tended to melt or burn litter items and therefore a cooler, longer drying cycle was used compared to typical laboratory drying procedures at 105⁰C (Allison et al., 1998a). The gross pollutant materials were then manually sorted and weighed. Different types of materials were sorted including vegetation (leaves and twigs), plastics (food and drink containers, sheeting), papers (newspapers, cardboard, food and drink packet), cans (cans and jars) and others (glass, clinical waste, clothes and miscellaneous items). A similar classification was also used by Allison et al. (1998a).

The pit water quality was measured in water samples collected below the CBI. The water samples were collected following standard procedures (DoW, 2009) and different water quality parameters such as, total suspended solid (TSS), orthophosphate (PO₄³⁻), ammonia-nitrogen (NH₃-N), nitrite- nitrogen (NO₂-N), and nitrate- nitrogen (NO₃-N) were measured. The TSS concentrations were measured by standard method 2540B (Eaton et al., 1995) using membrane filtration apparatus. The

concentrations of PO_4^{3-} , $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NO}_3\text{-N}$ were measured following standard methods given in APHA (1998) using an AQUAKEM 200 water analyzer (Labmedics Analytical Solutions; detection limit of 0.002 mg/L with a 1.5% measurement error at 95% confidence level). Two milliliters of each sample was filtered through 0.45 mm membrane filter (GE Water and Process Technologies) prior to nutrient measurement. In this study, PO_4^{3-} was considered as total phosphate (TP) and total nitrogen (TN) was calculated as the summation of $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ respectively (Chunyan et al., 2015).

Analyses for moisture content, pollutant size distribution and composition of solid samples were carried out using methods described previously (ASTM, 2014; ASCE, 2007; Allison et al., 1998a). The moisture content (% mass) was measured gravimetrically for each solid sample (Allison et al., 1998a). The pollutant size distribution was carried out using sieve analysis (ASTM Standard, 2014). Solid samples (100-500 g) from each CBI were taken for sieve analysis using ISO 3310: BS 410-1:2000 sieve sizes 0.075, 0.15, 0.3, 0.425, 0.6, 1.18, 2.36 and 4.75 mm.

The runoff for each CBI inlet (assuming the inlet runoff catchment area same for each inlet) was calculated using the rational formula (Subramanya, 2013; Standards Australia, 2003): $Q = CIA$, where, Q is the flow rate (m^3/sec), C is the runoff coefficient, I is the rainfall intensity (mm/hr) and A is the catchment area (m^2). The rational formula is commonly used to determine the peak flows and unit hydrographs, or kinetic wave approaches are used for runoff generation. The rational formula was used in this study because of the maximum accumulation of GPs occurring during the peak flow. Allison et al. (1998a) also showed that GP loads increased with increasing flow, reaching their maximum at peak flow. The runoff coefficient was taken as 0.9 for an unroofed impervious area (Standards Australia, 2003). The rainfall intensity was calculated from 1-minute rainfall duration depth data collected from the Bureau of Meteorology, Western Australia.

3.3 Results and Discussion

3.3.1 The effect of catchment characteristics on the extent of capture of gross pollutants

The amounts of gross pollutants observed in areas with different urban intensities of residential, commercial and industrial activities is related to climatic conditions such as wind, the volume of traffic, topography, population density and most importantly hydrological parameters. The hydrological parameters are energy factors that govern the mechanism of mobilisation and transportation of gross pollutants from the streets or pathways into stormwater systems. These factors relate to the number of stormwater drains in a given urban or catchment area, the fraction of imperviousness, the topography and the profile of the roadside gutter. In dry conditions, wind and traffic movement are likely to convey material into the drains while during rainfall events, it has been previously observed that approximately 77% of street litter enters the drains and as little as 2.6 mm of rainfall is adequate to provide the transport mechanism (Madhani et al., 2009).

In our study, the CBIs were found to effectively capture gross pollutants at the source during each servicing event. Gross pollutants including sediments >150 μm diameter can be captured in the CBIs, as shown in a separate filtration experiment (see Appendix C1) for the UST CBI geotextile material. As the site did not have coarser sediments, the main gross pollutants collected from the CBIs comprised vegetation and litter. The monthly servicing data are presented in Table 3.1, along with meteorological data and the calculated average dry load (kg/ha/CBI).

Table 3.1 Average monthly servicing data of four CBIs

^a Servicing dates	^b Total rainfall (mm)	^c Last rain from servicing dates	^d Total no. of rainfall events	^e Servicing Interval	^f Max. wind speed (km/hr)	^g Avg. dry load (\pm SD) (kg/ha/CBI)
13/05/15	130.6	8	7	28	37	51(\pm 20)
20/06/15	174	0	10	38	33	64(\pm 21)
25/07/15	132	2	13	35	28	53(\pm 10)
29/08/15	130	3	20	34	11	46(\pm 9)

26/09/15	68	11	8	27	37	17(±8)
27/10/15	20.8	7	5	30	22	20(±4)
29/11/15	62.3	1	8	31	33	13(±4)
22/12/15	15.4	15	4	23	48	10(±4)
05/01/16	0	--	0	14	28	26(±13)
09/02/16	10.6	16	2	34	56	38(±4)
16/03/16	2.6	14	2	37	52	21(±5)
22/04/16	67.4	5	7	36	56	25(±10)

^aThe date at which the servicing was done

^b Sum of rainfall between the interval of two consecutive servicing dates

^c Number of days from last rainfall prior to servicing date.

^d Number of rainfall events between the two consecutive servicing dates

^e Number of days between two consecutive servicing

^f Maximum wind speed recorded between the two consecutive servicing dates (BoM, 2016)

^g The average dry load found in the CBIs

The mass of captured pollutants (average dry load) was plotted against rainfall for both the whole year data and for the period of wet weather months (April-October) (Fig. 3.3). This showed that there was a strong relationship between the GP load and the rainfall in the latter (wet weather) period ($r^2=0.90$). This is consistent with a study by Allison et al. (1998a) who also found a similar relationship between event load and rainfall volume ($r^2=0.78$) in a stormwater drain during wet weather (May-August). However, for the whole year data in our study, this relationship did not hold, as shown by the lower r^2 value of 0.41 (Fig. 3.3). This indicates that GP load is affected by other factors such as wind. In wet weather, high runoff is the main driver for accumulation of GP into CBIs while strong wind (with low rainfall) appears to be the main mechanism to transport the material into the side entry pits during dry periods. The wind speed is not uniform over the month and that is why a low regression value ($r^2=0.10$) was obtained in a separate plot (not shown) for wind speed versus GP load. The variation of GP captured in each CBI was tested by ANOVA (at 5% significance level). There was no significant difference ($p>0.05$) between yearly pollutant loads captured in each of the different CBIs. When the data for each individual CBI was analysed, there was no significant difference in GP load within the wet months (April–September; $p>0.05$) and again, no significant difference within the dry months

(October–March). However, there was a significant difference between the dry period load and the wet period load ($p < 0.05$).

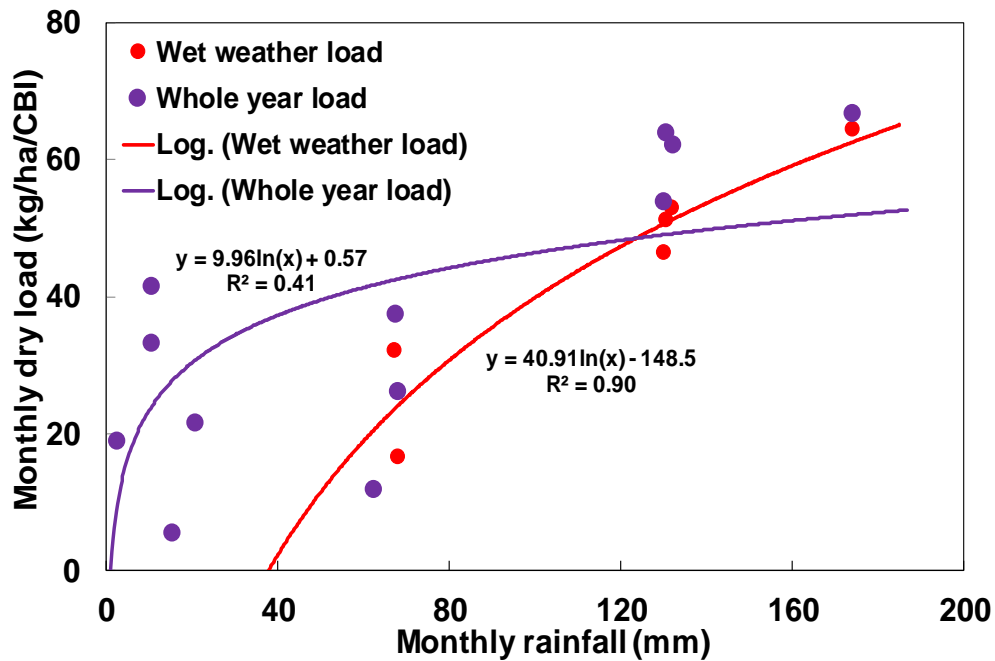


Fig. 3.3 Rainfall volume against dry load for wet weather and whole year

3.3.2 Total gross pollutants captured at source: comparison of devices

Total gross pollutants captured at source can be collected using a variety of devices such as, Catch basin inserts (CBI), continuous deflective system (CDS), inline netting system (NET), gross pollutant trap (GPT), at source pit traps (ASPT) and side entry pit trap (SEPT) (Allison et al., 1998a; Lewis, 2002; Chrispijn, 2004; Kostarelos and Khan, 2007). The photographs of each device are shown in Appendix C2. The amount of gross pollutant (mass basis) captured in different devices are shown in Table 3.2. To compare the total GP capture with other devices, only May–November data is presented. For the UST CBI tested in this study, the average accumulation of total GP load for each CBI were calculated as 384 kg/ha/yr (dry mass) and 919 kg/ha/yr (wet mass). These results are 13 times and 1.5 times higher than the similar study conducted in Melbourne and Sydney respectively (Allison et al., 1998a). The main difference between these studies is that Allison et al. (1998a) used SEPT and a CDS system which could not capture particles less than 5 mm, while the UST CBI captured particles down to 150 μm . In another study, Chrispijn (2004) found a GP load of 2250 kg (wet mass)

for a 7-month survey, which is equivalent to 4000 kg/yr for 63 devices in Hobart, Tasmania. In their study, significantly higher captured wet loads were found for Enviropod and Ecosols (1711 kg/ha/yr and 1427 kg/ha/yr respectively) compared to SEPTs (878 kg/ha/yr). The Enviropod showed a higher capture load as it could capture pollutants down to 200 μm while the screen sizes of the other two devices were 3 mm (Ecosol) and 33 mm (Council's SEPT). The pollutant load also depends on catchment characteristics, seasonal and climatic variations and causes for outliers such as land uses, illegal discharges, and pollutant hotspots.

The annual load in the devices (Table 3.2) may be affected by other parameters such as device dimensions, density of vegetation in the catchment and peak flows at the CBI inlets and hence the comparison of results should be normalized for these factors also. However, in this study, the captured load is normalized by their respective catchment areas per devices (last two columns of Table 3.2) because of the unavailability of other parameters. The results revealed that the UST CBI shows higher capture capacity (kg/ha) than the other devices throughout the year. However, the monthly dry load (kg) of the CDS system reported by Allison et al. (1998a) also shows a higher value because it was used at the outfall of a large catchment. The physical dimension of the CDS (usually 35 m^2) is much greater than that of the CBI ($<0.5 \text{ m}^2$), although this depends on multiple factors such as catchment area, site location, target pollutants and land use, expected pollution loads and storage volume to minimise lifecycle costs (ROCLA, 2016). A detailed description of the CDS system can be found in Allison et al. (1998a) and Birch et al. (2009). The smaller catchment area in our study gave a proportionally greater GP load than the other larger catchments, i.e. Table 3.2 also indicates that although Enviropod and UST CBI have nearly equal opening sizes but the UST CBI shows 8.25 times higher captured load (kg/ha) for 28 times smaller catchment area (2.83 ha versus 80 ha). These results suggest that the incoming flow in larger catchments is higher, possibly resulting in pollutants bypassing the devices and/or remobilisation of captured loads. A survey by Allison et al. (1998a) revealed that a combination of a CDS and 192 SEPT captured 225% higher GP load than a single CDS system for the same catchment area. These results confirm other reports (e.g. Chrispijn, 2004) that for optimal performance, the GP capture devices should be installed in relatively high density throughout the catchment. One advantage of the UST CBI is that since it is specifically designed to use existing drainage infrastructure

it can be easily retrofitted in most locations: comparable devices either need the infrastructure or drain to be replaced or have limited capture ability when fitted to existing infrastructure.

Table 3.2 Total gross pollutants captured in different devices

Reference	Survey year	Location	Catchment characteristics	Devices (*)	Screening size	Device dimensions (m ³)	**Peak flows per inlet (m/sec)	Collection months	Days between cleans	Weight (kg)		Weight (kg/ha/device)		Weight (kg/ha/yr /device)	
										Wet	Dry	Wet	Dry	Wet	Dry
This study	2015-16	Gosnells Perth	Commercial area (2.83 ha)	UST Catch Basin Insert (CBI) (4)	150 µm (geotex tile)	<0.5	0.035	May	28	53	19	18.7	6.7	3676	1536
								Jun	38	83	24	29.3	8.5		
								July	35	55	20	19.4	7.1		
								Aug	34	51	18	18.0	6.2		
								Sep	27	13	6	4.7	2.2		
								Oct	30	17	8	5.9	2.7		
								Nov	31	6	5	2.3	1.8		
Chrispijin (2004)	2002	Hobart Tasmania	Commercial area and majority of the stormwater system being tidally influenced (80 ha)	Enviropod Side Entry Pit Trap (SEPT) (20)	200 µm (filter bag)	<0.5	n.a.	May	27	147	n. a.	1.8	n. a.	1711	n. a.
								Jun	32	340	n. a.	4.3	n. a.		
								July	33	167	n. a.	2.1	n. a.		
				Ecosol SEPT (11)	3 mm (Steel mesh)			May	27	25	n. a.	0.3	n. a.	1427	n. a.
								Jun	32	113	n. a.	1.4	n. a.		

								July	33	38	n. a.	0.5	n. a.		
								May	27	81	n. a.	1.0	n. a.		
				Council's SEPT (32)	33 mm (Steel mesh)	n.a.		Jun	32	225	n. a.	2.8	n. a.	878	n. a.
								July	33	96	n. a.	1.2	n. a.		
Allison et al. (1998a)	1996	Coburg Central Melbourne	35% commercial and 65% residential land use with 192 road entrances to the drainage system (50 ha)	Continuous deflective system (CDS) (1)	5 mm	144 (6X6X4)	0.1	May	19	252	72	5.0	1.4	n. a.	n.a.
								Jun	34	348	111	7.0	2.2		
								July	27	422	122	8.4	2.4		
								Aug	27	n. a.	111	n. a.	2.2		
								Sep	32	n. a.	366	n. a.	7.3		
								Oct	15	n. a.	206	n. a.	4.1		
								Nov	31	n. a.	285	n. a.	5.7		
				CDS (1) + SEPT (192)	5 mm	n.a.	n.a.								

*Number of devices tested ** Normalized to the catchment area

3.3.3 Impact of moisture content of gross pollutants

Moisture content in the GPs can play a role in the rate of decomposition of vegetation and the release of nutrients to the environment. The moisture content was determined in each CBI and results are shown in Fig. 3.4. The mean moisture content (%) with their standard deviation found in CBIs varied between 24.05 (± 12.63) to 52.49 (± 13.85) for the whole year period. As expected, within the whole year period, the moisture content was higher during the wet season than during the dry period. A one-way ANOVA test (5% significance level) confirmed significant variation ($p < 0.05$) in moisture content in CBIs located on different sides of the road but no significant difference ($p > 0.05$) was observed among CBIs located on the same side of the road (e.g., CBI 6-8). The moisture content has an influence on the decomposition of materials captured within the CBI and hence their size distribution (see §3.4). As discussed, the presence of moisture content within the CBIs has implications on the decomposition of organic GP (such as leaves) that can increase dissolved nutrients to the runoff water coming in the next rain event (Selbig, 2016). As the CBI geotextile is not capable of removing any dissolved pollutants, it is necessary to service the CBIs well before the accumulated GPs are significantly decomposed.

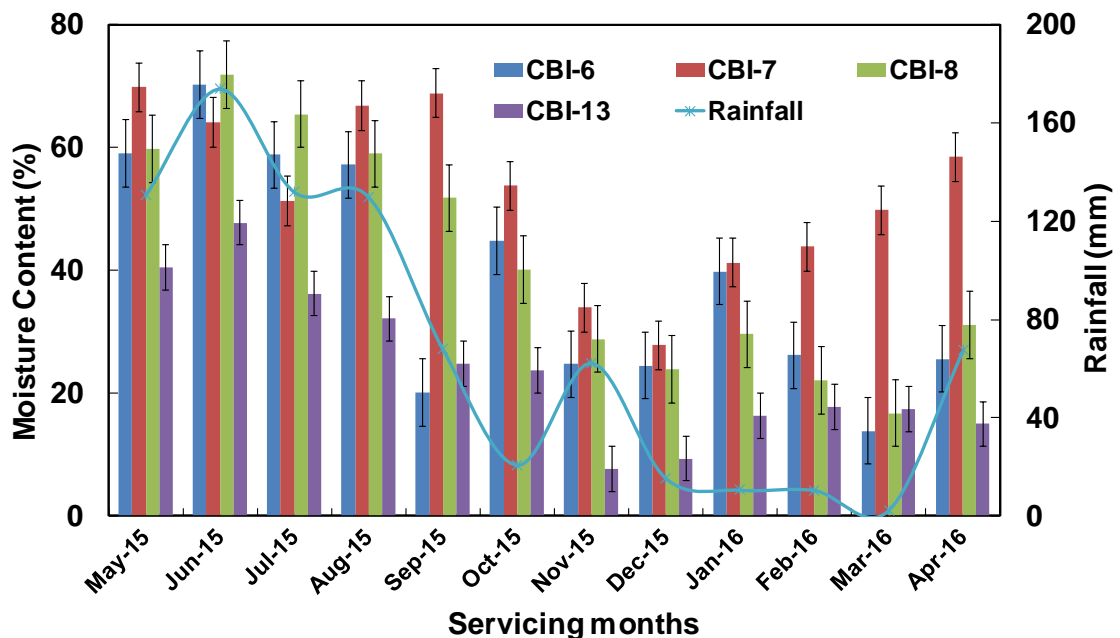


Fig. 3.4 Mean moisture content showing maxima and minima with corresponding monthly rainfall data in the different CBIs

3.3.4 Size distribution of captured gross pollutants

The size distribution of on-site GP captured depends on the land-use type, location and seasonal climate variability. The degree of variability describes the overall pollutant size distribution in each CBI. According to Selbig et al. (2016), the Shapiro-Wilk test (Helsel and Hirsch, 2002) for normality revealed that most of the individual particle size fractions, across a number of samples, did not show normal or log-normal distribution for skewness. Because of this degree of variability and the lack of normality in the data, the median distribution was chosen as the most appropriate representation of particle size distribution in each CBI. Usually, in highly skewed datasets, the median is a better representation of the population centre than the mean (Selbig et al., 2016). Hence, the median distribution (with standard deviation) for each sieve size calculated for the yearly GP captured in each CBI and tabulated in Appendix C3.

The results revealed that the percentage of GP retained on 4.75 mm sieve for CBI 6, 7 and 8 varied from 58.03- 68.24, indicating that 60-70% GP captured within these CBIs were larger than 4.75 mm. However, for CBI 13 the percentage was higher (>80%). The main reason for the difference was likely to be the moisture content and location of CBIs. Due to the low moisture content in CBI 13, the percentage of the breakdown of vegetation (mainly leaves) was lower. Since CBI 13 was located on the other side of the road as shown in Fig. 3.1, the larger size pollutants did not enter this CBI during periods of low rainfall. However, during the wetter months between May-August, larger pieces of vegetation (>150 mm) were more commonly found in this CBI because the heavier rainfall could transport these materials effectively (Fig. 3.5). The results indicate that the maximum percentage fines throughout the year in CBI 13 were less than 30%. From the median values, the pollutant sizes were arranged from higher to lower order as CBI 13>7≈8>6, i.e., the pollutants inside CBI 6 generally had a lower proportion of larger sizes (>4.75 mm) compared to other drains.

An ANOVA test confirmed that there was a significant difference (at 5% significance level) in yearly pollutant size distribution among four CBIs ($p < 0.05$) but there was no significant difference in pollutant sizes in different months of the year within the same CBI. This is because of the topographical location of each CBI. Similar sizes of

monthly vegetative loads were accumulated in the same CBIs. The results clearly revealed that the pollutant size distribution varied from one CBI to another for different months but did not vary in the GP captured in each individual CBI. Again there was a significant difference ($p < 0.05$) of pollutant size distribution in wet weather with respect to the dry period. This is because the size distribution may be affected in wet weather due to the higher moisture content enhancing the decomposition of vegetation.

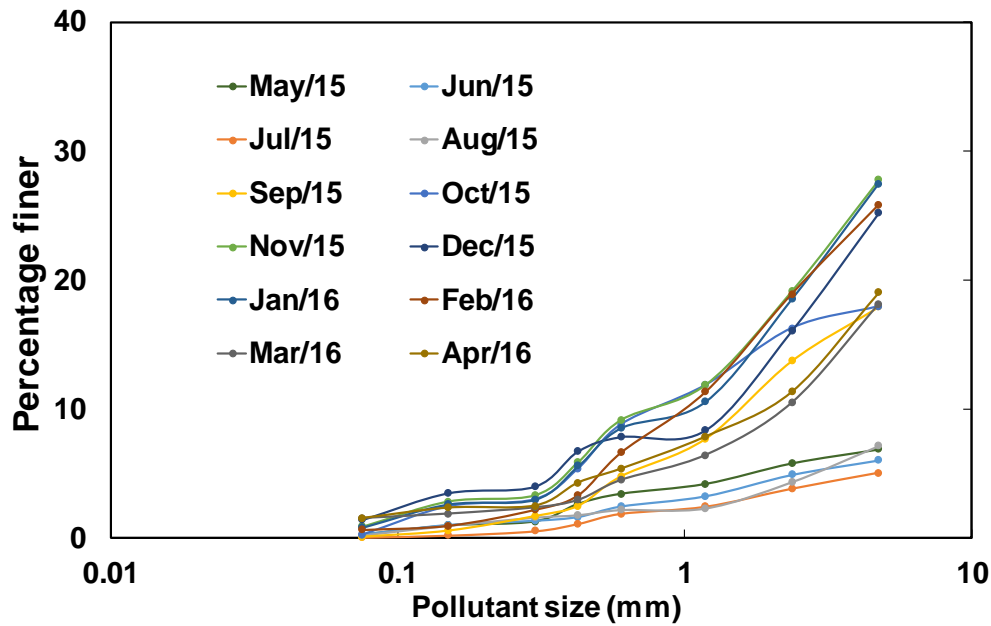


Fig. 3.5 Size distribution of gross pollutants captured in CBI 13

The loading rate coefficients (K) for different pollutant sizes captured in different CBIs are shown in Table 3.3. The K -value for each pollutant size indicates their relative accumulation in CBIs. The coefficients (K) were calculated with runoff and pollutant load data. These coefficients are similar to Event Mean Concentration (EMC), which is a flow-weighted average of constituent concentration (Lee et al., 2000). The EMC for an individual storm event can also be defined as the total pollutant load divided by total runoff volume which is known as loading rate coefficient (Lee et al., 2000, Lau et al., 2001). These loading rate coefficients have two systematic errors. The coefficients will be lower than the actual load as the CBI has a provision of bypass flow during heavy rainfall period. In contrast, it will be higher than the actual load if other controlling factors such as wind velocity and car speeds are considered for pollutant movement. These coefficients can be used as a first-order approximation of the GP load to be expected from the commercial sites in urban areas in a climate similar

to Perth, Western Australia. The results in Table 3.3 revealed that CBI 7 has the highest K-value (1.77) indicating higher relative accumulation of GP. This was because CBI 7 was closer to the pollutant source (trees, vegetation), which contributed to higher accumulation of GP in this CBI. These results are also comparable with those of Lau et al. (2001) who found the same range of coefficients for a commercial area. However, Lau et al. (2001) calculated the coefficients from one sampling data while yearly averaged (12 months' data) data were used in this study, which provides better representation of the field situation.

Table 3.3 Loading rate coefficients (*K*) of collected sample (kg/m³ of runoff)

Particle sizes (μm)	CBI number			
	CBI 6	CBI 7	CBI 8	CBI 13
>4750	1.03	1.25	0.99	1.03
1180-4750	0.28	0.29	0.19	0.12
300-1180	0.18	0.17	0.12	0.06
<300	0.06	0.06	0.05	0.03
Total (<i>K</i>)	1.55	1.77	1.34	1.24

3.3.5 Gross pollutant compositions

The GP accumulated in CBIs usually comprises a mixture of vegetation (leaves, clippings, and branches) and litter (plastic, paper, cans and other miscellaneous matter). The percentages of different types of GP in these categories revealed that the vegetation contribution was mostly above 90% of the total GP and that this composition remained reasonably consistent throughout the year. The amount of vegetation captured in CBIs depends on the surrounding environment, which in this case includes large eucalypt trees that shed copious quantities of leaves, branches, nuts and bark that enter the drainage systems through stormwater run-off and/or wind. In addition, a large proportion of trimmings from maintenance of grass verges enters the stormwater drains. During wet weather, the roadside gutter contains abundant organic matter especially grass clippings preventing a continuous flow of stormwater into the drains and causing blockages. The decomposing mass may contribute to the nutrients that enter the waterways, creating oxygen-depleting substances that are unfavourable to the aquatic environment.

Sustainable and green cities are the main foci of current urban planning. The city planners and designers are promoting the concepts of green (or 'living') walls and roofs in urban centres (Callaghan, 2008; Madhani et al., 2009). However, as these plans are implemented, the generation of green litter will proportionally increase, and buildings covered with vegetation will further add to the nutrient load in our waterways (Madhani et al., 2009). Additional elements included plastic, paper, cans and "others" made up the remainder of the GPs collected in the CBIs. "Others" mainly consisted of cigarette butts, glass, syringes, etc. which were primarily contributed by human activities. The current study site is a commercial land-use type surrounded by a shopping centre, a health centre, and a library, which are patronised heavily daily. Although CBI 13 is located on the other side of the road it showed a similar composition of pollutants to that in the other CBIs. The results revealed that a high percentage of vegetation may be found in stormwater systems, even for mixed activity urban areas.

Comparison of the UST CBI with previously described devices that capture GPs (e.g. GPT, CDS, SEPT, ASPT) showed that while the compositions of captured GPs were similar for all devices (Table 3.4), the major differences in the devices were in their screening sizes and operation and maintenance procedures. The GPT device has several disadvantages such as high construction costs, large visual impact usually on a recreational area and their frequency of trash rack blocking and subsequent overflowing including high maintenance program costs (Allison et al., 1998a). Maintenance of some GPTs may require large vertical clearances. Hence before construction of GPTs, it needs to be ensured that appropriate clearance zones (e.g. to trees, overhead power lines, awnings) are available for cleaning. The time to clean a single GPT unit is approximately 4 hours (including transportation and cleaning) and servicing occurs annually, depending on site characteristics. CDS and Vortex are also associated with high construction cost and require separate land area. SEPTs are baskets fitted below the entrance to drains from road gutters. When stormwater passes through the baskets to the drain, material larger than the basket mesh size (5-33 mm) is retained. This material remains in the basket until it is removed by a maintenance crew, typically every four to six weeks (Allison et al., 1998a). ASPT's units can be cleaned either manually or by an eductor truck. The total time taken for the clean,

including travelling time and disposal for four ASPT units is four hours (Watson, 2005). The UST CBI is usually serviced 10 times/year in the following manner: (a) truck pulls up next to the side entry pit and the drain lid or grate is removed or opened; (b) the CBI unit is lifted out of the drain by the Hiab crane or manually by two crews; (c) the geotextile basket with pollutant material is removed from the unit and a new one is installed on-site; the device is then reinstalled into the drain and the drain lid or grate is reinstalled or closed (Fig. 3.2). The whole process is carried out in this manner to keep traffic disruption to a minimum. The average time for a service is approximately 10 minutes. The collected geotextile bags with pollutant materials from the field are serviced/cleaned by reverse fluid flush back at the base where wastes are sorted for reuse or possible recycling which also takes roughly 10 minutes for each unit. The special type of geotextile used in the UST CBI is a key to its ease of use. The performance of the geotextile material is restored to near new condition by removing the captured sediment and vegetation with a high-pressure fluid flow (400 kPa) without destroying its original basket shape. It was found that newly developed urban areas generate significant quantities of silt and sediment run-off, which can fill up the swale pit even prior to the completion of the development. Trapping these pollutants into CBI units at-source will significantly reduce the sedimentation build-up in these pits and also on-going maintenance costs in downstream pipelines. The ability to fit CBI units to existing systems means that drainage lines serving pollutant-generating catchments such as schools, shopping precincts and central business districts, can be targeted for effective treatment of stormwater at significantly reduced cost. Each unit may be manufactured to suit the configuration of each individual pit. This is an important feature as there are a wide range of pit dimensions and depths across the different localities. There is a concern about stormwater treatment at source that the installation of devices may cause blockages resulting in localised flooding. However, the CBI unit has its unique design with a by-pass (Fig. 3.2) ensuring inflows passing continuously through the pit even when its collection unit is full.

Table 3.4 Composition of gross pollutants captured in different traps

Ref.	Survey year	Site description	Device types	Screening size	Vegetation Litter /Sediments		Method
					(%)		
This study	2015-16	Perth, Western Australia Federation parade, Gosnells (Commercial area)	CBI 6	150 µm (geotextile)	93	8	mass
			CBI 7		97	3	
			CBI 8		92	8	
			CBI 13		91	9	
Chrispijn (2004)	2002	Hobart, Tasmania, Australia Sullivan's Cove (Commercial, light Industrial, trafficked areas)	Enviropod	200 µm (filter bag)	98	2	mass
			EcoSol	3 mm (Steel mesh)	97	3	
			Council's SEPT	33 mm (Steel mesh)	94	6	
Allison et al., (1998a)	1996	Melbourne, Australia Coburg	CDS	5 mm	80	20	mass
Great lake councils (2002)	2001-02	Sydney, New South Wales, Australia Stroud Bulahdelah Nabiac Forster Tuncurry Tea Gardens Hawks Nest	ASPT	200 µm (mesh)	97	3	mass
					70	8	
					29	71	
					71	29	
					97	3	
					96	4	
					97	3	
Lewis (2002)	2001	Melbourne, Victoria, Australia Melbourne City Melbourne City St Kilda (Residential area) Frankston (Commercial/ shopping precinct)	NET ¹	n.a.	83	17	mass
					91	9	
			SEPT	3 mm	94	6	
					76	24	
Greenway et al., (2002)	1999-03	Brisbane, Queensland, Australia Brisbane (Residential area)	CDS	5 mm	97	3	mass
			vortex	5 mm	99	1	
Watson (2005)	2004	Tauranga, New Zealand	ASPT	200 µm (mesh)	82	18	mass
Lippner et al., (2000)	2000	Los Angeles, USA	drains	n.a.	60-80	-	mass
Kim et al., (2006)	2000-02	Southern California, USA	drains	n.a.	90	10	volume
Marais et al., (2004)	2000-01	Cape Town, South Africa (All residential area) Imizamo Yethu Ocean site Summer Greens Fresnaye Welgemoed Cape Town CBD Montague Gardens	SEPT & GPT	n.a.	21	79	mass
					60	40	
			64		36		
			100		0		
			GPT		100	0	
			SEPT & GPT		65	35	
			38		62		

¹inline netting system

3.3.6 Gross and aqueous phase pollutants in dry and wet seasons

The impact of CBIs on water quality was largely related to the retention of moisture within decaying vegetation which has been reported as promoting the release of nutrients. The accumulation of gross pollutants in dry and wet seasons and the subsequent aqueous phase contamination, total pollutant load and concentrations of nutrients and suspended solids are shown in Table 3.5. The pollutant load in the wet weather period was found to be higher because of the rainfall-runoff carrying these loads (Table 3.5). However, the vegetation in CBI 13 was lower because of its location, which is on the other side of the road further from the trees.

The pit water quality in terms of nutrient concentrations (TSS, TP and TN), averaged for dry (November- March) and wet (April-October) seasons (Table 3.5), is within the large range of values reported in the literature for fully developed urban areas in Australia (Wong et al., 2006). During the dry period TSS was higher than during the wet season because there appeared to be greater transport of fine particles in the dry period. TP and TN were higher in wet season possibly because the water-soluble components of nutrients are transported more readily by the road runoff from nearby market areas and parking lots. In addition, the moist vegetation accumulated in the CBIs may add to the nutrient load through decomposition. Ball and Ara (2010) and Allison et al. (1998b) confirmed the release of TP and TN from moist vegetation. Ball and Ara (2010) reported that more than 50% of phosphorous in leaves are released within 22 days of submergence. Allison et al. (1998b) indicated that 5-20% of nutrients can leach from vegetation under moist conditions. The decomposition of plant material may follow a first order exponential decay model (Olson, 1963; Ball and Ara, 2010): $P_t = P_0 e^{-kt}$ where P_0 is the initial nutrient content in vegetation, P_t is the amount of nutrient remaining after the time t , and t is the time in days. This indicates that there would be more release of nutrients into water if conditions inside the CBIs remain moist for the longer term, which will enrich the nutrient concentrations in the receiving water bodies. In this study, higher TP concentrations in the wet season (>the trigger value in ANZECC, 2000) may have resulted from stagnation of water in the pit and the accumulation of GPs within CBIs in moist condition for up to a month. Allison et al. (1998b) and Brich et al. (2009) found higher TP (0.14-0.6 mg/L) and TN (1.5-4 mg/L) concentrations in CDS effluent. The CDS are usually serviced annually and the

GPs remain under water for longer term in this device. However, the concentrations of TP and TN in CBI effluents were found lower in this study comparing with other literatures (Allison et al., 1998b; Brich et al., 2009). This was because the CBI is serviced monthly and GPs are accumulated within the basket.

The configuration of the side entry pit has a significant influence on stormwater infiltration and hence overall stormwater management. The side entry pit is primarily thought to function as a soak well but often the bottom of the pit becomes effectively sealed to water due to stormwater contaminants and accumulation of GPs. Hence it is necessary to capture the contaminants at source and then service the CBI on a regular basis. In this case, CBIs can be used since they provide easy access for cleaning both the CBI (e.g., servicing) and the pit. However, several operational parameters still require further research, such as the optimum frequency of servicing, which is dependent on the infiltration/retention capacity of CBI materials and site-specific conditions. Regular servicing of the CBI and maintenance of the side entry pit will allow the release of relatively clean water to aquifers and receiving water bodies and will also keep the storm drainage network free from blockages and ensure that it operates effectively.

Table 3.5 Total pollutant load and water quality parameters in dry and wet seasons

Parameter	Pollutant load (kg/ha) : Mean (\pm std dev)				
	Season	CBI-6	CBI-7	CBI-8	CBI-13
Vegetation	Dry	21(\pm 10)	24(\pm 14)	23 (\pm 10)	17(\pm 11)
	Wet	45(\pm 23)	48(\pm 0.5)	36(\pm 23)	23(\pm 13)
Litter	Dry	1.4(\pm 0.8)	1(\pm 0.9)	0.7(\pm 0.4)	1.5(\pm 0.6)
	Wet	4.5(\pm 0.8)	0.7(\pm 0.5)	3.7(\pm 2.4)	3.5(\pm 6.3)
Concentration in pit water (mg/L)					
TSS	Dry	368(\pm 352)	476(\pm 347)	-	135(\pm 75)
	Wet	309(\pm 238)	387(\pm 358)	-	101(\pm 118)
TP	Dry	0.02(\pm 0.02)	0.06(\pm 0.05)	-	0.02(\pm 0.02)
	Wet	0.07(\pm 0.08)	0.17(\pm 0.14)	-	0.04(\pm 0.06)
TN	Dry	0.32 (\pm 0.29)	0.27(\pm 0.13)	-	0.56(\pm 0.41)
	Wet	0.84(\pm 1.2)	0.37(\pm 0.49)	-	0.26(\pm 0.43)

3.4 Conclusion

This paper has demonstrated the nature, type and size of gross pollutants captured at source in a catch basin insert. A new type catch basin insert (CBIs), developed by UST, was trialled in an urban area in the City of Gosnells, Western Australia. Gross pollutants were collected from the CBI and water samples were collected from the side entry pit under each CBI during monthly servicing over the course of one year. The GP load was affected by seasonal conditions, being highest during the winter (wet) months due to mobilisation of pollutants by rainfall and storm events. In the dry months, the greatest factor in terms of GPs loading was thought to be median wind speed although sufficiently detailed wind speed data was not available. The prevailing wind patterns during the dry months are generally regular easterly in the morning with south-westerly sea breezes in the afternoon, whereas during the wet months most days are calm, but maximum wind speeds can be high during sporadic storm events. The GP compositions were evaluated, and vegetative waste was found to be the greatest contributor of all the GP types (93%) in all 4 CBIs. This reflected the nature of the site, which was an urban commercial area near parkland with numerous trees and indicated the site specificity for GP characteristics. The moisture content of the GPs varied between 24-52.5%. The sizes of captured GP were found to be of similar distribution in all CBIs for the sizes varying between 0.075-4.75 mm. The sieve size of 0.075 mm showed less than one percent of solids accumulation, indicating the CBI is suitable for capturing GPs above 150 microns. The loading rate coefficient (K), showing relative accumulation of GPs, was found to be higher in the CBIs located near trees. The GP capture capacity of different types of devices was reviewed and it was found that the UST CBI has higher potential to capture GP per unit area above 150 microns. Comparison of this study with previous studies confirmed the importance of the density of capture devices in terms of their effectiveness. Large catchments with high flow and a low density of capture devices can result in a significant portion of the GP load by-passing the devices and/or remobilisation of the captured loads. Higher densities of smaller devices, as was the case in this study, may be more effective in capturing GPs than larger devices spread further apart. However, this study was carried out at one site only and further investigation is required for site specific information on the performance of the CBI, e.g. in a range of brownfield and/or greenfield sites.

List of Abbreviations

ANOVA	analysis of variance
ASPT	at source pit traps
ASTM	American Society for Testing and Materials
BMP	best management practices
BS	British Standard
BOD	biochemical oxygen demand
CBD	central business district
CBI	catch basin insert
CDS	continuous deflective system
CSIRO	Commonwealth Scientific and Industrial Research Organisation
EMC	event mean concentration
GP	gross pollutant
GPT	gross pollutant trap
ISO	International Organization for Standardization
NET	in line netting system
NSW	New South Wales
SEPT	side entry pit trap
SS	suspended solids
TN	total nitrogen
TPH	total petroleum hydrocarbon
TP	total phosphorous
TSS	total suspended solids
UST	Urban Stormwater Technologies Pty Ltd

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CHAPTER 4

IMPROVING STORMWATER QUALITY AT SOURCE USING CATCH BASIN INSERTS

Abstract

Stormwater runoff transports contaminants, including gross pollutants (GPs) accumulated on surfaces to nearby receiving water bodies. These may clog storm drainage systems, seal side entry pits and increase dissolved pollutants in receiving water bodies. Best management practices (BMPs) such as oil and grit separators, grassed swales, vegetated filter strips, retention ponds, and catch basin inserts (CBIs) are implemented to reduce stormwater pollutants in urban runoff. CBIs are devices used to remove GPs at source without requiring any extra land use because they are typically mounted within a catch basin (e.g. side entry pit) or existing drain. In this study, improvement of stormwater quality was investigated at two different sites (Subiaco, a residential area and Hillarys Boat Harbour, a commercial-marine-recreational area; Western Australia) where a new CBI made of non-woven polypropylene geotextile was installed in side entry pits to capture GPs at source. Influent and effluent water from the CBIs was collected and analysed for BOD, COD, TSS & PO₄-P with maximum improvements in water quality of 90%, 88%, 88% & 26% respectively. Heavy metal concentrations were found to be below their maximum guideline values. Analysis of particle size distribution, specific surface area of solids, SEM images and heavy metal content (Cu, Fe, Ni, Pb, Zn, Cd) in solids showed that the residential area contained more finer particles than the commercial area but that solids in the commercial area contained greater concentrations of heavy metals than those from the residential area. The specific surface area was found to be higher in the residential area and particles were thought to be largely sourced from traffic. However, the morphology of grain sizes in particles from traffic-related soils is complex and not well understood.

Key Words: Stormwater; Catch Basin Inserts; Treatment; Sediments; Water Quality

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4.1 Introduction

Urban development (e.g., urbanization) has significant effects on the water quality of nearby water bodies receiving urban runoff (Miguntanna et al., 2010). Urbanization alters the natural surface, transforming pervious to impervious surfaces. These human transformations affect the hydrologic cycle by altering the percentage of rainfall that contributes to groundwater, evapotranspiration and runoff relative to the natural ground cover (Balousek et al., 2007). In nature, stormwater runoff commonly is soaked into the ground to replenish groundwater or absorbed for plant growth. It has been found that impervious surfaces associated with urbanization can lead to reducing infiltration and increasing surface runoff (USEPA, 2012). The surface runoff consists of various pollutants including gross pollutants (debris and litter), suspended solids, nutrients, oxygen demanding substances, heavy metals and hydrocarbons (oil and surfactants). Excessive nutrient levels in water bodies can result in growth of algae, and other aquatic plants that clog waterways. The decrease in dissolved oxygen (DO) can lead to depletion of aquatic organisms, therefore degrading aquatic ecosystems. Eutrophication, the phenomenon of excessive aquatic plant growth such as macrophytes and algae, has become a serious environmental threat in urban areas (Lewitus et al., 2008). The presence of heavy metals in urban stormwater runoff is of concern due to their potential toxicity level in receiving waters. Marsalek et al. (1999) reported that heavy metals such as lead (Pb), cadmium (Cd), zinc (Zn) and copper (Cu) are the most prevalent metals in urban stormwater runoff and mercury (Hg), chromium (Cr) and nickel (Ni) are found to a lesser extent (Sartor and Boyd, 1972). Heavy metals in urban stormwater runoff originate from traffic-related sources such as brake linings, tires, pavement wear and automobile exhaust (Gunawardana et al., 2012). Corrosion of building materials and atmospheric deposition are also potential sources of heavy metals in urban stormwater runoff (Gunawardana et al., 2012; Amato et al., 2011).

Various researchers showed that stormwater from different catchments consist of different levels of pollutants (Zhao et al., 2007; Kim et al., 2005; Lee and Bang, 2000). Nazahiyah et al., (2007) and Lee et al., (2002) reported that total suspended solids (TSS) and chemical oxygen demand (COD) are the primary pollutants which can result in degradation of water quality in residential areas. Chemical oxygen demand (COD)

is an indicative measure of the amount of oxygen that can be consumed by reactions in a measured solution (Clair et al., 2003). Zhang et al., (2010) verified that vehicular traffic density in commercial and industrial areas is higher than in residential areas. This implies that the characteristics of pollutants and their accumulation level depend on the number of people that utilize the area and also the types of activities carried out. Again, rainfall characteristics such as runoff volume, antecedent dry weather periods and rainfall intensity are the major factors affecting the magnitude of stormwater pollutants in receiving waters (Gupta and Saul, 1996; Le Boutillier et al., 2000). Huang et al. (2007) reported that the strongest rainfall event following the longest period of dry days can result in the highest concentration of TN, TSS and COD in urban waterways.

This has led to the development of stormwater quality improvement devices at the point of waste generation such as drain basket/side entry pit trap (SEPT) to clean stormwater from street borne pollution (Allison et al., 1998a). The other type of device for pollutant removal is the gross pollutant trap (GPT) but for this device there are difficulties in periodical cleaning and it is not very effective for removing pollutants less than 5 mm. The GPT is not effective in treating stormwater at source because it is placed at outlets of piped drainage systems and captures mainly litter and debris (Ab Ghani et al., 2011; Allison et al., 1997; Allison et al., 1998a; Madhani and Brown, 2015; Sidek et al., 2016). A few studies have focused on capturing pollutants using drain baskets (also termed catch basin insert-CBI) in side entry pits before they enter the drainage system (CIWMB, 2005; GeoSyntec and UCLA, 2005; ICBIC, 1995; MacLure, 2009). Kostarelos and Khan (2007) and Kostarelos et al. (2011) evaluated pollutant removal efficiency of six CBIs under laboratory and field conditions. They studied the removal of five water quality parameters including total suspended solids (TSS), total nitrogen (TN), total phosphorus (TP), total petroleum hydrocarbon (TPH), and biochemical oxygen demand (BOD₅) at three different flow rates (50, 150 and 300 mg/L) with three contaminant concentrations (low, medium, high). BOD is the amount of dissolved oxygen required by aerobic biological organisms to break down organic matter present in a given water sample at certain temperature over a specific time period (Clair et al., 2003). This study focused on the installation characteristics, durability and maintenance of CBIs. The authors concluded that these CBIs can be used as a pre-treatment device with other stormwater structural practices as none of

them can consistently remove all the five water quality parameters according to the New York State Stormwater Management Design Manual (CWP, 2003). Their field studies revealed that these CBIs were easy to operate and maintain and have comparable annual maintenance cost (approximately \$640 per year, Kostarelos and Khan, 2007) except one CBI (i.e., Passive Skimmer). A similar study was performed by GeoSyntec and UCLA (2005) to remove oil and grease in four CBIs. Crispijn (2004) did a field survey for 63 ‘at source’ stormwater pollutant traps (ASPT) out of 300 SEPT in Hobart, Tasmania. Three different ASPT namely Enviropod Filter, Ecosol RSF 100 and SEPTs (designed by Hobart City Council) were used in this study and a small number of traps from each type were installed in comparable locations in and around Sullivans Cove, Hobart, Tasmania Australia. A wet weight of 2.25 tons of polluted materials was captured in the 63 traps with variable retention capacity of pollutant materials. Lau et al. (2001) performed field and laboratory tests on CBIs in the City of Santa Monica, USA, collecting the GP from CBIs twice during their testing period to determine the pollutant size distribution. Recently, Alam et al. (2017a) carried out a field survey on UST (Urban Stormwater Technologies Pty Ltd) CBIs through a period of a year and found efficient (>90%) for capturing gross pollutants, mainly vegetation. However, although different types of trapping devices are now available there is a lack of information on physio-chemical characteristics and removal efficiencies of captured pollutants in CBIs. Pollutant characteristics captured in CBIs have not been fully tested in field conditions under the influence of seasonal variations especially for a Mediterranean climate (such as Perth, Western Australia) where high rainfall intensity in short duration prevails.

Based on the regulations, proper stormwater management must be undertaken to remove pollutants to the required levels. Best management practices (BMPs) for stormwater management include bioretention devices, swales, infiltration basins, stormwater ponds, engineered wetlands, gross pollutant traps and CBIs. Among these, only a few BMPs can capture GPs at source but there is no device that can capture GPs down to 150 μm . It is essential to capture the gross pollutants at source so that the storm drainage system is free of blockages. Fine particles may contribute to the sealing of the bottom of the side entry pit and limit the infiltration (Alam et al., 2017a). Among the available BMPs, the catch basin insert (CBI) is a device that can be used to remove GP at source without requiring any extra land use because it is typically mounted within a

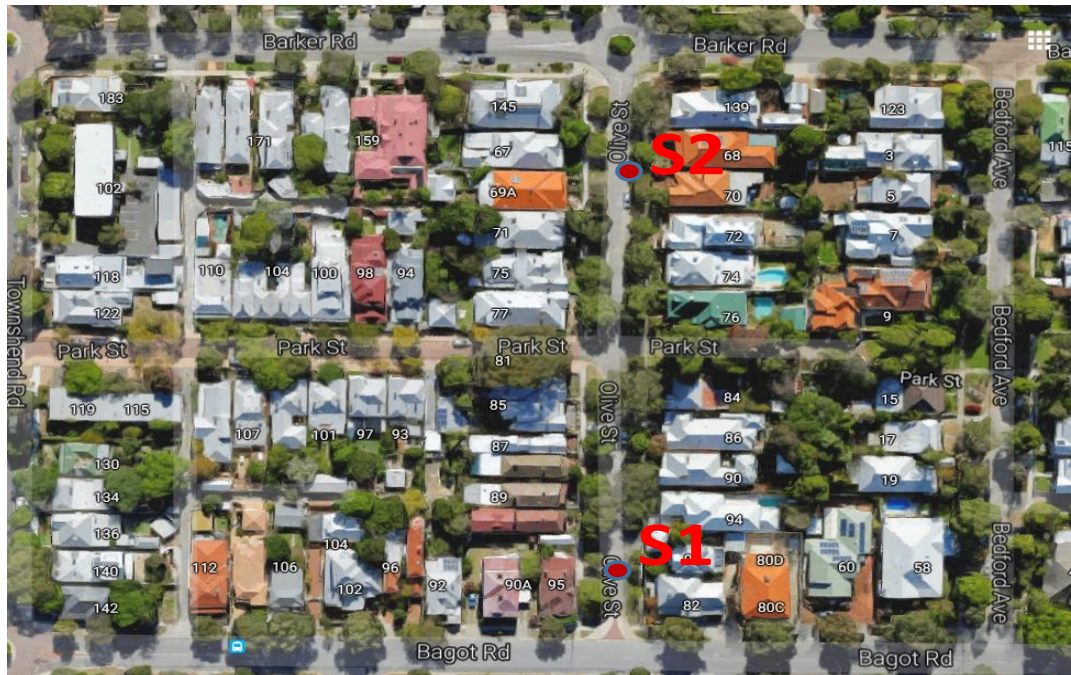
catch basin (e.g. side entry pit drain). As reported by Alam et al. (2017a) and (2017b), the UST CBIs (made of non-woven polypropylene geotextile) can capture sediments down to 150 μm . The study of Alam et al. (2017a) was conducted in a commercial land use type site located in the vicinity of a market and library surrounded by trees with the major GPs being vegetation. The study mainly focused on the physical characteristics of the captured GPs but it is important to also understand the chemical characteristics of pollutants removed in order to implement BMPs for the improvement of stormwater quality at source. In this paper, the quality of stormwater and captured solids in CBIs were investigated for a variety of both physical and chemical environmental parameters. The CBIs studied were located side entry pits which are the beginning (i.e. source) of the stormwater collection (i.e. drainage) system. The water quality parameters of influent and effluents of CBIs are discussed in this paper and the physico-chemical characteristics of captured solids are illustrated.

4.2 Materials and methods

4.2.1 Selection of study area

In this study, two different sites (i) Olive Street, Subiaco and (ii) Southside Drive, Hillarys in Western Australia were selected where UST has installed CBIs in the side entry pits to capture GP at source (Fig. 4.1). A total number of 17 and 14 CBIs were installed in Olive St and Southside Dr respectively. Among them, 2 CBIs (S1 and S2) from Subiaco and 4 CBIs (H1, H2, H3 and H4) from Hillarys were selected based on the criteria of receiving maximum amount of stormwater runoff. The CBIs in Hillarys were selected at the junction of roads and near the car park area as shown in Fig. 4.1. Similarly, the CBIs in Subiaco were selected near the end and middle of the side road (Fig. 4.1) with relative downward slope considering that these will receive all kinds of pollutants. The CBI may therefore represent the outlet points of the basin. A detailed description of UST CBIs and its solid removal characteristics can be found in Alam et al. (2017a) and (2017b). The selected catchments are mixed land use type areas. The land use in Subiaco catchment (25.5 ha) is mostly residential with high vegetation waste (such as leaves and twigs) and located 3 km from Perth CBD. Hillarys is located on the coast approximately 18 km northwest of the Perth CBD. Hillarys is a recreational and commercial area that includes more than 2700 car parking bays. The catchment area of Hillarys is approximately 45.5 ha. The city of

Subiaco and Hillarys provides comprehensive street sweeping (weekly), butt out bin and street bin cleaning (fortnightly), as well as litter control services (City of Subiaco, 2017; City of Joondalup, 2017). Similarly, street sweeping practices are monitored and audited to ensure that street waste is kept out of drains.



(a)



(b)

Fig. 4.1 Location of the study area: (a) Olive St, Subiaco and (b) Southside Dr, Hillarys, Western Australia

4.2.2 Method of sampling

Duplicate sets of water and solid samples were collected from 2 CBIs at Subiaco (S1 and S2) and 4 CBIs at Hillarys (H1, H2, H3 and H4) during the wet season of 2014. Two storm events (June and July 2014) were targeted and influent and effluent stormwater samples were collected from different sampling points at both study sites. Two storm events were selected in wet weather condition because the pollutant load is washed out during the wet season with surface runoff (Alam et al., 2017a). The monthly rainfall pattern for 2014 is shown in Fig. 4.2 (BoM, 2017). Side entry pits are designed to operate as soak wells but in practice, many of them were found to be sealed due to accumulation of GPs and other pollutants because of insufficient maintenance. Stagnant water was found in most pits: the water inside the CBIs was considered as influent and water outside the CBIs was considered effluent in this study. The samples were collected after few rain events on the basis of the assumption that after successive rain events these CBIs act as a permeable reactive filter due to the accumulation of different sizes of soil/wood particles (0-10000 μm). The accumulated fine particles within the CBI may act as an adsorbent medium for dissolved pollutants and thus releasing the cleaner water outside of CBI.

The influent and effluent water samples were collected in 1L polyethylene bottles from selected CBIs at both sites and were kept below 4°C to minimize any changes in water characteristics. Soil samples were collected at a depth of 0 to 5 cm from within the CBIs and stored in a polystyrene bag in ice boxes to maintain the temperature below 4°C. The collected samples were immediately transferred from the site to the laboratory for analysis. The collected water samples were analyzed for TSS and $\text{PO}_4\text{-P}$ at water laboratory of civil engineering department, Curtin University while BOD, COD, heavy metals (HMs) and particle size distribution (PSD), density, specific surface area and scanning electron microscope (SEM) analyses were performed at the CSIRO Laboratory.

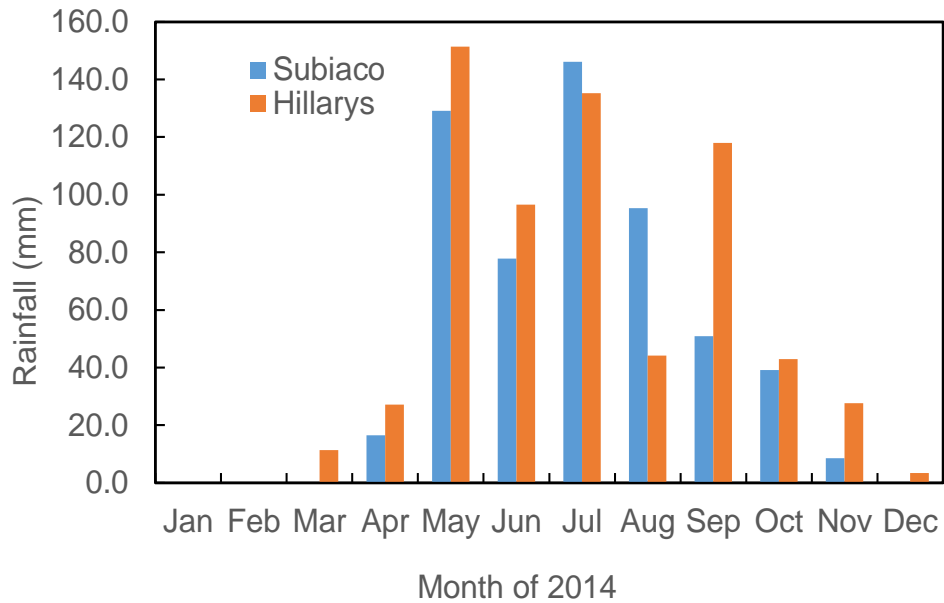


Fig. 4.2 Monthly rainfall pattern in 2014

4.2.3 Analytical method

The water samples were analyzed for total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD) and phosphate (PO₄-P). TSS was measured by filtering samples (100 mL) through a 0.45 µm glass fiber filters (GE Water and Process Technologies) using the Standard Method 2540D (APHA, 2005). PO₄-P was measured using an AQUAKEM 200 Discrete Photometric analyzer (Labmedics Analytical Solutions; detection limit of 0.002 mg/L with a 1.5% measurement error at 95% confidence level). A VELP Sensor (BOD Sensor), was used to measure BOD in accordance with the Standard Method 5210D for Water and Wastewater (APHA, 2005). COD was measured using the standard Reactor Digestion Method 8000 (APHA, 2005). Water samples (inlet and outlet of CBIs) were also analyzed for heavy metals using ICP-MS (Agilent ICPMS 7700).

Solid samples collected from each CBI were analysed for particle size distribution, solid density, specific surface area and heavy metals content. The particle size distribution of solid samples was determined using the wet screening method (500-10000 µm) and the laser diffraction method (0.02-500 µm) using a Malvern Mastersizer Particle Size Distribution Analyzer 2000. The Malvern Mastersizer analyser used a reverse Fourier lens and was able to analyse particles in the range 0.05-

10000 μm and specified a reading accuracy of $\pm 1\%$ of the volume median diameter. The solid density was analysed using Helium multipycnometer (Quantachrome instruments). The specific surface area of solid samples was analysed using TriStar 3000 (Micromeritics Instrument Corporation) using either the options BET or Langmuir surface area. SEM images of solids captured in CBIs were also obtained for both sites. The solid samples were analysed for heavy metals using ICP-MS (Agilent ICPMS 7700) according to Method 3125B (APHA, 2005). External standards were used in all analyses. The blanks and duplicate samples were also analysed and the mean values (standard error ≤ 0.01) were reported. The rational formula ($Q = CIA$, where, Q is the flow rate (m^3/sec), C is the runoff coefficient, I is the rainfall intensity (mm/hr) and A is the catchment area (m^2) was used to calculate the runoff of each CBI (assuming the inlet runoff catchment area same for each inlet) (Alam et al., 2017a).

4.2.4 Efficiency calculation

This is an efficiency ratio method based on log transformed influent and effluent pollutant concentrations (Barret, 2003). This methodology was used because catch basin inserts exhibit similar characteristics to sand filtration systems. The soils are accumulated within CBIs and it acts as a soil fabric filtration system. In the efficiency ratio method, the test data are assumed to be log-normally distributed. The mean (μ) and variance (s^2) of the log transformed pollutant event mean concentrations were calculated as,

$$\mu = \frac{\sum x}{N} \quad (4.1)$$

where x is the natural log of pollutant concentrations (mg/L); $\sum x$ is the summation of data points (x); and N is the number of data points (x). The mean of pollutant concentrations (a) was calculated as $a = e^{(\mu + \frac{s^2}{2})}$; where s^2 is the variance of the transformed pollutant concentrations. The removal efficiency of the soil fabric filtration system was then determined as,

$$\text{Removal efficiency} = \left(\frac{a_{inf} - a_{eff}}{a_{inf}} \right) \times 100 \quad (4.2)$$

where a_{inf} is the average influent concentration (mg/L); and a_{eff} is the average effluent concentration (mg/L).

4.2.5 Statistical analysis

To compare the results of six CBIs for several parameters such as influent and effluent water qualities and particle size distribution/soil textures, a hypothesis test was performed by using one-way ANOVA with 5% level of significance. The null hypothesis assumed that one parameter is equal to the other. The level of significance (p) was considered as the probability of rejecting null hypothesis when it was actually true. Hence, the critical p value for a hypothesis analysis was the rejection probability. When the critical p value was very small, it was safe to reject the null hypothesis (Ayyub and McCuen, 2011).

4.3 Results and discussion

4.3.1 Improving the stormwater quality

The UST CBIs are generally serviced at least 10 times/year to maintain their effectiveness for filtration. The servicing consists of removing the GPs from CBIs and cleaning of the CBI geotextile with surfactant solution under high pressure fluid flow (400 kPa) and reinstalling it into the side entry pit (Alam et al., 2017a). The details of monthly servicing data are shown in Table 4.1 along with meteorological data (BoM, 2017) and the water quality data are presented in Table 4.2. The number of CBI servicing/cleanings carried out in Subiaco and Hillarys were 12 and 10 times respectively in the study year 2014. Table 4.1 shows that the inlet catchment area per CBI in Subiaco is approximately twice that of Hillarys. This is because Hillarys is situated in the vicinity of the ocean and hence the total rainfall of Hillarys was found to be more than that of Subiaco (Table 4.1). However, the water quality data of Hillarys was better than that of Subiaco (Table 4.2) due to lower catchment area per CBI. The similar findings were also noted in Alam et al. (2017a) for captured gross pollutant load in CBI. Water quality parameters in samples of the influent and effluent of CBIs showed that use of these devices resulted in significant water quality improvements particularly for BOD, COD and TSS (Eq. 4.2; Table 4.2). Overall the influent

concentrations of all parameters were higher in Subiaco than Hillarys. This may be because Subiaco has greater number of trees on both sides of the street and gross pollutants (mainly vegetation) accumulating in the CBI on a monthly basis. Hence there is a possibility of releasing pollutants from leaves to the aqueous phase (Alam et al., 2017a; Ball and Ara, 2010; Allison et al., 1998b) within the CBI. BOD values were also higher in Subiaco than Hillarys (Table 4.2). Stormwater runoff contains organic matter in the form of decaying plant detritus, manure and/or even food scraps which accumulate within the CBIs. During the microbial breakdown of organic matter, the dissolved oxygen concentrations in the water may decrease: BOD provides a good indication of the amount of organic material in stormwater that will lead to the consumption of dissolved oxygen. In this study, the BOD levels in the influent water samples were much higher than the ANZECC freshwater limit (>15 mg/L) but this decreased substantially as the water passed through the CBIs, with a removal efficiency of 87-90%. This may have been due to biological filtration, involving microorganisms within the CBIs material and/or in the sediments accumulated at the base of the CBIs degrading the BOD, and effectively cleaning the water. Suspended solids add to BOD load and therefore the removal of TSS would also result in lower BOD values. Further evidence to support the suggestion that microbial activity within the CBIs contributed to BOD removal is provided by the decrease in the ratios of BOD/COD as water passed through the CBIs. COD is the total equivalent of oxidant required to chemically oxidise organic substances in water and is an indicator of organic pollution that is measured by BOD as well as other oxidisable organic material that is not readily biodegraded (e.g. from industry sources). The ratio of BOD/COD therefore indicates the biodegradability of organic matter with higher ratios indicating increasing biodegradability of the organic matter. The BOD/COD ratio reduced from 0.47 to 0.29 at Subiaco and 0.46 to 0.19 at Hillarys (Table 4.2), showing that organic matter biodegradation within CBIs occurred at both of these sites. Qualitatively the organic matter at both sites was fairly similar as shown by the comparable BOD/COD ratios. As mentioned above the overall lower values of both BOD and COD in the Hillarys samples were probably due to the lower vegetation density at this location (Fig. 4.1). Our results are in agreement with other studies (e.g. Lau et al., 2001) that showed that CBIs generally improve water quality by reducing pollutant loads to the receiving waters. However, there have been few studies that demonstrated the

reduction specifically in BOD due to biodegradation processes occurring within the CBI.

Table 4.1 Monthly servicing and meteorological data during sampling times

Site	^a Sampling dates during servicing	^b Total rainfall (mm)	^c Total no. of rainfall events	^d Servicing Interval (days)	^e Highest daily rainfall (mm)	^f Maximum Runoff area/CBI (m ²)	^g Maximum Runoff volume/CBI (mm)
Subiaco	04/06/14	85.20	17	24	31.0	945	3.61
	31/07/14	146.5	20	30	39.0		3.58
Hillarys	04/06/14	179.8	16	38	50.4	500	2.63
	31/07/14	135.3	13	29	36.0		2.34

^a The date at which the servicing was carried out and the samples were collected

^b Sum of rainfall between the interval of two consecutive servicing dates

^c Number of rainfall events between the two consecutive servicing dates

^d Number of days between two consecutive monthly servicing

^e Highest daily rainfall

^f Maximum Runoff area/CBI

^g Maximum Runoff volume/CBI

Table 4.2 Water quality parameters in CBI sites (mg/L)

Parameters (ANZECC limit)	Site	Influent (mg/L)	Effluent (mg/L)	Removal efficiency (%)
BOD (<15 mg/L)	Subiaco	164(±98)	23(±15)	90
	Hillarys	58(±20)	7(±2)	87
COD (<40 mg/L)	Subiaco	352(±211)	110(±51)	78
	Hillarys	125(±44)	37(±25)	88
BOD/COD (n/a)	Subiaco	0.47(±0.46)	0.21(±0.29)	-
	Hillarys	0.46(±0.45)	0.19(±0.08)	-
TSS (<40 mg/L)	Subiaco	165(±28)	68(±28)	71
	Hillarys	155(±18)	63(±19)	80
PO ₄ -P (<0.1 mg/L)	Subiaco	0.04(±0.2)	0.02(±0.01)	11
	Hillarys	0.17(±0.16)	0.07(±0.05)	26

TSS is an important parameter in stormwater runoff that mainly depends on the distributions of land use types and watershed size. Stormwater runoff particulates are generated from construction activities, agriculture, unpaved surfaces, and waste management, with less evident sources including highways, parking lots, and air emissions. The TSS concentrations in this study were similar to a previous study on sites at comparable locations (Alam et al., 2017a). Similar to the observations for BOD, in this study, TSS also appeared to be significantly removed from the influent water as it passed through the CBIs geotextile material (Table 4.3). TSS in the influent water was higher than the ANZECC value for point discharge criteria (<40 mg/L) but this was removed by the CBIs to concentrations lower than the guideline value, with removal efficiencies of 71-80%. Currently there is no guideline value for stormwater (nonpoint source) discharge hence the reference to point source discharge criteria for freshwater was considered. Significant removal of TSS by the CBI was as expected since it has previously been shown that the UST geotextile material can remove particles down to diameters of 150 μm (Alam et al., 2017a).

Phosphate is an important nutrient used by living organisms for growth but excessive concentrations in waterways lead to increased algal productivity and eutrophication which causes a myriad of water quality and environmental problems. In this study, the $\text{PO}_4\text{-P}$ concentrations were slightly lower at the Subiaco site than at the Hillarys site, again possibly due to the higher abundance of vegetation at Subiaco. The removal of $\text{PO}_4\text{-P}$ by the CBIs was much lower than for organic carbon and TSS, although some phosphate removal was observed. The percentage of reduction of $\text{PO}_4\text{-P}$ was 11 to 26% for Subiaco and Hillarys, respectively (Table 4.2), which is encouraging considering that the CBIs was not designed for the purpose of nutrient removal. It should be noted that $\text{PO}_4\text{-P}$ in the water may increase if the leaves remain submerged for longer periods (Alam et al., 2017a; Ball and Ara, 2010; Allison et al., 1998b). An ANOVA analysis (5% significance level) confirmed that there was no significant difference ($p>0.05$) between influent and effluent concentrations of different water quality parameters (Table 4.2) among CBIs in two different sampling times. However, a significant variation ($p<0.05$) was observed between the influent and effluent concentrations of water quality parameters for the same sampling time among different CBIs (5% significance level).

4.3.2 CBIs pollutant removal efficiencies

Removal efficiency is typically expressed as the percentage reduction in the concentration or load for the pollutant of concern based on flow-weighted samples collected before and after treatment. Removal efficiency depends on the structural design, characteristics of the filter materials and the effective maintenance of CBIs. The CBIs used in this study showed good removal efficiencies compared to other CBIs in previous studies for the relevant pollutants (TSS, TP, BOD and COD; Table 4.3). Reported causes of low efficiency are generally related to clogging of the filter or material bypassing the filter (Morgan et al., 2005; Geosyntec and UCLA, 2005). Fine screens/meshes or filter materials in some of the devices can be overwhelmed or blinded by debris and clogged by sediment. Blinding can be defined as a mechanism when coarse particles retained by a filter material/geotextile intercept finer particles effectively forming an impervious layer over the coarse particles. Clogging results when the coarse particles migrate at the upstream face of the filter/geotextile and become entrained at the entrance of the pores (Rollin and Lambard, 1988). This phenomenon of formation of multilayer natural filters disrupts the normal behaviour of filtration of a CBI. The volume of the insert can also fill with GP so that there is little space for stormwater to accumulate and to create sufficient pressure to maintain flow through the filter surface/screen. During this study, the captured material caused both blinding due to large items, such as vegetation, plastic bags and newspaper, and clogging due to sediment. The sediment coated the screens at the bottom of the insert appearing as a moist mud layer in wet inserts. After the insert dried out, the mud layer formed a largely impermeable barrier (Geosyntec and UCLA, 2005).

CBIs generally require significant maintenance. Inadequate maintenance procedures of CBI and catchment area/basin results in poor performance of the stormwater collection system. For example, Morgan et al. (2005) identified the following maintenance issues for two CBIs, the AquaShield and the AbTech. Geosyntec and UCLA (2005) used four different CBIs for budgetary and technical feasibility testing and their lab tests showed that most of the inserts could remove particles $>250 \mu\text{m}$. The DrainPac and FloGuard CBIs remove TSS by screening. These two CBIs have larger capacities and finer screens and hence are able to retain bulk solids effectively. Efficient capture of bulk solids consequently helped continued to facilitate pollutant

capture until the accumulated GP caused bypass. The HydroKleen removes TSS by sedimentation in the first compartment and then filtration in the second compartment. These studies demonstrated the efficiency increases with efficient maintenance. They also suggested a need for developing strong communication networks between the respective stakeholders. The UST CBI units can be readily cleaned manually by two people expelling the geotextile basket from the steel frame, with servicing of four CBIs units in one hour (Alam et al., 2017a). A special type of geotextile was used as a part of UST CBIs which is reusable. This geotextile become noticeably cleaner and more permeable by evacuating the captured residue and vegetation with a low pressure, high flow of water without changing its original insert shape.

Construction activities in new business and residential developments tend to produce significant amounts of silt and sediment runoff, which can rapidly fill and clog swale pits. Capturing these pollutants using CBIs units at-source will decrease the sedimentation developed in these pits and thereby the on-going maintenance costs for downstream pipelines. The capacity to fit CBIs units to existing stormwater drainage systems means that effective treatment of stormwater can be focused on drainage channels serving pollutant generating catchments, for example, schools, strip malls and CBDs, at fundamentally lessened cost. There is some concern about stormwater treatment at source i.e., the establishment of CBIs may cause blockages which can lead to localized flooding. However, the UST CBI unit has a by-pass which allows water to flow through the pit even when the CBI is full (Alam et al., 2017a).

Table 4.3 Pollutant removal efficiencies of different catch basin inserts (CBIs)

Sl. No	Device name and description	Test conditions	Removal efficiency (%)				Site /origin	Ref.
			TSS	TP	BOD ₅	COD		
1	UST CBI: This has a bypass flow section for high flow to avoid flooding, a diffuser to dissipate energy within the CBI, geotextile which can capture particles down to 150 µm. Multiple reuse capabilities without losing original shape.	Field test:	71	11	90	78	Subiaco Hillarys	This study
		Rain events	80	26	87	88		
2	Vortechs®: This contains two chambers- one is a grit chamber promoting a gentle spinning motion helping sediments to deposit in the center. The other chamber consists of a baffle wall that separates oil and grease.	Field test:	50	28	44	n.a.	Hauppa-uge & Bayshore, Long Island, NY, USA	Kostarelos and Khan, (2007)
3		Rain events	-21	7	3	n.a.		
4	Siltsack®: Permeable geotextile to remove silt and sediment. Requires inspection after every major rain event or every 2-3 weeks.		24 to 70	-90 to 14	4 to 59	n.a.	Polytechnic University, USA	
5	Stream Guard™: Equipped with encapsulating polymer. May overflow within 20 minutes in high flow ≥ 300 L/min	Lab. exp.	70 to 86	-20 to 19	34 to 61	n.a.		
6	FloGard®+PLUS: Metal frame with plastic netting and four walled adsorbent pillow liners. Liner maintenance is complicated.	i) grain size: 0.037-2 mm	-34 to 81	1.5 to 50	-56 to 56	n.a.		
7	Hydro-Kleen™: Dual chambered CBI, first chamber collects sediment; second chamber contains two adsorbent pillows and one activated carbon filter media pillow. Clogging issues and issues with ponding of water.	ii) flow rate: 50, 150 and 300 L/min	5 to 85	6 to 31	-62 to 69	n.a.		
8	AbTech Ultra: CBI has a hard box structure, hence requires space for storage.		-5 to 96	6 to 84	-6 to 68	n.a.		
9	Stream Guard™Passive Skimmer: Pillow containing adsorbent polymer attached to two floating booms. Can be hooked/connected to the catch basin through the connector hardware and line.		29 to 90	-3 to 76	27 to 54	n.a.		
10	AbTech Ultra: Same as 8	Lab exp.	45	n.a.	n.a.	n.a.		

11	AquaShield™ : Constructed from stainless steel and high-density polyethylene. Stainless steel flange used for hanging the insert from catch basin frame. An upper compartment provides for settling of sediments; lower compartment contains an adsorbent pillow for oil and grease adsorption.	i) grain size: <0.6 mm	10	n.a.	n.a.	n.a.		Edwards, F. (2003)
12	DrainPac™ : Metal frame to which a plastic mesh is suspended and a bag filter into the mesh for straining and adsorption.	i) flow rate:	22	n.a.	n.a.	n.a.	University of Arkansas, USA	
13	HydroCartridge™ : Fiberglass unit hung from side entry pit frame on flanges moulded into the insert. Water flows through catch basin grate forced to the bottom of the insert, then back up in annular space on two sides where it discharged from the insert over horizontal weirs on each side of the insert. CBI uses sedimentation, flotation, and absorption. An absorbent sock suspended in the gullet of the insert absorbs oil and grease.	0.013-0.014 m ³ /sec	40	n.a.	n.a.	n.a.		
14	Up flow filter : The insert sediment removal mechanism involves physical sedimentation and filtration using filter media.	Field test: Rain events	34	18	n.a.	27		Tuscaloosa City Hall, Alabama, USA
15	FloGard®+PLUS : Same as 6	Lab exp.	15	n.a.	n.a.	n.a.	Uni. of California, Los Angeles, USA	Geosyntec and UCLA, (2005)
16	DrainPac™ : Same as 12	i) grain size: 0.045-0.43 mm	66	n.a.	n.a.	n.a.		
17	Curb Inlet : A multi-stage, removable filtration basket that was designed to capture a range of materials including hydrocarbons, sediment, grass clippings, and miscellaneous GPs. Constructed from fiberglass with stainless steel filter screens, backed by heavy-duty aluminum grating.	ii) flow rate:	40	n.a.	n.a.	n.a.		
18	Hydro-Kleen™ : Same as 7	5-50 gpm	87	n.a.	n.a.	n.a.		

4.3.3 Particle size characterization

Sediments play important roles in the functions of aquatic ecosystems. Fine sediment is the portion of organic and inorganic material with a particle size of less than 2 mm, consisting of sand, silt and clay particles. Coarse sediment particles are greater than 2 mm and include gravel and cobble. Fine sediments, in particular, can lead to various adverse impacts on the receiving water bodies. Particle size analyses in this study classified sediments into six textural categories: clay (<4 μm), silt (4-62 μm), fine sand (62-250 μm), medium sand (250-500 μm), coarse sand (500-2000 μm) and gravel (>2000 μm) and shown in Table 4.4. Sample site S1 in Olive Street, Subiaco had the highest silt (36.97%) and clay (6.86%) content among all sites. The sites in Hillarys contained more sandy soil with respect to silt or clay. Hillarys is adjacent to the coast and open dune and beach and there is therefore significant influence from Aeolian transport of sand. The samples were collected in June after the strong rain event in May 2014 (Fig. 4.2 and Table 4.1). During rain events, surface runoff is the main driver that leads to accumulation of gross pollutants (e.g. leaves or sediments) into side entry pits. The CBI is a potential device to capture these sediments to avoid blockages in the stormwater drainage systems.

Table 4.4 Soil textural class of captured solids

Catchment	Site	% Clay (<4 μm)	% Silt (4-62 μm)	% Fine sand (62-250 μm)	% Medium sand (250- 500 μm)	% Coarse sand (500- 2000 μm)	% Gravel (>2000 μm)
Subiaco	S1	6.86	37.0	11.5	5.21	7.30	32.2
	S2	1.96	12.1	8.55	21.7	28.6	27.1
Hillarys	H1	1.85	7.57	12.2	14.9	30.9	32.6
	H2	1.63	10.9	14.1	13.8	30.1	29.5
	H3	2.62	17.7	14.5	15.2	17.3	32.7
	H4	1.57	11.1	9.71	5.88	21.7	50.0

Land use type, location and climatic variability are the main factors for the variation of particle size distribution of on-site sediments captured in CBI. The overall particle size distribution was illustrated by the degree of variability in each CBI. The Shapiro-Wilk test (Helsel and Hirsch, 2002) for normality showed that most of the individual particles size distribution across a number of samples did not show normal and log-normal distribution for skewness (Selbig et al., 2016). Therefore, assuming emphasis on degree of variability and due to the lack of normality in the data, the median distribution was chosen as the most appropriate representation for particle size distribution. This is because median is the better demonstration of population centre in highly skewed datasets than the mean (Selbig et al., 2016). Hence, the particle size distribution for each CBI and their median values were shown in Fig. 4.3. Furthermore, the different indices characterizing the grain sizes were estimated and presented in Table 4.5. The effective particle size (D_{10}) was measured from Fig 4.3 which is defined as the size at which 10 percent of the material is finer. The effective particle diameter of a hypothetical sphere is assumed to exhibit the behaviour of quiescent sedimentation similar to the actual particles of irregular shape accumulated in the CBI. The median diameter (D_{50}) of the particle sizes is at which 50 percent is finer. The uniformity coefficient (C_U) is defined by:

$$C_U = \frac{D_{60}}{D_{10}} \quad (4.3)$$

The value of C_U provides an indication of the distribution of particle sizes. A value of $C_U=1$ uniform size and a large value of C_U indicates well graded materials that the D_{10} and D_{60} particles differ significantly. The parameter known as the coefficient of concavity (C_c) can also be determined using particle size distribution curve (Fig. 4.3). The coefficient of concavity measures the shape of the particle size distribution curve between the grain sizes of D_{60} and D_{10} which may be defined as:

$$C_c = \frac{D_{30}^2}{D_{10}D_{60}} \quad (4.4)$$

Varying C_c greatly from 1 indicates more missing particles between D_{60} and D_{10} .

The mean diameter (D_m) and the size variability (standard deviation, σ) of the particle sizes were determined mathematically using the following equations:

$$D_m = \frac{\sum_{i=1}^n k_i D_i}{\sum_{i=1}^n k_i} \quad (4.5)$$

$$\sigma = \left[\frac{\sum_{i=1}^n k_i (D_i - D_m)^2}{\sum_{i=1}^n k_i} \right]^{1/2} \quad (4.6)$$

Where D_i is the mean size of the i^{th} class, k_i is the sample percentages of i^{th} class and n is the number of classes.

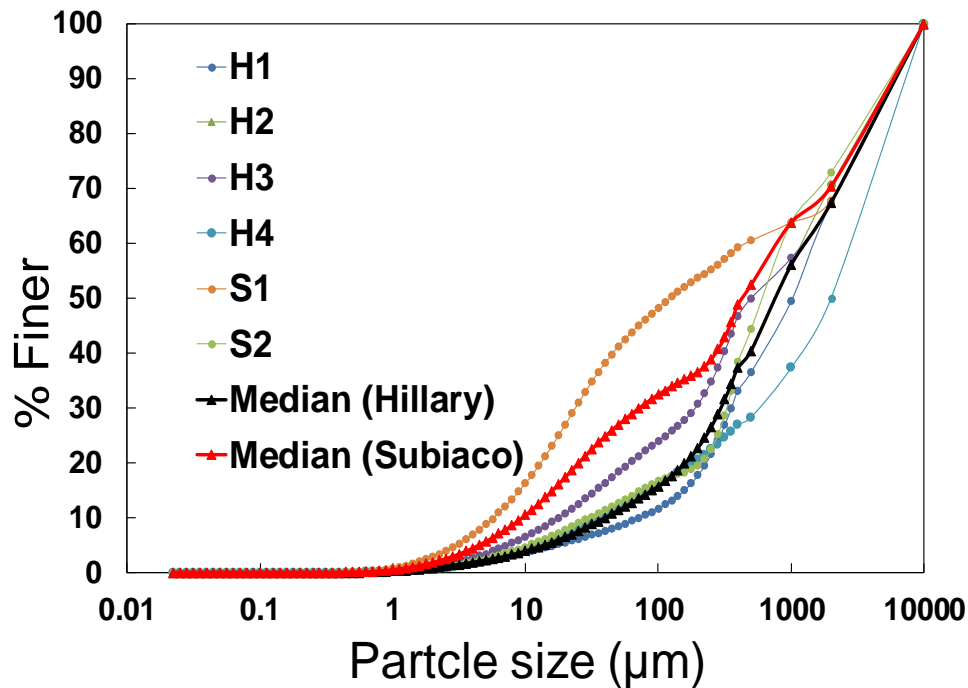


Fig. 4.3 Cumulative particle size distribution of captured solids

Analysis of soil textural class showed variations in this parameter between CBIs at the Subiaco site, whereas the same soil texture was found in each of the CBIs at Hillarys (Table 4.4; as confirmed by ANOVA, 5% confidence level). As shown in Table 4.5, the solid particles captured at the Hillarys site were primarily gravel type sand with uniform grade in accordance to unified soil classification system ($C_u > 4$ & $1 < C_c < 3$; Holtz, R. and Kovacs, 1981). One exception is site H4 in which particle sizes did not conform with those from the other sites probably due to influence from trees which are in close proximity to the site. Sites at Subiaco did not demonstrate a uniform grade probably because of the landscape and site characteristics. Subiaco is a residential area and the particles are probably mainly sourced from vegetation. Rain rather than wind

is likely to be the main driving factor to accumulate sand particles into the CBIs, in contrast to Hillarys which is much more open, located adjacent to a sandy beach and subject to more consistent and stronger winds. Alam et al. (2017a) showed that the size distribution of pollutant varied from one CBI to another CBI for an area consisting of vegetation. They also found a correlation between wind speed and pollutant load ($r^2=0.10$) for their study area (Alam et al., 2017a). Hence, the wind and rainfall can both influence the transport mechanism for accumulation of different sizes of sand particles into the CBIs depending on their site characteristics.

Table 4.5 The particle size distribution indices for GP captured at two different sites

Catchment	Site	D_{10} (μm)	D_{30} (μm)	D_{50} (μm)	D_{60} (μm)	D_m (μm)	C_U	C_c	σ (μm)
Subiaco	S1	6	25	130	450	785.1	75.0	0.231	892.3
	S2	30	320	600	900	998.4	30.0	3.792	752.9
Hillarys	H1	70	370	1000	1500	1115	21.4	1.304	752.4
	H2	40	300	760	1200	1043	30.0	1.875	764.3
	H3	18	200	500	1200	955.7	66.7	1.851	830.6
	H4	40	600	2000	2800	1312	70.0	3.214	792.4

A CBI is not an idealized settling basin due to the turbulence that occurs within the catch basin during high flow. Hence the smaller particles may not be captured in CBIs. The particle sizes captured in different CBIs are presented in Table 4.6. The results from the field test of Edwards (2003) showed that 68% of the particles captured were larger than 600 μm . Allison et al. (1997) also reported a particle size distribution (not shown in the Table) of litter for side entry pit traps in which 90% (by mass) of the material would be retained by a 20 mm size mesh screen. This was because the captured material was mostly litter and the screening size of the side entry pit trap was 5 mm. Alam et al. (2017a) also showed that more than 70% GPs captured in CBIs was vegetation (>4750 microns) due to the site characteristics. Therefore, the size distribution of onsite GP captured in CBI greatly varies with the land use type and site characteristics (Alam et al., 2017a). However, the particle sizes of solids captured in this study was found to be within the range of the previous studies (Table 4.6).

Table 4.6 Size distribution of samples captured in different CBIs

Device Name	Sieve sizes (µm) / Percentage retained					Site characteristics	Location	Method of analysis	Ref.
	4750	2360	1190	600	<600				
UST	7	13.8	16	29.8	33.4	i) Residential	Subiaco, WA	Wet sieving and laser diffraction	This study
	7	12	14.7	30.5	35.8	ii) Commercial -marine-recreational	Hillarys, WA		
UST	73.4	8.7	5.3	3.7	8.9	Commercial	Gosnells, WA	Dry sieving	Alam et al., (2017a)
AquaShield™	17.6	22.7	14.5	14	31.5	i) Commercial ii) Vehicle maintenance yard	i) WAC parking lots, USA	Dry sieving	Edwards, F. (2003)
AbTech™	38.9	20.2	16.5	12	11.9		ii) Uni. of Arkansas, USA		
DrainPac™	8.5	9.3	12.9	16	53.5				

4.3.4 Specific surface area

Metal cations can interact with surfaces of solid particles, such that the pollutants are retained on the surfaces thereby improving the overall water quality. The specific surface area (SSA) of solids captured in each CBI was analyzed in the laboratory using the Langmuir method where the surface area is related to the volume of gas adsorbed as a monolayer. The theoretical specific surface area, a_m (m²/g) also can be calculated from the soil textural classes given in Table 4.7:

$$a_m = \frac{6}{\rho_s} \sum \frac{M_i}{d_i} \quad (4.7)$$

Where ρ_s is the solid density (g/cm³), M_i is the mass fraction of particles of average diameter d_i . The solid density was determined in the laboratory using a multipycnometer and the results of the specific surface area are shown in Table 4.4. In general, the density in the Hillarys samples was higher than that for the Subiaco sites which in turn provided lower SSA. In general, SSA decreases with increasing grain sizes. If the quartz content is high in the mineralogical composition of a coarse soil, it can lower the SSA values (Gunawardana et al., 2014) since it is a three-dimensional framework silicate mineral which has low surface area (Sparks, 2003). In order to further investigate the solid surfaces, SEM analyses were performed for each of the captured soil samples. A typical SEM image of solid samples from Subiaco and

Hillarys sites is shown in Fig 4.4. The SEM images indicate that the soils in Hillarys have greater numbers of larger particles with angular or rounded surfaces with less porous materials whilst the soils in Subiaco show more fine particles of irregular shapes with more porous materials. SSA analyses did not show consistent trends and are not readily interpreted, probably because even though the sediments at Hillarys are primarily sand and those from Subiaco are thought to be mainly from traffic, the composition of these mixtures is still very complex. Gunawardana et al. (2014) reported that the SSA depends on the mineralogical composition and morphology of fine particles rather than soil organic content. For example, clay forming minerals (e.g., albite, microcline, chlorite and muscovite) reduce the size of the particle and hence increase the SSA. Although traffic related soils may comprise finer particles, potentially increasing the SSA, the morphology of grain sizes in this soil is very complex (Milani et al., 2004). The tyre wear activities may provide metal deposition on the road surface, but it does not indicate how it increases the SSA. Road deposits and their effect on SSA are not clearly understood at this stage and further research is needed.

Table 4.7 Specific surface area of captured solids

Catchment	Sample site	Solid density ρ_s (g/cm ³)	Specific surface area (m ² /g)	
			Langmuir	Eq 4.7
Subiaco	S1	1.3	0.670 ± 0.047	1.359
	S2	1.8	0.325 ± 0.009	0.334
Hillarys	H1	2.5	-	0.204
	H2	2.3	1.172 ± 0.003	0.235
	H3	1.5	0.179 ± 0.010	0.541
	H4	1.4	0.312 ± 0.023	0.364

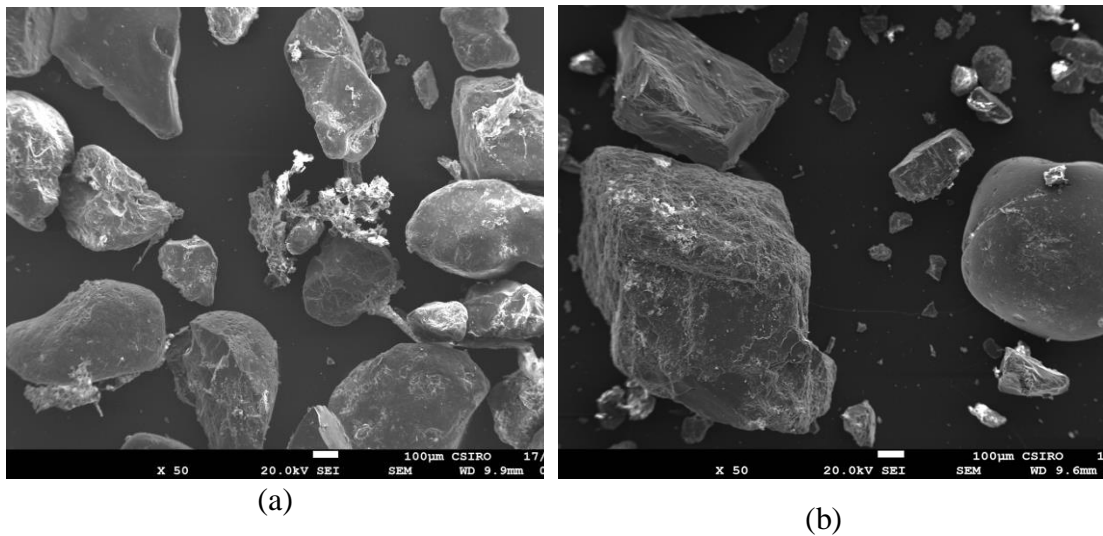


Fig. 4.4 Typical scanning electron microscope (SEM) images of the captured sediments in (a) Subiaco and (b) Hillarys area

4.3.5 Heavy metals

Trace metals are of concern in environmental waters due to their potential toxicity. Analysis of the chemical composition of solid samples collected from CBIs is another approach for source identification of the solids accumulated within the devices. The content of heavy metals in the sediment within CBIs can indicate the extent of particles generated due to traffic flows or related activities. Heavy metal analyses were carried out for two samples in Subiaco and two samples in Hillarys. Only two CBIs were considered because the CBIs are located close to each other and it was assumed that the solids in both areas accumulated in the CBI would have similar chemical characteristics. ANOVA analysis also confirmed that there was no significant difference ($p > 0.05$) in metal concentrations in the different CBIs for the two study sites. It indicated that the heavy metal concentrations did not vary from one CBI to another in the same area. However, a significant difference was found ($p < 0.05$) for the different metal concentrations in solid sample in each CBI.

The grain size of sediment is a significant factor because it determines the mobility of the particles and their associated pollutant concentrations. The results of this study and a comparison with other studies for the heavy metals and grain size (GS) found in road dust and curb side dust are presented in Table 4.8. Heavy metals elemental analysis

indicates the presence of traffic related metals associated with these particles. Traffic maps and counting data (Main Roads, Western Australia 2017) shows significantly high number of vehicles travelled in Southside Drive at Hillarys (17353) than the Olive Street, Subiaco (11453) in 2013-2014. This is because of the site in Hillarys situated in a commercial area consisting of a boat harbor, boardwalk, tavern, retail outlets, swimming area including water slides and the Aquarium of Western Australia which attracts many visitors every day. Solid samples contained some heavy metals (Fe and Cu) at significantly higher concentrations in Hillarys than Subiaco (Table 4.8) possibly because the heavy metals are mainly generated from anthropogenic activities such as traffic and vehicle wear and emissions. Car parking in Hillarys is highly affected by vehicular emission such as engine oil and exhaust gases. High volumes of traffic in Southside drive in Hillarys also provides more tyre wear sediments containing heavy metals. Similar elemental composition (Zn: 3000 mg/L; Cu: <634 mg/L; Fe: 27,700 mg/L) of tyre wear sediments are also found in previous studies (Kreider et al., 2010). Therefore, high amounts of particles in build-up of solids are generated from traffic related activities (Gunawardana et al., 2014).

Amongst both catchments, Fe was shown to be the dominating metal while Cd was present in the lowest abundance. The Fe content in Hillarys was found to be greater than at the Subiaco site (Table 4.8). This is because of greater intensity of traffic with low speed in Hillarys (mainly parking area) which causes more use of brakes in this area than that in Subiaco. Potential origins of Fe are vehicle component rust, brake lining materials, Fe products in brake-pads and vehicle exhaust (Gunawardana et al., 2012; Amato et al., 2011; Adachi Tainosho, 2004; Manno et al., 2006) or soil sources (Pierson and Brachaczek, 1983). However, iron in soil is particularly abundant and it is therefore difficult to pinpoint the source of this metal in our samples (Obaidy and Mashhadi, 2012). After Fe, Zn was the most abundant metal element found in all of the particle sizes regardless of the study site. The Zn content varied from 120-180 mg/kg which is greater than the reported average value (100 mg/kg) of unpolluted soil (Kabata-Pendias and Pendias, 2001). The Zn concentration in soils is mainly associated with anthropogenic activities such as fertilizer and pesticide in agriculture, vehicular traffic, building waste and industry input. The sources of Zn in CBIs sediment coming from street dust are also primarily from tyre wear as found in previous literature (Adachi and Tainosho, 2004). Among the six metals studied, Cd

was the least detected in all of the sites followed by Ni and Pb. Surprisingly, the Pb and Cd concentrations were found to be lower in this study than in other countries (Table 4.8). Similar results were also found in a study in Gold Coast, Australia (Gunawardana et al., 2012). Cd is usually required for plating in brake pads to prevent corrosion and Ni can originate from tyre and brake pad wear (McKenzie et al., 2009). The Cu concentration in the soils of commercial areas (213.5 mg/kg) was much higher than the residential areas (15.5 mg/kg) indicating the Cu contribution in Hillarys may also be sourced from combustion of lubricating oils and atmospheric deposition. Furthermore, the main difference between the sites is that Hillarys is very close to the ocean while Subiaco is a suburb, about 10km inland. The ratios of Fe to Cu and Zn do not indicate that aerosols blown onto the land from the sea could have contributed to any of the increased concentrations of any of these metals. However, corrosion rates are much greater in close proximity to the ocean, so the higher contribution of Fe may be due to increased corrosion of infrastructure at Hillarys, mobilizing Fe into the runoff, as well as via particulates. Cu and Zn may also enter the system as corrosion products since there are many brass fittings on buildings in the vicinity. Sources of these metals are likely to be a combination of street dust (tyre wear and wear metals from traffic) and dust from corrosion of infrastructure and buildings in the vicinity, as well as dust blown from inland locations.

Table 4.8 A comparison of heavy metal contents in street dust found in studies in Australia and other cities worldwide (unit of heavy metal contents: mg/kg, and unit of grain size GS: μm)

Location	Characteristics of sites	Concentrations						GS	Method of collection and metal detection	Ref.
		Cu	Fe	Ni	Pb	Zn	Cd			
Subiaco, Western Australia	Residential with high vegetation	14(\pm 3)	1950(\pm 150)	2(\pm 1)	22(\pm 2)	135(\pm 15)	<0.4	<10000	Side entry pit, ICP-MS (Agilent ICPMS 7700)	This study
Hillarys, Western Australia	Commercial-cum-recreational areas	213(\pm 157)	4800(\pm 700)	3(\pm 1)	27(\pm 11)	175(\pm 5)	<0.4			
Clearview, Gold Coast, Australia	Residential area	131(\pm 26)	7220(\pm 4000)	8(\pm 5)	33(\pm 12)	297(\pm 78)	0.5(\pm 0.1)	<425	Road dust, ICP-MS	Gunawardana et al., (2012)
Nerang, Gold Coast, Australia	Industrial area	65(\pm 20)	4230(\pm 1200)	6(\pm 2)	26(\pm 11)	176(\pm 100)	0.2(\pm 0.1)			
Benowa, Gold Coast, Australia	Residential, Industrial, commercial area	98(\pm 24)	5730(\pm 1900)	7(\pm 2)	29(\pm 5)	237(\pm 42)	0.35(\pm 0.1)			
Surfers Paradise, Gold Coast, Australia	commercial area	79(\pm 20)	2980(\pm 100)	5(\pm 1)	38(\pm 10)	90(\pm 23)	0.5(\pm 0.1)	<2000	Road side dust, ICP-AES (Perkin-Elmer Optima 3300DV)	Li. et al., (2001)
Special administrative region, Hongkong	Urban parks and recreational areas	173(\pm 190)	n.a.	n.a.	181(\pm 93)	1450(\pm 869)	3.8(\pm 2.3)			
Asturias, Spain	Port area, 20000 vehicles/day of 20% heavy vehicles	104-374	1.67-3.24 ^a	18-50	330-964	2422-23400	9.6-104	<147	Street dust, ICP-AES	Ordonez et al., (2001)
Bursa city, Turkey	Low and high-density traffic road	n.a.	n.a.	n.a.	210	57	3.1	<200	Street dust, FAAS (Perkin-Elmer Model 3110)	Arslan (2001)

Amman, Jordan	Low to high density traffic area	47-477	294-6994	22-50	219-373	n.a.	2.5-3.4	>0.045	Sediments associate with street runoff, FAAS	Jiries et al., (2001)
Linda Teruya, City and County of Honolulu, Hawaii	Mixed traffic areas, <3200-45200 vehicles/day	167(±46)	6.59 (±0.79) ^a	177(±34)	106(±38)	434(±94)	n.a.	<125	Sediment from curbside areas near side entry pit, ICP-AES	Sutherland and Tolosa, (2000)
Central London, UK	Quiet to busy commercial area	191-204	2.28-2.42 ^a	n.a.	2008-4053	1171-1176	5.2-7.9			
Manhattan, New York, USA	Quiet commercial/residential area	171-540	3.22-3.37 ^a	n.a.	2213-2952	984-2638	4.6-11.4			
Halifax, Nova Scotia, Canada	Quiet to busy commercial/residential area	54-119	3.21-5.86 ^a	n.a.	674-1919	315-620	0.6-1.4	<963	Footpath or gutter dust, FAAS	Fergusson and Ryan, (1984)
Christchurch, NZ	Busy commercial and light industrial area	48-258	2.36-5.82 ^a		887-1294	365-850	0.8-1.1			
Kingston, Jamaica	Busy, main thoroughfare junction	59-72	533-996	n.a.	817-909	533-996	0.8			
Lancaster, London, UK	Urban road and car park areas	71-312	n. a.	n.a.	660-2540	260-539	2.68-4.91	<600	Street sweeping along the edge of road, AAS (Perkin-Elmer 280)	Harrison et al., (1981)

FAAS: flame atomic adsorption spectrometry; ICP-AES: inductively coupled plasma optical emission spectrometry, ICPMS: inductively coupled plasma mass spectrometry; ^a concentration as (%)

Testing for heavy metals in the water samples collected from the inlets and outlets of CBIs showed that concentrations of these metals were very low in water both inside and outside CBIs: concentrations were less than the limit of ANZECC trigger values (ANZECC, 2000) for the protection of aquaculture species (Table 4.9). Heavy metals (i.e., Fe, Al, Pb etc.) adsorb strongly to TSS and particulates within CBIs (Herngren et al., 2005). In our study Fe and Zn concentrations were shown to decrease in water that had passed through the CBIs. This is in agreement with Lau et al. (2001) who showed that CBIs can remove up to 96% of heavy metals with the adsorption of suspended solids captured in CBIs. This indicates that if the gross pollutants are captured at source (e.g., CBIs in this case), the stormwater quality may be significantly improved before it discharges to the drainage systems. However, the data in this study is limited to only a few CBIs at two sites and more data is needed for planning an informed stormwater management system. The total accumulation of gross pollutants and their characteristics may be monitored for longer term for CBIs installed in different locations to check the effectiveness of CBIs used in this study.

Table 4.9 Mean of heavy metals presence in water samples

Catchment	Concentration (mg/L)											
	Cu		Fe		Ni		Pb		Zn		Cd	
	in	out	in	out	in	out	in	out	in	out	in	out
Subiaco	<0.01	<0.01	0.75	0.78	<0.02	<0.02	<0.03	<0.03	0.08	<0.02	<0.01	<0.01
Hillarys	0.002	0.002	77	10	0.002	0.001	<0.001	<0.001	0.007	0.003	<0.0001	<0.0001
ANZECC Trigger value	<5		10		100		<1		<5		<0.2	

4.4 Conclusion

In this study, analyses of water and solid samples collected from CBIs located in two suburban areas in Western Australia showed that the use of CBIs could lead to improvements in stormwater quality. The two areas were selected to show the effects on CBIs from two different types of land use patterns: Subiaco, a residential area was compared with Hillarys, a recreational-marine-commercial area. CBIs led to improved water quality by decreasing BOD, BOD/COD ratio (the biodegradability of the organic matter), TSS and heavy metal content. A small amount of phosphate removal was also

observed but this may have been affected by concomitant release of phosphate by decomposition of vegetation. The CBI mainly captured gross pollutants including sediments, reducing sediment pollution in stormwater but it may also reduce the dissolved pollutants to some extent when the accumulated soil/wood materials act as adsorbents. The release nutrients into the water during biodegradation of the captured organic waste gross pollutants may cause problems in stormwater drainage systems if the CBIs is not serviced on a regular basis. Though the BOD/COD was lower in the effluent water because of the biological activity occurring within the CBIs but it may affect the effluent water by decreasing the DO of the effluent water. The particle size distribution showed more fine particles in the residential area than the commercial/coastal area, but heavy metal concentrations were generally higher in the commercial area. The higher numbers of service station and high vehicle movements in commercial areas may produce elevated levels of heavy metals through normal vehicle wear and repair work and also due to vehicle emissions. However, this study is limited to a few CBIs in two different areas only and further research is substantiated the effectiveness of CBIs.

List of notations

<u>Notation</u>	<u>unit</u>	
Q :	flow rate	m^3/sec
C :	runoff coefficient	dimensionless
I :	rainfall intensity	mm/hr
A :	the catchment area	m^2
A :	mean of pollutant concentration	mg/L
a_{inf} :	average influent concentration	mg/L
a_{eff} :	average effluent concentration	mg/L
D_m :	mean diameter	μm
$D_{10}, D_{30}, D_{50}, D_{60}$:	the grain diameter at 10%, 30%, 50% and 60% passing respectively	μm
a_m :	theoretical specific surface area	m^2/g
ρ_s :	the solid density	g/cm^3
C_U :	coefficient of uniformity	dimensionless
C_c :	coefficient of curvature	dimensionless

List of abbreviations

ANOVA	:	analysis of variance
ANZECC	:	Australian And New Zealand Environment and Conservation Council
APHA	:	American Public Health Association
ASPT	:	at source pit traps
ASTM	:	American Society for Testing and Materials
BMP	:	best management practice
BOD	:	biochemical oxygen demand
CBD	:	central business district
CBI	:	catch basin insert
CIWMB	:	California Integrated Waste Management Board
COD	:	chemical oxygen demand
CSIRO	:	Commonwealth Scientific and Industrial Research Organization
DO	:	dissolved oxygen
GP	:	gross pollutant
GPT	:	gross pollutant trap
GS	:	grain size
HM	:	heavy metals
ISO	:	International Organization for Standardization
PSD	:	particle size distributions
SEM	:	scanning electron microscope
SEPT	:	side entry pit trap
SSA	:	specific surface area
TN	:	total nitrogen
TPH	:	total petroleum hydrocarbon
TP	:	total phosphorous
TSS	:	total suspended solids
UCLA	:	university of California, Los Angeles
UST	:	Urban Stormwater Technologies Pty Ltd
WA	:	Western Australia

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CHAPTER 5

STORMWATER SOLIDS REMOVAL CHARACTERISTICS OF A CATCH BASIN INSERT USING GEOTEXTILE

Abstract

Suspended solids in urban runoff have multiple adverse environmental impacts and create a wide range of water quality problems in receiving water bodies. Geotextile filtration systems inserted within catch basins have the potential to mitigate these effects, through flow attenuation and pollutant removal. This study modelled a catch basin in a column and assessed the hydraulic and solids removal characteristics of a new type of non-woven geotextile (NWG1) in the capture of solids from stormwater runoff. The new geotextile was compared with two others readily available on the market (NWG2, NWG3). Synthetic stormwater containing TSS (200 mg/L) was used with two particle size distributions of 0-180 μ m (P1; D_{50} :106 μ m) and 0-300 μ m (P2; D_{50} :150 μ m). The results revealed that the desired stormwater TSS concentration (<30 mg/L; ANZECC, 2000) could be achieved with a short ripening process (e.g., 1-2 kg/m² of suspended solids loading) for trials using the larger particle size distribution (P2). In addition, 36% more suspended solids were captured in trials using the soil with the larger range of particle sizes (P2) than for the soil with smaller particle sizes (P1). Geotextile fibre pattern appeared to have a significant influence on the TSS removal capacity. The NWG1 has higher permittivity than NWG3 but similar to NWG2. NWG1 could capture overall more TSS (which also resulted in earlier clogging) than NWG2 and NWG3 because of the special fibre structure of NWG1. The experimental data shows that these geotextiles may start to clog when the hydraulic conductivity reaches below 1.36×10^{-5} m/s. The overall hydraulic performances of geotextiles showed that the NWG1 has better potential for use in CBIs because of its higher strength and multiple reuse capability.

Keywords: Stormwater; Suspended solids; Geotextiles; Catch basin insert; Water quality

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5.1 Introduction

Urban runoff caused by increasing areas of impervious surfaces such as roads, parking lots, and building rooftops is a major contributor to pollution of water bodies and is a major concern globally (Franks et al., 2015, Hsieh and Davis, 2005). Stormwater solids such as total suspended solids (TSS) originated from pervious or impervious surfaces are transported to receiving waters which may have a wide range of detrimental effects in aquatic systems (Alam et al., 2017a; Zhao and Li, 2013). Various best management practices (BMPs) have been introduced for sediment control which include gross pollutant traps, constructed wetlands, retention ponds, detention basins, grass swales, vegetated filter strips, biofilters, sand filters and catch basin inserts (CBIs) (Alam et al., 2017a; Ghani et al., 2011, Hatt et al., 2009). Most of these technologies can effectively reduce the concentration of stormwater particulates (e.g., total suspended solid-TSS) but require significant land area and incur costs to maintain filter media after clogging.

Among all of the above technologies, CBI is a promising tool for solids removal from stormwater runoff at source. CBIs are typically mounted within catch basins (e.g. side entry pits) that do not require any extra land. A few studies have focused on TSS removal using CBIs in side entry pits prior to entry into the drainage system (ICBIC, 1995; Lau et al., 2001; CIWMB, 2005; GeoSyntec and UCLA, 2005; Kostarelos and Khan, 2007). The ICBIC (1995) tested five different CBIs under field conditions and found TSS removal efficiency up to 73% for particle sizes less than 600 μm . Edwards et al. (2004) evaluated four different inserts (i.e., AbTech Industries, Aqua Shield, Inc., Geotechnical Marine Corporation and PacTec, Inc) in the laboratory using a pilot scale catch basin and synthetic stormwater containing sand particles up to 600 μm . The removal efficiency for a TSS concentration of 225 mg/L with influent flow rate 0.013-0.014 m^3/sec was found to be 11-42%. The CBIs used in their study consisted of an adsorbent media for oil and grease removal but no information related to particle removal characteristics was reported. Lau et al. (2001) briefly described the results of two prototype CBIs consisting of two adsorbents (OARS polymer and polypropylene) under laboratory and field conditions for the removal of oil and grease, litter and suspended solids. The first one consisted of an OARS sorbent placed in a metal boxes with open tops and screened bottoms and the second insert used polypropylene cloth

as an adsorbent medium supported by a geotextile for stabilizing solids. The TSS removal efficiency was found to be 78% and 99% for the smallest and largest particles respectively in lab testing and 21% for field testing for the OARS adsorbent and 95-98% for polypropylene cloth. However, the clarity of smallest and largest particle sizes was not mentioned for a particle sizes of 120-400 μm used for laboratory test. Their results indicated that 100% TSS can be removed in field tests for particle sizes larger than 800 μm and that particles down to 100 μm can be removed in lab tests. Morgan et al. (2005) reported a TSS removal efficiency of 11-42% for a series of controlled tests using CBI with a flow rate 18.9 L/min and a TSS concentration of 225 mg/L but they did not study the effect of the particle size distribution. Kostarelos and Khan (2007) studied the removal of TSS in six CBIs in field and lab condition. They used three flow rates (50, 150 and 300 L/min), three contaminant concentrations (low, medium and high) and particle sizes 0.037 to 2 mm for lab conditions and found the removal efficiency up to 96%. The removal efficiency was found to be up to 50% in field conditions for more than one-year duration and covering four seasons. Particle sizes were not mentioned. Although different types of CBIs are now available, there is a dearth of information on TSS removal characteristics for capturing solids from stormwater.

Geotextile, a permeable geo-synthetic, is a potential candidate to filter and separate debris and impurities from water which has been widely applied in geotechnical and environmental fields (Leverenz et al., 2000, Nagahara et al., 2004, Bouazza et al., 2006, Muthukumaran and Ila mparuthi, 2006, Vaitkus et al., 2007, Lamy et al., 2013). Geotextile fabric commonly comprises woven or nonwoven polypropylene or polyester. Woven fabric is designed for separation and reinforcement applications (Bouazza et al., 2006). Nonwoven (needle punched) geotextile is designed for filtration (Leverenz et al. 2000, Lamy et al., 2013), separation (Vaitkus et al., 2007), liner protection (Nagahara et al., 2004) and drainage applications (Muthukumaran and Ilamparuthi, 2006). Franks et al. (2012) reported on criteria for retention of sand particles on geotextiles for two particle size distributions (0-106 μm , D_{50} : 25 μm (G1) and 0-180 μm , D_{50} :106 μm (G2) in stormwater runoff, observing that a geotextile filter with an apparent opening size (AOS) of 150 μm is effective in reducing the TSS concentration.

A new type of CBI has recently been introduced by Urban Stormwater Technologies Pty Ltd (UST) to remove stormwater pollutants at source in the drainage systems of few city councils in Western Australia (Rothleitner, 2011). Recently, Alam et al. (2017a) carried out a field survey to characterize the gross pollutants (GP) captured in the geotextile of UST CBI. The GPs may be defined as vegetation (plant-based debris), litter (paper, plastic, cans and others) and sediments of different sizes. The geotextile used in UST CBI was capable of capturing GPs down to 0.15 mm. The UST CBI uses a special type of non-woven geotextile. To date, no data on this UST geotextile has been reported in the literature for the removal of stormwater solids (TSS) in CBI applications. The objective of this research was to investigate the solids removal characteristics of this new UST geotextile for using it in CBI. Filtration experiments were also carried out for two other types of commercially available geotextiles and the hydraulic performances of solid removals are discussed.

5.2 Materials and methods

5.2.1 Geotextiles selection

Three types of geotextiles (NWG1, NWG2, NWG3) were selected for this study. Among these, the NWG1 is a new type of non-woven geotextile developed by UST while the other two (NWG2 and NWG2) are readily available on the market. The NWG1 is a special type of geotextile which has unique fiber arrangement compared to NWG2 and NWG3. The speciality in the structure of NWG1 is that it is made of multiple pieces of fabric used in composite to make it stronger and more durable, allowing it to keep its original shape for heavy loading and multiple reuses. The soil particles in stormwater are only captured on the external layer of geotextile. Thus, the captured particles can easily be removed or cleaned by reverse flushing with high water flow (400-450 kPa) and reused more than 10 times, keeping its original shape intact (Alam et al., 2017a). Due to its reusable properties, the disposal load of this non-biodegradable polypropylene (NWG1) material will be reduced and after the end of its use as a CBI insert, the polymer can be reused as a raw material for other products. The selection criteria of other two geotextiles were based on their apparent opening sizes (AOS), thickness and G-rating. The apparent opening size is the primary variable that dictates the removal of TSS from stormwater. The G-rating and thickness are used as criteria to describe the capacity of geotextile to hold its original shape for fitting

into the CBI after several reuses. The G-rating is the geometric mean of Drop Cone and California bearing ratio (CBR) Burst test results (Alexander, 2001). The Drop Cone is a test used to measure resistance of geotextiles to puncture from a defined load falling from a known height. The CBR test is carried out by forcing a CBR plunger through a sample of fabric that is fixed over a frame. The apparent opening size (AOS) is defined as the size at which 95% of the pore sizes are of that size or smaller. The NWG2 was chosen because of its similar thickness and permittivity to NWG1. The NWG3 was chosen based on its G-rating, thickness and the fiber arrangement similar to NWG2. The physical and hydraulic properties of each geotextile are given in Table 5.1.

Table 5.1 Physical and hydraulic properties of geotextiles used in this study

Hydraulic properties						Mechanical properties		
Name	Structure and materials	Flow rate, Q (L/min/m ²) Mean	Permittivity ψ (s ⁻¹)	Hydraulic conductivity, K (m/sec)*10 ⁻⁴	Apparent opening size (AOS)-O ₉₅ (mm)	Unit wt. (g/m ²)	Thick-ness, T (mm)	G-Rating
NWG1	NP, STF, PP	3080	0.68	23.85	0.10	525	3.5	n.a.
NWG2	NP, STF, PP	4800	0.8	24.8	0.075	450	3	6000
NWG3	NP, STF, PP	2100	0.35	14.7	0.06	1200	4	11700

NWG: nonwoven geotextiles, NP: needle-punched, STF: staple fibre, CF: continuous filament, PP: polypropylene, all properties are AS 3706 & Austroads standards and manufacturer's minimum average roll value (MARV) for each geotextile, Tensile strengths are machine direction values, permittivity is equal to hydraulic conductivity normalized by thickness. n.a.: Not available

5.2.2 Soil samples and stormwater preparation

Washed chemical free sandy and silty soils were collected from Cook Industrial Minerals (CIM, Perth Western Australia) and used to prepare suspended solids. The suspended solid samples were prepared by sieve analysis method AS 1289.3.6.1 (Standard Australia, 2009) with ISO 3310: BS 410-1:2000 sieve sizes 20, 63, 75, 106, 150, 180 and 300 μm . Hydrometer tests were conducted according to AS 1289.3.6.3 (Standard Australia, 2009) to determine the PSD of fine grained soil passing through the BS standard sieve size 75 μm . The D_{50} of urban runoff varies from 8 μm to 570 μm for different land use types (Charter et al., 2015) but a weak trend of very fine particles (<8 μm) concentration was found relatively constant in the road runoff (Brodie and Peter, 2009). Selbig et al. (2015) mentioned that no single distribution of

particles can be applied uniformly to runoff in urban environments. Therefore, the synthetic stormwater was prepared with two soil types, P1 and P2: soil type P1 was prepared by combining graded soil samples to obtain a PSD of 0-180 μm with a D_{50} of 106 μm , while P2 contained particle sizes measuring 0-300 μm with a D_{50} of 150 μm (Fig. 5.1). The PSD of P1, P2 and the D_{50} was similar to the particle size distributions in previous studies (Gironas et al. 2008; Siriwardene et al. 2007; Wong et al. 2006). The range of P2 was also similar to previous field surveys conducted in various studies (Brodie and Peter, 2009; Charter et al., 2015; Selbig et al., 2015). The D_{50} for P1 was similar to that of particles typically found under a sand filter passing through an underground detention basin (Li et al., 2008). The uniformity coefficient (C_U) and coefficient of curvature (C_c) of P1 and P2 were calculated as 27, 0.25 and 4.25, 2 respectively. The synthetic stormwater of TSS concentration (200 mg/L) was prepared by mixing the soil samples, P1 and P2 (6 g each) with tap water (30 L) at ambient temperature. The TSS concentration of this study was similar to the average event mean concentration (EMC) for TSS found in urban stormwater runoff (Hallberg and Renman, 2008; Kim and Sansalone, 2008; Li and Davis, 2008; Flint and Davis, 2007; Taebi and Droste, 2004; Sansalone et al., 2005).

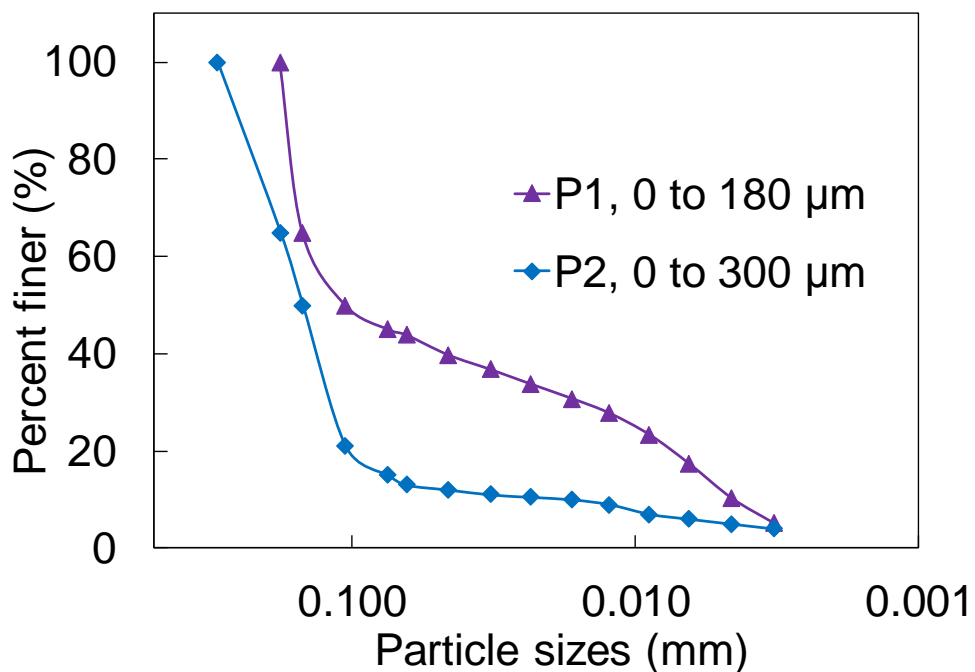


Fig. 5.1 Particle size distributions of suspended solids used in this study.

5.2.3 Experimental set up

A plexiglass laboratory column of 130 mm diameter and 350 mm length was constructed to model the CBI for capturing solids from storm drainage systems (Fig. 5.2). Other materials used for the column experiments included a pump, a stirrer, a 30-litre plastic tub to hold the synthetic stormwater, tubing to carry synthetic runoff into the column, 500-mL plastic sampling containers, the geotextile filters and a diffuser for energy dissipation while pumping stormwater into the column. The energy dissipater was placed 30 cm above the geotextile filter which replicates the field application of Alam et al. (2017a). However, the height of the diffuser should be carefully determined depending on the pollutant distribution of the area.

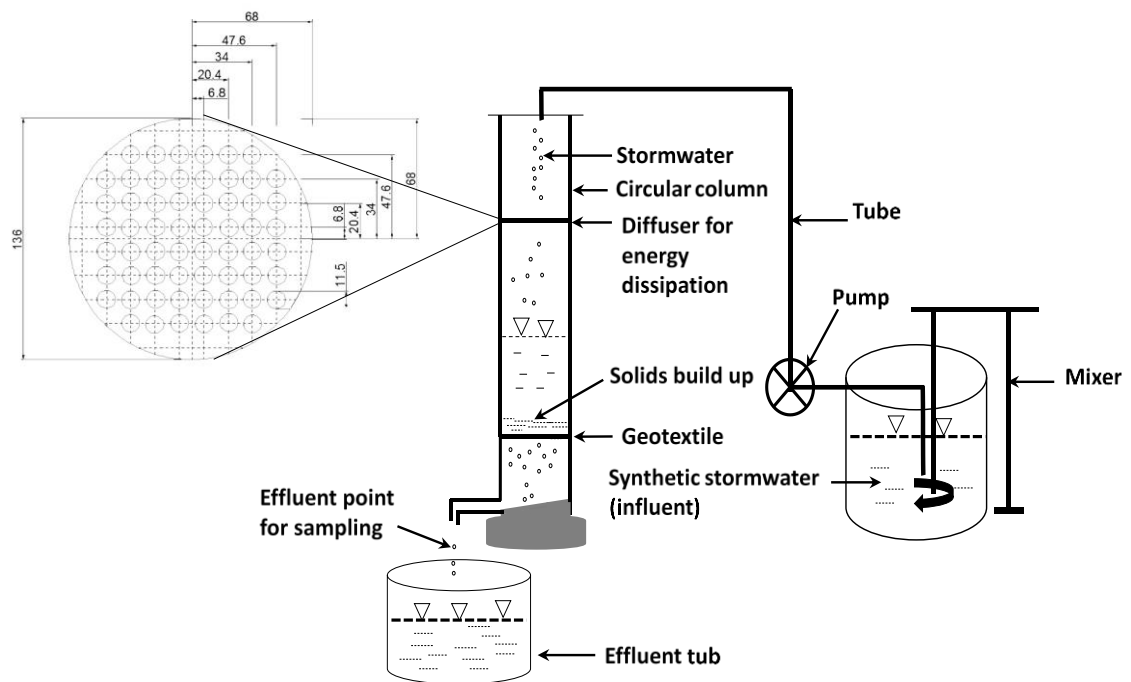


Fig. 5.2 Schematic diagram of experimental set up (all dimensions in mm).

5.2.4 Experimental method

The synthetic stormwater was pumped into the column similar to the flow of a road runoff. The column arrangement was such that it could simulate the stormwater flow into the CBI. A mechanical stirrer agitated the stormwater solution at 100 RPM to maintain particles as a suspension. Uniformity of the TSS concentration in the inlet

tank was ensured by monitoring of subsamples taken periodically at different tank depths during each experiment. The stormwater flow rate into the column was 6 mL/sec and the hydraulic loading rate (HLR) was 0.45 mm/sec (64 in/hr). This flow rate was calculated using rational formula and assuming a runoff to stormwater drainage (storm sewerage) area ratio of 50 and rainfall intensity of 3.4 cm/hr (Franks et al., 2012). Two 250 ml of influent and effluent samples were collected every 10 minutes and the TSS concentrations were measured following the Standard Method 2540B and SSC B (Nordqvist et al., 2014, Eaton et al., 1995). The effluent flow rate was measured to check the outflow reduction due to sediment accumulation. The head loss due to sediment deposition was measured by the water level rise in the column. The hydraulic conductivity was calculated assuming the total head loss occurred across the full depth of soil fabric system. A total of 4-6 data points of head losses were obtained in each test; the average value of the points that were within a relative standard deviation of 25% or less were used to determine the hydraulic conductivity. Hydraulic conductivities were calculated for each geotextile using the same method. Each test duration was 80 minutes. Ten influent and effluent samples were collected during each event and TSS concentrations for all samples were used to determine the event mean concentration (EMC) using the following equation (Rees et al., 2006):

$$EMC = \frac{\sum_{i=1}^N C_i Q_i \Delta t_i}{\sum_{i=1}^N Q_i \Delta t_i} \quad (5.1)$$

where, C_i is the TSS concentration of each sample within an event i , Q_i is runoff flow rate of the sample calculated by measuring the volume of water exiting the column in a given amount of time; and Δt_i is the time interval between the samples (Taebi and Droste, 2004).

The filter system was air dried for 1-2 days in between consecutive runs. A total of 15-92 experimental runs were carried out for one set of filter fabrics depending on particle size distributions until clogging occurred. The filter system was assumed to be clogged whenever the water level in the column reached the top of the column within 20 minutes of testing or until the filter was clogged, similar to the methodology of Franks et al. (2012) who assumed a linear increase in head loss in a typical underground sand column system. An increase of water level in a typical vertical clearance (1 m) of an

underground sand column system within the average duration of a rainfall event (1 hr) is equivalent to reaching the water level in the column at the top (30 cm) in 20 minutes of testing. Duplicates of each test were carried out and if the standard error was more than 5%, the test was repeated.

Stereomicroscopic images were obtained for both virgin and used geotextiles (NWG1, NWG2 and NWG3) by cutting 3 to 5 specimens to obtain three cross sections and one to two planar sections. The geotextile specimens (25 × 25 mm) were air dried at room temperature (20°C) for 24 hrs and placed on a square flat surface to ensure that a cleaned and smooth surface was obtained for image analysis under a low magnification light stereomicroscope (Aydilek et al., 2002); Nikon SMZ800 stereomicroscope with a Schott KL1500 LCD light source, a Toupcam UCMOS14000KPA camera and ToupView 3.7 software; microscope lens Plan 1X, zoom range 1x to 6.3x.

5.3 Results and discussions

5.3.1 TSS removal

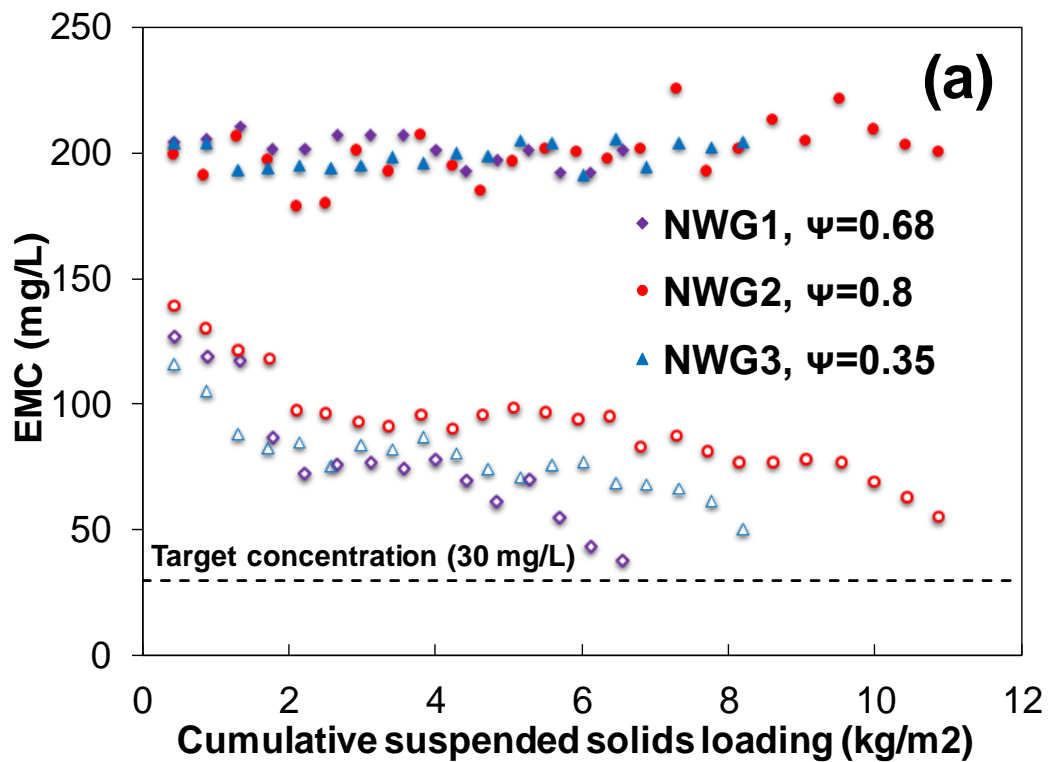
Tests for TSS removal were performed to check the optimum capacity of the geotextile fabrics to capture suspended solids while allowing water to pass through freely. The influent and effluent TSS concentrations were measured at 10 minute intervals: effluent concentrations were found to decrease with increasing influent solids loading. EMCs of influent and effluent were calculated as a function of cumulative mass loaded to each geotextile for both particle sizes (Fig. 5.3). EMC values were calculated for each test (80 minutes) until clogging occurred. For P1, for all three geotextiles, the targeted effluent concentration of 30 mg/L (ANZECC, 2000 Table 4.4.2) could not be attained prior to clogging occurring (Fig. 5.3a), although it was attained for P2 (Fig. 5.3b).

TSS accumulation on geotextiles is said to follow the filter ripening process, as the effluent concentration decreases gradually, while the removal efficiency of the filter increases (Clark et al., 1992). The ripening process may be explained as the particles built up in and on the filter to enhance the filter retention capacity (Mao et al., 2006). Ripening has a drastic effect on the removal efficiency of a filter because of the subsequent effect of the captured particles on solids accumulation. The effect of

ripening process increased the removal efficiency of solid particles of all geotextile filters and as a result the concentration of effluent decreases (Fig. 5.3). The ripening process for NWG1, NWG2 and NWG3 occurred at a total suspended solid loading of 1.35, 1.72 and 0.88 kg/m² respectively for both particle size distributions. The ripening process of NWG3 occurred earlier because of its smaller apparent opening sizes.

Due to the difference in fibre structure, more of the smaller particulate material was removed and consequently, effluent TSS concentrations in NWG1 decreased rapidly in the latter stage of the test, with clogging of the filter occurring faster than for the other two (total loading 6.56 kg/m²). Effluent TSS in NWG2 was higher due to its larger AOS and permittivity, as also noted by Kutay and Aydilek (2004). Their study revealed that the percentage of solids passing through the geotextiles increases with increasing AOS and permittivity (the hydraulic conductivity normalized by the thickness). A similar range of ripening period (1-2 kg/m²) was observed by Franks et al. (2012) but the corresponding drop in TSS differed slightly from this study because of differences in PSD. Though the range of soil particles of P1 (0-180 µm; $D_{50} = 106$ µm) was similar to the soil G2 (0-180 µm; $D_{50} = 106$ µm) of Franks et al. (2012) but the soil uniformity coefficient ($C_U=27$) of this study was found to be two times greater than their soil ($C_U=12$). Unit value of C_U indicates uniform soil while larger value indicates well graded materials. This shows the importance of soil gradation in applications such as geotextile filtration, i.e. the importance of different grain distribution parameters, in addition to D_{50} (Coduto, 2011). Additionally, the properties of geotextile (AOS, permittivity, thickness and hydraulic conductivity) used in this study differed from this previous research (Franks et al., 2012). TSS removal also depends on the AOS of geotextile and the median grain sizes (D_{50}). The D_{50} of P1 (106 µm) indicates that 50% of the particles in this sample were larger than the AOS of geotextiles (Table 5.1). However, the geotextiles captured more than 50% of stormwater TSS, with the extent of capture increasing due to the ripening process (Fig. 5.3a). The clogging points were obtained when the effluent concentrations of NWG1, NWG2 and NWG3 had decreased to 82%, 73% and 75% of their initial concentrations respectively. Even though the AOS of NWG1 was the highest, it clogged first because of its special type of fibre structure.

The total solids at the clogging point for P2 was found to be higher than for P1 because of the greater range of particle sizes. Clogging occurred at the lowest total solids loading for NWG1 (6.56 kg/m²), followed by NWG3 (8.21 kg/m²) and NWG2 (10.86 kg/m²) respectively for P1. A similar trend was also observed for P2: NWG1 (25.03 kg/m²) < NWG3 (33.77 kg/m²) < NWG2 (39.79 kg/m²). Higher permittivity is expected to result in a greater mass of solids loaded to the filter before its final clogging point (Kutay and Aydilek, 2004) which was observed for NWG2 and NWG3 but not for NWG1. Although the permittivity of geotextiles varied between 0.35-0.8 (s⁻¹) (Table 5.1), the fibre structure of NWG2 and NWG3 was completely different than NWG1. The special type of internal fibre structure of NWG1, led to faster clogging than for the other two geotextiles.



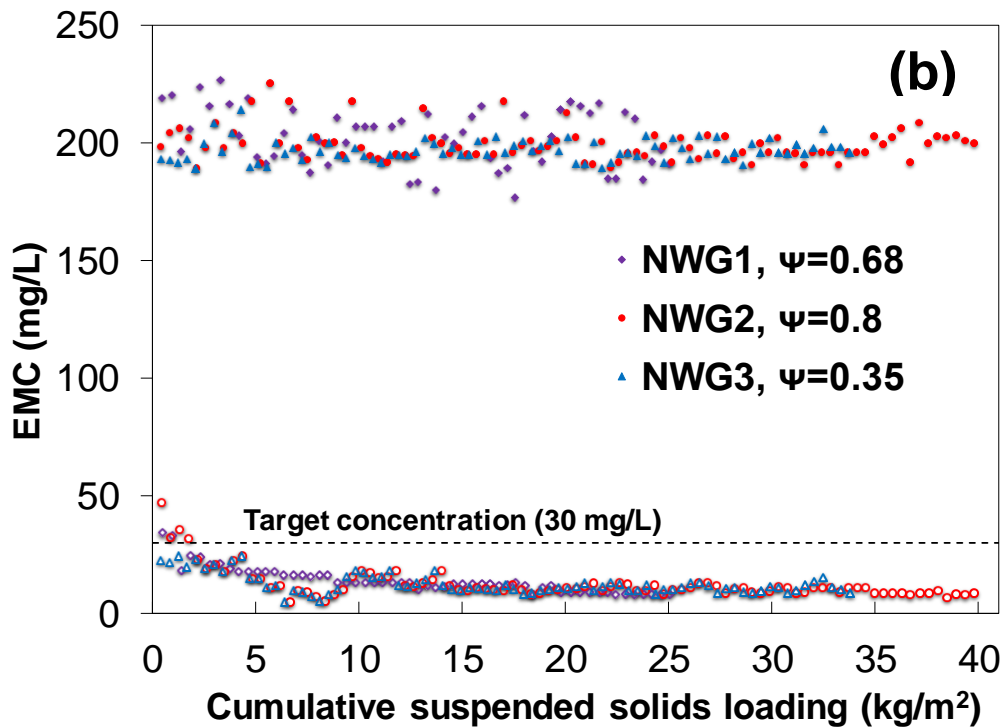


Fig. 5.3 Effect of cumulative mass loaded to each filter for TSS concentration of 200 mg/L for particle size distribution (a) P1 (0-180 μm) and (b) P2 (0-300 μm). Filled symbols indicate influent concentration and open symbols indicate effluent concentration. Initial permittivity values are given in legend for each geotextile.

5.3.2 Effect of geotextile fibre pattern on filtration

Even though the influent concentration was constant for all tests, the effluent TSS concentration showed significant variation for the different geotextile filter materials. NWG2 had the greatest TSS effluent concentration (EMC) for P1 followed by NWG3 and NWG1 respectively (Fig. 5.3a). This shows that NWG1 has the capacity to capture the greatest amount of TSS from stormwater runoff prior to clogging. This observation can be partly explained by analysis of the arrangement of fibres within the different geotextiles materials. The NWG1 material was designed to provide specific water filtration qualities using a patent pending process (Rothleitner, 2011). Stereomicroscopic imaging of planar and cross-sectional views of the geotextiles clearly indicates the differences in fibre arrangement between the geotextiles (Fig. 5.4). The NWG2 and NWG3 images show similar patterns which differ from NWG1. Although the pore size of NWG1 (150 μm) is larger than for NWG2 and NWG3, the permittivity of NWG1 is similar to that of NWG2 (Table 5.1). As shown in Fig. 5.4

(d), the bulk of TSS particles were captured in the top portion of the filter in NWG1 while in NWG2 and NWG3, the particles were distributed throughout the entire thickness of the material. In NWG1, at least half of the filter thickness was relatively free of the particulates whereas in NWG2 and NWG3 the particulates had permeated through the filter material. The images in Fig. 5.4 suggest that particles are more easily able to pass through NWG2 and NWG3 than NWG1, explaining the observation that NWG1 has greater capacity to capture the smaller particles. For NWG1, breakthrough of small particles is less likely and the clogging of NWG1 occurs when the material has captured the maximum amount of small particles; however, for the other two materials, breakthrough occurs preferentially, allowing the small particles to pass through the filter.

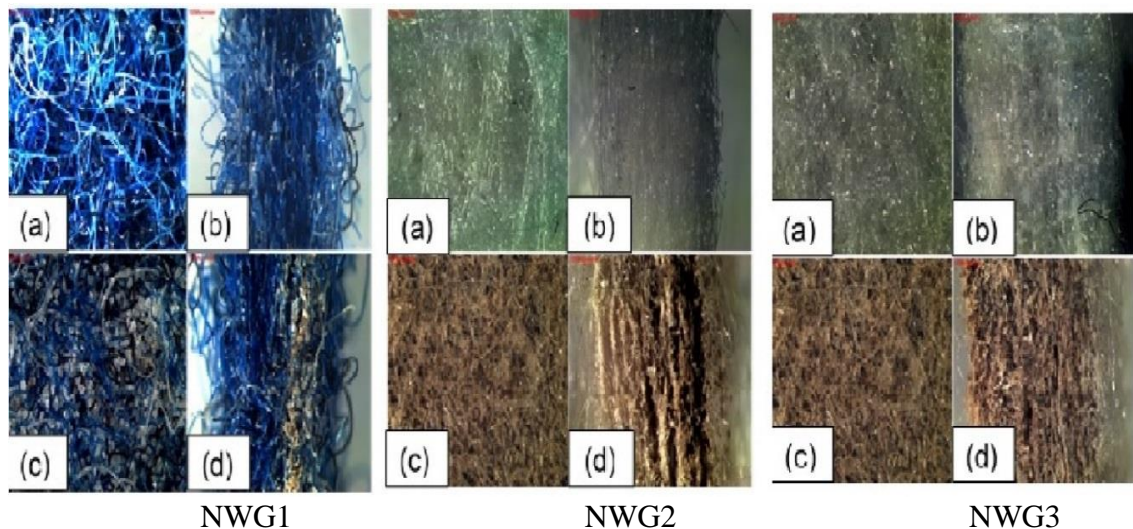


Fig. 5.4 Stereomicroscopic image of NWG1, NWG2, NWG3 respectively (a) planar and (b) cross-sectional images of the virgin geotextile and (c) planar and (d) cross sectional images of the clogged geotextile.

5.3.3 Effect of PSD on filtration

For all three geotextile materials tested, the soil type with the larger PSD range was more effectively captured and generally resulted in more efficient filtration. The total solids loaded and captured for both soil types (P1 and P2) were calculated from the EMC of influent and effluent (Table 5.2). For P1 (0-180 μm), NWG1 and NWG3 showed similar capture capacities of 61%, slightly higher than for NWG2 (54%), which may have been due to differences in hydraulic properties and the apparent

opening sizes (AOS) of the geotextiles. In contrast, the cumulative TSS loaded for the sand sample, P2, was significantly larger than for P1 (around 93% solids captured; Table 5.2). The three geotextiles clogged at an average of 8.54 kg/m² suspended solids loaded, with 4.94 kg/m² suspended solids captured for P1, while geotextiles with P2 were clogged at an approximately 30.74 kg/m² captured with TSS loading 32.86 kg/m². Therefore, on average, 35.11% (average of three geotextiles in Table 5.2 column 5) more suspended solids were captured in the sample with the larger particle size distribution than for the smaller size particles, indicating that smaller particle sizes led to clogging much more readily than samples containing larger particles. For P1 the geotextiles became clogged after 15-23 experiments, while for P2, 59-92 experiments were needed for the materials to clog, which indicates that the number of rain events required to clog the CBI insert materials would be 4 times higher for soil types of P2 (larger PSD and larger range of PSDs) than for P1 soil types. This phenomenon also suggests that the material was able to capture a greater percentage of P2 sediments while achieving a slower clogging rate, compared to the results with P1 sediments has potentially significant benefits for achieving high effectiveness at reduced maintenance demand. This is due to the effect of ripening and captured solids in a filter, which depends on the grain size distribution and morphology of the previously captured particles in the media depth of the filter (Clark et al., 1992). Statistical analysis (two-tailed t-test) confirmed (1% level of significance) that there was no significant difference ($p > 0.01$) of cumulative TSS captured for P1 among the geotextiles. However, a significant variation ($p < 0.01$) was found for NWG1 with respect to NWG2 and NWG3 but no significant difference was found between NWG2 and NWG3 for P2. A significant difference ($p < 0.01$) for cumulative TSS captured was found between P1 and P2 for each type of geotextile at 1% level of significance. Capture and accumulation of smaller, more uniform particles creates denser packing which leads to earlier clogging. During the experiments, suspended solids in the stormwater mixture accumulated to form a cake layer on the surface of the geotextile (Clark et al., 1992). This accumulated cake layer formed another filter zone above the geotextile which effected further retention of particles. As the cake layer increased, smaller particles were entrapped in the voids of the existing layer, reducing the overall porosity and void ratio which ultimately resulted in clogging. The sand sample P2 (0-300 μm) had a higher accumulation of sand particles than P1 (0-180 μm), forming a thicker cake layer, demonstrating how the greater range of particle sizes has generally

higher porosity with the same mass of solids captured as compared to poorly graded particles. As larger particle sizes (e.g., P2) were captured on the geotextile, the retained suspended solids overlapped on the surface of the geotextile forming a graded filter zone. This zone may be more porous allowing more particles to settle before clogging, and thereby allowing effective filter operation for a higher number of rain events. Similar observations on the impact of particle size distribution on solids capture were reported by Franks et al. (2012) (Table 5.2). These authors used two particle size distributions G1 ($C_U = 35$) and G2 ($C_U = 12$) with median grain sizes of 50 and 106 μm respectively and three non-woven geotextiles with AOS of 180 μm (Geo 1), 150 μm (Geo 2) and 150 μm (Geo 3) respectively. In their study, the larger particle size distribution G2 (0-180 μm) was captured, on average, 29% more effectively than the smaller particle size distribution G1 (0-106 μm) for the three geotextiles. However, a greater removal for a similar particle size range (0-180) was shown in their study but lower solids capture was attained before clogging (Table 5.2).

Table 5.2 Summary of total solid loaded and captured

PSD	Geotextile types	Total solids loaded (kg/m^2)	Total solids captured (kg/m^2)	Percentage captured	Ref.
P1 (0-180 μm)	NWG1	6.56	3.98	60.74	This study
	NWG2	10.87	5.86	53.89	
	NWG3	8.21	4.97	60.51	
P2 (0-300 μm)	NWG1	25.03	23.31	93.12	
	NWG2	39.79	37.29	93.72	
	NWG3	33.77	31.62	93.63	
G1 (0-106 μm)	Geo 1	3.75	0.25	6.67	Franks et al., (2012)
	Geo 2	4.33	3.57	82.45	
	Geo 3	3.41	2.57	75.37	
G2 (0-180 μm)	Geo 1	10.80	8.10	75.00	
	Geo 2	6.37	5.57	87.44	
	Geo 3	4.17	3.76	90.17	

The effect of PSD on the solids capturing capacity can be further explained by the use of classic steady state filtration theory (Tufenkji & Elimelech, 2004):

$$\frac{C_e}{C_0} = \exp\left(-\frac{3(1-n)}{2d_c}\alpha\eta T\right) \quad (5.2)$$

where C_0 and C_e are influent and effluent TSS concentrations, n is the filter bed porosity, α is the striking coefficient (determined from column test, Li and Davis, 2008), η is the single collector contact efficiency, d_c the diameter of spherical collector (media particle) and T is the media depth (e.g., geotextile thickness). Equation (5.2) indicates a sharp exponential decrease of particle concentration throughout the media depth, i.e., the increase in media depth will decrease the effluent concentration (AWWA, 1999). However, equation (5.2) is used in the context of a clean bed and therefore does not account for the accumulation of solids deposited in the filter. In addition, in this study, the outlet flow rate was not constant due to solids accumulation and therefore the conditions were not in a steady state. Therefore, the assumption of steady state was made using granular bed filtration theory, as was also done in the study by Franks et al. (2012). In the first set of experiments, the geotextile may be considered as a clean bed and this equation was used for the results obtained from the first test. To make the equation (5.2) simple, the variables α , η and d_c in equation (5.2) are transformed into a single constant, Z :

$$\frac{C_e}{C_0} = \exp\left(-\frac{3}{2}Z(1-n)T\right) \quad (5.3)$$

The Z values obtained from six tests (for geotextile as clean bed) using equation (5.3) are listed in Table 5.3. The results of the Z value increase with decreasing permittivity and increasing unit weight (Table 5.1 and 5.3). Again, if it is assumed that α , the striking coefficient and η , the single collector collision/contact efficiency remain constant for all three geotextiles for one particle size distribution, an increase in Z indicates a decrease in d_c (diameter of the spherical collector). Therefore, it can be explained that the unit weight and diameter of a spherical collector behaves similar to permittivity. These results indicate that decreasing the diameter of the spherical collector also decreases the pore spaces between the particles and as a result, the filter media become less permeable. Similar explanations can be drawn for unit weight of geotextiles. Values in Table 5.3 indicate larger Z values for P2 particle size distribution than for P1. Further if it is assumed that α and d_c remain constant for the same

geotextile then η , the single collector collision efficiency depends on particle size distribution. This phenomenon follows the granular filtration theory that larger particles have an affinity to collide more with a collector via sedimentation and interception mechanism. These results are similar to those of Li and Davis (2008).

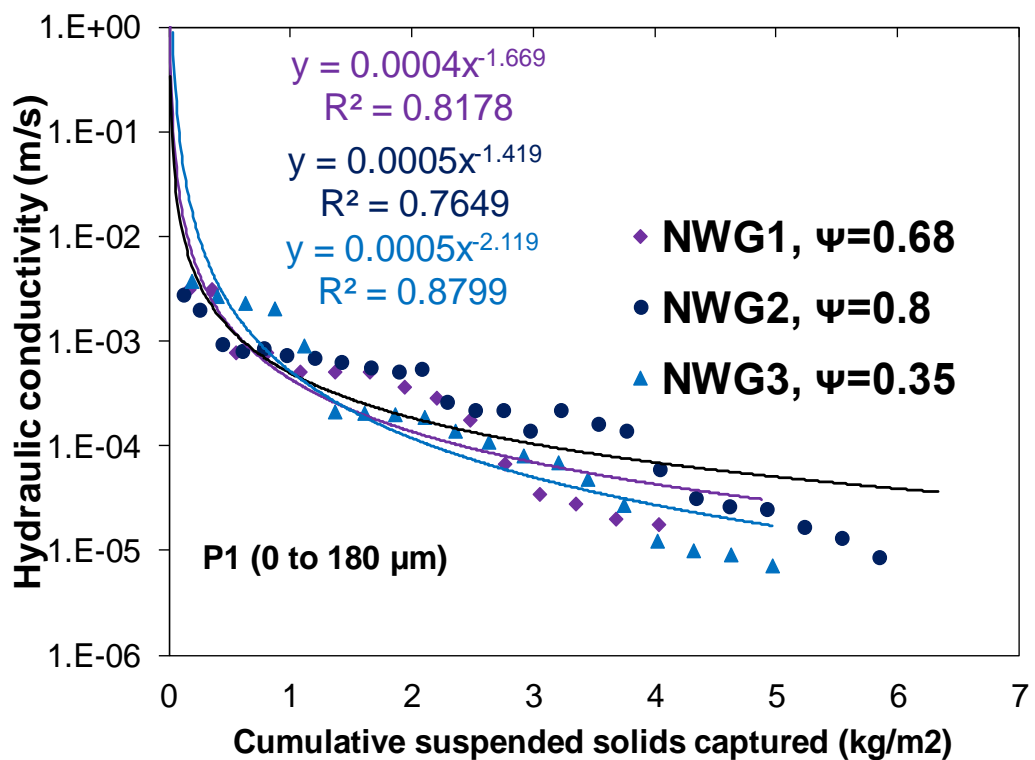
Table 5.3 Trend analysis of Z for the reduction of initial concentration for six tests

PSD	P1			P2		
	NWG1	NWG2	NWG3	NWG1	NWG2	NWG3
C_o	205	199	204	219	198	193
C_e	126	139	116	34	47	22
Z	457	396	472	1765	1596	1793

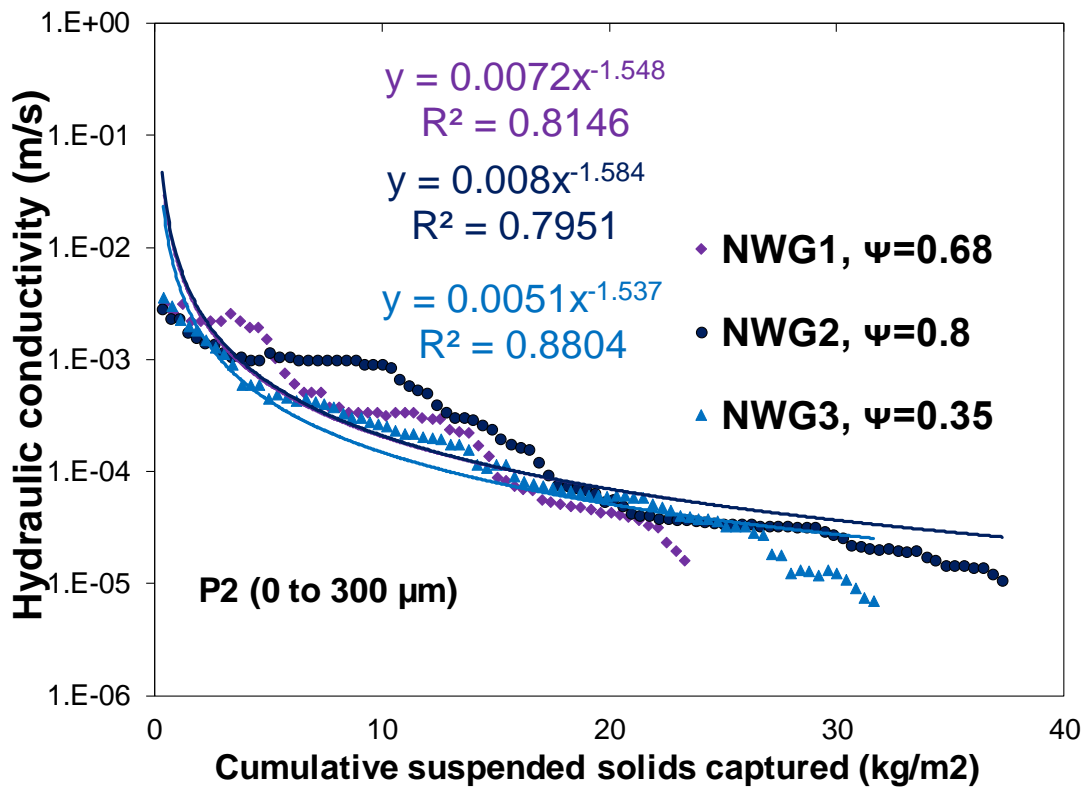
5.3.4 Hydraulic conductivity

Hydraulic conductivity was calculated by taking the average of 4-5 readings of head losses for each 80-minute test (equivalent to one rain event). The standard deviation of hydraulic conductivity was found to be between $0.65-1.02 \times 10^{-3}$ and $6.5-9.05 \times 10^{-4}$ for P1 and P2 respectively from the beginning to clogging of all geotextiles. Hydraulic conductivities for each test event (15-92 test events) as a function of cumulative suspended solids captured for P1 and P2 are shown in Fig. 5.5 (a-b). These tests showed that more cumulative mass was captured with P2 (0-300 μm) than P1 (0-180 μm) for the same hydraulic conductivity. For instance, NWG2 captured 3.5 times more P2 sand samples than P1 for the same hydraulic conductivity of 1.3×10^{-5} m/s. Similarly, NWG1 and NWG3 captured 6.3 and 7.3 times more P2 than P1 with hydraulic conductivities of 1.9×10^{-5} m/s and 1.2×10^{-5} m/s respectively. This shows that for the soil with a larger range of particle size diameters, more soil would be captured than for soil that has a smaller range of particle sizes at the same hydraulic conductivity. Hence, the filtration rate of geotextiles will be more in an area with larger particle size distributions (i.e., a construction or newly developed area) than an area with smaller particle size distributions (i.e., heavy traffic) and more particles will be captured.

In addition to the effect of PSD on hydraulic conductivity, there were also differences due to other factors such as geotextile type. As shown in Fig. 5.5, the hydraulic conductivities for all three geotextiles at the clogging point varied between 0.85×10^{-5} - 1.36×10^{-5} m/s. NWG2 had the highest average hydraulic conductivity followed by NWG1 and NWG3 respectively. Similar hydraulic conductivities for nonwoven geotextiles at the clogging point were also found by Franks et al., (2012). Therefore, in general, the geotextiles would start to clog when the hydraulic conductivity reached below 1.36×10^{-5} m/s. However, the variation of hydraulic conductivity at the clogging point depends on the type of geotextile and soil sample gradation.



(a)



(b)

Fig. 5.5 Hydraulic conductivity of each geotextile filter as a function of cumulative suspended solids captured for particle size distribution (a) P1 (0-180 µm) and (b) P2 (0-300 µm).

The hydraulic conductivities found in this study are similar to those of mixed media filters (such as sand filters and geotextiles) and hence they can be compared with other media-based stormwater filtration systems (Clark and Pitt, 2009). Urbanas (1999) developed an equation describing the performance of different natural filters which shows that the unit flow velocity through a natural media is directly related to the amount of sediment loaded onto the filter surface. Clark and Pit (2009) later applied and validated this equation for mixed media filtration systems. Franks et al. (2012) used this equation directly for geosynthetic filtration for cumulative captured solids onto geotextiles and the suggested power equation of Urbanas (1999) for predicting the unit flow velocity (u) is:

$$u = X \left(\frac{M_m}{A} \right)^{-y} \quad (5.4)$$

where X and y are the best fitted parameters for empirical flow through and exponential constant, M_m is the loaded (L_m) or captured solid (C_m) mass onto geotextile filter and A is the loaded or captured cross sectional area of the geotextile. It was assumed that the filtration process for a soil fabric filtration system is similar to that for mixed-media filters: the different parameters of equation (5.4) were calculated and compared for this study and for those of Clark and Pitt (2009) who used a mixed media filter of fine sand, peat moss, activated carbon and compost, and Franks et al. (2012) (Table 5.4).

Table 5.4 The empirical flow through and exponential constant parameters for geotextile and sand filtration system

Ref.	Filtration media	Conc. (mg/L)	Clogging K (m/s)	Model parameters			Model equation
				X	y	R^2	
This study	NWG1-P1	200	9.73×10^{-6}	3.82×10^6	1.67	0.818	$u = X \left(\frac{C_m}{A} \right)^{-y}$
	NWG2-P1		1.03×10^{-5}	7.78×10^6	1.42	0.765	
	NWG3-P1		8.90×10^{-6}	1.02×10^8	2.12	0.880	
	NWG1-P2		1.44×10^{-5}	2.73×10^7	1.55	0.814	
	NWG2-P2		8.35×10^{-6}	5.46×10^7	1.58	0.795	
	NWG3-P2		1.36×10^{-5}	1.89×10^7	1.54	0.878	
Franks et al., (2012)	Geo 1- G1	200	3.76×10^{-4}	N/A	N/A	N/A	$u = X \left(\frac{C_m}{A} \right)^{-y}$
	Geo 2-G1		4.85×10^{-6}	5.11×10^5	1.76	0.886	
	Geo 3- G1		3.48×10^{-6}	2×10^9	2.96	0.959	
	Geo 1- G2		1.64×10^{-5}	2.77×10^2	0.59	0.653	
	Geo 2-G2		4.16×10^{-6}	1.02×10^4	1.22	0.868	
	Geo 3- G2		3.05×10^{-6}	4.17×10^5	1.75	0.904	
Clark and Pitt, (2009)	Sand	400		4.45×10^4	1.02	0.734	$u = X \left(\frac{L_m}{A} \right)^{-y}$
	Carbon sand		n.a.	1.4×10^4	0.77	0.611	
	Peat sand			2×10^3	0.71	0.818	
	Compost sand			1.6×10^{13}	4.09	0.998	
	Sand	150		1.55×10^3	0.22	0.882	
	Carbon sand			6.3×10^{13}	5.17	0.541	
	Peat sand		n.a.	5.1×10^3	0.40	0.581	
	Compost sand			1.6×10^{13}	4.09	0.997	

* L_m/A and C_m/A are cumulative loaded and captured mass of solids on/in filters (g/m^2) respectively.

Clark and Pitt. (2009) used the constant head method to determine hydraulic conductivity while this study used the falling head method similar to Franks et al. (2012). As indicated in Table 5.4, the values of X in Franks et al. (2012) and Clark and Pitt. (2009) vary between 2.77×10^2 to 2×10^9 and 1.55×10^3 to 6.3×10^{13} respectively and the values of y vary between 0.594-2.96 and 0.227-5.17 respectively. The values of X and y found in this study are within the range of this previous research. However, Franks et al. (2012) found that the X and y values for their geotextiles decreased with the increasing AOS and permittivity. The results in this study also showed that the X and y values for all geotextiles decreased with increasing AOS and permittivity for P1 (0 to 180 μm). However, this trend was not evident for P2 (0 to 300 μm) presumably due to its larger particle size distribution. This observation shows that AOS and permittivity cannot be used as the sole parameters for modelling of hydraulic conductivity as a function of solids loading and that particle size distribution must also be considered when modelling TSS removal from stormwater using geotextiles.

Geotextiles used in this study showed significant potential for TSS removal from stormwater but the selection of geotextile type for CBI needs careful consideration including physical and hydraulic properties. With an influent concentration of 200 mg/L and a runoff coefficient of 0.9 (Alam et al., 2017), the NWG1, NWG2 and NWG3 were found to clog at 0.72- 1.2 m (P1) and 2.77-4.42 m (P2) of total rainfall. Considering the average yearly rainfall of Western Australia 1 m (BoM, 2015), the NWG1, NWG2 and NWG3 would require maintenance of 262, 422 and 332 days respectively for P1. The maintenance time of NWG1 was found to be less than this because it becomes clogged more rapidly. Under current operation, NWG1 in CBI is currently serviced (e.g. maintained) 10 times a year (Alam et al., 2017a). The servicing frequency of CBI is an important parameter that depends on other factors such as runoff characteristics, location, season and traffic volume. When the geotextiles are used in water with high organic content (especially road runoff and runoff from parking lots), biological growth may also occur in and on the geotextile (Palmeira et al., 2008; Korkut et al., 2006). This biological activity may limit the hydraulic conductivity of geotextile enhancing early clogging. The PSDs chosen for this study were quite coarse compared to what has been reported elsewhere for actual stormwater runoff samples, so the expected performance of the new NWG being tested may not be as high in field conditions as found in this study. Therefore, further research is

needed to determine the servicing frequency of geotextile CBIs in field conditions for their optimum efficiency. It is also not obvious that high intensities are critical elsewhere; it would be more interesting to observe longer events.

5.4 Conclusion

This study evaluated the hydraulic performance of a new type of geotextile for use in CBIs and compared it with two commercially available geotextiles. Two types of TSS with different particle size distributions (PSD) were used for synthetic stormwater. The filtration performances of the geotextiles were found to be dependent on the geotextile physical properties and the PSD of the suspended solids. It was found that the effluent TSS concentration target value of 30 mg/L (ANZECC 2000 Table 4.4.2) could be attained for the sandy soil type with the larger PSD (P2; 0-300 μm) after a short filter ripening period. The ripening period for both particle size distributions occurred between 0.88-1.72 kg/m^2 of cumulative suspended solids loading. The cumulative solids loading onto geotextiles varied between 6.56-39.79 kg/m^2 depending on particle size distribution and the results indicate that 36% more of the larger particle size distribution (P2) was captured than the smaller particle sizes (P1: 0-180 μm). In general, the TSS with coarser particle size distribution (P2) resulted in a greater percentage of solids captured (93%) than the finer particle size distribution (P1) solids because clogging occurred at a lower percentage of solids captured (53-60%). The hydraulic conductivity values were also consistently larger for the experiments with larger particle size distribution (P2), because of the expected formation of a more permeable graded filter zone. The clogging point is an important hydraulic parameter for geotextile filtration and it occurs between hydraulic conductivities of 0.85×10^{-5} m/s to 1.36×10^{-5} m/s. Based on the results, it was shown that the new type of geotextile (NWG1) is suited for use as a stormwater CBI, assisted by its unique structure and capacity for reuse over the other two materials tested. Solids capture occurs through only half of the thickness of the material, leading to more efficient capture with less breakthrough of fine particles. In addition, the material allows multiple reuse with good retention of the original shape of the basket even after numerous (at least 10) back flushing and cleaning cycles. However, this study considered only three geotextiles and two particle size distributions and further research is needed to select

appropriate geotextile types from a wide range of geo-fabrics and soil types for optimum efficiency in CBIs to clean stormwater at source.

List of notations

<u>Notation</u>	<u>unit</u>
A :	loaded/captured area of geotextile m^2
C_i :	influent EMC mg/L
C_e :	effluent EMC mg/L
C_U :	coefficient of uniformity dimensionless
C_c :	coefficient of curvature dimensionless
C_m :	cumulative captured solid mass onto geotextile at the time clogging gm
D :	particle sizes μm
D_{50} :	the grain diameter at 50% passing respectively μm
d_c :	the diameter of the spherical collector dimensionless
K :	hydraulic conductivity m/sec
L_m :	cumulative loaded solid mass onto geotextile at the time clogging gm
M_m :	cumulative loaded or captured mass of solid onto geotextile gm
n :	the filter bed porosity dimensionless
O_{95} :	apparent opening size μm
O :	geotextile pore sizes μm
Q :	unit flow rate L/min/m ²
Q_i :	unit flow rate in a given amount of time L/min/m ²
T :	thickness of filter mm
u :	unit flow velocity m/day
X :	flow through constant dimensionless
y :	exponential constant dimensionless
Z :	transformed constant dimensionless
Δt_i :	the time interval between the samples s
Ψ :	permittivity s-1
α :	the striking coefficient dimensionless
η :	the single collector contact efficiency dimensionless

List of abbreviations

ASTM	:	American Society for Testing and Materials
ANZECC	:	Australian and New Zealand Environment and Conservation Council
AOS	:	apparent opening sizes
ARI	:	average recurrences interval
AS	:	Australian Standard
AWWA	:	American Water Works Association
BMP	:	best management practice
BoM	:	Bureau of Meteorology
BS	:	British Standard
CBI	:	catch basin insert
CBR	:	California bearing ratio
CIM	:	Cook Industrial Minerals
CF	:	continuous filament
DoW	:	Department of Water
EMC	:	event mean concentration
GP	:	gross pollutant
Geo	:	geotextile
HLR	:	hydraulic loading rate
ISO	:	International Organization for Standardization
MARV	:	manufacturer's minimum average roll value
NWG	:	nonwoven geotextile
NP	:	needle-punched
PSD	:	particle size distributions
PP	:	polypropylene
RPM	:	radiation per minute
SS	:	suspended solid
STF	:	staple fibre
TSS	:	total suspended solids
UST	:	Urban Stormwater Technologies Pty Ltd
WA	:	Western Australia

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CHAPTER 6

REMOVAL OF NITROGEN SPECIES FROM WATER USING *EUCALYPTUS WANDOO* BIOCHAR

Abstract

Eucalyptus wandoo (EW) biochar was characterised for its surface morphology and tested for removing aqueous phase nitrogen species (NO₃-N, NO₂-N and NH₃-N) in batch adsorption. Different surface characterisation tests including Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), nitrogen adsorption-desorption isotherm and SEM image confirmed the EW biochar a good adsorbent because of its H4 hysteresis type mesoporous structure with amorphous materials. The adsorption batch tests (varying initial concentration: 0.5-5mg/L; dosage: 2-10 g; pH: 4-9; and contact time: 0-24 hr) results showed 100% removal for NO₂-N and NH₃-N at lower concentrations (0.5-1 mg/L) but the removal of NO₃-N was found <1%. The adsorption capacity was inversely related to dosage and the most suitable pH was found 4-5. The adsorption kinetics followed the pseudo second order model for both NO₂-N and NH₃-N adsorption. The isotherm study showed that adsorption of both species followed Langmuir model better than Freundlich model.

Keywords: Adsorption; *Eucalyptus wandoo*; Biochar; Nitrogen; Water quality

6.1 Introduction

Due to the expansion of urbanization, the volume of urban stormwater runoff has also been increased significantly (Alam et al., 2017a & b). This urban runoff consists of significant number of pollutants including nutrients, heavy metals, oil, grease and hydrocarbons. These chemicals may be released from vehicle emissions and fluid leaks from vehicles, domestic fertilizer, pesticides, refuse and pet faeces (Harmayani and

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Anwar, 2016). One of the major constituents found in urban stormwater runoff is nitrogenous matter including nitrate-nitrogen ($\text{NO}_3\text{-N}$), nitrite-nitrogen ($\text{NO}_2\text{-N}$) and ammonia-nitrogen ($\text{NH}_3\text{-N}$). The presence of excessive nitrogen species in urban runoff may produce algal blooms (eutrophication) in receiving water bodies such as lakes, wetlands, streams, rivers or coastal waters. When the algae starts to decompose, the bacteria grows and consumes dissolved oxygen (DO) from water and depletes the required DO which endangers the marine ecosystem (Chislock et al., 2013). It is therefore of utmost importance to treat the wastewater/stormwater to remove these contaminants to maintain water quality for sustainable ecosystems.

The dissolved nitrogen species in water may be removed either by biological processes (e.g. nitrification or denitrification) or physical adsorption. Nitrogen removal methods include reverse osmosis, electro dialysis, activated carbon adsorption, adsorption by green media and ion exchange with synthetic resins (Wanielista & Chang, 2008). Among these methods, adsorption was found to be the most cost-effective and environment-friendly process because of its operational simplicity and economic viability (Hameed et al., 2007). Xuan et al. (2010) and Kim et al. (2003) used different types of low cost green sorption media such as tree bark, wood chips, wheat straw, tire crumbs, sawdust, alfalfa, mulch compost, paper (newspaper), cotton, and sulfur/limestone. Kim et al. (2003) found 100% nitrate removal using Alfalfa and newspaper but only 60% with mulch compost. Recently, Harmayani and Anwar (2016) used *radiata pine* sawdust to remove aqueous phase nitrogen species and found it to be very effective for $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ removal (100%). Other researchers have shown biochar to be a suitable medium for treating waste water (Iqbal et al., 2015; Reddy et al., 2014a; Mohanty et al., 2014). Biochar is a charcoal-like material produced by heating biomass to high temperatures (300-1000°C) under low oxygen conditions (i.e., pyrolysis) (Chen et al., 2011). Reddy et al. (2014a) used wood-derived biochar (pyrolysis at 520°C) to treat stormwater and found the following removal percentages: TSS (86%), $\text{NO}_3\text{-N}$ (86%), $\text{PO}_4\text{-P}$ (47%) and heavy metals (18-75%). The removal percentage using biochar varies due to the variation in its molecular structure and its porosity. This is because of the variation in the original biomaterial and temperature in the pyrolysis process (Reddy et al., 2014a). To date, no study has been undertaken using biochar as medium to remove nitrogenous species ($\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$) from the aqueous phase. Due to the microporous structure and cation

exchange capacity (CEC) of biochar, it may be used as a good adsorbent for removing nitrogen species from water. This study considers wood (*Eucalyptus wandoo-EW*)-derived biochar for the first time to remove nitrogen species (NO₃-N, NO₂-N and NH₃-N) from water. The *EW* commonly known as ‘white gum’, was formerly harvested as a commercial source of tannin in Western Australia and is used in both light and heavy construction (FPC, 2016). The increasing use of *EW* in the construction industry has produced abundant amounts of wood waste such as wood chips, wood shavings and wood pellets. These wood wastes can be used to produce bio-energy in the pyrolysis process, leaving biochar as a by-product. Previously biochar was mainly used in agriculture as fertilizer (EFA, 2016) and its use in treating wastewater/stormwater is relatively new. In this study, detailed surface characterization of *EW* biochar was performed by FTIR, TGA, XRD, SEM and nitrogen adsorption–desorption isotherms. The kinetics of NO₂-N and NH₃-N adsorption process were studied for pseudo first and second order models. Equilibrium isotherms were investigated using Freundlich and Langmuir models and an overall adsorption mechanism process was evaluated. The batch experiments were conducted with varying initial concentrations, biochar dosage, pH, and contact time.

6.2 Materials and method

6.2.1 *EW* Biochar

The *EW* biochar was collected from ‘Energy Farmers Australia Pty Ltd’ in Geraldton, Western Australia. The fine particles from biochar were removed by two-step sieve analysis using dry and wet sieving methods (Reddy et al., 2014a). Deionised water was used in the wet sieving method with one to two hundred grams of biochar (ISO 3310: BS 410-1:2000 sieve size 2.36 mm). Biochar of particle size of 2.36 mm diameter was selected as an adsorbent in this study for effective filtration. The sieved biochar was washed with deionized water and the wash water (2 mL) was analysed for any possible nitrogen residues remaining in the biochar. After 6–7 washes, the nitrogen content in the washed water was found to be negligible. The samples were oven dried and stored in an air-tight container at room temperature (22±2°C).

6.2.2 Biochar characterisation

Scanning electron microscopy (SEM) imaging and energy dispersive X-ray spectroscopy (EDS) of biochar samples were conducted to characterise and observe the morphology of biochar and identify its surface elements. Sample preparation involved platinum coating (approximately 3 nm) using a Baltec MED 020 coater. The sample was observed through an ion beam scanning electron microscope (Zeiss Neon 40 EsB) at 15.0 kV and 11.0 mm working distance. An X-ray diffractometer (D8 Advance-Bruker aXS) was used for powder X-ray diffraction (PXRD) patterns employing Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at an accelerating voltage of 40 kV and current of 40 mA for 2θ ranging from 5 to 60°.

A thermogravimetric analysis (TGA) instrument (TGA/DSC1 STAR^e system, Mettler Toledo) was used for investigation of the thermal stability of biochar, using an alumina pan (150 μL) and heated to 700°C in air with a flow rate of 10 mL/min.

Fourier transform infrared spectroscopy (FTIR) was performed by 650 to 4000 cm^{-1} scanning with a resolution of 4 cm^{-1} on a spectrum 100 FTIR Spectrometer (Perkin Elmer) by an attenuated total reflectance (ATR) technique.

A Micromeritics Tristar II3020 was employed to measure nitrogen adsorption-desorption isotherms to obtain the surface area, pore size and pore volume. Prior to nitrogen adsorption-desorption measurements, biochar samples were prepared at 180 °C for 12 hr under high vacuum.

The pH value of raw biochar was measured electrometrically by using a combined electrode (HACH 40d with PHC 101 HAC electrode) calibrated against 3 buffers. The point of zero charge (pH_{pzc}) was measured by the solid addition method (Oh et al., 2012). Biochar (0.1 g) was mixed with NaCl solution (50 mL; 0.01 M) in a 250 mL Erlenmeyer flask. The solutions were initially adjusted to pH of 4-8 by either adding 0.1M HCl or 0.1M NaOH and securely capped immediately. The equilibrium pH of the supernatant was measured after 48 hours by placing the Erlenmeyer flask on a 16-flask capacity shaking platform (Innova 2100, New Brunswick Scientific) and shaken

at 100 rpm at room temperature ($22\pm 2^\circ\text{C}$). The difference between the initial and final pH value ($\Delta\text{pH}=\text{pH}_0-\text{pH}_f$) was plotted against pH_0 and the point of intersection of the resulting null pH corresponded to the point of zero charge (pH_{PZC}).

6.2.3 Nitrogen solutions

Aqueous solutions containing $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ (0.5-5 mg/L) were prepared using analytical grade chemicals purchased from Thermo Fisher Scientific, Sydney, Australia. These nitrogen concentrations were chosen based on Australian Runoff Quality (Wong, 2006; Alam et al., 2017a) and similar to other studies for nutrient adsorption (Harmayani and Anwar, 2016; Reddy et al., 2014a & b). Stock solutions of $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ were prepared from NaNO_3 , NaNO_2 and NH_4Cl respectively (Harmayani and Anwar, 2016). Fresh solutions were prepared by diluting the stock standard solutions with deionized water before each experiment. The pH of the solutions were adjusted by dosing NaOH (0.1 M) or HCl (0.1 M) and measured using a pH meter (HACH 40d with PHC 101 HAC electrode).

6.2.4 Adsorption experiments

A series of batch adsorption experiments was conducted with varying initial concentrations (0.5-5 mg/L), biochar dosages (2-10 g) and pH (4-8). Each biochar dosage (2.36 mm diameter) was mixed with nitrogen solution (0.5-5 mg/L; 100 mL) in a 250 mL Erlenmeyer flask. The pH values were kept constant at $6.5(\pm 0.5)$ except the experiments with varying pH (4-8). Parafilm was used to cover the flasks to avoid any evaporation of the solution. The flasks were placed on a 16-flask capacity shaking platform (Innova 2100, New Brunswick Scientific) and shaken at 100 rpm at room temperature ($22\pm 2^\circ\text{C}$). Two millilitres of solution was extracted using a syringe and filtered through a $0.45\ \mu\text{m}$ syringe filter (GE Water and Process Technologies) at a predetermined time interval (5-60 minutes). The filtered water samples were analysed for nitrogen species ($\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$) using an AQUAKEM 200 water analyser (Labmedics Analytical Solutions; nominal detection limit of 0.002 mg/L with a 1.5% measurement error at 95% confidence level) following standard methods given in APHA (1998). The data was recorded until the equilibrium concentrations were

reached. All experiments were carried out in duplicate/triplicate and the average values are reported. The variance between any replicate measurements was smaller than 1%. The experimental data were recorded and the equilibrium adsorption of biochar was calculated (Sun et al., 2013; Harmayani and Anwar, 2016):

$$q_e = \left(\frac{C_o - C_{eq}}{W} \right) \times V \quad (6.1)$$

where q_e is the equilibrium adsorption ($\mu\text{g/g}$), C_o and C_{eq} are the initial and equilibrium concentration (mg/L), W is the weight of biochar (gm) and V is the volume of solution (L). The percentage removal was calculated by the ratio of difference between the initial concentration (C_o) and the concentration obtained at specific time (C_t) until equilibrium is reached.

$$Removal (\%) = \frac{C_o - C_t}{C_o} \times 100 \quad (6.2)$$

6.2.5 Adsorption kinetics

The kinetic batch experiments were similar to those of the equilibrium test. The samples were taken at various time t intervals and the nitrogen concentration (C_t) was analysed using the same analytical technique (APHA, 1998). The amount of adsorption q_t ($\mu\text{g/g}$) at specific time t was calculated using the following equation (Harmayani and Anwar, 2016):

$$q_t = \left(\frac{C_o - C_t}{W} \right) \times V \quad (6.3)$$

The adsorption kinetics show the contaminant uptake rate and occurred in two phases: a rapid adsorption rate followed by a slow adsorption process before reaching equilibrium. Experimental data fitted into either pseudo-first and second order kinetic models. Fit to the pseudo-first order model suggested that the contaminants are attracted to the biochar via physical forces while the pseudo-second order relationship suggested that a chemisorption mechanism plays an important role between the

adsorbent molecules and adsorbate ions in the aqueous solution. The pseudo-first-order and second order models are expressed as follows (Sun et al., 2013):

Pseudo-first order kinetic model:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (6.4)$$

K_1 (1/min) is the first order adsorption reaction constant determined using the linear plot of $\log(q_e - q_t)$ versus t .

Pseudo-second order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6.5)$$

K_2 (g/mg h) is the second order adsorption reaction constant determined using the linear plot of t/q_t versus, t .

To verify the validity of kinetic models, the normalized standard deviation Δq (%) was calculated:

$$\Delta q (\%) = 100 \sqrt{\frac{\sum \{(q_{exp} - q_{cal}) / q_{exp}\}^2}{i-1}} \quad (6.6)$$

where q_{exp} and q_{cal} refer to the experimental and calculated values of adsorption capacity respectively and i is the number of data points.

6.2.6 Adsorption isotherm

The Langmuir and Freundlich isotherms were considered as models to fit the experimental data. The Langmuir isotherm is an empirical model with the assumption that adsorption only occurs in a monolayer model at identical, equivalent and finite localised sites. The Langmuir isotherm essentially describes the equilibrium adsorption as a reversible process (Foo and Hameed, 2010):

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \left(\frac{1}{C_e} \right) + \frac{1}{q_m} \quad (6.7)$$

where, q_e (mg/gm) is the equilibrium adsorption, q_m (mg/gm) is the maximum capacity that the absorbent has for the adsorbate, K_L is the Langmuir constant (dimensionless) which can be obtained by plotting $1/q_e$ versus $1/C_e$ graph and C_e (mg/L) is the concentration of the compound of interest (adsorbate) in solution at equilibrium. Another dimensionless parameter, the adsorption intensity (R_L) is used to indicate the type of adsorption process (Sari et al., 2007):

$$R_L = \frac{1}{1 + K_L C_o} \quad (6.8)$$

$R_L = 0$ indicates irreversible adsorption, $0 < R_L < 1$ indicates favourable adsorption, $R_L = 1$ indicates linear adsorption and $R_L > 1$ indicates unfavourable adsorption.

The linear form of the Freundlich isotherm is described as follows (Foo and Hameed, 2010):

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \quad (6.9)$$

where the constants K_F (mg/gm) and n_F are the adsorption capacity and adsorption intensity respectively. These constants are obtained from a plot of $\log q_e$ versus $\log C_e$. The Freundlich isotherm is widely used for heterogeneous materials. The slope of the line of best fit is indicative of the heterogeneity of the adsorbent material, i.e. the smaller the slope of the greater the heterogeneity. The $1/n_F$ value indicates whether the adsorption process involved cooperative adsorption or chemisorption (Foo and Hameed, 2010).

6.2.7 Statistical analysis

A one-way analysis of variance (ANOVA) was conducted and least significant difference tests were used to compare differences between various compositions, as

well as the differences between compositions at various concentration levels. Differences were considered to be significant at $P \leq 0.05$.

6.3 Results and discussion

6.3.1 Characterization of *EW* biochar

The biochar used in this study was produced by [Energy Farmers](#), Geraldton, Western Australia from the waste wood of '*Eucalyptus wandoo*' at a pyrolysis temperature of 400°C for approximately 10-15 minutes, although temperatures can vary through the kiln (EFA, 2016). The pyrolysis is a continuous process, processing up to 250 kg/hr of feedstock, yielding 30% biochar by weight. The biochar production rate varies between 21.7-51.5% on a mass basis; the percentage yield has an inverse relationship with the pyrolysis temperature (Yao et al., 2012). The elemental composition and production process of *EW* biochar was supplied by [Energy farmers](#) (Appendix D) and the physical parameters were determined in our lab. The results are shown in Table 6.1 together with other biochars derived from different sources. Table 6.1 shows carbon as the main constituent of biochar which was confirmed by results of other tests, e.g. EDS (Fig. 6.1). The biochar in this study was acidic in nature which is similar to the biochar used by Yao et al. (2012) and Oh et al. (2012) (Table 6.1).

Nitrogen adsorption-desorption isotherm was shown in Fig. 6.2 and it indicated that N_2 isotherm is of type IV with strong hysteresis in adsorption-desorption branches indicating mesoporous nature of biochar. Apparently, hysteresis is H4 type, however, instead of eliminating at $p/p_0 = 0.45$, it continued till $p/p_0 = 0.1$, indicating heterogeneity of carbon material (Azhar et al., 2016).

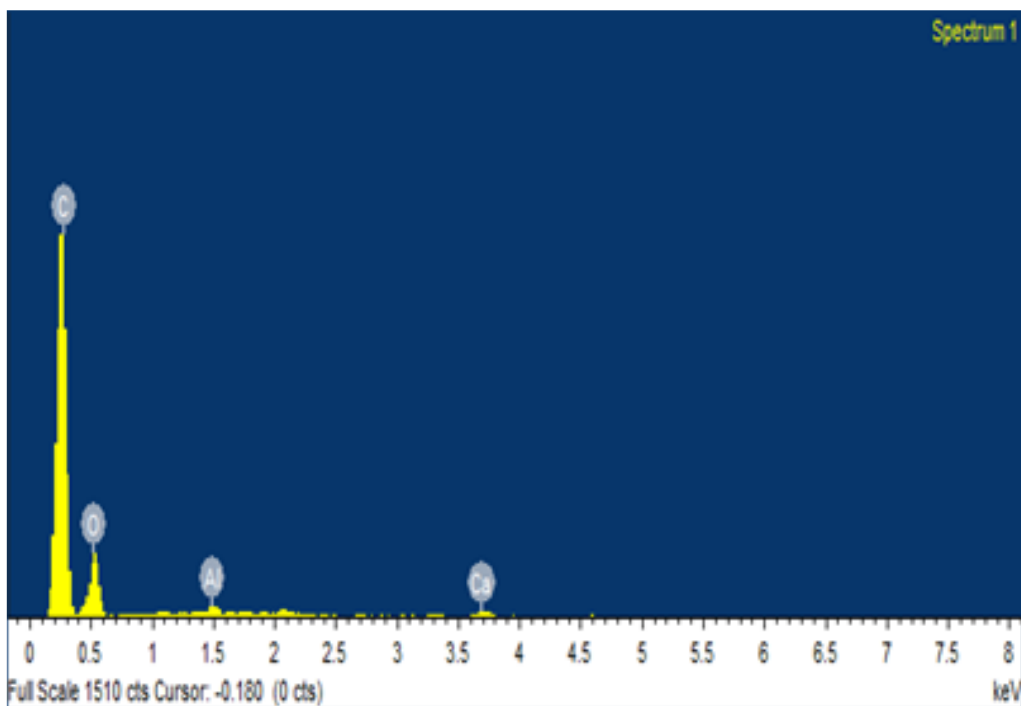


Fig. 6.1 Energy dispersive spectroscopy (EDS) of *EW* biochar

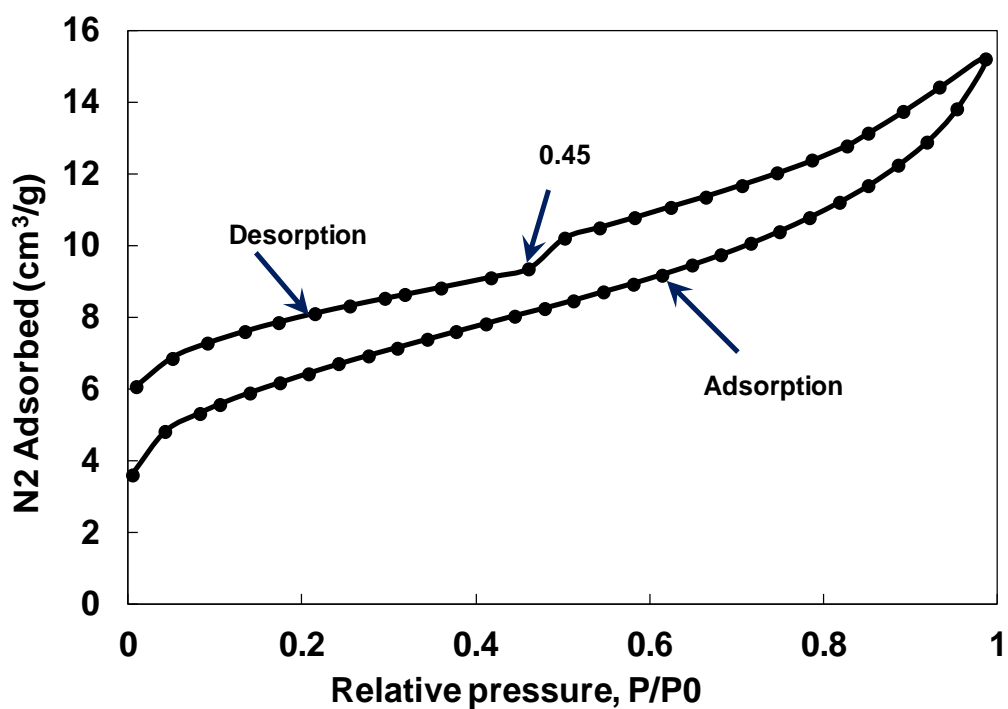


Fig. 6.2 N₂ adsorption-desorption isotherms of *EW* biochar in BET method

Table 6.1 Physiochemical properties of biochar produced from different sources and their removal characteristics for different pollutants

Biochar sources	Elemental composition ^a (%)	Production process			Physical properties					Target compound (s)	Removal efficiency (%) /adsorption capacity (µg/g)	Reference s
		Pyrolysis temperature (°C)	Yield (%)	heating rate (°C/min)	Micro pore volume (cm ³ /g)	Surface area, BET (m ² /g)	Pore width, BJH (nm)	Particle size (mm)	pH			
Eucalyptus wandoo	C:61.2 H:5, O:18, N:<1	400	30	5	0.0235	22.48	4.19	2.36	5.2 ^b	NH ₃ -N, NO ₂ -N NO ₃ -N	100% <1%	³ This study
Eucalyptus deglupta	C:82.4, O:13.7, N:0.57	350	n.a.	n.a.	n.a.	7	n.a.	2	n.a.	Biological N ₂ fixation	n.a.	² Rondon et al., (2007)
Digestion residue	C:63.5 H:5.28, O:18.1, N:0.94	400	n.a.	n.a.	0.013	7.6	6.7	0.25-0.83	8.8	Cationic MB ^c	99.4-99.9%	Sun et al., (2013)
Palm bark	C:68.9 H:5.38, O:20.8, N:0.88		n.a.	n.a.	0.0039	2.46	4.75		7.1			
Eucalyptus	C:77.8 H:5.38, O:18.3, N:0.41		n.a.	n.a.	0.0059	10.35	2.29		7.47			
Poultry litter	C:38, N:3.75	500	n.a.	n.a.	n.a.	5.01	n.a.	0.8-1	10.5	NH ₄ ⁺	adsorption capacity: 150 µg/g	Tian et al., (2016)
Poultry litter	C:79, N:0.25	400	n.a.	n.a.	n.a.	15.39	n.a.		7.5		260 µg/g	
Hard wood	C:84, N:0.3	500	n.a.	n.a.	n.a.	26.65	n.a.		8.1		28 µg/g	
Hard wood	C:63 H:5, N:1	400	36	8	n.a.	1.8	n.a.				45 µg/g	
Sugarcane bagasse	C:69.5 H:4.2, O:24.5, N:0.9	300	33.4	21.7 -51.5	n.a.	5.2	n.a.	0.5-1	7.2	NO ₃ -N, NH ₄ ⁺	0.12-3.7% (Pyrolysis temp.>600°C) 1.8-15.7%	¹ Yao et al. (2012)
Sugarcane bagasse	C:78.6 H:3.5, O:15.5, N:0.9	450	28		n.a.	15.3	n.a.	0.5-1	7.9	PO ₄ -P	3.1%	

Sugarcane bagasse	C:76.5 H:2.9, O:18.3, N:0.8	600	26.5		n.a.	4.2	n.a.	0.5-1	7.9			
Peanut hull	C:73.9 H:3.9, O:19.1, N:1.6	300	38.4		n.a.	0.8	n.a.	0.5-1	7.8			
Peanut hull	C:81.5 H:2.9, O:13, N:1	450	21.7		n.a.	21.8	n.a.	0.5-1	8.2			
Peanut hull	C:86.4 H:1.4, O:10, N:0.9	600	30.8		n.a.	27.1	n.a.	0.5-1	8			
Brazilian pepper wood	C:59.3 H:5.2, O:34.1, N:0.3	300	51.5		n.a.	81.1	n.a.	0.5-1	6.6			
Brazilian pepper wood	C:77 H:2.2, O:17.7, N:0.1	600	28.9		n.a.	234.7	n.a.	0.5-1	9.1			
Bamboo	C:66.2 H:4.7, O:27.7, N:0.4	300	73.2		n.a.	1.3	n.a.	0.5-1	6.7			
Bamboo	C:76.9 H:3.6, O:18.1, N:0.2	450	26.3		n.a.	18.2	n.a.	0.5-1	5.2			
Bamboo	C:80.9 H:2.4, O:14.9, N:1	600	24		n.a.	470.4	n.a.	0.5-1	7.9			
Oak wood	C:82.83 H:2.7, O:8.05, N:0.3	400-450	n.a.	n.a.	1.06	2.7	n.a.	n.a.	11.6	Cr(VI)	adsorption capacity: 3000 - 4930 µg/g	Mohan et al., (2011)
Oak bark	C:71 H:2.63, O:13, N:0.46	450	n.a.	n.a.	0.41	1.9	n.a.	n.a.	11.6		adsorption capacity: 4600 - 7500 µg/g	
Orange peel	C:41.9 H:6.4, O:47.9, N:1	0	n.a.	n.a.	-	24	n.a.	<2	4.1	F-	apparent fluoride adsorption 100 %	Oh et al., (2012)
	C:68.4 H:4.8, O:19.8, N:2	400	n.a.	n.a.	-	428	n.a.		11.6			
	C:74.7 H:2.1, O:13.4, N:1.7	600	n.a.	n.a.	-	137.1	n.a.		12.1			
	C:74.8 H:1.6, O:13.4, N:1.7	700	n.a.	n.a.	-	110.2	n.a.		12.3			
Water treatment Sludge	C:6.6 H:1.8, O:15.3, N:0.3	0	n.a.	n.a.	-	93.5	n.a.		5.7			
	C:8.5 H:1, O:6.4, N:0.3	400	n.a.	n.a.	-	126.4	n.a.		6.2			
	C:8.4 H:0.6, O:2, N:0.2	600	n.a.	n.a.	-	114.4	n.a.		6.5			
	C:8.1 H:0.5, O:0.6, N:0.2	700	n.a.	n.a.	-	135.2	n.a.		6.2			

^a Elemental composition (% , mass based); ^b pHpzc; ^c Methylene blue;

FTIR is a fast and convenient method to follow the progress of adsorption. The FTIR described only for the characterization of biochar. FTIR after adsorption was also carried out but no major peak was found. Hence, this FTIR was not included in the thesis. The FTIR spectra of *EW* biochar samples shown in Fig. 6.3 is indicative of the functional groups on the biochar surface. The functional groups were identified using data from the literature (Sun et al., 2013; Table 6.2). The peaks at 780 and 1400 cm^{-1} in the spectra of biochar produced were assigned to the carboxylate ($-\text{COO}^-$) deviational vibration and symmetric stretching. The peaks at 1563 cm^{-1} for the biochar samples were assigned to $-\text{COO}^-$ anti-symmetric stretching indicated aromatization occurred during the biochar preparation (Li et al., 2016). The peaks at 1653 cm^{-1} were assigned to the band out of the plane C-H bending. The peaks at 3331 cm^{-1} assigned to the free hydroxyl (from structural hydroxyl groups and interlayer water molecules) stretching (Özçimen and Ersoy-Meriçboyu, 2010).

Table 6.2 FTIR spectral characteristics of *EW* biochar

IR Peak	Frequency (cm^{-1})	Assignment
1	875	Aromatic C-H out of the plane deformation
2	1218, 1353	C=O stretching and bending of ketones
3	1563	C=O stretching of carboxylic acid
4	1653	Out of plane C-H bending
6	3331	Free O-H stretching

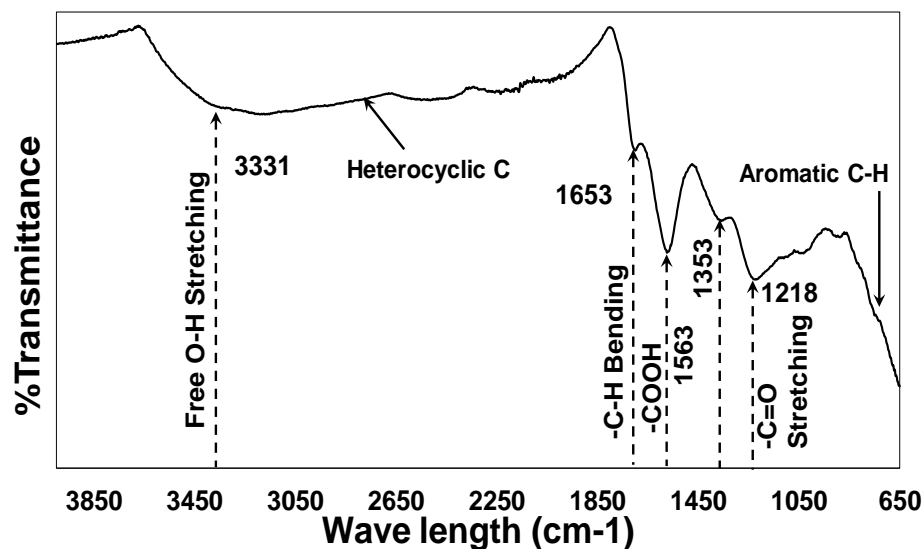


Fig. 6.3 FTIR Spectra of *EW* biochar before adsorption

TGA analysis of the *EW* biochar showed a mass loss of 4.5% below 100°C which was attributed to moisture and other small molecules (Fig. 6.4). With increasing temperature, a plateau occurred until around 325°C, in which no effective loss of mass was observed after which there was a continuous weight loss of approximately 95% up to 575°C. This was attributed to loss of carbon, including oxygenated functional groups such as COO and COOH. Decomposition of organic content remaining in biochar such as cellulose and hemicellulose has been observed at this temperature (Yang et al., 2007). There was no distinct degradation pattern of the carbon skeleton at one fixed temperature indicating an irregular amorphous carbon structure with a porous structure as shown in the SEM image in Fig. 6.5 (Melo et al., 2013). This effect may be due to the result of the melting and fusion process of the lignin and other small molecule compounds (e.g., pectin and inorganic compounds) as illustrated by Liu et al. (2010) for pinewood biochar produced at 300°C and 700°C respectively.

To analyse the structure of biochar, XRD examination was carried out with 2θ range of 10°–60° and shown in Fig 6.6. The obtained XRD patterns presented a broad peak around 18°–28° which can essentially be attributed to the presence of amorphous materials.

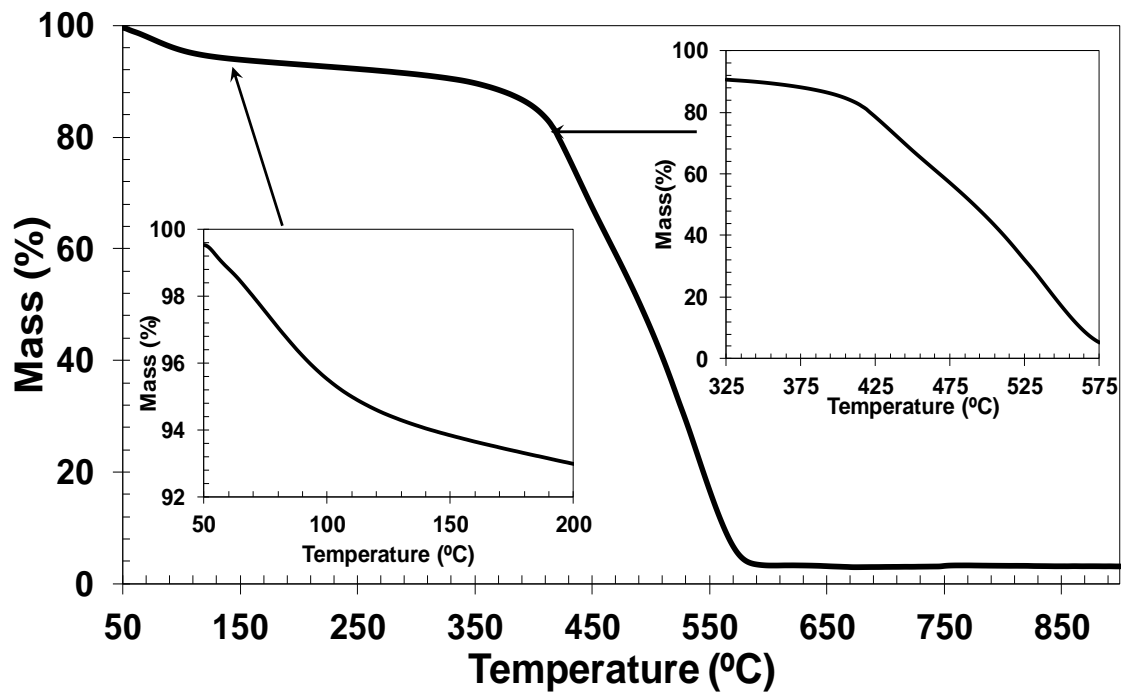


Fig. 6.4 Thermogravimetric analysis (TGA) of *EW* biochar

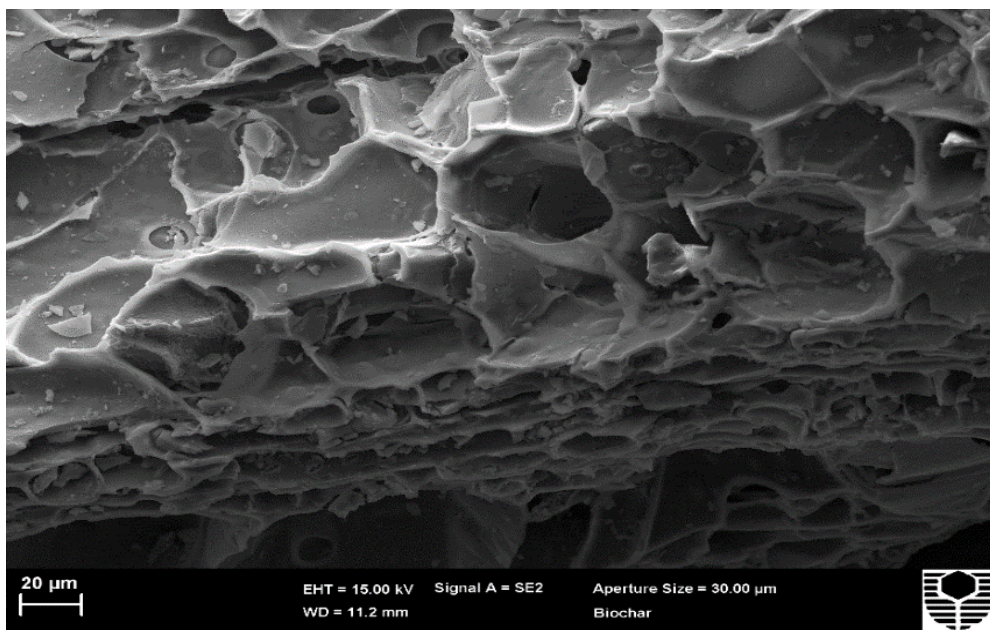


Fig. 6.5 Scanning electron microscopy (SEM) image of *EW* biochar

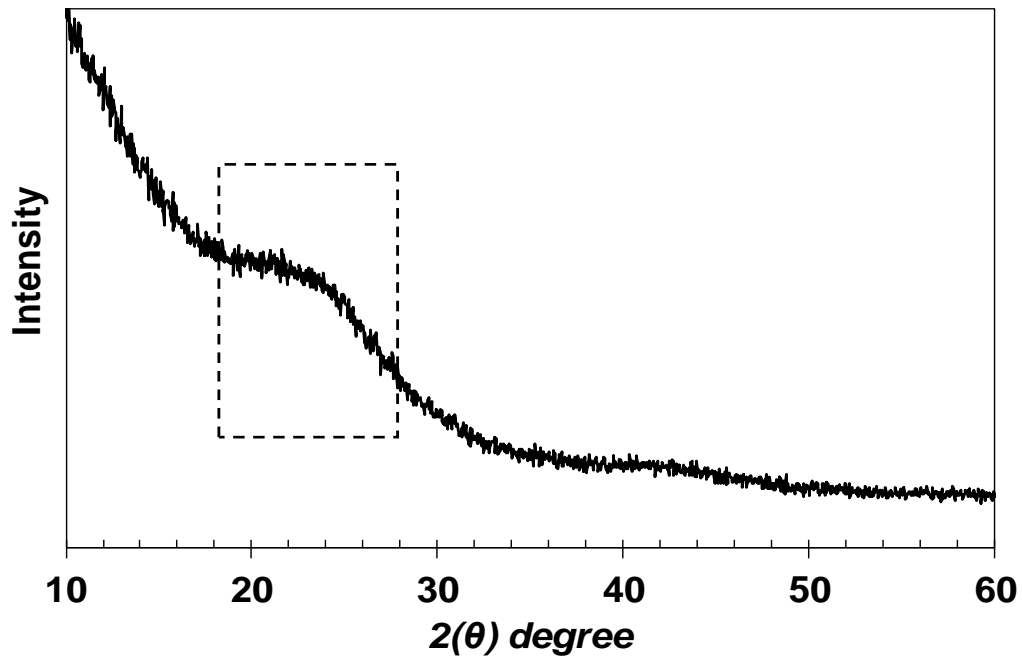


Fig. 6.6 X-ray diffraction (XRD) patterns of *EW* biochar

6.3.2 Adsorption of nitrogen species onto *EW* biochar

6.3.2.1 The effect of concentration and contact time

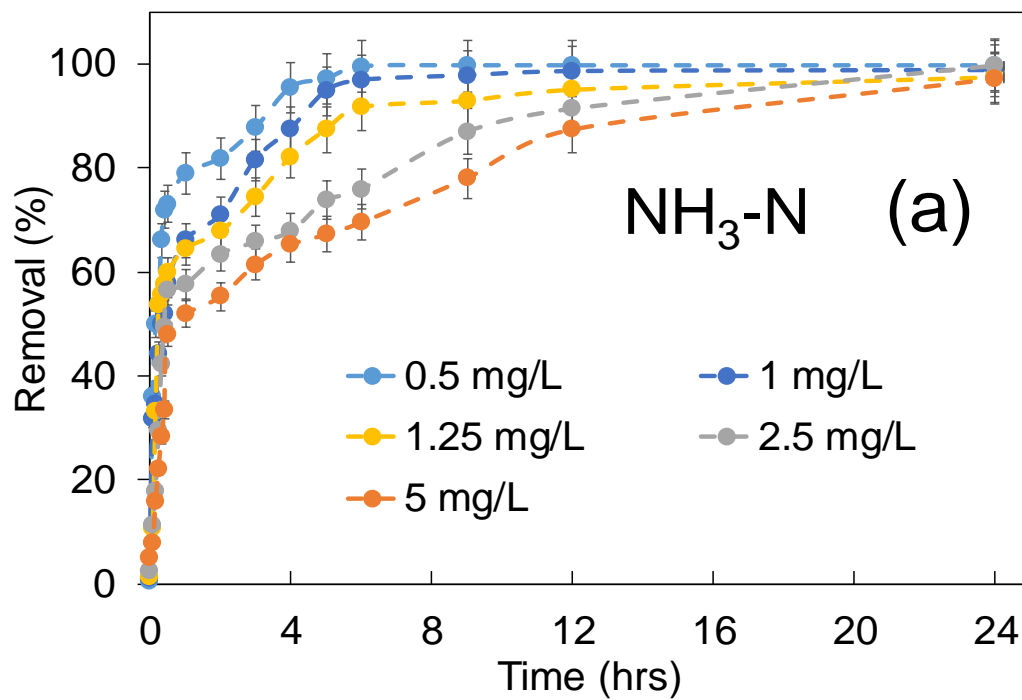
The adsorption process may be defined as the bond of atoms/molecules of multi-components through physical or chemical attraction forces onto the surfaces of solid adsorbent (Foo and Hameed, 2010). Therefore, in this study the most suitable adsorption isotherm model was determined in order to quantify the adsorption capacity of biochar. The adsorption models would also enable prediction of adsorbent performance under different conditions via quantitative comparisons with other adsorbent materials as reported in previous studies (e.g., Harmayani and Anwar, 2016; Foo and Hameed, 2010).

In order to determine the adsorption characteristics of biochar for $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$, a series of batch adsorption tests was conducted at different initial concentrations between 0.5- 5 mg/L at constant pH (6.5 ± 0.5) at a dosage of 10 gm biochar of particle size 2.36 mm. The removal of $\text{NO}_3\text{-N}$ was found negligible (<1%) in all experiments. This was due to the lower pyrolysis temperature (400°C) used to produce the *EW* biochar (Yao et al. 2012; Mizuta et al. 2004). Yao et al. (2012) found the removal of $\text{NO}_3\text{-N}$ was higher for biochar made at higher temperature 600°C

(0.12%-3.7%, Table 1). Mizuta et al. (2004) also reported that bamboo biochar made at 900°C had relatively higher NO₃-N adsorption capacity even compared to a commercial activated carbon. Therefore, the results of NO₃-N are not presented further in this thesis. The effects of initial concentration and contact time on removal of NH₃-N and NO₂-N are shown in Fig. 6.7(a-b). Faster removal was observed for both of these N species at the beginning of experiments. In first one hour of experiment with 0.5 mg/L concentration, 79% removal of NH₃-N and 91% removal of NO₂-N were observed. The removal percentage was eventually increased to 100% at its equilibrium condition after 12 hrs for these initial concentrations and maximum contact times. Harmayani and Anwar (2016) showed 100% removal of NO₂-N but 55% removal of NH₃-N when raw sawdust of radiata pine was used as the adsorbent. The increase of NH₃-N removal in this study may be due to the difference in wood species, particle sizes and also the preparation process (i.e., pyrolysis process for biochar). However, the maximum removal (>90%) of NO₂-N was found to be 3-4 times faster than NH₃-N at lower concentration (0.5-1.25 mg/L) as shown in Fig. 6.7(a) -(b). This may be due to cation exchange facilitating the adsorption of the ionized ammonia from aqueous phase to the solid phase (Vymazal, 2007; Reddy et al., 2014a). This is confirmed by increased adsorption of NH₃-N at pH 4.0, decreasing as pH increased to 8.0 (Section 3.2.3). The ammonia species adsorbed onto the solid phase remain in free form and can readily be desorbed back into the aqueous phase if any change in concentration occurs in the aqueous phase (i.e. to retain the equilibrium between sorbed and aqueous NH₃-N). A certain amount of NH₃-N is adsorbed onto biochar to saturate the empty sorption sites for a given concentration of NH₃-N. However, the NH₃-N concentration in the aqueous phase may decrease due to nitrification. Hence, a portion of the sorbed NH₃-N will desorb to regain the chemical equilibrium and the aqueous phase concentration will change. This may partly explain the slower removal rate of NH₃-N when compared with NO₂-N.

The removal rate with initial concentrations above 2.5 mg/L was lower for both contaminants. A one-way ANOVA analysis also confirmed that there was significant difference ($p > 0.01$) of removal efficiency among different initial concentrations of NH₃-N with respect to time but no significant variation ($p < 0.01$) was found for NO₂-N at the 1% significant level. The maximum adsorption capacity increased (5-50 µg/g) with increasing concentration (0.5-5 mg/L) because of higher availability of

nitrogenous ions in the solution for both contaminants (Fig. 6.7c). Concentration provides an important driving force to overcome the mass transfer resistance of ions between aqueous and solid phase (Harmayani and Anwar, 2016). There is therefore a higher probability of collision between the ions and biochar surface due to the higher numbers of nitrogenous ions that are present at the higher concentrations. Similar results were attributed for ammonium sorption by poultry litter and wood biochar (Sun et al., 2013) and $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ sorption by sawdust (Harmayani and Anwar, 2016). No significant difference ($p < 0.01$) was observed in ANOVA analysis (1% significance level) for the adsorption capacities of both contaminants for different initial concentrations.



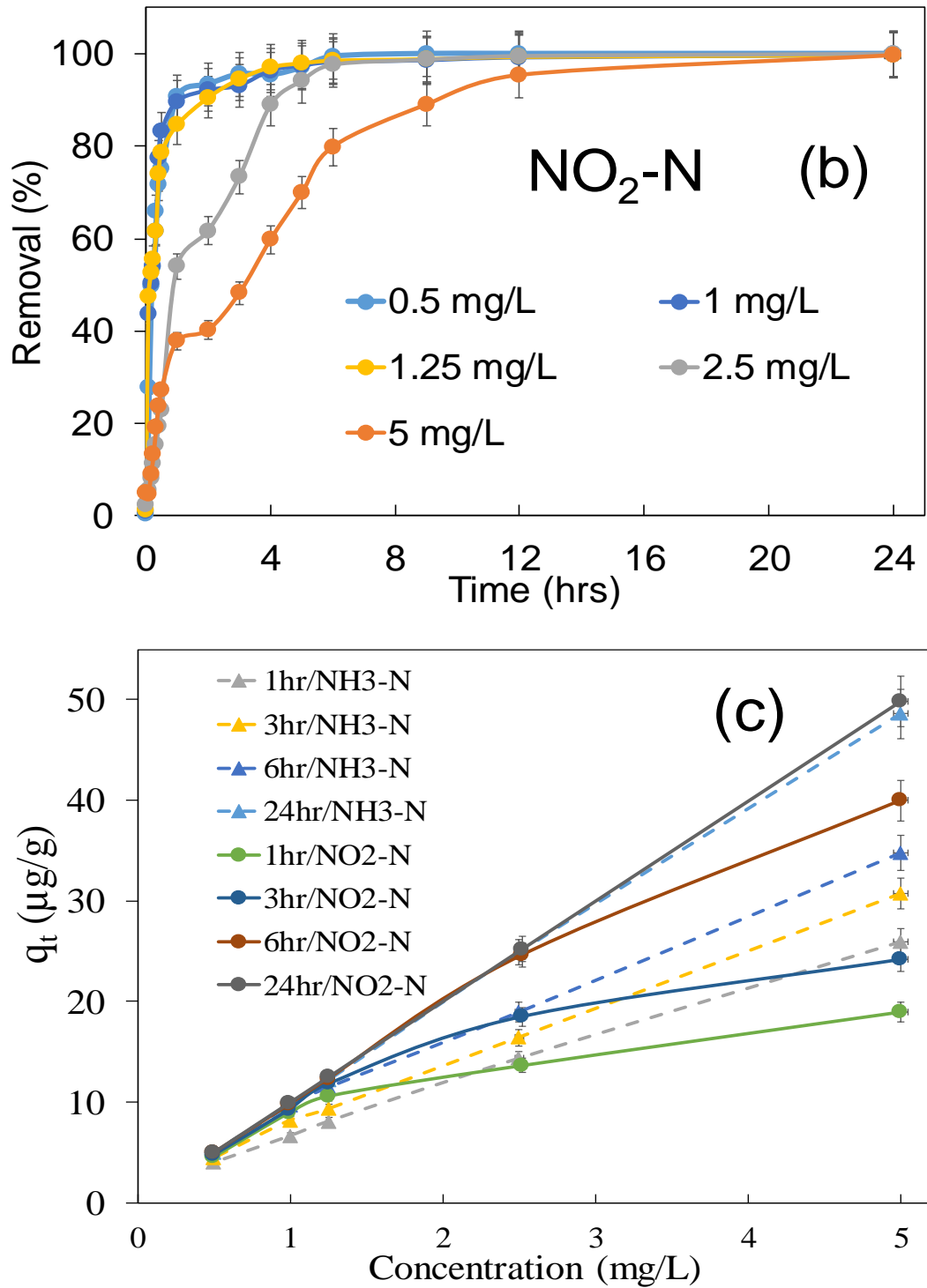
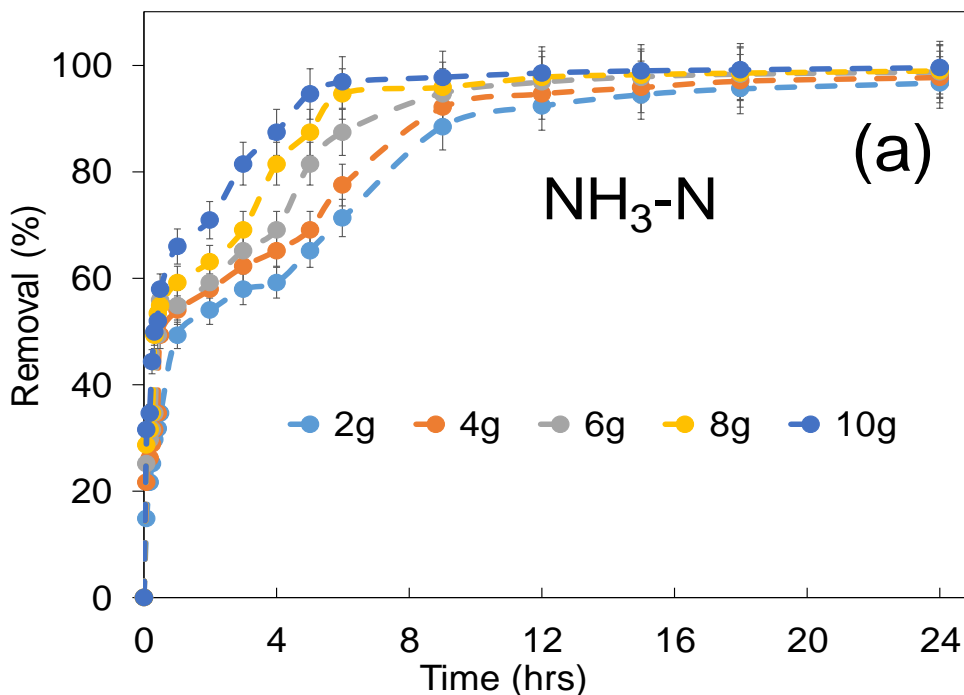


Fig. 6.7 (a-b) The effects of initial concentration and contact time on (a) NH₃-N and (b) NO₂-N removal, (c) Adsorption of NH₃-N and NO₂-N onto *EW* biochar (µg/g) [C₀: 0.5-5 mg/L; dose of *EW* biochar: 10 gm; particle size: 2.36 mm; T: 22±2°C; shaker speed: 100 rpm; P^H: 6.5±0.5]

6.3.2.2 The effect of adsorbent dosage

The effect of adsorbent dosages (2-10 g of 2.36 mm) on nitrogen removal was investigated with constant initial concentration (1 mg/L) and the results are shown in Fig. 6.8 (a-b) for $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ removal. Increasing doses increased the surface area and therefore the adsorption sites and as a result, improved the removal process. The increasing rate of removal was faster for $\text{NO}_2\text{-N}$ adsorption than for $\text{NH}_3\text{-N}$ for all dosages. The removal efficiency over 1 hr increased from 57.2 to 89.7% and 49.4 to 66.2% for $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ adsorption respectively with an increase of biochar dosage from 2 to 10 gm. However, the adsorption capacity showed a decreasing trend with biochar dosage (Fig. 6.8c). This is because of less availability of nitrogen ions per unit mass of biochar when the initial biochar concentration remained constant. These observations are consistent with those of Sun et al. (2013) for methylene blue adsorption with biochars derived from Eucalyptus, palm bark and anaerobic digester residue (Table 6.1). Babu and Gupta (2008) also found similar results for adsorption of methylene blue for an increasing dosage of 2 to 8 gm. ANOVA analysis (1% significance level) confirmed significant variation ($p > 0.01$) in removal efficiency but no significant difference ($p < 0.01$) for adsorption capacity for increasing dosage (2-10 gm).



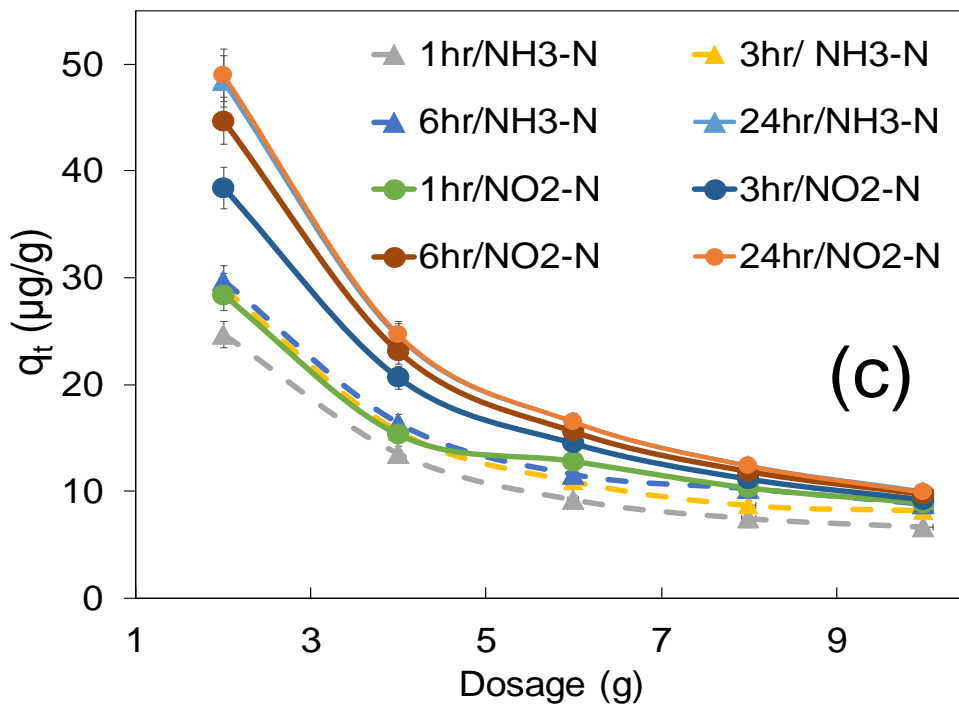
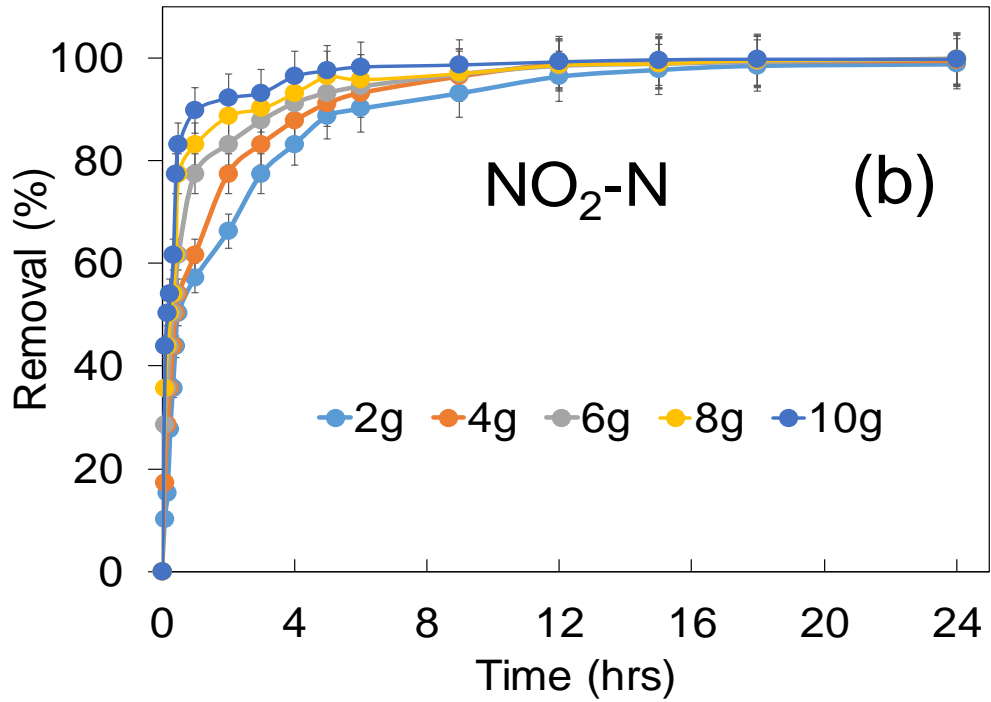


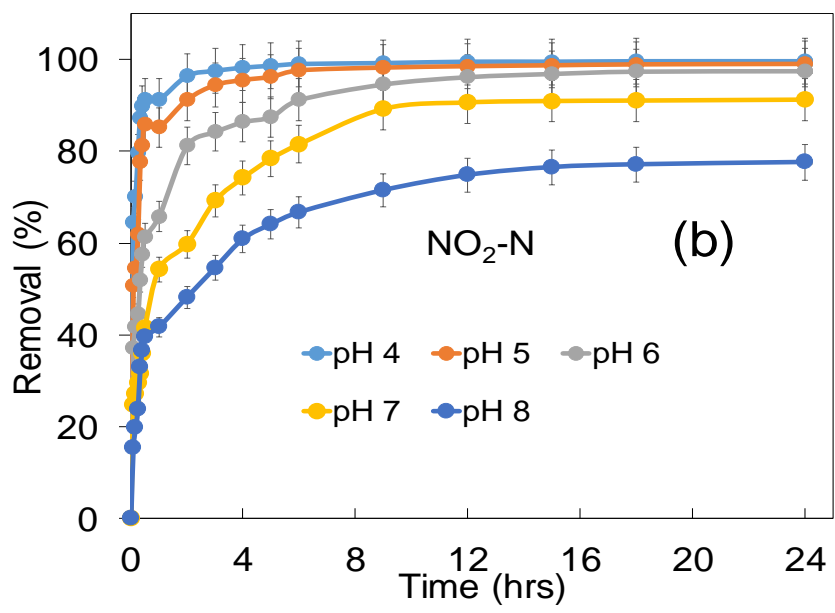
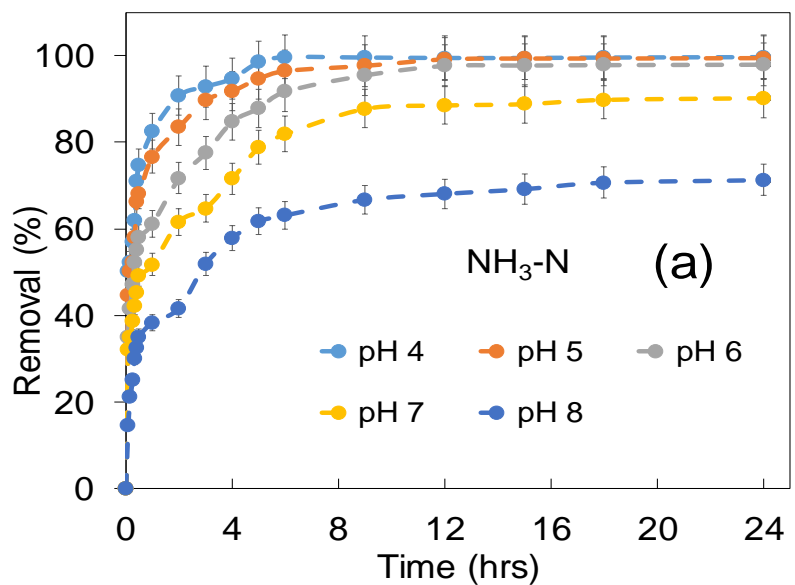
Fig. 6.8 (a-b) The effect of dosages and contact time on the removal of NH₃-N and NO₂-N, (c) Adsorption of NH₃-N and NO₂-N onto *EW* biochar (µg/g). [*C*₀: 1 mg/L; doses of *EW* biochar: 2-10 gm; particle size: 2.36 mm; T: 22±2°C; shaker speed: 100 rpm; P^H: 6.5±0.5]

6.3.2.3 The Effect of pH

Biochar contains surfaces that are charged, with the charge dependent on the pH of the solution (Ahmad et al., 2014) and thus the relative effect of ionic strength on adsorption onto these surfaces is also pH dependent. In general, the effect of ionic strength on adsorption onto biochar can be positive or negative depending on pH or pHPzc (point of zero charge) of the biochar. Therefore, it is important to observe the effects of solution pH and pHPzc on adsorption to understand its mechanism. The impact of pH on adsorption is dependent on biochar type and the contaminants of interest because it influences the adsorbent surface charge, as well as the level of ionization and speciation of the adsorbate (Li et al., 2013). Biochar carries surface functional groups, largely carboxylate (-COOH) and hydroxyl (-OH) as evidenced by the FTIR analysis (see SI). The characteristics of these surface groups change as solution pH changes. Many of the functional groups on biochar (carboxylate and phenolate) may become protonated and positively charged at lower pH (Sun et al., 2013).

The effect of solution pH on NH₃-N and NO₂-N removal is shown in Fig. 6.9(a-b). The pHPzc for this biochar was 5.2 (Table 6.1). The effect of pH (4-8) was investigated with an initial concentration of 1 mg/L and a biochar dosage of 2 g. While the solution pH < pHPzc, the biochar surface is positively charged which promotes the adsorption of the anions (i.e. NO₂-N) due to electrostatic attraction (Oh et al., 2012; Abdel-Fattah et al., 2015). Fig. 6.9(a-b) shows that lower pH values (4-5) achieved a higher percentage of removal in comparison to higher pH values (6-8) indicating the role of electrostatic repulsion between negatively charged adsorbent and anionic adsorbate at pH > 5. This was also clearly observed in terms of the adsorption capacity of biochar shown in Fig. 6.9(c-d). The decrease in removal with increasing pH may be also explained as the increase of OH⁻ competition for NO₂-N species for the adsorption sites of biochar and electrostatic repulsion on adsorption. The increase in removal for pH < pHPzc may be attributed to the strong electrostatic interaction between positively charged functional group of biochar and negatively charged NO₂-N (Abdel-Fattah et al., 2015). Similar results were obtained by Oh et al. (2012) using orange peel and water treatment sludge biochar and Dong et al. (2011) using sugar beet tailing biochar for the adsorption of negatively charged fluoride and chromate ions respectively. The

optimum pH for nitrogen removal was found to be 4-5 with a removal of 45-65% within 5 mins and decreased 23-30% at pH 8 for NH₃-N and NO₂-N respectively. Nazari et al. (2017) also showed that at pH<8, the NH₃-N mostly converts into NH₄⁺-N. They found a sharp increase of NH₄⁺-N removal and generation of NH₃-N at pH above 8.3 due to substitution of carboxylic group of raw brown coal. ANOVA analysis (1% significance level) confirmed significant variation (p>0.01) in adsorption between NH₃-N and NO₂-N but no significant difference (p<0.01) was found for variation in pH (4-8). It is interesting to note that the adsorbate and adsorbent in suspension have no charge at pHPzc (5.2) but still the adsorption is continuing, suggesting some other factors may affect the removal process (e.g., ion inclusion into pores and/or surface precipitation as discussed in Section 6.3.5).



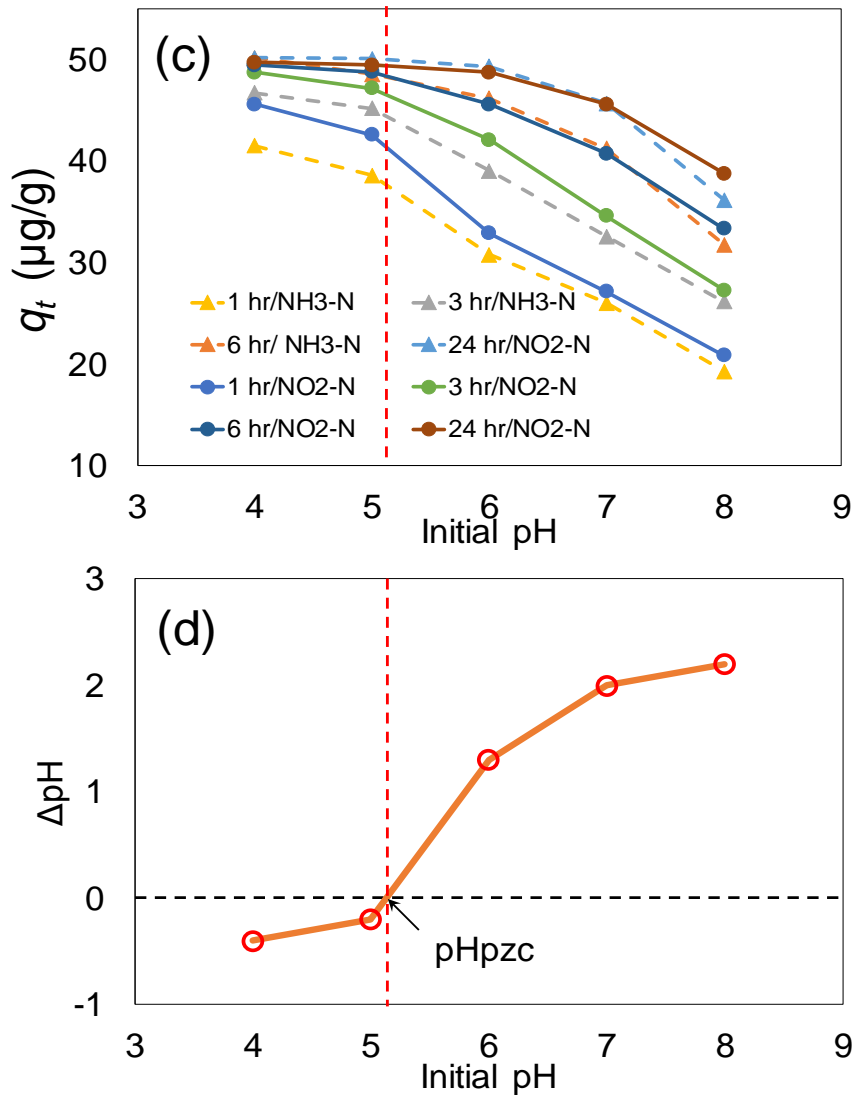
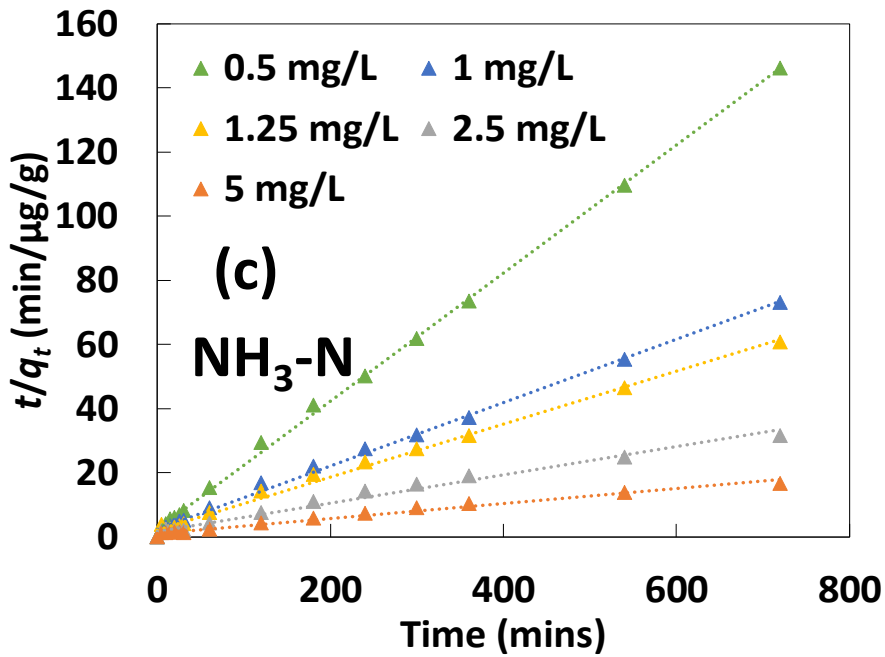
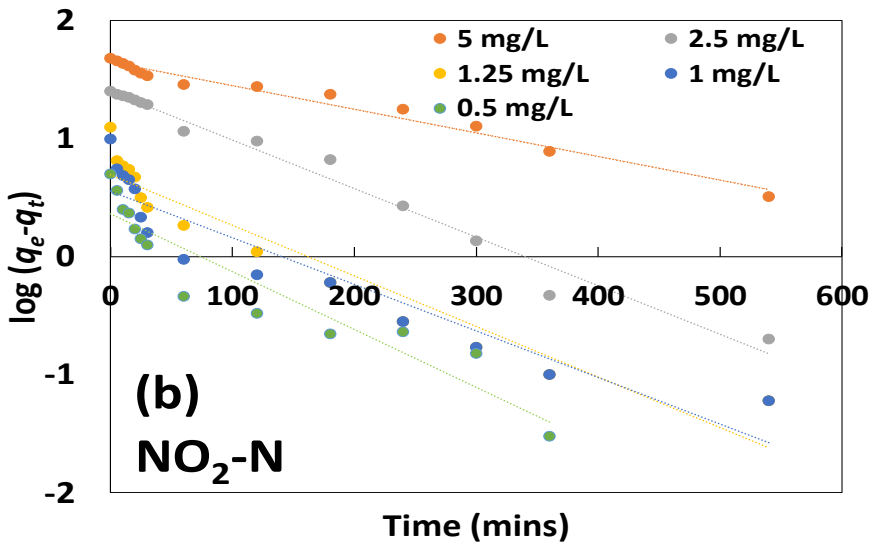
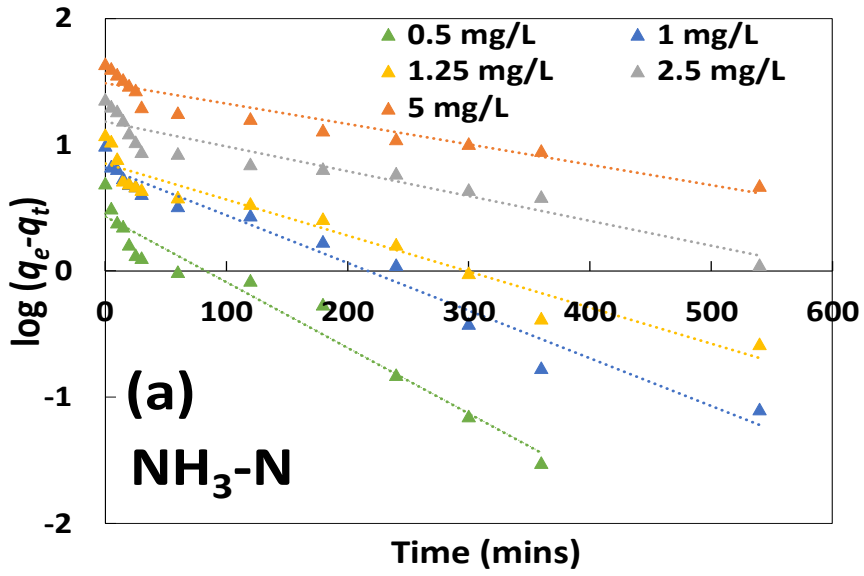


Fig. 6.9 (a-b) The effect of pH on $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ removal and (c) Point of zero charge (pH_{pzc}) of *EW* biochar and (d) adsorption of $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ at different pH level. [C_0 : 1 mg/L; dose of *EW* biochar: 10 gm; particle size: 2.36 mm; T: $22 \pm 2^\circ\text{C}$; shaker speed: 100 rpm; P^{H} : 4-8]

6.3.3 Adsorption kinetics

The physical and/or chemical characteristics of biochar strongly affect the adsorption kinetics. The results of adsorption kinetics influence adsorption mechanisms that involve mass transport and chemical reaction processes (Harmayani and Anwar, 2016). The adsorption of $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ onto *EW* biochar reached equilibrium after 12 hrs and therefore the batch test data prior to 12 hrs was used to fit pseudo first and second order kinetics using Eq 6.4 and Eq 6.5, respectively. The model parameters

are presented in Table 6.3 and the fitted graphs are included in Fig. 6.10. The fitted regression coefficients of the pseudo second order kinetic model for both species ($R^2 = 0.9673-0.9998$) were higher than the pseudo first order kinetic model ($R^2 = 0.8846-0.9812$). Again, the normalized standard deviation (Δq , Eq. 6.6) for the pseudo first order kinetics were ($\text{NH}_3\text{-N}$: 14.8-22.5%; $\text{NO}_2\text{-N}$: 0.76-32.0%) higher than those for the pseudo second order kinetic equation ($\text{NH}_3\text{-N}$: 0.29-1.27%; $\text{NO}_2\text{-N}$: 0.45-9.57%). Based on the high R^2 and low Δq values, both $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ adsorption were found to follow the pseudo second order model. The pseudo first order kinetic model was based on the assumption that physical adsorption and the solute uptake rate with time is directly proportional to the ratio of the solute concentration and the amount of solid (Shawabkeh and Tutunji, 2003). On the other hand, the pseudo second order kinetic model relies on the assumption that the rate-limiting step may be chemical sorption or chemisorption comprising valence forces through sharing or exchange of electrons between sorbate and sorbent (Ho and McKay, 1998). This indicates the nitrogen ions were adsorbed onto the biochar mostly associated with chemical reactions. The adsorption for the pseudo second order kinetic model increased from 5.01 to 43.1 $\mu\text{g/g}$ and 5.08 to 53.19 $\mu\text{g/g}$ for $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ respectively when increasing the initial concentration from 0.5 to 5 mg/L. However, the values of kinetic rate constants were decreased for both $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ adsorption with increasing initial concentrations. This may occur due to the large number of $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ ions interacting with one another in solution rather than adsorbing onto the biochar. The large variation in the observed rate constants with increasing initial concentration of adsorbate indicated that the adsorption process is very complex and multiple adsorption processes may occur simultaneously, as suggested in Section 6.3.5.



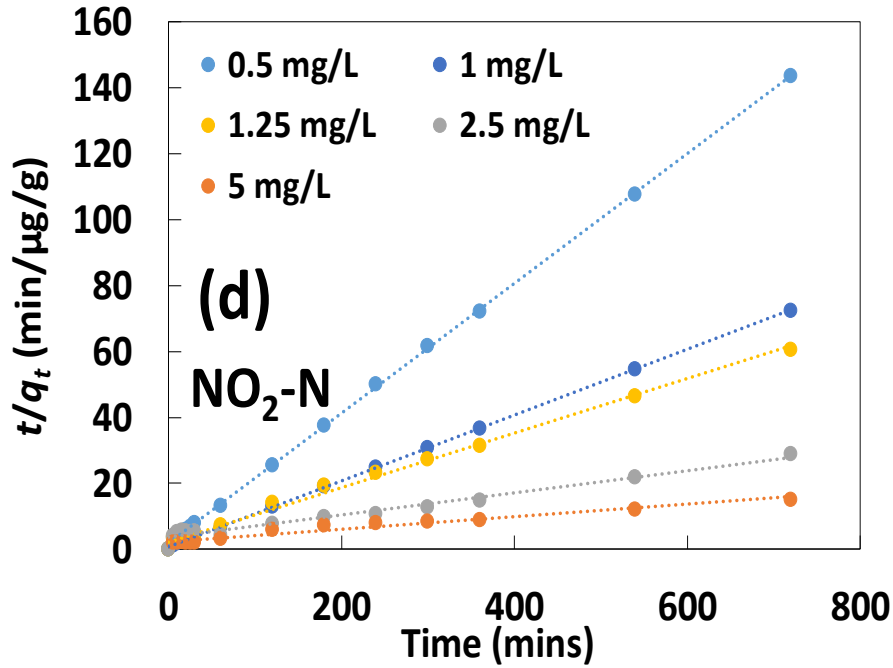


Fig. 6.10 Pseudo first and second order plots of nitrogen adsorption onto *EW* biochar. [C_0 : 0.5-5 mg/L; dose of *EW* biochar: 10 gm; particle size: 2.36 mm; T: $22\pm 2^\circ\text{C}$; shaker speed: 100 rpm; P^{H} : 6.5 ± 0.5]

Table 6.3 Kinetic parameters of the pseudo first and pseudo second order kinetic models

Nutrient	C_0 (mg/L)	$q_{e, \text{exp}}$ ($\mu\text{g/g}$)	pseudo-first order				pseudo-second order			
			$q_{e, \text{cal}}$ ($\mu\text{g/g}$)	K_1 (1/min)	R^2	Δq (%)	$q_{e, \text{cal}}$ ($\mu\text{g/g}$)	K_2 (g/mg min)	R^2	Δq (%)
$\text{NH}_3\text{-N}$	0.5	4.93	2.70	0.0119	0.9539	22.5	5.01	0.0165	0.9991	0.68
	1	9.86	6.58	0.0087	0.9690	16.6	10.1	0.0042	0.9967	0.29
	1.25	11.9	7.10	0.0067	0.9352	20.1	12.1	0.0032	0.9950	0.89
	2.5	22.8	15.2	0.0046	0.8966	16.7	22.7	0.0012	0.9925	1.27
	5	43.7	30.7	0.0036	0.8952	14.8	43.1	0.0005	0.9879	0.68
$\text{NO}_2\text{-N}$	0.5	5.01	2.31	0.0112	0.8867	26.9	5.08	0.0198	0.9997	0.68
	1	9.92	3.57	0.0089	0.8846	32.0	10.02	0.0120	0.9998	0.45
	1.25	11.9	4.94	0.0099	0.9209	30.1	12.09	0.0032	0.9950	0.89
	2.5	24.8	25.2	0.0094	0.9812	0.76	29.59	0.0003	0.9673	9.57
	5	47.7	44.5	0.0046	0.9761	3.31	53.19	0.0002	0.9616	5.74

6.3.4 Adsorption isotherms

The adsorption equilibrium data were analysed using Langmuir and Freundlich models and the isotherm parameters were calculated using Eq 6.7 and 6.9 and the results are presented in Table 6.4. The results revealed that the adsorption of both species follow Langmuir model ($R^2=0.93-0.98$) better than Freundlich model ($R^2=0.86-0.96$). The maximum Langmuir adsorption capacities (q_m) for $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ were found to be 36.49 and 41.15 $\mu\text{g/g}$ respectively. The K_L values in Langmuir model was found very high ($K_L > 1$) for both species indicating the high adsorption process. However, n_F value is lower than 2 for both species shows a complexity adsorption characteristic. The better fit of the Langmuir model from the experimental data showed that the adsorption was predominantly monolayer adsorption, which comprises both chemical and physical mechanisms. This observation is in agreement with previous studies such as methylene blue adsorption onto biochar prepared from eucalyptus, palm bark, anaerobic digester residue (Sun et al., 2013) and also onto activated carbon prepared from hazelnut husks (Ozer et al., 2012), rotten saw dust (Hameed et al., 2007). Harmayani and Anwar (2016) also indicated similar characteristics for the adsorption of nitrogenous species onto Radiata pine saw dust.

Table 6.4 Langmuir and Freundlich isotherm constants

Nutrient	Langmuir constants			Freundlich constants		
	q_m ($\mu\text{g/g}$)	K_L	R^2	K_F	n_F	R^2
$\text{NH}_3\text{-N}$	36.49	6.3	0.98	62.53	1.47	0.96
$\text{NO}_2\text{-N}$	41.15	3.62	0.93	186.17	0.87	0.86

The adsorption intensity (R_L) with initial concentration 0.5-5 mg/L of aqueous solution was calculated by Eq 6.8 and shown in Fig. 6.11. The value of R_L in the range $0 < R_L < 1$ at all initial concentrations confirms favourable adsorption (Babu and Gupta, 2008). These results indicate that the biochar may be used as a cost-effective medium for removing $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ from aqueous solution such as stormwater and/or wastewater.

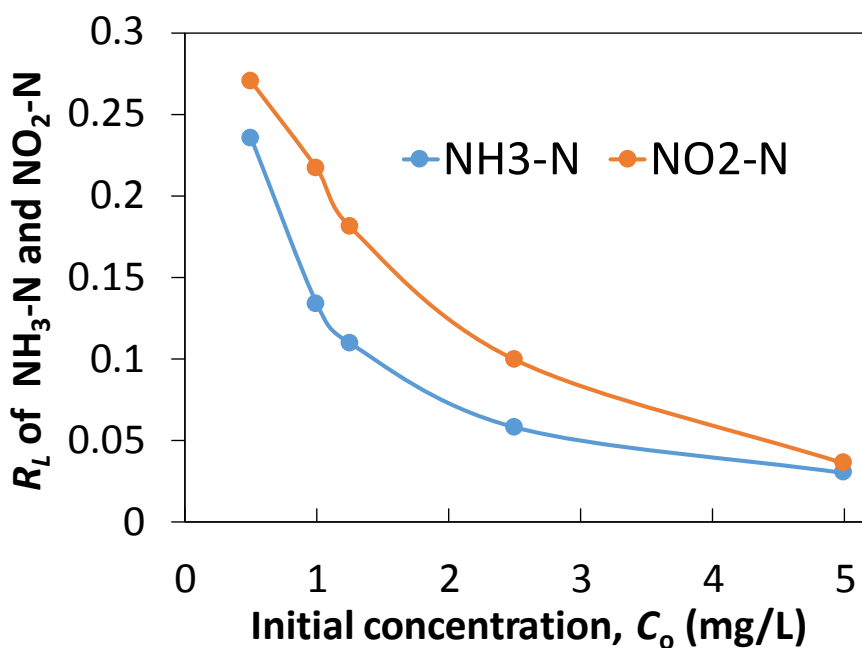


Fig. 6.11 Variation of adsorption intensity (R_L) with initial concentration

6.3.5 Adsorption mechanism

The various mechanisms that may be occurring in the interaction of biochar with $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ are summarized in Fig. 6.12. The most important physical properties of biochar which might govern the $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ retention are its surface area, pore size and pore structure. For example, a material having a larger pore diameter is likely to retain a higher amount of moisture and hence a lower amount of $\text{NH}_4^+\text{-N}$ (Sarkar and Naidu, 2015). The biochar used in this study has a surface area two to three times larger and a micro pore volume four times larger than other Eucalyptus biochar pyrolysed at the same temperature (Table 6.1). The characteristics of surface area and pore size were found to be important for sorption of $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ onto *EW* biochar (Lou et al., 2011). The *EW* biochar produced at higher temperature (400°C) has high surface area and micro-area development which is more effective for adsorption due to its porous carbonized fractions (Ahmad et al., 2012).

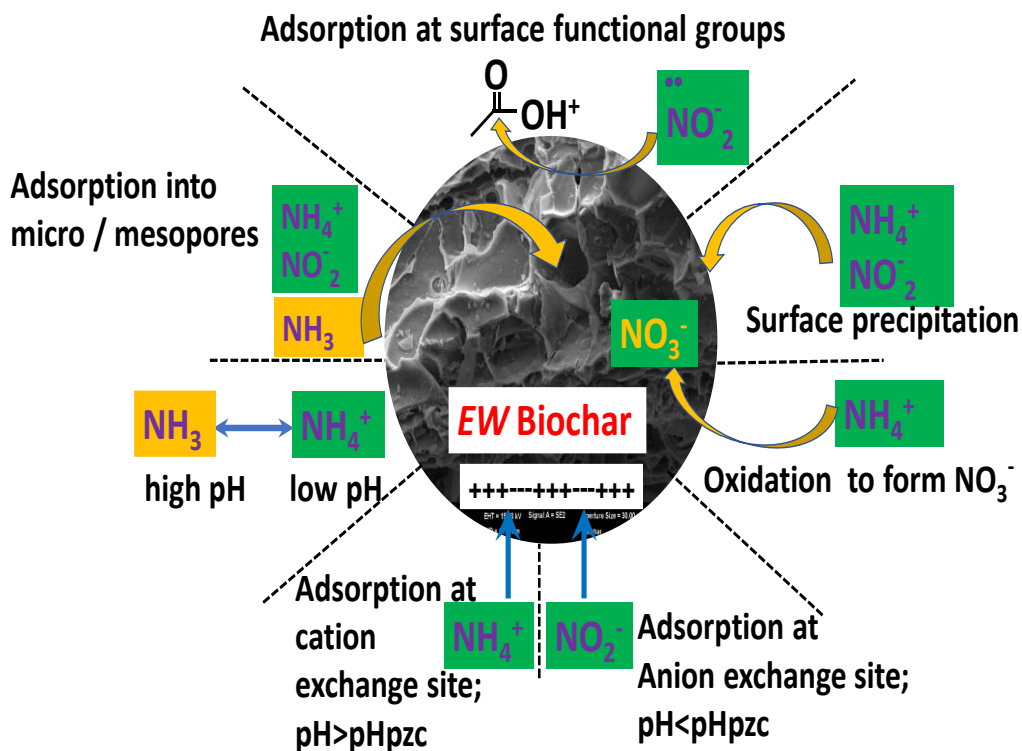


Fig. 6.12 Schematic diagram illustrating the mechanisms between solid (biochar) and contaminants ($\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$) phases.

The surface charge of biochar and anionic nature of adsorbate may be other factors in the adsorption process. Fig. 6.9 (c-d) showed that the electrostatic attraction/repulsion between anionic $\text{NO}_2\text{-N}$ and biochar is another possible adsorption mechanism. The biochar surfaces are positively charged when $\text{pH} < \text{pHPzc}$, which could facilitate the electrostatic attraction of negatively charged anionic compounds. However, both electron rich and electron poor functional groups are present in high temperature derived biochar; therefore, they are theoretically capable of interacting with both anions and cations (Sun et al., 2012). $\text{NH}_3\text{-N}$ is largely present as the ammonium ion (NH_4^+) under the conditions of the experiment, although around 5% would be in the form of NH_3 under the highest pH used in this study (pH 8.0). Under these conditions NH_3 may be adsorbed within meso/micro pores in the biochar. NH_4^+ would be adsorbed by negatively charged species

An electrostatic repulsion between negatively charged anionic compounds and biochars could promote H-bonding and induce adsorption. This phenomenon was

described by Teixido et al. (2011). The anionic sulfamethazine adsorption on hardwood derived biochar produced at 600°C was presented in their study. Hydrogen bonding may occur between NO₂-N and carboxylate or phenolate groups available on biochar (Teixido et al., 2011). Inclusion of both NO₂-N and NH₃-N into micro and meso pores, as well as adsorption onto cation and anion exchange sites could occur at pH_{pzc} > 5.2 (as shown in Fig. 6.9 (c-d)), explaining the continued removal of these compounds at the higher pH values. NO₂-N removal capacity was slightly higher than that of NH₃-N, possibly because the biochar has a higher abundance of positively charged functional groups at low pH (ROOH⁺).

The results can be explained that functional groups on surface of biochar were involved in providing active sites for NH₃-N and NO₂-N binding (Suksabye et al., 2009). The NH₃-N and NO₂-N were bound to the biochar surface through complexation and precipitation (Hsu et al., 2009) or released into the solution (Yue et al., 2009).

This novel adsorbent material (*EW* biochar) studied in this research shows its potential use in removing NH₃-N and NO₂-N from stormwater and/or wastewater but the same biochar may not be suitable for NO₃-N removal. In order to check for NO₃-N removal, *EW* biochar produced through higher pyrolysis temperature (>600°C) is recommended. The *EW* biochar (pyrolysis temperature 400°C) used in this study may be used in bio-retention ponds and/or catch basin inserts for removing dissolved NH₃-N and NO₂-N from stormwater. Since biochars are secondary waste materials produced from bio-energy production the use of biochar for stormwater/wastewater treatment will open a new window for sustainable water management using green media. However, this research is limited to batch experiments only and further investigations are required for its field application in treating wastewater/stormwater.

6.4 Conclusion

The surface characteristics of *EW* biochar made it a good choice for removing NH₃-N and NO₂-N from wastewater/stormwater because of its mesoporous structure and larger irregular amorphous carbon surfaces. Adsorption of nitrogen species onto *EW* biochar was checked in batches and found 100% removal of NH₃-N and NO₂-N while

NO₃-N adsorption shown negligible removal (<1%). The higher removal was achieved using low concentrations of adsorbate and high dosages of biochar under the most suitable pH of 4-5. Kinetic studies showed both NH₃-N and NO₂-N following the pseudo second order model. Isotherm studies showed that Langmuir model fit better for both species than Freundlich model. The *EW* trees are abundant, and a huge amount of *EW* wood wastes are produced in the wood industry which can be reused for bio-energy leaving biochar as by-product. This *EW* biochar can be used as a low-cost adsorbent for treating wastewater and/or stormwater.

List of notations

<u>Notations</u>	<u>unit</u>
C_0 :	initial concentration mg/L
C_e :	equilibrium concentration mg/L
V :	volume of solution L
W :	weight of biochar gm
C_t :	concentration at specific time mg/L
q_t :	amount of adsorption at specific time μg/g
q_e :	equilibrium adsorption μg/g
q_m :	maximum capacity constant of adsorbent for adsorbate μg/g
q_{exp} :	experimental adsorption capacity μg/g
q_{cal} :	calculated adsorption capacity μg/g
pH_{PZC} :	point of zero charge dimensionless
K_L :	Langmuir constant dimensionless
R_L :	adsorption intensity dimensionless
K_F :	Freundlich constant for adsorption capacity mg/g
n_F :	Freundlich constant for adsorption intensity dimensionless
K_1 :	first order adsorption reaction constant 1/min
K_2 :	second order adsorption reaction constant g/mg h
Δq :	normalized standard deviation %
ΔpH :	difference between the initial and final pH value
i :	number of data points

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CHAPTER 7

REMOVAL OF NITROGEN AND PHOSPHOROUS SPECIES FROM WATER USING *EUCALYPTUS WANDOO* BIOCHAR AND ALUM SLUDGE

Abstract

The mixture of *Eucalyptus Wandoo* (*EW*) biochar and dewatered alum sludge was used as adsorbents to remove nitrogen and phosphorous species from aqueous phase. The characterization of alum sludge was carried out by Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS) and N₂ adsorption-desorption isotherms. The surface area, pore diameter and micropore volume of alum sludge was found 179.13 m²/gm, 8.66 nm and 0.3276 cm³/g respectively and they were 7, 2 and 14 times higher than the *EW* biochar respectively. The feasibility of *EW* biochar and dewatered alum sludge for nitrogen and phosphate removal was tested in batch experiments and the maximum percentage removal was found 98.2%, 99.4% and 99.8% for NH₃-N, NO₂-N and PO₄-P respectively for 1 mg/L. The maximum removal was decreased by 10% and 8% for NH₃-N and NO₂-N respectively for increasing initial concentration from 1 mg/L to 5 mg/L but no drop was found for PO₄-P for all concentration. The percentage removal of PO₄-P was found >90% within 5 minutes of commencement of experiment for all concentrations whereas NO₂-N and NH₃-N took 2 and 4 hours respectively for 1 mg/L. The maximum adsorptions for NH₃-N, NO₂-N and PO₄-P were increased from 6.15-55.22 µg/g, 6.21-57.64 µg/g, 25.41-246.1 µg/g respectively for increasing initial concentrations 0.5 to 5 mg/L. Pseudo second order model was the most suitable to describe the adsorption kinetics of all nutrients. The adsorption of NH₃-N followed both Langmuir and Freundlich model, but NO₂-N and PO₄-P fitted better with Freundlich than Langmuir model.

Keywords: Adsorption; biochar; alum sludge; nutrients; water quality

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7.1 Introduction

Stormwater pollution originates from point and non-point sources. Point sources include the pipe or drain discharge of industrial waste or stormwater and non-point sources include stormwater runoff from large areas such as highways, parking bays or agricultural land (Hvitved et al., 2010). Stormwater runoff contains variety of pollutants including heavy metals, polycyclic aromatic hydrocarbons (PAHs), nutrients, suspended solids and microorganisms (Reddy et al., 2014b). High amount of nutrients (nitrogen and phosphorous species) in catchment runoff will result in eutrophication which is caused by rapid algae growth due to the excessive amount of nutrients being discharged into the local water reservoirs (Alam et al., 2017a). As a result, rapid consumption of dissolved oxygen by the increased algae will endanger marine ecosystems. The Cooperative Research Centre (CRC) for catchment hydrology has discovered that the gross pollutant in stormwater falls in the range of 20-40 kg/ha/yr in typical Australian urban areas (Chiew et al., 1997) which is also a source of nutrients into receiving water bodies (Alam et al., 2017a). “Nutrient run-off from agricultural land represents the largest source of nutrients entering estuaries in south-west Western Australia threatening the health of estuaries in the region. The challenge of sustaining productive agriculture and healthy estuaries is shared by farmers, catchment managers and industry. New and innovative approaches and ways of working together will be necessary to achieve healthy estuaries alongside thriving agriculture” (Polyakov et al., 2014). Major concerns in terms of public health and environment were raised as stormwater is recycled and reused in Australia. Therefore, the implementation of bioaugmented materials into in-ground permeable reactive filter (PRF) has been considered to improve water quality for a sustainable future.

Various types of best management practices (BMPs) such as dry extended detention basins, wet/retention basins, constructed wetlands, infiltration trenches, grass swales and bioretention systems are used to remove suspended solids, heavy metals and nutrients from stormwater (Alam et al., 2017a; Reddy et al., 2014b). Bioretention systems in particular, categorized as an infiltration practice, are gaining popularity due to their incorporation of both vegetative and filtration systems in the removal of pollutants from urban runoffs (Weiss et al., 2007). One of the limitations of BMPs include time limitations as the filtration process requires a certain amount of retention

time. Another limitation is spatial boundaries as it requires specified amounts of space for construction. Therefore, the application of BMP is not feasible in extreme weather conditions with unexpected peak flow of stormwater and in urban settings, which may result in flash floods (Reddy et al., 2014a; Trowsdale et al., 2011). Therefore, greater attention has been focused to find out the potentiality of in-ground permeable reactive filtration (PRF) systems for removing stormwater contaminants due to its compressed dimensions and its ability to allow sufficient flow in stormwater channels (Reddy et al., 2014b; Reddy et al., 2013). Synthetic polymers are currently being used as a filter material in most filtration system but not feasible due to depletion of natural resources such as petroleum. Therefore, wood chips, saw dust, rice husk, coconut fibre, and wood mulch etc. were studied as alternative biomaterials for filter media to remove contaminants from stormwater. On the basis of that biochar has been used for the removal of runoff contaminants (e.g. nutrients) in stormwater management practices. Previous research revealed that alum sludge is good for phosphorous adsorption (Yao et al., 2012; Yang et al., 2006). In this research, biochar and alum sludge will be mixed together for the first time to remove nitrogen and phosphorous simultaneously.

Biochar originates from the pyrolysis of solid wastes and alum sludge is produced by the coagulation process in water treatment plants as waste material (Sohi et al., 2010; Adhikari et al., 2016). The solid waste and alum sludge generally end up in landfill sites (Yang et al., 2006; Boving and Neary, 2004). Wood-derived biochar are produced from timber construction wastes. For example, *Eucalyptus wandoo* (*EW*) is a wood species commonly known as ‘white gum’, formerly harvested as a commercial source of tannin in Western Australia. *EW* is mainly used in both light and heavy construction such as flooring, finishes and poles (FPC, 2016). The increasing usage of *EW* in the construction industry has produced an abundant source of construction waste such as *EW* wood chips, wood shavings and wood pallets. One of the waste management strategies of timber is to conduct pyrolysis producing bioenergy and the by-product, biochar. Biochar is used in agriculture to increase the fertility of soil. Alum sludge is produced in large amounts by water treatment plant. Australian water authorities have reportedly produced an alarming 150 to 43,500 tons of alum sludge per annum (Maiden et al., 2015; Dassanayake et al., 2015). Victorian water industry, Australia was assessed that a total cost of \$6.2 million per annum required to dispose alum sludge into landfills and sewers (Maiden et al., 2015; Dassanayake et al., 2015).

Therefore, the use of *EW* biochar and alum sludge would decrease the cost of disposing alum sludge and timber construction wastes, reduce the land pollution and help to protect water resources. Hence, the biochar and alum sludge mix may be used in stormwater management for a sustainable future.

The objective of this research was to examine the adsorption characteristics of this mixed adsorbent to remove nutrients: nitrite ($\text{NO}_2\text{-N}$), dissolved ammonium ($\text{NH}_3\text{-N}$) and phosphate ($\text{PO}_4\text{-P}$) from synthetic stormwater. The quantification of adsorption capacity will help urban waterways managers to design and implement the stormwater treatment facilities in a cost-effective way.

7.2 Materials and method

7.2.1 Material selection

The *EW* biochar was collected from Energy Farmers Australia Pty Ltd in Geraldton, Western Australia (EFA, 2016) and the dewatered alum sludge were obtained from Neerabup ground water treatment plant, Perth, Western Australia. To get better adsorption a two-step method was applied to prepare the washed samples of biochar (Reddy et al., 2014a). Firstly, removal of fine particles via dry sieving and then removal of remaining fine particles through wet sieving with deionized water. However, only dry sieving method was followed for the alum sludge due to its drained-out possibilities during wet sieving. Solid samples (100-200g) were taken for sieve analysis (ISO 3310: BS 410-1:2000; sieve size 2.36 mm). The sieved samples were washed again with deionized water for 8-10 times to make it free from any impurities. 2 mL of washed water were analyzed after each washing for any possible nitrogen and phosphorus residues coming from biochar and dewatered alum sludge. After 6–7 washes, the nutrient content in the washed water was found negligible. Next, the samples were oven dried at 105°C for 48 hrs and stored in air-tight container at room temperature ($22\pm 2^\circ\text{C}$).

7.2.2 Synthetic stormwater preparation

The synthetic stormwater containing $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ was prepared as it is easy to control than the natural stormwater. NaNO_2 , NH_4Cl and NaH_2PO_4 were used

to prepare the stock solutions of $\text{NO}_2\text{-N}$, $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ respectively. The chemicals used in this study were bought from Thermo Fisher Scientific and Sigma-Aldrich, Australia and prepared to the required concentrations by chemical dilution based on Australian Runoff Quality and previous literatures (Alam et al., 2017a; Harmayani and Anwar, 2016; Wong, 2006). Fresh solutions were prepared before each experiment to avoid any possible deterioration in concentration. pH values were measured by a pH meter (HACH 40d with PHC 101 HAC electrode).

7.2.3 Characterisation of *EW* biochar and alum sludge

The characterization of alum sludge was carried by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and N_2 adsorption-desorption isotherms by following similar method as discussed in chapter 6. However, the characterization of biochar discussed in chapter 6.

7.2.4 Batch experiment

Batch experiments were conducted similar to Chapter 6. The experiments were carried out with varying concentrations of contaminants (0.5-5 mg/L) and exposure time of *EW* biochar/dewatered alum sludge and synthetic stormwater. As stormwater contains both nutrients (nitrogen and phosphorous) together, biochar and alum sludge with different proportion but same diameter (2.36 mm) was poured in Erlenmeyer flasks which contain 100 mL of the selected concentration of solutions. The initial pH values of solution were kept constant at $6.5(\pm 0.5)$ by adding 1 M NaOH and 1 M HCl. Aluminium foil was used to cover the opening of the flasks to protect any evaporation of the solution. The flasks were then placed on a 16-flask capacity shaking platform (Innova 2100, New Brunswick Scientific) and shaken at 100 rpm at room temperature ($22\pm 2^\circ\text{C}$). Then 2 mL of solution sample was extracting using a syringe and filtered through a $0.45\ \mu\text{m}$ syringe filter (GE Water and Process Technologies) from the flasks at a predetermined time interval of 5 to 60 minutes until the equilibrium concentration was reached. Each sample solutions concentrations were measured using AQUAKEM 200 water analyser (Labmedics Analytical Solutions; detection limit of 0.002 mg/L with a 1.5% measurement error at 95% confidence level). Duplicate/triplicate tests

were conducted to minimize the errors and the mean values were reported. Results that showed above 0.01 mg/L difference between duplicate samples were discarded.

The equilibrium adsorption and removal percentages of the adsorbents were calculated by following equations 6.1 and 6.2 in chapter 6.

7.2.5 Adsorption kinetics

The adsorption kinetics analysis was carried similar to chapter 6. The amount of contaminant adsorption onto the adsorbents at any given time was calculated by following equation 6.3. The pseudo-first-order and second model parameters were determined by equations 6.4 and 6.5 in chapter 6. The normalized standard deviation Δq (%) was determined by the following equation 6.6 to verify the accuracy of the model.

7.2.6 Adsorption isotherm

The Langmuir isotherm model is an empirical model with the assumption that adsorption only occurs in a monolayer surface at identical, equivalent and finite localised sites (Foo and Hameed, 2010) and is given in the equation 6.7 (Chapter 6). A dimensionless parameter known as adsorption intensity (R_L) usually used to indicate the type of the adsorption process and is specified in equation 6.8. The Freundlich isotherm model is widely implemented into heterogeneous materials and determined by following equation 6.9 in chapter 6.

7.2.7 Statistical analysis

The least significant difference tests were used to compare differences between various mixes by one-way analysis of variance (ANOVA). This was also used to compare the differences between compositions at various concentration levels. When the P value is less than or equal to 0.05, the differences were considered to be significant.

7.3 Results and discussion

7.3.1 Adsorbents characterisation

The characterization of biochar has been discussed in chapter 6 and the characteristics of alum sludge is presented in this section. The surface area and pore diameter were determined by N₂ adsorption-desorption isotherms. The surface area of this alum sludge was found 148.55-179.13 m²/gm by BET, Langmuir and single point method which was 7 times higher than the *EW* biochar. The pore diameter and micropore volume was found 8.66 nm and 0.3276 cm³/g by Barret-Joyner-Halenda (BJH) method which was 2 and 14 times higher than *EW* biochar.

One of the most common coagulant used in ground water treatment process is Aluminium sulphate (Yang et al., 2006; Adhikari et al., 2016). The SEM image of alum sludge in Fig. 7.1 (a) showed that it possesses heterogeneous structure and properties. This is because alum sludge has produced from the by-product through a series of complex reactions (Sujana et al., 1998; Yang et al., 2006). The process includes the dissipation of the alum sulphate into Al³⁺ and SO₄²⁻ ions which produce various hydrolytic products such as [Al(H₂O)₅OH]²⁺. These hydrolytic products endure complex adsorption and alteration of surface charge creates colloids in the raw water which eventually formed alum sludge (Yang et al., 2006; Matilainen et al., 2010; Duan et al., 2002). This sludge is then dewatered and discarded as waste at disposal sites after flocculation, sedimentation and filtration in the water treatment process (Adhikari et al., 2016; Yang et al., 2006). The EDS of alum sludge sample shown in Fig. 7.1 (b) confirmed the contents of oxygen (O), aluminium (Al), iron (Fe), silicon (Si), calcium (Ca), carbon (C). Alum sludge is most effective to remove fluoride and phosphorus from aqueous solution via adsorption process because of the significant levels of aluminium that exists in it (Adhikari et al., 2016, Babatunde et al., 2010; Zhao et al., 2007; Aguilar et al., 2002). The high removal of phosphate is due to the plentiful presence of Al³⁺ forming ligand interactions on the solid surface of the alum sludge increase the adsorption process and chemical precipitation (Yang et al., 2006).

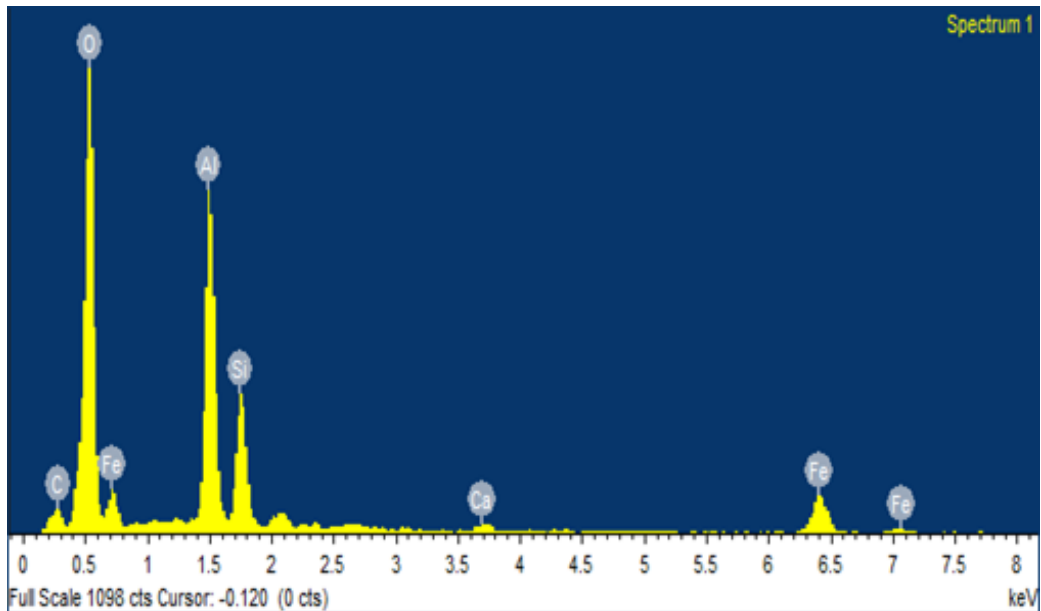
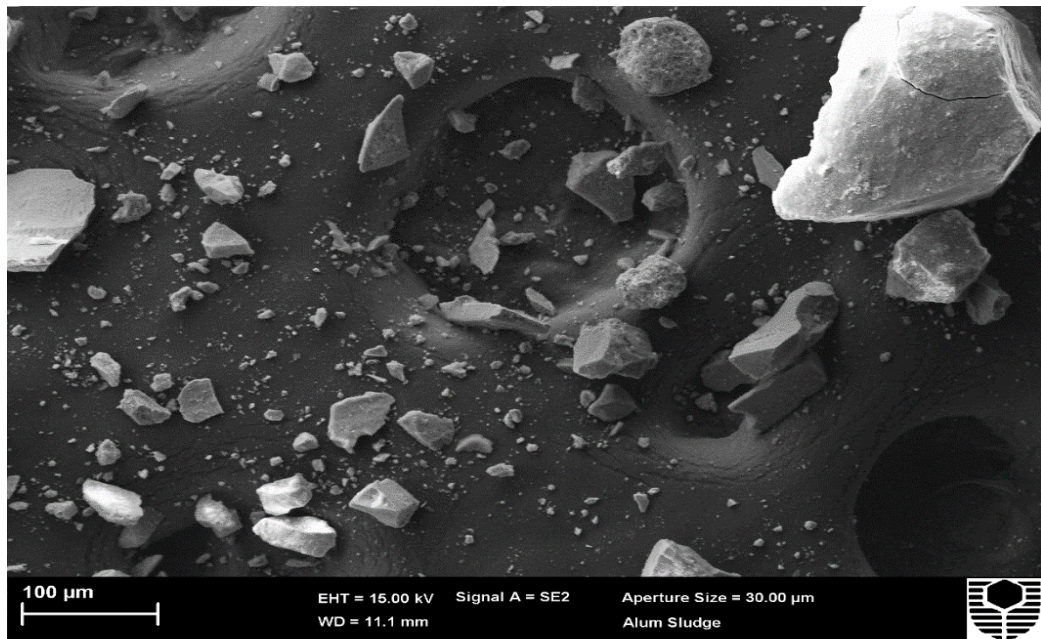


Fig. 7.1 (a) Scanning electron microscopy (SEM) and (b) Energy dispersive spectroscopy (EDS) of dewatered alum

7.3.2 Removal efficiency

Removal efficiency has typically been stated as parentage reduction in the concentration or load for the pollutant of concern based on the flow-weighted samples collected from treated and untreated samples. A series of batch test was conducted at different initial concentrations (0.5-5 mg/L) and constant pH 6.5(\pm 0.5) in a mixture of

biochar and alum sludge (8 gm biochar and 2 gm alum sludge). The removal percentages (Eq 6.2) of $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ are shown in Fig. 7.2 (a-c). The maximum percentage was considered when the concentration reached equilibrium condition. The maximum percentage removal was found 98.2%, 99.4% and 99.8% for $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ respectively for 0.5 mg/L (Fig. 7.2 (a-c)). However, the maximum percentage removal decreased by 20% and 10% for $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ respectively for increasing initial concentration from 1 mg/L to 5 mg/L but no removal drop was found for $\text{PO}_4\text{-P}$ for all concentration. The percentage removal of $\text{PO}_4\text{-P}$ was found >90% within 5 minutes of beginning of the experiment for all concentrations whereas $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ took 2 and 4 hours respectively for 1 mg/L concentration. The removal of $\text{PO}_4\text{-P}$ was much faster than nitrogen species ($\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$) because the adsorption width and surface area of alum sludge was 2 and 7 times higher than that of *EW* biochar. Increasing the initial concentration from 2.5 to 5 mg/L increased the equilibrium time from 4 to 6 hours for both $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ respectively. The removal efficiency of $\text{NO}_2\text{-N}$ was similar to Harmayani and Anwar (2016) but double for $\text{NH}_3\text{-N}$. They found the 100% and 55% removal efficiency for $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ respectively with raw saw dust adsorbent. The difference of removal efficiency may be due to different particle size, sources (i.e. tree species) and preparation condition (pyrolysis process of *EW* biochar). The difference of percentage removal was not significant ($p>0.05$) for all nitrogen and phosphorous species for increasing the initial concentration from 2.5 mg/L to 5 mg/L.

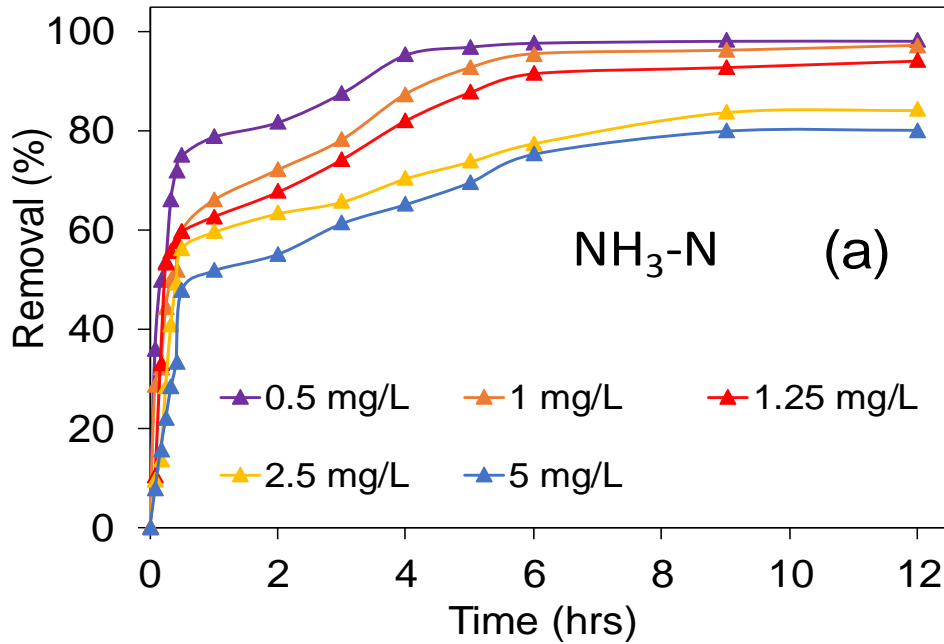


Fig. 7.2 (a) The effect of initial concentrations (0.5-5 mg/L) and contact time on NH₃-N removal by *EW* biochar and alum sludge [doses: 8 gm *EW* biochar and 2 gm Alum sludge; particle size: 2.36 mm; T: 22±2°C; shaker speed: 100 rpm; P^H: 6.5±0.5].

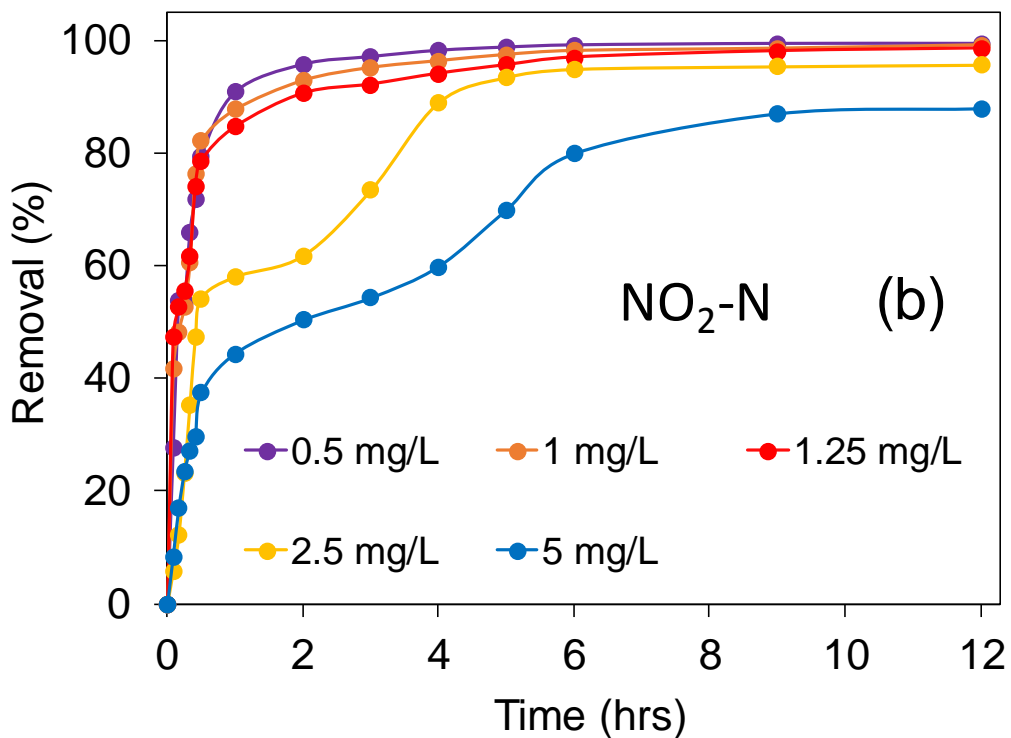


Fig. 7.2 (b) The effect of initial concentrations (0.5-5 mg/L) and contact time on NO₂-N removal by *EW* biochar and alum sludge [doses: 8 gm *EW* biochar and 2 gm Alum sludge; particle size: 2.36 mm; T: 22±2°C; shaker speed: 100 rpm; P^H: 6.5±0.5].

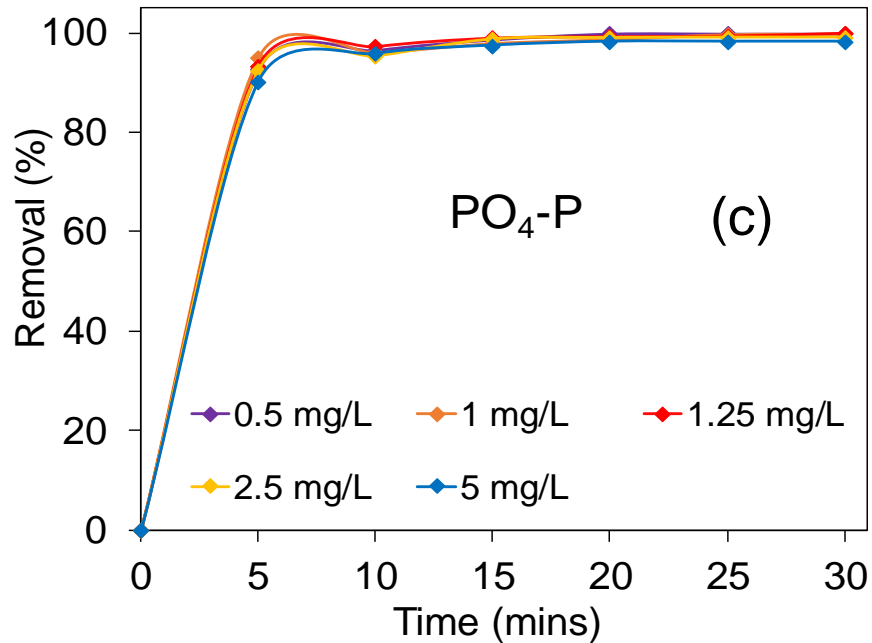


Fig. 7.2 (c) The effect of initial concentrations (0.5-5 mg/L) and contact time on PO₄-P removal by the mixture of *EW* biochar and alum sludge [doses: 8 gm *EW* biochar and 2 gm Alum sludge; particle size: 2.36 mm; T: 22±2°C; shaker speed: 100 rpm; P^H: 6.5±0.5].

7.3.3 Adsorption capacity

The adsorption capacity of nitrogen and phosphorous species was calculated using Eq 6.1 and shown in Fig. 7.3 (a-c). The maximum adsorption for NH₃-N, NO₂-N and PO₄-P was increased from 6.15-55.22 μg/g, 6.21-57.64 μg/g and 25.41-246.1 μg/g respectively for increasing initial concentrations (0.5-5 mg/L). This characteristic also observed by the slope and y intercept values of trendline equations as shown in Table 7.1. It showed that the slope and y intercept values increased with increasing of initial concentrations. The maximum adsorption was found to increase with increasing concentration for higher availability of nitrogenous and phosphorus ions in the solution. It provides an important driving force to overcome the mass transfer resistance of ions between aqueous and solid phase (Harmayani and Anwar, 2016). Higher concentrations increase the probability of collision between adsorbate (nitrogenous and phosphorus ions) and adsorbent (biochar and alum sludge). Similar outcomes were reported for ammonium sorption by poultry litter and wood biochar (Sun et al., 2013), NH₃-N, NO₂-N sorption by sawdust (Harmayani and Anwar, 2016)

and PO₄-P adsorption by dewatered alum sludge and red mud (Adhikari et al., 2016, Huang et al., 2008). The adsorption of PO₄-P was found to be 4-4.5 times larger than NH₃-N and NO₂-N. The regression analysis of Fig 7.3 (a-c) showed a direct relationship in y-intercept values for adsorption capacities of three species (Table 7.1). The y intercept values for the three species are in a trend of PO₄-P>NO₂-N>NH₃-N. The adsorption of NH₃-N was found lower because the ammonia species adsorbed onto the solid phase are remaining in free form and it can desorb easily by changing the water chemistry of aqueous phase. A certain amount of NH₃-N is adsorbed onto biochar to saturate the empty sorption place for a given concentration of NH₃-N. But the NH₃-N concentration in aqueous phase may reduce due to nitrification process. Hence, a portion of NH₃-N will desorb to regain its chemical equilibrium and the aqueous phase will have new concentration. Therefore, the removal rate of NH₃-N was found lower than NO₂-N. The adsorption capacity of PO₄-P was much faster than nitrogen species because the adsorption width and surface area of alum sludge was 2 and 7 times higher than that of *EW* biochar.

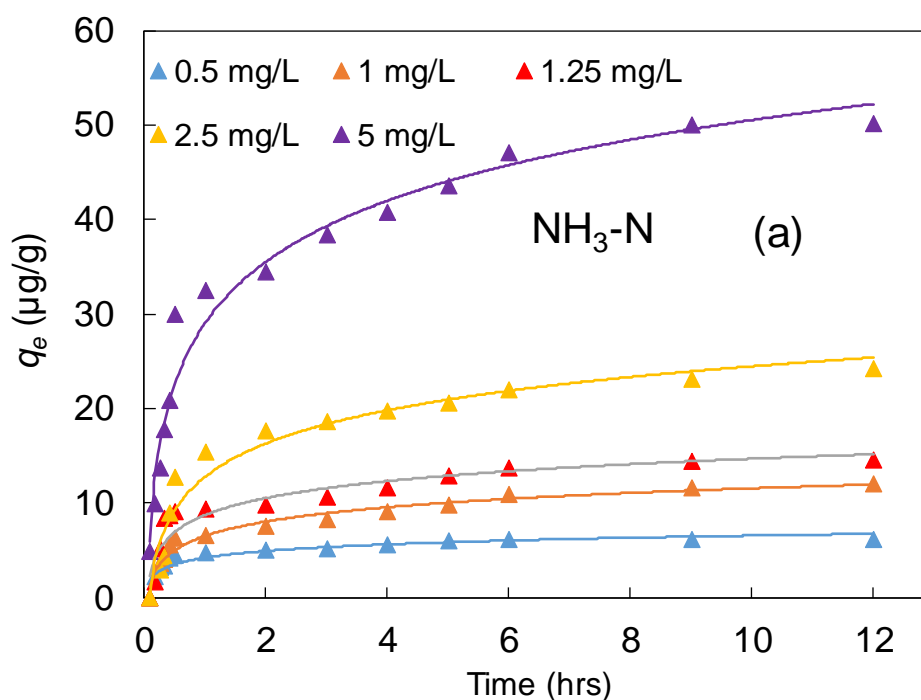


Fig. 7.3 (a) The effect of initial concentration (0.5-5 mg/L) and contact time on NH₃-N adsorption by *EW* biochar and alum sludge [doses: 8 gm *EW* biochar and 2 gm Alum sludge; particle size: 2.36 mm; T: 22±2°C; shaker speed: 100 rpm; P^H: 6.5±0.5].

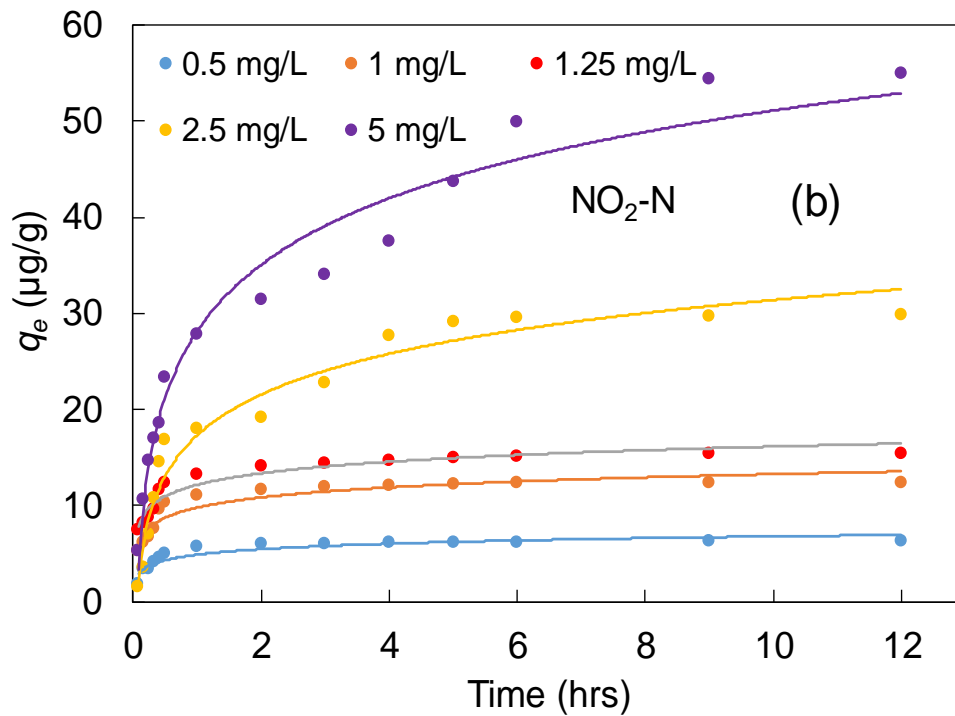


Fig. 7.3 (b) The effect of initial concentration (0.5-5 mg/L) and contact time on $\text{NO}_2\text{-N}$ adsorption by *EW* biochar and alum sludge [doses: 8 gm *EW* biochar and 2 gm Alum sludge; particle size: 2.36 mm; T: $22\pm 2^\circ\text{C}$; shaker speed: 100 rpm; P^{H} : 6.5 ± 0.5].

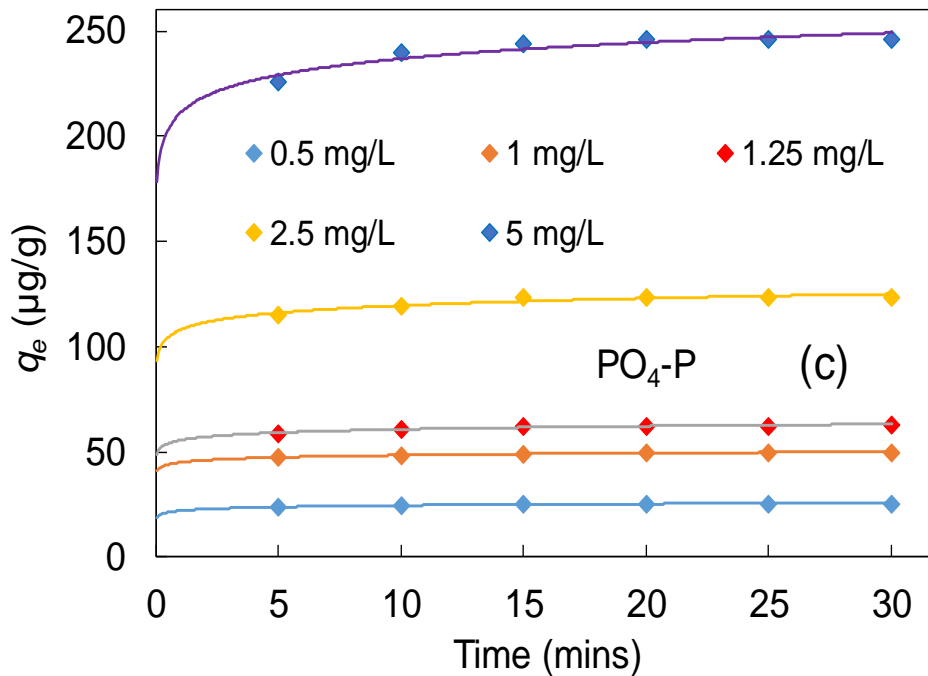


Fig. 7.3 (c) The effect of initial concentration (0.5-5 mg/L) and contact time on $\text{PO}_4\text{-P}$ adsorption by *EW* biochar and alum sludge (doses: 8 gm *EW* biochar and 2 gm Alum sludge; particle size: 2.36 mm; T: $22\pm 2^\circ\text{C}$; shaker speed: 100 rpm; P^{H} : 6.5 ± 0.5].

Table 7.1 Trendline analysis of adsorption capacities of nitrogen and phosphorous

Nutrients	C_0 (mg/L)	Trendline equations	R^2
NH ₃ -N	0.5	$y = 1.01\ln(x) + 4.21$	0.8633
	1	$y = 2.18\ln(x) + 7.24$	0.9649
	1.25	$y = 2.58\ln(x) + 8.73$	0.8827
	2.5	$y = 5.04\ln(x) + 12.8$	0.9479
	5	$y = 9.77\ln(x) + 21.4$	0.9822
NO ₂ -N	0.5	$y = 0.83\ln(x) + 4.80$	0.8611
	1	$y = 1.51\ln(x) + 9.76$	0.8761
	1.25	$y = 1.72\ln(x) + 12.1$	0.9214
	2.5	$y = 6.13\ln(x) + 17.3$	0.9553
	5	$y = 10.1\ln(x) + 28.3$	0.9661
PO ₄ -P	0.5	$y = 1.08\ln(x) + 21.9$	0.9361
	1	$y = 1.46\ln(x) + 44.9$	0.9637
	1.25	$y = 2.23\ln(x) + 55.5$	0.9197
	2.5	$y = 4.98\ln(x) + 108$	0.9039
	5	$y = 11.2\ln(x) + 211$	0.8752

7.3.4 Adsorption kinetics

The physical and/or chemical characteristics of biochar has a strong relationship with adsorption kinetics. Nutrients (i.e., NH₃-N, NO₂-N and PO₄-P) adsorption as a function of time and concentration was fitted with the pseudo first order and pseudo second order kinetic models. Pseudo second order kinetic model graphs were shown in Fig. 7.4 (a-c) while the parameters for both models were expressed in Table 7.2. Both models fit the results based on the correlation coefficient R^2 and the actual test results. The R^2 values of pseudo second order kinetics (0.985-1) were higher than pseudo first order kinetic (0.734-0.965) and the calculated q_e values were closer to the experimental q_e values for all species. These results indicate that the adsorption kinetics is better represented by the pseudo second order kinetic model for all nutrients. The normalized standard deviation Δq for the pseudo first order kinetics was between 29.40-52.42%, 4.46-49.29%, and 20.10-86.54% for NH₃-N, NO₂-N, PO₄-P respectively, which are

higher than those for the pseudo second order kinetic equation. The pseudo second order kinetic model indicated the lowest Δq values, which ranged from 2.45-9.69%, 5.42-9.89%, and 0.87-8.00% for $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ respectively. Based on the highest R^2 values and the lowest Δq values, the pseudo second order model was the most suitable to describe the adsorption kinetics of nutrients onto the mixture of *EW* biochar and alum sludge. The pseudo first order kinetic model was based on the assumption of physical adsorption and the solute uptake rate with time is directly proportional to the ratio of the solute concentration and the amount of solid (Shawabkeh and Tutunji, 2003). On the other hand, the pseudo second order kinetic model relies on the assumption that the rate-limiting step may be chemical sorption or chemisorption comprising valence forces through sharing or exchange of electrons between sorbate and sorbent (Ho and McKay, 1998). This indicates the nitrogen and phosphorous ions adsorbed onto the biochar and alum sludge mostly associated with chemical reactions. The adsorption of $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ for pseudo second order kinetic model increased from 5.90-50.0 $\mu\text{g/g}$, 6.31-59.52 $\mu\text{g/g}$ and 25.4-243.9 $\mu\text{g/g}$ respectively as the concentrations of these compounds increased from 0.5 mg/L to 5 mg/L. When comparing with previous studies, the adsorption of phosphate onto red mud samples treated with HCl, dewatered alum sludge and lime sludge were 0.58 mg /g, 55 mg/g and 44.5 mg/g (Adhikari et al., 2016, Huang et al., 2008). Similarly, the adsorption capacity of $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ onto raw saw dust was found 2.59-17.57 $\mu\text{g/g}$ and 5-49.53 $\mu\text{g/g}$ respectively. The difference probably because of the differences in original materials, particle size, and the preparation conditions of biochar in the present study. However, the adsorption of biochar and alum sludge mixture used in this study were better than those raw saw dust prepared from radiata pine (Harmayani and Anwar, 2016).

Table 7.2 Kinetic parameters of the pseudo-first and pseudo-second order kinetic models

Nutrient	C_0 (mg/L)	q_e, exp ($\mu\text{g/g}$)	Pseudo-first order				Pseudo-second order			
			q_e, cal ($\mu\text{g/g}$)	K_1 (1/min)	R^2	Δq (%)	q_e, cal ($\mu\text{g/g}$)	K_2 (g/mg min)	R^2	Δq (%)
$\text{NH}_3\text{-N}$	5	48.81	34.46	0.0060	0.946	29.4	50.00	0.0005	0.999	2.45
	2.5	25.75	16.03	0.0060	0.860	37.7	26.88	0.0011	0.993	4.40
	1.25	13.73	8.02	0.0088	0.833	41.6	15.06	0.0026	0.987	9.69

	1	11.60	7.46	0.0094	0.917	35.6	12.45	0.0035	0.990	7.37
	0.5	5.49	2.61	0.0200	0.734	52.4	5.90	0.0135	0.999	7.53
	5	54.39	44.81	0.0053	0.932	17.6	59.52	0.0002	0.974	9.44
	2.5	29.58	28.26	0.0129	0.883	4.46	32.36	0.0006	0.985	9.43
NO ₂ -N	1.25	14.15	9.71	0.0433	0.915	31.4	15.55	0.0069	0.999	9.89
	1	11.63	8.93	0.0484	0.965	23.2	12.55	0.0093	0.999	7.92
	0.5	5.98	8.93	0.0484	0.965	49.3	6.31	0.0194	0.999	5.42
	5	246.1	164.29	0.3137	0.908	33.2	243.9	0.0420	1.000	0.87
	2.5	115.5	85.94	0.3355	0.895	25.6	123.5	0.0820	1.000	6.86
PO ₄ -P	1.25	58.6	46.84	0.4053	0.600	20.1	62.9	0.1204	1.000	7.29
	1	47.5	24.26	0.2952	0.863	48.9	50.0	0.1379	1.000	5.24
	0.5	23.6	3.17	0.3213	0.935	86.5	25.4	0.3510	1.000	8.00

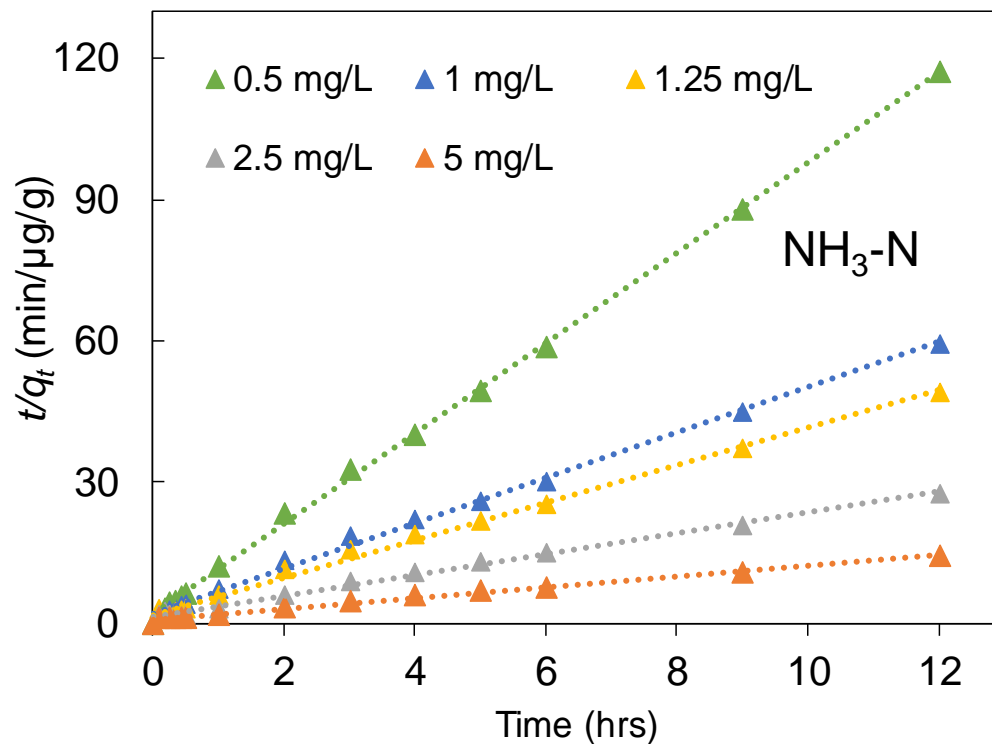


Fig. 7.4 (a) Pseudo second order plots of NH₃-N adsorption [doses: 8 gm *EW* biochar and 2 gm Alum sludge; particle size: 2.36 mm, T: 22±2°C; shaker speed: 100 rpm; P^H: 6.5±0.5].

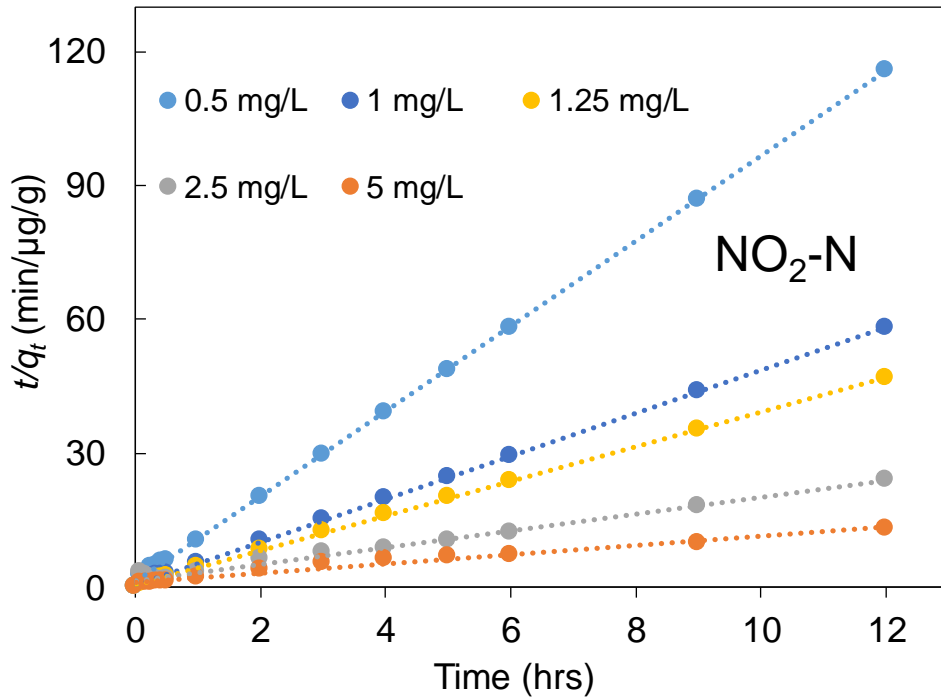


Fig. 7.4 (b) Pseudo second order plots of $\text{NO}_2\text{-N}$ adsorption [doses: 8 gm *EW* biochar and 2 gm Alum sludge; particle size: 2.36 mm, T: $22\pm 2^\circ\text{C}$; shaker speed: 100 rpm; pH : 6.5 ± 0.5].

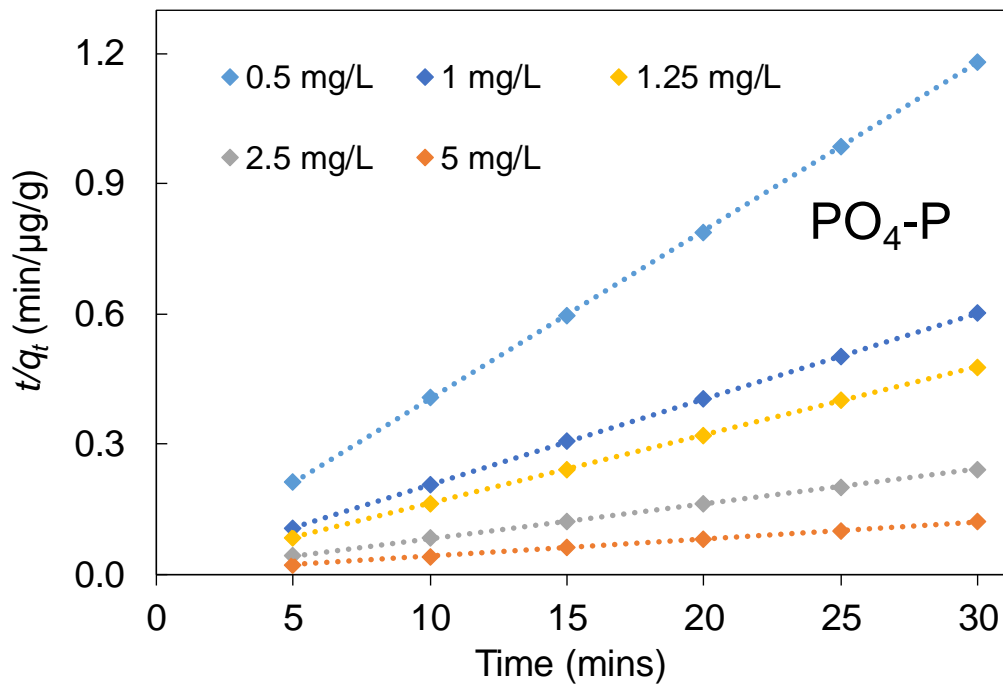


Fig. 7.4 (c) Pseudo second order plots of $\text{PO}_4\text{-P}$ adsorption [doses: 8 gm *EW* biochar and 2 gm Alum sludge; particle size: 2.36 mm, T: $22\pm 2^\circ\text{C}$; shaker speed: 100 rpm; pH : 6.5 ± 0.5].

7.3.5 Adsorption isotherm

Adsorption equilibrium data were analyzed with Langmuir and Freundlich isotherm models (Eq 6.7 and 6.9) and the isotherm parameters obtained with the model equations were shown in Table 7.3. The NH₃-N adsorption fitted with both Langmuir and Freundlich isotherm model ($R^2=0.97-0.99$) but NO₂-N and PO₄-P followed Freundlich model (0.96-0.99) better. The maximum Langmuir adsorption for nitrogen and phosphorous species were between 93-2500 $\mu\text{g/g}$ and 5000 $\mu\text{g/g}$ respectively. The value of n was found to be greater than 1, which reveals a positive position of adsorption condition. The perfect fit for Langmuir model shown in the experimental data of NH₃-N suggests that the adsorption process was predominantly monolayer adsorption, which comprises both chemical and physical mechanisms. Similar results were indicated in previous literature such as methylene blue adsorption onto biochar prepared from eucalyptus, palm bark, anaerobic digestion residue (Sun et al., 2013) and also onto activated carbon prepared from hazelnut husks (Ozer et al., 2012). Phosphorous and nitrogenous species adsorption by alum sludge and Radiata pine saw dust were also showed similar trends (Adhikari et al., 2016, Harmayani and Anwar, 2016). The adsorption intensity (R_L) was calculated by equation 6.8 for 1-5mg/L initial concentrations and shown in Fig. 7.5. The value of R_L confirms favourable adsorption as the value lies between 0 to 1 (Babu and Gupta, 2008). Overall the study indicates that *EW* biochar and alum sludge blend can be used as effective adsorbents to remove nitrogen and phosphorous species from aqueous phase such as stormwater and/or wastewater.

Table 7.3 Langmuir and Freundlich isotherm constants

Species	Langmuir			Freundlich		
	Q_m ($\mu\text{g/g}$)	$Kads$	R^2	n	K	R^2
NH ₃ -N	93	0.49	0.99	1.13	68	0.97
NO ₂ -N	2500	1.58	0.94	1.18	81	0.99
PO ₄ -P	5000	0.14	0.90	1.19	476	0.97

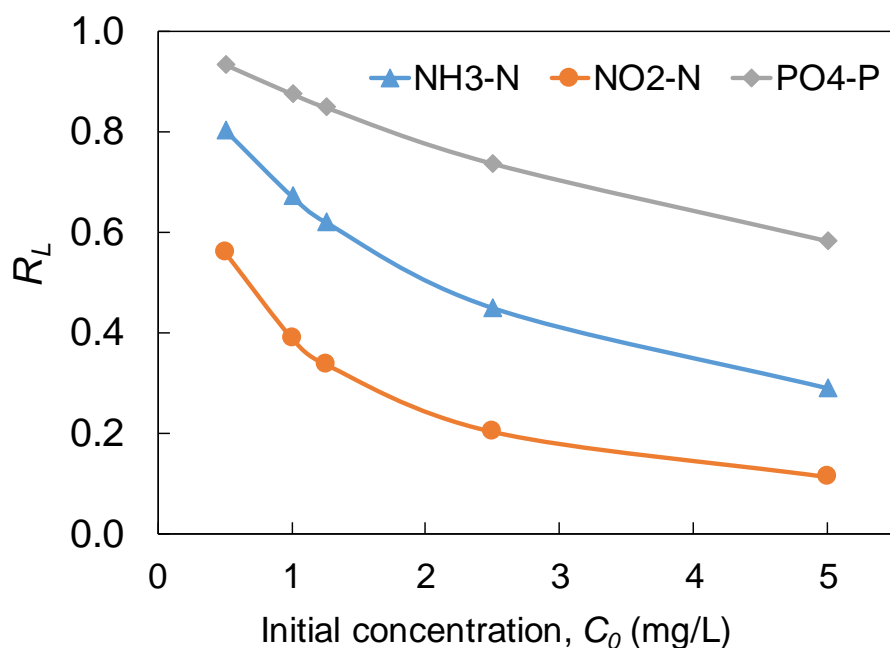


Fig. 7.5 Variation of adsorption intensity (R_L) with initial concentration.

7.4 Conclusion

Chapter six presented the removal of nitrogen species from water/stormwater using *EW* biochar. However, urban runoff also consists of another nutrient such as phosphorous. The unacceptable levels of nutrients (i.e., $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$) in urban runoff may cause multiple negative environmental impacts on the receiving waters. In this chapter, a mixed adsorbent (*EW* biochar and alum sludge) was used to remove these nutrients. The maximum removal was found 98.2%, 99.4% and 99.8% for $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ respectively for 0.5 mg/L. This efficiency decreased by 20% and 10% for $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ respectively for increasing initial concentration from 1 mg/L to 5 mg/L but no efficiency drop was found for $\text{PO}_4\text{-P}$ for all concentration. The percentage removal of $\text{PO}_4\text{-P}$ was found >90% within 5 minutes of the beginning of experiment for all concentrations whereas $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ took 2 and 4 hours respectively for 1 mg/L concentration. The maximum adsorption for $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ was increased from 6.15-55.22 $\mu\text{g/g}$, 6.21-57.64 $\mu\text{g/g}$, 25.41-246.1 $\mu\text{g/g}$ respectively for increasing initial concentrations (0.5-5 mg/L). Pseudo second order model was the most suitable to describe the adsorption kinetics of all nutrients. Langmuir and Freundlich both model fitted with $\text{NH}_3\text{-N}$ adsorption whereas $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ followed Freundlich better than Langmuir model. *EW* trees are

abundant in Australia and the dewatered alum sludge is a waste material. Therefore, the use of biochar produced from *EW* trees and alum sludge as low-cost adsorbent will be a sustainable approach for the treatment of stormwater and/or wastewater.

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CHAPTER 8

REMOVING NITROGEN AND PHOSPHOROUS IN DYNAMIC CONDITION AND DEVELOPING A MODIFIED CATCH BASIN INSERT

Abstract

Urban stormwater runoff is contaminated with harmful constituents such as sediments and nutrients wash from roadways, parking lots, and open spaces. The subsequent discharge into water sources can pose adverse effects on public health and the water environment. Although several best management practices have been developed to treat urban stormwater, catch basin inserts can be best suited in urban site-constrained settings. This chapter investigates the effectiveness of a mixed adsorbent (*EW* biochar and alum sludge) to treat nitrogen and phosphorous species in dynamic condition and proposed a modified CBI for nutrients and sediments removal from stormwater. The column experiments were carried out with varying concentrations (1-5 mg/L) and a uniform flow rate of 10 mL/min. Column study revealed that increase of initial concentration from 1-5 mg/L, the equilibrium adsorption capacity increased from 62.5-88.3 $\mu\text{g/g}$; 46.3-84.2 $\mu\text{g/g}$ and 22.5-346 $\mu\text{g/g}$ for $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ respectively. The CBI is modified to have two chambers: top geotextile basket will remove the sediments and gross pollutants and the bottom geotextile basket containing adsorbent materials will remove the dissolved nutrients. The overall maintenance period for the bottom basket was calculated based on the column results which were found to be 78-151, 78-161 and 73-166 days for $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ respectively when concentrations drop 5 mg/L to 1 mg/L. On the other hand, the top geotextile basket needs a maintenance period of 262-1030 days depending on the particle sizes. The proposed modified CBI shows great potential to remove sediments and nutrients simultaneously from urban stormwater runoff.

Keywords: Catch basin inserts; nutrients; sediment; stormwater; water quality

8.1 Introduction

One of the major sources of pollution that enter the natural water environment is urban stormwater runoff. Point and non-point sources are the origin of urban runoff. Point sources include the discharge that can be traced back to a certain area and non-point sources include stormwater runoff from large areas such as large farming areas, highways, parking bays (Hvitved et al., 2010). Urban runoff from different areas such as parking areas, industrial sites, freeways, commercialized areas and open spaces contain multiple contaminants often exceed admissible limits. These contaminants include TSS (i.e., sediments), toxic organics, heavy metals, PAHs, litter, microorganisms and nutrients; primarily nitrogen and phosphorous (DoEH, 2000). Sediments have negative hydrologic and environmental impact on receiving water bodies (Alam et al., 2017b). Excessive amount of nitrogen and phosphorous in waterbody will result a phenomenon defined as eutrophication. The excessive amount of nutrients being discharged into aquatic biota will lead to rapid algae growth (Alam et al., 2017a). As a result, speedy consumption of dissolved oxygen by the increasing amount of algae will endanger marine creatures that coexists in the marine environment. Several best management practices (BMP) have been developed especially oil and grit separators, grassed swales, vegetated filter strips and retention ponds and catch basin inserts (CBIs) to reduce stormwater pollutants (Reddy et al., 2014b, Kumar et al., 2012, Llyod et al., 2002). However, most of these practices are not practicable for urban zones with limited free area as these required spaces for construction (Sample et al., 2012; Tafuri and Field, 2012). Another difficulty of BMPs are maintenance problem as the filtration process requires maintenance after a certain period. As a result, greater attention and research have been focused in the development of potential of filtration systems which will be compact in size and easy to maintenance. A CBI is a device that can be hanged in a side entry pit without requiring any extra land. This device is also easy to maintain because of its compact size (Alam et al., 2017a). A new form of CBIs has recently been introduced by Urban Stormwater Technologies Pty Ltd to remove stormwater pollutants at source in the drainage systems and installed in few city councils of Western Australia. This CBI consist of a special type of non-woven geotextile which can only remove pollutants up to 150 μm but can't remove any dissolve pollutants (e.g., nutrients, Alam et al., 2017b). Chapter 7 showed the batch adsorption study of biochar and alum sludge for significant

removal of nitrogen and phosphorous from aqueous solution. In this chapter, the adsorption of these species will be tested in a series of column experiments and a new modified CBI will be proposed by integrating this adsorbent medium with CBI to remove both sediment and nutrients simultaneously from stormwater runoff.

8.2 Materials and method

8.2.1 Material selection

The *EW* biochar and the dewatered alum sludge was used in batch tests in chapter 7. The same adsorbent materials are used in column test in this chapter to check the dynamic adsorption. Two-step method was applied to prepare the washed samples of biochar before packing in column (Reddy et al., 2014a). Firstly, fine particles were removed via dry sieving and then remaining fine particles removed through wet sieving with deionized water. However, dry sieving method was applied only for the alum sludge sample preparation due to its drained-out possibilities during wet sieving. The material size of 2.36 mm was chosen for column study (ISO 3310: BS 410-1:2000; sieve size 2.36 mm). To make it free from impurities, the sieved samples were washed again with deionized water for 8-10 times. Two millilitres of washed water were analyzed after each washing for any possible nitrogen and phosphorus residues coming from biochar and dewatered alum sludge. The nutrient content in the washed water was found negligible after 6–7 washes. The samples were then oven dried at 105°C for 48 hrs and stored in air-tight container at room temperature (22±2°C).

8.2.2 Synthetic stormwater preparation

The synthetic stormwater containing NH₃-N, NO₂-N and PO₄-P was prepared from NaNO₂, NH₄Cl and NaH₂PO₄. The chemicals used to prepare solution of NO₂-N, NH₃-N and PO₄-P was analytical grade. The concentrations of nutrients were prepared based on Australian Runoff Quality and previous literatures (Alam et al., 2017a; Harmayani and Anwar, 2016; Wong, 2006). Fresh solutions were prepared before each experiment to avoid any possible deterioration in concentration. pH values were measured by a pH meter (HACH 40d with PHC 101 HAC electrode).

8.2.3 Column set up

The plastic column of inner diameter of 3.9 cm and a length of 30 cm was constructed as shown in Fig 8.1. Continuous flow adsorption experiments were conducted with two adsorbents (i.e., biochar and alum sludge) in layer. The column was packed with 20 mm (15 g) of alum sludge and a 160 mm (60 g) of biochar. This ratio (by weight) of biochar and alum sludge (4:1) was taken based on the results found in chapter 7. Pea gravel of 40 mm (20 g) height is added at the top and bottom layer in order to avoid the floating of biochar and alum sludge during the excessive build-up of the synthetic stormwater within the column. Geofabrics was placed at the bottom layer of pea gravel to prevent the possibilities of drain out of alum sludge with effluent which may cause turbidity in effluent water. Steel wire mesh was provided to separate each layer and provide stability. This also prevents the passing of materials between each layer or with the effluent.

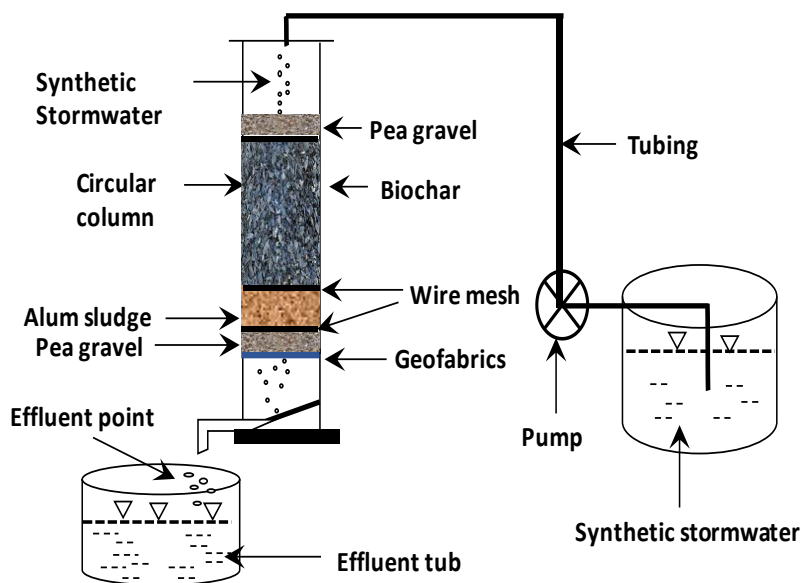


Fig. 8.1 Schematic of the column filter system

8.2.4 Column experiment

The synthetic stormwater was prepared by mixing $\text{NO}_2\text{-N}$, $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ as these contaminants found in mixed condition in stormwater. At the beginning of the test the

deionized water was passed through the column set up at a constant flow rate of 10 mL/min for 30 min. The effluent sample was collected as blank sample. This flow rate was chosen assuming a runoff area to drainage area ratio of 50 (Alam et al., 2017b; Franks et al., 2012) and rainfall intensity of 1 cm/hr, which is 3 times greater than rainfall intensity found for 20 years average recurrence interval (ARI) for 1-hour rainfall intensity in Perth, Western Australia (BoM, 2015). The hydraulic loading rate was 0.15 mm/sec (21.25 in/hr). A measured concentration based on batch experiment (1, 2.5 and 5 mg/L) was passed through the column with above mentioned flow rate. The subsamples were collected at influent and effluent after passing through the column at different predetermined time intervals (5-60 min). The influent and effluent samples of synthetic stormwater and initial clean water were analysed for contaminants. The P^H of synthetic stormwater was kept at pH 6(±0.5) as stormwater in field condition have the similar P^H level (Wong, 2006). The nutrients concentration was measured with Aqukem 200 water analyser (Labmedics Analytical Solutions; detection limit of 0.002 mg/L with a 1.5% measurement error at 95% confidence level). The Duplicate/triplicate tests were conducted to minimize the errors and the mean values were reported. Results that showed above 1% difference for nutrients between duplicate samples were discarded.

8.2.5 Column data analysis

The breakthrough appearance and the outline of breakthrough curve are very crucial for explaining the operation and dynamic behaviour of a column adsorption. The breakthrough curve for column studies can be obtained by plotting C_t/C_0 (effluent to influent nutrient concentration) versus time, t . Adsorption only occurs in a particular region of the bed, known as the mass transfer zone (MTZ), which moves through the bed. Therefore, it's crucial to know the information of MTZ in a fixed bed column which is given by the following equation (Rout et al., 2017):

$$MTZ = L \left(\frac{t_e - t_b}{t_e} \right) \quad (8.1)$$

where MTZ is the adsorption zone length (cm), L is the adsorbent length in the column (cm), t_b is the breakthrough time (hr) and t_e is the exhaustion time (hr).

The Thomas model is one of the most general and widely used models in column performance theory (Han et al., 2007). The data obtained in column in continuous mode studies was used to calculate maximum solid phase concentration of nutrients on adsorbent by Thomas model. The Thomas model is given as follows (Han et al., 2007):

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{TH}q_0x}{V_f} - k_{TH}C_0t\right)} \quad (8.2)$$

where q_0 is the equilibrium adsorption capacity (mg/g), k_{TH} is the Thomas rate constant (L/mg.hr), x is the amount of adsorbent in column (gm), V_f is the linear flow velocity (mL/min). The values of k_{Th} and q_0 can be determined from a plot of C_t/C_0 against t using nonlinear regression analysis. In this study, column adsorption capacity was considered the adsorption capacity at 90% exhaustion point (Negrea, 2011).

8.3 Results and discussion

8.3.1 Interpretation of adsorbent and the process of adsorption

The detailed characterization of the adsorbents was described in chapter 6 and 7 respectively. The process of nitrogen and phosphorous adsorption by *EW* biochar and alum sludge was accomplished by analytical techniques including SEM, EDS, FTIR, XRD etc. and was described in detail in previous chapters. Alum sludge predominantly consists of aluminium, iron, silicon, calcium and *EW* biochar consist of carbon materials. N_2 adsorption-desorption approach using surface area analyser exposes the presence of micro pore for both adsorbents. The other textural parameters such as micro pore volume, pore width/adsorption width determined by similar method also signify that the adsorbent is prone to adsorption. Phosphate ions react with iron and aluminium oxides by ligand exchange forming inner-sphere complexes and the existence of calcium ion smooths phosphate removal via precipitation (Rout et al. 2017). On the other hand, the functional groups on the surface of *EW* biochar were involved in providing active sites for NH_3-N and NO_2-N binding (Suksabye et al., 2009). The biochar surface integrates the NH_3-N and NO_2-N through complexation and precipitation (Hsu et al., 2009) or released into the solution (Yue et al., 2009). The

surface charge of biochar and anionic nature of adsorbate (i.e., $\text{NO}_2\text{-N}$) may be other factors in the adsorption process. Altogether, the manifestation of the mentioned phases, Al, Fe, Ca of alum sludge and carbon materials of *EW* biochar, specific textural parameters and intrinsic surface characteristics of adsorbents play a dynamic role in nitrogen and phosphorous adsorption from aqueous phase.

8.3.2 Effect of initial concentration

The effect of the initial concentration on the breakthrough curve was investigated by varying initial concentrations (1, 2.5 and 5 mg/L) and maintaining flow rate of 10 mL/min. The sorption breakthrough curves obtained by changing inlet concentration for $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ were shown in Fig. 8.2 (a-c) and corresponding experimental parameters were tabulated in Table 8.1. It was clearly shown from the results that a decreased inlet initial concentration gave delayed breakthrough curves and the treated volume increased. It clearly indicates that breakthrough time (and volume) and exhaustion time (volume) are inversely related to the initial nutrient concentration. At higher nutrient concentration (5 mg/L) the adsorbent bed saturated quickly leading to steeper breakthrough curves and earlier breakthrough and exhaustion time. In contrast, flatter breakthrough curves and slower bed saturation were observed with a shorter mass transfer zone at lower nutrient concentration (MTZ, Eq. 1; Table 8.1). This can be explained by intra-particle diffusion control adsorption process and the diffusion process is concentration dependent. The change in concentration gradient affects the breakthrough time as well as saturation rate (Rout et al., 2014). Higher initial nutrient concentration creates higher driving force to overcome the mass transfer resistance and exhibited quick exhaustion of the bed (Rout et al., 2017) and the lower initial nutrient concentration gradient caused slower transport due to decreased diffusion/mass transfer coefficient and contribution to prolonged exhaustion time of the column (Padmesh et al., 2005).

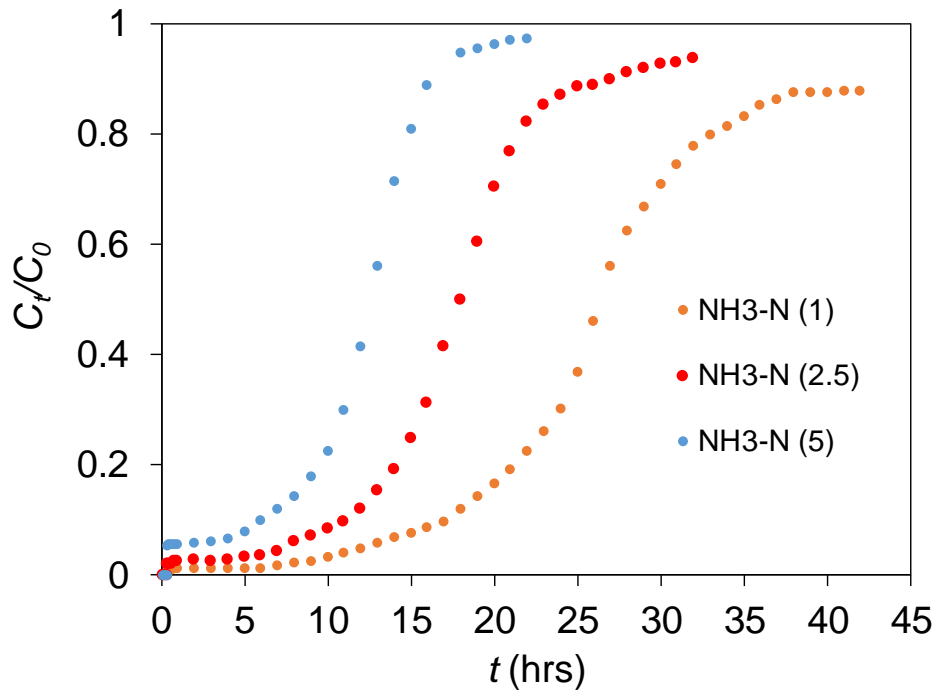


Fig. 8.2 (a) Breakthrough curves: the effect of initial concentration on nutrient adsorption.

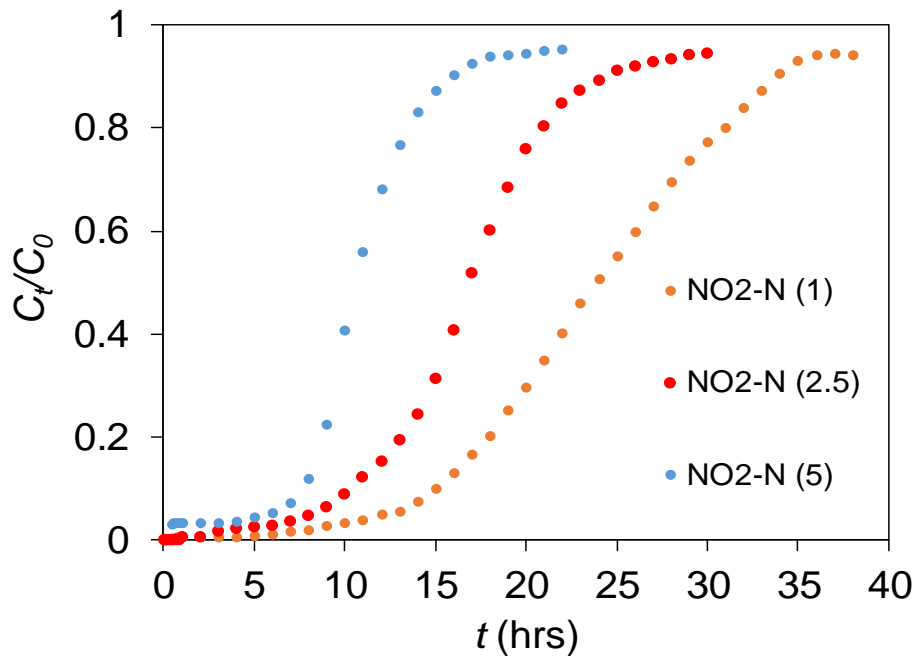


Fig. 8.2 (b) Breakthrough curves: the effect of initial concentration on nutrient adsorption.

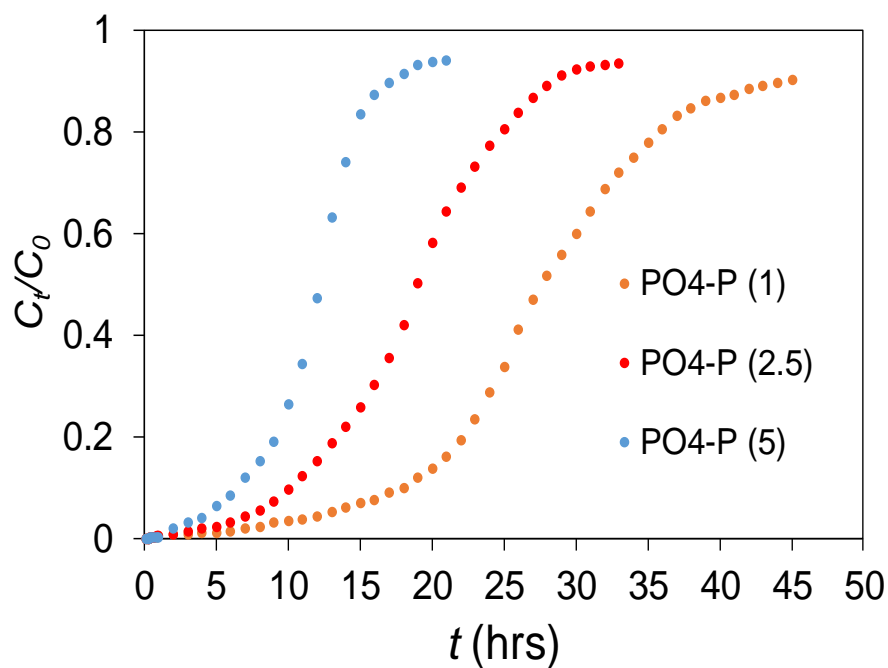


Fig. 8.2 (c) Breakthrough curves: the effect of initial concentration on nutrient adsorption.

Table 8.1 Experimental parameters of breakthrough curves for nitrogen and phosphorous adsorption by biochar and alum sludge layered column

Species	C_0 (mg/L)	t_b (hr)	t_e (hr)	MTZ (cm)	K_{TH} (L/mg.hr)	q_0 (μ g/g)
NH ₃ -N	1	13	42	11.04	0.0253	62.5
	2.5	8	32	12.00	0.0148	71.3
	5	4	21	12.95	0.0102	88.3
NO ₂ -N	1	14	36	9.772	0.0271	46.3
	2.5	9	30	11.20	0.0149	71.7
	5	6	19	11.43	0.0108	84.2
PO ₄ -P	1	13	44	1.401	0.0229	22.5
	2.5	8	31	1.482	0.0131	297
	5	4	20	1.603	0.0103	346

8.3.3 Adsorption capacity

The equilibrium nutrient adsorption capacity (q_0) was calculated by Eq. 2 and shown in Table 8.1. It indicated that the increase of initial concentration from 1 to 5 mg/L, the adsorption capacity of $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ was found to increase from 62.5-88.3 $\mu\text{g/g}$; 46.3-84.2 $\mu\text{g/g}$ and 22.5-346 $\mu\text{g/g}$ respectively. The concentration drop was observed to increase due to increase of initial concentration. This may be higher driving force for diffusion improved adsorbate loading rate with increased in initial concentration of $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$. The variation in adsorption capacity can also be explained with breakthrough curves of each species as shown in Fig. 8.2 (a-c). The saturation of adsorbent active sites took place by means of improved breakthrough values and enhance the adsorption capacity. The increasing of influent nitrogen and phosphorous concentration showed a decreased trend of K_{TH} values but q_0 values increased (Table 8.1). This can be explained the difference in driving force for adsorption resulting from the concentration difference. Similar findings were described by previous literatures (Rout et al., 2014, 2017; Padmesh et al., 2005).

8.4 Developing a modified CBI

Filtration is a process to separate impurities, particles and suspended solids from the fluid by flowing it through a porous media. Filtration is carried out to remove and capture solids to reduce the particles concentration of the fluid. An ideal geotextile should have minimal pore size to capture the suspended particles by allowing ample of water to pass through freely. The primary function of the geotextile filter was to capture TSS from influent solution and thus reduce its concentrations. Field study showed that UST CBI can capture pollutants down to 150 μm with the special type NWG1 geotextile (Chapter 3; Alam et al., 2017a). Field study also showed sufficient capacity of UST CBI to capture gross pollutants in field condition (>90%, Alam et al., 2017a). Chapter 5 showed that the NWG1 geotextile is suitable than other geotextiles (NWG2 and NWG3) to treat TSS from stormwater (Alam et al., 2017b). Therefore, NWG1 may be chosen for using it in CBI to remove gross pollutants and TSS. Again, stormwater not only contains gross pollutants (pollutants>150 μm) but also has dissolve pollutants. Existing CBI with NWG1 does not have the capacity to remove dissolved pollutants such as nutrients. Therefore, a new modified CBI is proposed in

this study to remove gross and dissolved pollutants simultaneously from urban stormwater runoff (Fig. 8.3).

Chapter 6 and 7 proposed the good adsorbent behaviour of *EW* biochar and alum sludge to remove nitrogen and phosphorous species from water. The proposed modified CBI has two chambers and both chambers can hold geotextile baskets. A diffuser can be placed in the top chamber to dissipate the energy during high flow. The bottom chamber may be filled up with the adsorbent media of biochar and alum sludge (4:1). A steel mesh may be used on top of the adsorbent media in bottom chamber to keep the media intact. The top chamber (basket) will capture the gross pollutants and release the stormwater in the bottom chamber to pass through the layers of adsorbent media. The filtration and hydraulics of top chamber will be similar to the results found in chapter 3, 4 and 5. The adsorption characteristics of bottom chamber will be similar to the results found in chapter 6, 7 and 8. The dimensions of the proposed modified CBI (e.g., height/volume of both chambers) will depend on the amount of pollutants and runoff generation based on the different land use type.

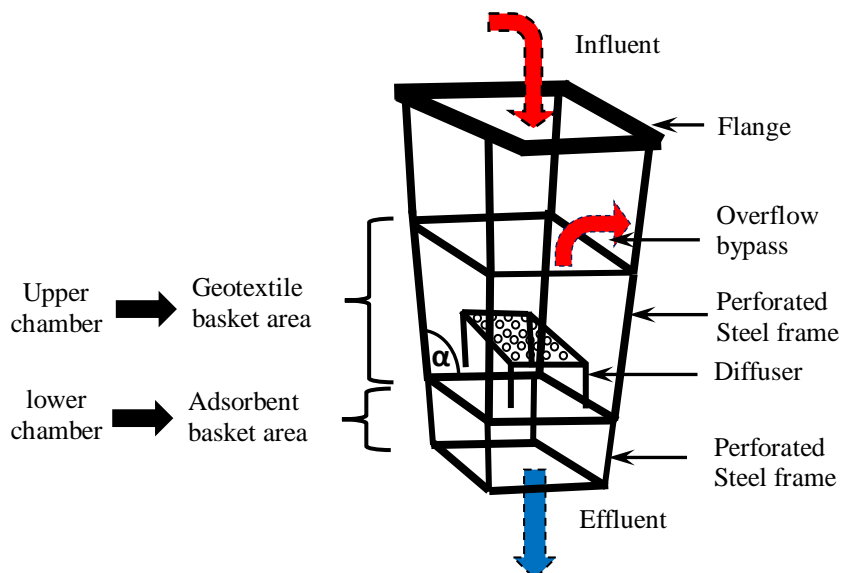


Fig. 8.3 Sketch of proposed modified CBI

8.5 Maintenance period of proposed CBI

The proposed CBI will be comprised of two distinct chambers. Therefore, the servicing can be done separately or combinedly. The individual servicing time (maintenance period) of two chambers are shown in Table 8.2. One important aspect of assessing the viability of a new filter is the duration in which it will function before becoming clogged or saturated. Based on the total solids loaded to geotextile filter at clogging during laboratory testing the filters would require maintenance after 15 and 59 rain events for soil type P1 and P2 respectively (Chapter 5; Alam et al., 2017b). On the other hand, the column test with adsorbents indicated that $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ was continued for 16-31, 16-33 and 15-34 rain events when concentrations drop 5 mg/L to 1 mg/L (considering 80 mins for one rain events similar to geotextile test criteria). Considering the average yearly rainfall for Western Australia is 1 m (Alam et al., 2017b), scaling up by 50 (runoff area to drainage area ratio) and runoff coefficient of 0.9 (Alam et al., 2017a & b), the maintenance days of the proposed CBI has shown in Table 8.2. A longer filter lifespan will result lower material costs caused by less frequent replacement. It will also lower the labour costs associated with training, oversight, and performance of filter maintenance. The current practise of maintenance of UST CBI was more than 10 times in a year. This indicates that the modified CBI would be more suitable for treating TSS and nutrients in field condition. However, further studies are recommended for evaluating optimum servicing frequency (maintenance period) and long-term performance under variable field conditions.

Table 8.2 Servicing frequency (maintenance period) of proposed CBI

Chamber location	Filter medium	Pollutants	C_0 (mg/L)	Rain events	Life span days
Upper	Geotextile (NWG1)	P1 soil	200	15	262
		P2 soil		59	1030
Lower	<i>EW</i> biochar and alum sludge	NH ₃ -N	1	31	151
			2.5	24	117
		5	16	78	
		NO ₂ -N	1	33	161
			2.5	25	122
		5	16	78	
		PO ₄ -P	1	34	166
			2.5	25	122
5	15	73			

8.6 Conclusion

Innovative stormwater treatment methods are crucial for preventing the negative impacts of stormwater runoff. This study measured the removal of nitrogen and phosphorous species in column experiment and proposed a new modified CBI to treat nutrients and sediment simultaneously from stormwater. The column test with mixed adsorbents (*EW* biochar and alum sludge) in layer indicated that NH₃-N, NO₂-N and PO₄-P was lasted for 16-31, 16-33 and 15-34 rain events respectively when concentrations drop 5 mg/L to 1 mg/L. The adsorption capacity of NH₃-N, NO₂-N and PO₄-P was found to increase from 62.5-88.3 µg/g; 46.3-84.2 µg/g and 22.5-346 µg/g respectively for increasing initial concentration from 1 to 5 mg/L. The maintenance days of the proposed CBI for geotextile and adsorbent chamber was found 262-1030 days and 73-166 days respectively. The current maintenance practice of CBI is 10 times per year indicated that the proposed modified CBI with adsorbent media would be suitable for treating both sediment and nutrients from stormwater at source.

List of notations

<u>Notation</u>		<u>unit</u>
C_0	: initial concentration	mg/L
C_t	: concentration at any time t	mg/L
V_f	: volumetric flow rate	L/hr
L	: adsorbent length in the column	cm
x	: amount of adsorbent in column	gm
t_b	: breakthrough time	hr
t_e	: exhaustion time	hr
q_0	: column adsorption capacity	mg/g
k_{TH}	: Thomas rate constant	L/mg.hr

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CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

This research addresses the different aspects of catch basin insert (CBI) for stormwater treatment at source. Firstly, it focuses on the characterisation and performance of CBI in field condition (chapter 3 and 4). Secondly, an effort has been made to find a suitable geotextile material for sediment removal using a prototype model in the laboratory (chapter 5). Thirdly, laboratory batch experiments were conducted using a low-cost adsorbent medium (i.e., *EW* biochar and alum sludge) to remove nutrients from stormwater (chapter 6 and 7). Finally, column experiment was conducted to check the dynamic behaviour of nutrient adsorption onto the mix adsorbent of *EW* biochar and alum sludge. Based on these results, a modified CBI is proposed by integrating suitable geotextile and adsorbent medium to remove sediments and nutrient simultaneously (chapter 8). Each chapter has conclusion specific to the chapter objectives but an overall conclusion and recommendation are presented in this chapter.

9.1 Conclusions

- Field investigations on gross pollutants (GPs) of UST CBI showed that it can effectively capture gross GPs down to particle sizes of 150 microns. The main GP component was found vegetation (93%) with a moisture content variation of 24-53%. The average accumulation of total GP load for each CBI was 384 kg/ha/yr (dry mass) and it is affected by seasonal environments. GPs accumulation showed a strong relationship ($r^2=0.9$) with rainfall especially during the wet season due to mobilization of pollutants by rainfall and storm events. The loading rate coefficient (K) which describes relative accumulation of GPs was found higher in the CBIs near trees. The results on the stormwater quality improvement of CBI shows that the concentrations of BOD, COD, TSS and PO₄-P were reduced by 90%, 88%, 88% & 26% respectively. The current UST CBI is not designed to remove dissolved pollutants but it may reduce the concentrations of some of the dissolved pollutants when the accumulated soil/wood materials act as adsorbents. However, the higher densities of smaller devices (e.g. CBI) may be more effective in

capturing GPs than larger devices spread further apart.

- In order to find a suitable geotextile for using it in CBI, the hydraulic performances of three selected geotextiles (NWG1, NWG2, NWG3) revealed that the filtration capacity is dependent on the geotextile texture and the soil grain sizes. It was found that the desired stormwater TSS concentration at outlet (<30 mg/L; ANZECC, 2000) was achieved within a short ripening process (e.g., 1-2 kg/m² of suspended solids loading) for larger particle sizes (P2, 0-300 µm). The overall capturing of P2 was 36% more than the smaller particle sizes (P1: 0-180 µm). The NWG1 could capture more TSS with maximum amount of small particles (which also resulted in earlier clogging) than NWG2 and NWG3 because of its special internal fiber structure. The clogging point is an important hydraulic parameter for geotextile filtration and it occurred between hydraulic conductivities of 0.85×10^{-5} m/s to 1.36×10^{-5} m/s. The overall hydraulic performances of geotextiles showed that the NWG1 may be considered with higher potential for using it in CBIs because of its higher strength and multiple reuse capability.
- The geotextile alone in CBI is capable to capture mainly the GPs. To remove the dissolved pollutants from stormwater using adsorbents and to integrate it in CBI, batch experiments conducted with *EW* biochar (as adsorbent) shows that it could remove NH₃-N and NO₂-N effectively (100% removal at lower concentration). However, the removal of NO₃-N was less than 1%. In order to remove nitrogen (NH₃-N and NO₂-N) and phosphorous (PO₄-P) simultaneously, another batch experiments were conducted with *EW* biochar and alum sludge together and the results show that 90% of PO₄-P was removed within 5 minutes for all concentrations but > 90% removal of NH₃-N and NO₂-N were achieved within 2-4 hours for lower concentration (1 mg/L). Based on the nutrient removal capacity, kinetics and isotherm data, the mixture of *EW* biochar and alum sludge was suggested to use it as adsorbent media in CBI.
- In order to test the mix adsorbent media (*EW* biochar and alum sludge) in dynamic condition (so as the case of CBI) to remove the nutrients, the column study was performed and the results revealed that the adsorbent bed provides steeper and

earlier breakthrough with a larger mass transfer zone at higher initial concentration. Adsorption capacities of all nutrients increase with increasing initial concentration. The results further suggest that the nutrient adsorptions may last for approximately 15-33 rain events for the concentration drops of 5 to 1 mg/L (considering one rain event lasts for 80 minutes). Based on the experimental data and the West Australian hydrologic data, the life span of the mix adsorbents was found varying between 73 to 161 days depending on nutrient types and their initial concentrations. Finally, a modified CBI comprising of two chambers is proposed integrating this mix adsorbent media. Both chambers will contain geotextile basket (may be NWG1). The upper geotextile basket will capture the GPs (including sediments) and the lower chamber basket will contain the mix adsorbent media (biochar and alum sludge) to remove nutrients from stormwater. As catch basin is the first point of stormwater collection system, this proposed modified CBI will be very useful to treat stormwater at source by capturing GPs and removing nutrients before releasing it to the storm drainage system.

9.2 Recommendation for future works

This research has been enclosed a comprehensive range of work for removing pollutants from stormwater using CBI. Several aspects of cleaning stormwater using CBI has been covered for removing GPs and dissolved nutrients. However, still there are many issues unresolved because of limited scope of this study which can be further investigated in future. These are summarized below:

1. The field investigation was limited to few CBIs and three sites only. In order to provide site specific information on the use of CBI, further investigation is required in many other sites with CBIs such as a range of brownfield and/or greenfield sites. Traffic parameters, such as vehicles during storm and vehicle intensity during storm may provide a more accurate representation of gross pollutants buildup in CBIs.
2. The water samplings of this study were done manually and other meteorological parameters (such as rainfall, temperature, wind speed etc.) were collected from meteorological departments. Further research can be carried out with automatic

sampler to collect the real-time specimen. Modern instruments (e.g., wireless anemometer, rain gauge etc.) can be set up at sampling site to measure the meteorological parameters more precisely.

3. While selecting geotextiles for using in CBIs, this study was limited to three geotextiles and two particle size distributions. Further research can be carried out with a wide range of geo-fabrics and soil types to select appropriate geotextile types and optimum efficiency in CBIs. Maintenance period of CBI was calculated under controlled condition with comparatively coarser particles. More finer particles and field investigation may be required considering other factors such as runoff characteristics, location, season and traffic volume for optimum maintenance period of CBI. Again, CBI may come in contact with high organic content from road and parking lot runoff. This may lead to biological growth onto CBI geotextile. This biological activity may limit the hydraulic conductivity of CBI geotextile enhancing early clogging and hence may be considered for future study.

4. The adsorbent and adsorbate in this study were limited to two materials (*EW* biochar and alum sludge) and two pollutants (i.e., nitrogen and phosphorous species) only. Further research may be conducted with some varieties of adsorbents (e.g., wood mulch, lime sludge, saw dust, biochar from different sources etc.) to select the best one for using it in CBI. Modification of these adsorbents (e.g., acidified/alkaline/Mg-Al layered adsorbents) with more stormwater pollutants such as heavy metals, PAHs, BOD, COD, oil and grease can also be considered for further investigations.

APPENDICES

APPENDIX A

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Title: Characterising stormwater gross pollutants captured in catch basin inserts

Author: Md Zahanggir Alam, A.H.M. Faisal Anwar, Dipok Chandra Sarker, Anna Heitz, Craig Rothleitner

Publication: Science of The Total Environment

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Cc: wsud2018@engineersaustralia.org.au <wsud2018@engineersaustralia.org.au>; kristy.chandler@coterra.com.au <kristy.chandler@coterra.com.au>;

Good afternoon Zahanggir,

I'm pleased to advise that Engineers Australia is happy for you to include the author version of your full paper (in a word document format) within your PhD thesis.

Best regards,

Kristen Smith | Conference & Events Coordinator
National Conferences & Events Team, Engineers Australia
T: (07) 3226 3028 | Ext: 4028 | engineersaustralia.org.au
Engineering House, 447 Upper Edward Street, Brisbane QLD 4000



From: Md. Zahanggir Alam [mailto:m.alam11@postgrad.curtin.edu.au]
Sent: Monday, 12 March 2018 5:29 PM
To: kristy.chandler@coterra.com.au
Cc: wsud2018@engineersaustralia.org.au
Subject: Permission

Dear Kristy,

I attended the last WSUD 2018 conference (attached certificate). This paper is part of PhD research and I will include this in my thesis. Therefore, could you please send me a permission letter (an email) to include this in my thesis.

Regards,

Md. Zahanggir Alam
PhD Candidate
Department of Civil Engineering

APPENDIX B

Written statements of the co-authors

To Whom It May Concern

I, Md Zahanggir Alam, as a first author declare that this work was primarily designed, sample collected from field, data collected from different sources, experimentally executed, interpreted and written by me to the publication entitled "Alam, M. Z., Anwar, F., Sarker, D.C., Heitz, A. and Rothleitner, C., 2017. Characterising stormwater gross pollutants captured in catch basin inserts. Science of The Total Environment, 586, pp.76-86, <http://dx.doi.org/10.1016/j.scitotenv.2017.01.219>"




(Signature of Candidate)

I, as a Co-Author, endorse that this level of contribution by the candidate indicated above is appropriate.


A. H. M. Faisal Anwar
(Full Name of Co-Author 1)


(Signature of Co-Author 1)

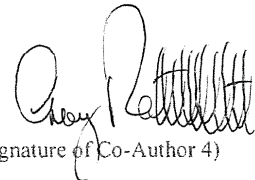
Dipok Chandra Sarker
(Full Name of Co-Author 2)


(Signature of Co-Author 2)

Anna Heitz
(Full Name of Co-Author 3)


(Signature of Co-Author 3)

Craig Rothleitner
(Full Name of Co-Author 4)


(Signature of Co-Author 4)

To Whom It May Concern

I, Md Zahangir Alam, as a first author declare that this work was primarily designed, sample collected from different sources, experimentally executed, interpreted and written by me to the publication entitled "Alam, M. Z., Anwar F., and Heitz, A., 2017. Stormwater solids removal characteristics of a catch basin insert using geotextile, Science of The Total Environment, 618, pp. 1054-1063, [https://doi.org/ 10.1016/j.scitotenv.2017.09.091](https://doi.org/10.1016/j.scitotenv.2017.09.091) "



(Signature of Candidate)

I, as a Co-Author, endorse that this level of contribution by the candidate indicated above is appropriate.

A. H. M. Faisal Anwar

(Full Name of Co-Author 1)



(Signature of Co-Author 1)

Anna Heitz

(Full Name of Co-Author 2)



(Signature of Co-Author 1)

To Whom It May Concern

I, Md Zahangir Alam, as a first author declare that this work was primarily designed, sample collected from different sources, experimentally executed, interpreted and written by me to the publication entitled "Alam, M. Z., Anwar, F., and Heitz, A, 2018. Removal of nutrients from stormwater using a mixed biochar-alum sludge adsorbent. Creating water sensitives communities, WSUD 2018 & HYDROPOLIS 2018 12th_15th February 2018, Perth, Western Australia. https://wsud2018.org.au/wp-content/uploads/2018/02/Alam_Removal-of-Nutrients.pdf"



(Signature of Candidate)

I as a Co-Author, endorse that this level of contribution by the candidate indicated above is appropriate.

A H. M. Faisal Anwar

(Full Name of Co-Author 1)



(Signature of Co-Author 1)

Anna Heitz

(Full Name of Co-Author 2)



(Signature of Co-Author 2)

APPENDIX C

Supplementary material of chapter 3

C1 Determination of particle size distribution (PSD) of particles retained by UST CBI

In order to determine the size distribution of particles retained by the UST CBI filter material, a sample of water representative of real conditions was prepared by making a slurry of drain litter in water. This water sample was passed through the UST CBI filter material. The particle size distribution (PSD) was analysed in the water sample prior to passing through the filter (Figure C1a) and after passing through the filter (Figure C1b). In the water that had passed through the filter, there were no detectable particles above 150 μm and 99% of particles below 150 μm were removed.

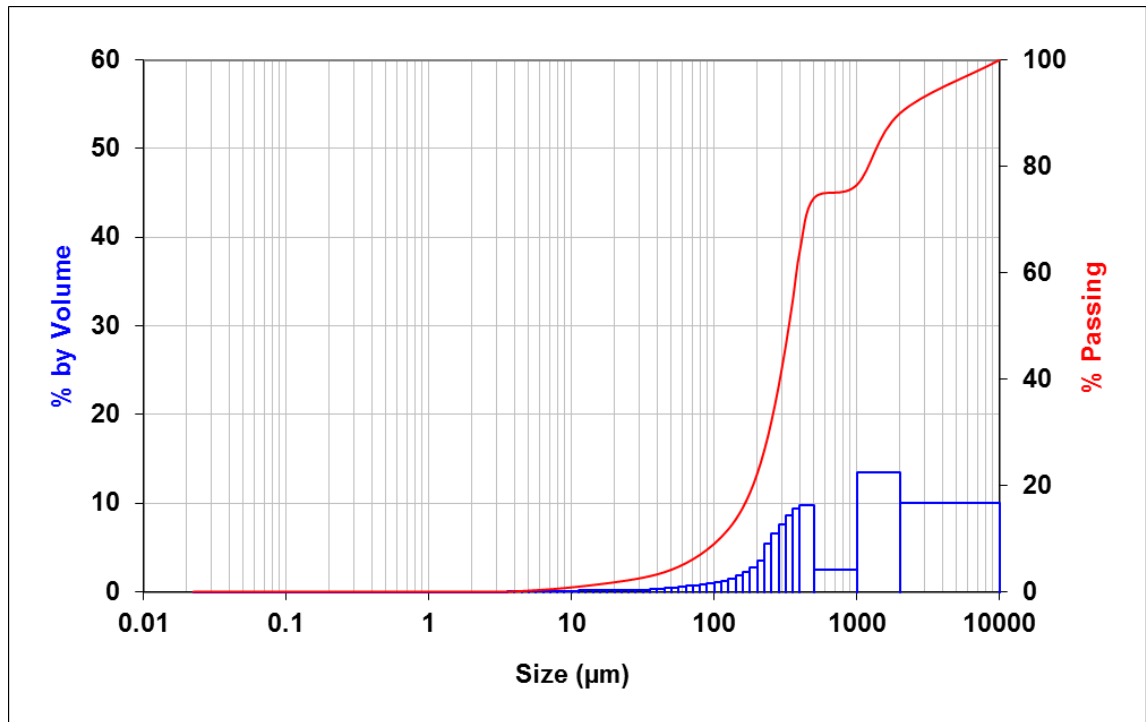


Fig. C1a: PSD of slurry of drain litter sample. The red line indicates the equivalent spherical volume of particles (volume % undersize)

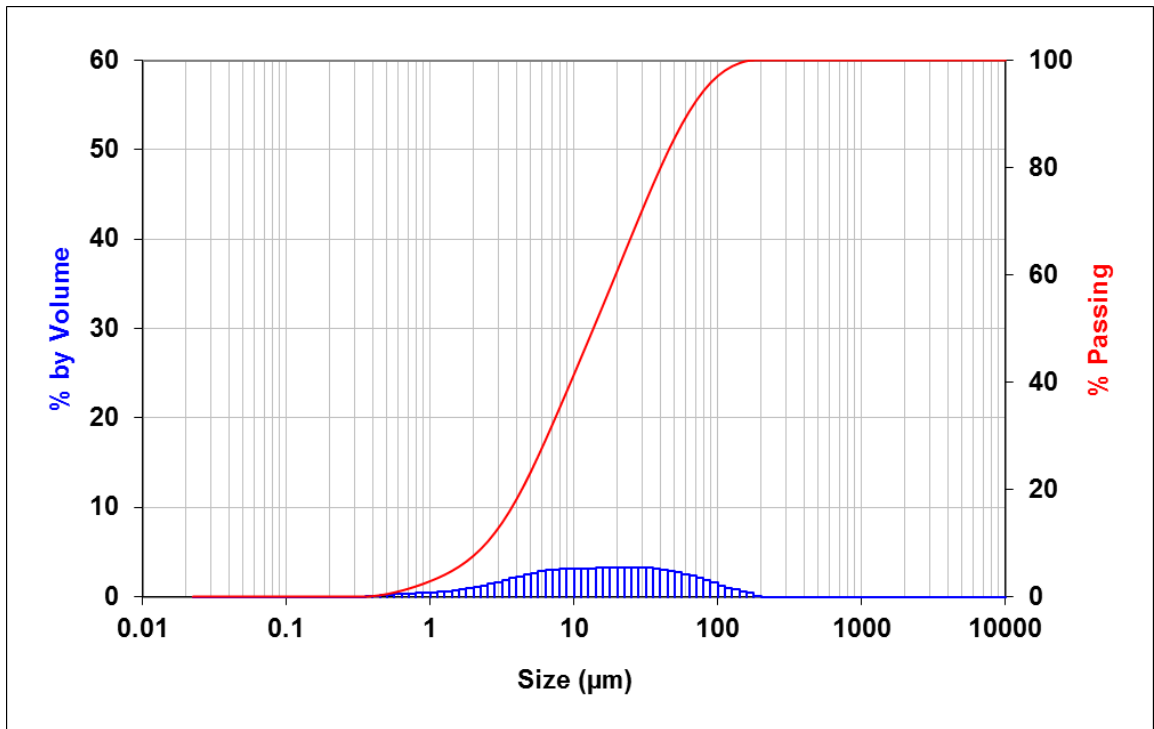


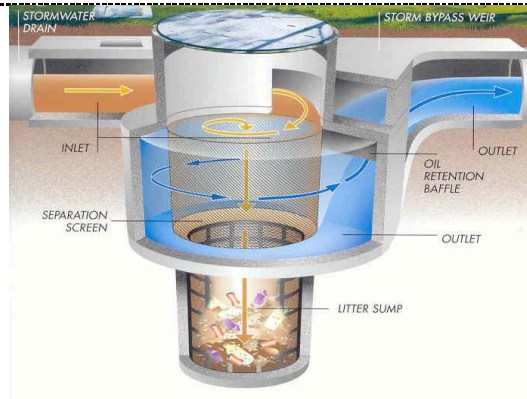
Fig. C1b: PSD of slurry of drain litter sample after sieving through UST CBI filter material, i.e. PSD of particles in water that had passed through the filter material. The red line indicates the equivalent spherical volume of particles (volume % undersize)

C2. Current available technologies to capture gross pollutants

Table C1: Different types of technologies for capturing gross pollutants.

Device name	Pictures/diagrams	References
Catch Basin Inserts		GeoSyntec and UCLA, (2005)

Continuous Deflective
System



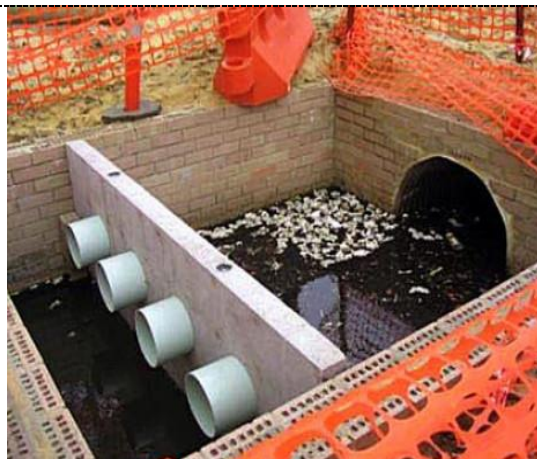
Allison et al.,
(1998a);
ROCLA (2016)

In line netting system
(NET)



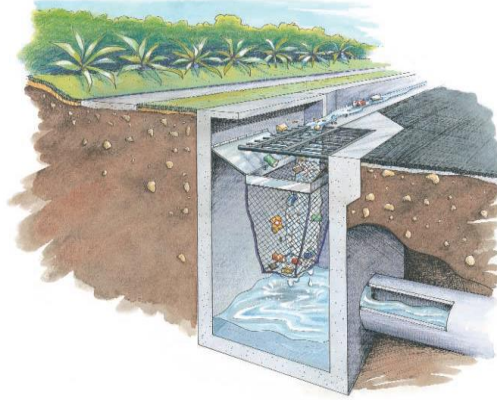
Lewis (2002)/
Hobart city
council website
(2016)/
[http://www.
Hobart
city.com.au/Envir
onment/Stormwat
er_and Waterwa
ys/Stormwater Qu
ality and Water
Conservation/](http://www.Hobartcity.com.au/Environment/Stormwater_and_Waterways/Stormwater_Quality_and_Water_Conservation/)
(accessed
13.09.2016)

Gross Pollutant Trap



Department of
water (Western
Australia)
(2016)/
[http://lgam.wiki
dot.com/gross-
pollutant-trap/](http://lgam.wiki dot.com/gross-pollutant-trap/)
(accessed
22.09.2016)

At Source Pit Trap



Chrispijn
(2004)/
Great lake
councils (2002)

Side Entry Pit Traps/

Litter basket



Allison et al.,
(1998a)/

[Kogarah City
Council website](http://www.kogarahcitycouncil.com.au)

(2016)

[/http://lgam.wiki
dot.com/ litter-
basket/](http://lgam.wiki dot.com/ litter- basket/)

(accessed

23.09.2016)

C3. GP particle size distributions for each CBI (May/2015- April/2016)

Table C3 GP particle size distributions for each CBI (May/2015- April/2016)

Particle sizes (mm)	Percentage fines that passed through each respective sieve for each CBI: Median (\pm Std. dev.)			
	6	7	8	13
>4.75	41.97(\pm 14.34)	29.57(\pm 6.78)	31.76(\pm 8.32)	18.05(\pm 8.95)
2.36-4.75	26.32(\pm 8.04)	20.53(\pm 4.64)	19.80(\pm 8.03)	12.52(\pm 6.19)
1.18-2.36	21.41(\pm 6.89)	13.64(\pm 3.56)	13.36(\pm 8.02)	7.77(\pm 3.75)
0.6-1.18	15.08(\pm 5.33)	9.30(\pm 2.22)	9.16(\pm 5.99)	5.08(\pm 2.75)
0.425-0.6	9.34(\pm 3.67)	5.34(\pm 1.72)	5.79(\pm 4.51)	3.13(\pm 1.73)
0.3-0.425	5.45(\pm 2.38)	3.43(\pm 1.38)	3.48(\pm 1.92)	2.27(\pm 0.87)
0.15*-0.3	3.03(\pm 1.18)	1.88(\pm 0.82)	2.59(\pm 1.65)	1.44(\pm 0.94)
<0.075	0.92(\pm 0.42)	0.53(\pm 0.35)	0.96(\pm 0.99)	0.44(\pm 0.52)

*Material found below 150 microns comprises the residue produced from decomposition of
vegetation

APPENDIX D

External laboratory (SGS) data sheet

CLIENT DETAILS		LABORATORY DETAILS	
Contact	EUAN	Manager	Ros Ma
Client	ENERGY FARMERS AUSTRALIA PTY LTD	Laboratory	SGS Newburn Environmental
Address	164 AUGUSTUS STREET GERALDTON WA 6530	Address	10 Reid Rd Newburn WA 6105
Telephone	(Not specified)	Telephone	(08) 9373 3500
Facsimile	(Not specified)	Facsimile	(08) 9373 3556
Email	euan@energyfarmers.com.au	Email	au.environmental.perth@sgs.com
Project	Bio Char	SGS Reference	PE091024 R0
Order Number	(Not specified)	Report Number	000090871
Samples	1	Date Reported	31 Jul 2014
Date Started	28 Jul 2014	Date Received	24 Jul 2014

COMMENTS
 Accredited for compliance with ISO/IEC 17025. NATA accredited laboratory 2562(898/20210).

SIGNATORIES

Hue Thanh Ly Metals Team Leader	Michael McKay Inorganics and ARD Supervisor	Ros Ma Laboratory Manager

Sample Number	PE091024.001
Sample Matrix	Carbon
Sample Date	24 Jul 2014
Sample Name	Bio Char

Parameter	Units	LOR
Moisture Content Method: AN002		
% Moisture	%	0.5

pH in soil (1:5) Method: AN101		
pH	pH Units	-
		5.0

Total Recoverable Metals in Soil by ICPOES Method: AN320AN321			
Arsenic, As	mg/kg	1	<1
Cadmium, Cd	mg/kg	0.3	<0.3
Chromium, Cr	mg/kg	0.5	4.2
Copper, Cu	mg/kg	0.5	2.7
Lead, Pb	mg/kg	1	6
Nickel, Ni	mg/kg	0.5	1.7
Zinc, Zn	mg/kg	2	9

Mercury in Soil Method: AN312			
Mercury	mg/kg	0.05	<0.05

SVOC In Soil Method: AN420			
OCs			
Alpha-BHC	mg/kg	0.1	<0.1
Hexachlorobenzene (HCB)	mg/kg	0.1	<0.1
Beta-BHC	mg/kg	0.1	<0.1
Gamma-BHC (Lindane)	mg/kg	0.1	<0.1
Delta-BHC	mg/kg	0.1	<0.1
Heptachlor	mg/kg	0.1	<0.1
Aldrin	mg/kg	0.1	<0.1
Heptachlor epoxide	mg/kg	0.1	<0.1
Iaodrin	mg/kg	0.1	<0.1
Gamma-chlordane	mg/kg	0.1	<0.1
Alpha-chlordane	mg/kg	0.1	<0.1
Alpha-endosulfen	mg/kg	0.2	<0.2
p,p'-DDE	mg/kg	0.1	<0.1
Dieldrin	mg/kg	0.2	<0.2
Endrin	mg/kg	0.2	<0.2
Beta-endosulfen	mg/kg	0.2	<0.2
p,p'-DDD	mg/kg	0.1	<0.1
Endosulfen sulphate	mg/kg	0.1	<0.1
p,p'-DDT	mg/kg	0.1	<0.1
Endrin ketone	mg/kg	0.1	<0.1
Methoxychlor	mg/kg	0.1	<0.1
Mirex	mg/kg	0.1	<0.1

Sample Number PE091024.001
 Sample Matrix Carbon
 Sample Date 24 Jul 2014
 Sample Name Bio Char

Parameter Units LOR

SVOC in Soil Method: AN420 (continued)

OPs

Dichlorvos	mg/kg	1	<1
Dimethoate	mg/kg	1	<1
Diazinon (Dimpylate)	mg/kg	0.5	<0.5
Fenitrothion	mg/kg	0.2	<0.2
Malethion (Maldison)	mg/kg	0.2	<0.2
Chlorpyrifos (Chlorpyrifos Ethyl)	mg/kg	0.2	<0.2
Parathion ethyl (Parathion)	mg/kg	0.2	<0.2
Bromophos ethyl	mg/kg	0.2	<0.2
Methidathion	mg/kg	0.5	<0.5
Ethion	mg/kg	0.2	<0.2
Acetophen-methyl (Guthion)	mg/kg	0.2	<0.2

SVOC Surrogates

2-fluorobiphenyl (Surrogate)	%	-	104
d5-phenol (Surrogate)	%	-	81
2,4,6-tribromophenol (Surrogate)	%	-	-
d14-p-terphenyl (Surrogate)	%	-	78
d5-nitrobenzene (Surrogate)	%	-	76

Total Carbon and TOC by LECO Furnace Method: AN203

Total Organic Carbon (TOC)	%dw	0.02	81
----------------------------	-----	------	----

MB blank results are compared to the Limit of Reporting
 LCS and MS spike recoveries are measured as the percentage of analyte recovered from the sample compared to the amount of analyte spiked into the sample.
 DUP and MSD relative percent differences are measured against their original counterpart samples according to the formula: the absolute difference of the two results divided by the average of the two results as a percentage. Where the DUP RPD is 'NA', the results are less than the LOR and thus the RPD is not applicable.

Mercury In Soil Method: ME-(AU)-(ENV)AN812

Parameter	GC Reference	Units	LOR	MB	DUP %RPD	LCS %Recovery	MS %Recovery	MSD %RPD
Mercury	LB066020	mg/kg	0.05	<0.05	0%	110%	101%	1%

Molature Content Method: ME-(AU)-(ENV)AN002

Parameter	GC Reference	Units	LOR	DUP %RPD
% Moisture	LB066008	%	0.5	2%

pH In soil (1:6) Method: ME-(AU)-(ENV)AN101

Parameter	GC Reference	Units	LOR	DUP %RPD	LCS %Recovery
pH	LB066008	pH Units	-	0 - 2%	99%

SVOC In Soil Method: ME-(AU)-(ENV)AN420

OCs

Parameter	GC Reference	Units	LOR	MB	DUP %RPD	LCS %Recovery	MS %Recovery	MSD %RPD
Alpha-BHC	LB066071	mg/kg	0.1	<0.1	0%			
Hexachlorobenzene (HCB)	LB066071	mg/kg	0.1	<0.1	0%	NA	NA	NA
Beta-BHC	LB066071	mg/kg	0.1	<0.1	0%			
Gamma-BHC (Lindane)	LB066071	mg/kg	0.1	<0.1	0%	91%	86%	1%
Delta-BHC	LB066071	mg/kg	0.1	<0.1	0%			
Heptachlor	LB066071	mg/kg	0.1	<0.1	0%	90%	82%	1%
Aldrin	LB066071	mg/kg	0.1	<0.1	0%	92%	86%	2%
Heptachlor epoxide	LB066071	mg/kg	0.1	<0.1	0%			
Isoctin	LB066071	mg/kg	0.1	<0.1	0%	95%	86%	2%
Gamma-chlordane	LB066071	mg/kg	0.1	<0.1	0%	90%	85%	1%
Alpha-chlordane	LB066071	mg/kg	0.1	<0.1	0%			
Alpha-endosulfen	LB066071	mg/kg	0.2	<0.2	0%			
p,p'-DDE	LB066071	mg/kg	0.1	<0.1	0%	96%	87%	0%
Dieldrin	LB066071	mg/kg	0.2	<0.2	0%	91%	86%	1%
Erdin	LB066071	mg/kg	0.2	<0.2	0%	90%	86%	1%
Beta-endosulfen	LB066071	mg/kg	0.2	<0.2	0%			
p,p'-DDD	LB066071	mg/kg	0.1	<0.1	0%			
Endosulfen sulphate	LB066071	mg/kg	0.1	<0.1	0%			
p,p'-DDT	LB066071	mg/kg	0.1	<0.1	0%			
Erdin ketone	LB066071	mg/kg	0.1	<0.1	0%			
Methoxychlor	LB066071	mg/kg	0.1	<0.1	0%			
Mirex	LB066071	mg/kg	0.1	<0.1	0%	99%	93%	7%

OPs

Parameter	GC Reference	Units	LOR	MB	DUP %RPD	LCS %Recovery	MS %Recovery	MSD %RPD
Dichlorvos	LB066071	mg/kg	1	<1	0%			
Dimethoate	LB066071	mg/kg	1	<1	0%			
Diazinon (Dimpylate)	LB066071	mg/kg	0.5	<0.5	0%	86%	81%	2%
Fenitrothion	LB066071	mg/kg	0.2	<0.2	0%			
Malethion (Maldison)	LB066071	mg/kg	0.2	<0.2	0%			
Chlorpyrifos (Chlorpyrifos Ethyl)	LB066071	mg/kg	0.2	<0.2	0%	86%	77%	1%
Parathion ethyl (Parathion)	LB066071	mg/kg	0.2	<0.2	0%	93%	80%	2%
Bromophos ethyl	LB066071	mg/kg	0.2	<0.2	0%			
Methidathion	LB066071	mg/kg	0.5	<0.5	0%	88%	82%	2%
Ethion	LB066071	mg/kg	0.2	<0.2	0%			
Acetiphos-methyl (Duthion)	LB066071	mg/kg	0.2	<0.2	0%			

SVOC Surrogates

MB blank results are compared to the Limit of Reporting
 LCS and MS spike recoveries are measured as the percentage of analyte recovered from the sample compared to the amount of analyte spiked into the sample.
 DUP and MSD relative percent differences are measured against their original counterpart samples according to the formula: the absolute difference of the two results divided by the average of the two results as a percentage. Where the DUP RPD is 'NA', the results are less than the LOR and thus the RPD is not applicable.

SVOC In Soil Method: ME-(AU)-(ENV)AN420 (continued)

Parameter	GC Reference	Units	LOR	MB	DUP %RPD	LCS %Recovery	MS %Recovery	MSD %RPD
2-fluorobiphenyl (Surrogate)	LB066871	%	-	106%	6%	102%	90%	0%
d5-phenol (Surrogate)	LB066871	%	-	89%	0%	104%	85%	1%
d14-p-terphenyl (Surrogate)	LB066871	%	-	90%	0%	100%	86%	2%
d5-nitrobenzene (Surrogate)	LB066871	%	-	72%	5%	96%	78%	7%

Total Carbon and TOC by LECO Fumaoc Method: ME-(AU)-(ENV)AN203

Parameter	GC Reference	Units	LOR	MB	DUP %RPD	LCS %Recovery
Total Organic Carbon (TOC)	LB066967	%wt	0.02	<0.02	0%	92 - 100%

Total Recoverable Metals in Soil by ICPOES Method: ME-(AU)-(ENV)AN320AN321

Parameter	GC Reference	Units	LOR	MB	DUP %RPD	LCS %Recovery	MS %Recovery	MSD %RPD
Arsenic, As	LB066920	mg/kg	1	<1	0%	107%	104%	1%
Cadmium, Cd	LB066920	mg/kg	0.3	<0.3	0%	98%	103%	1%
Chromium, Cr	LB066920	mg/kg	0.5	<0.5	6%	96%	92%	1%
Copper, Cu	LB066920	mg/kg	0.5	<0.5	4%	87%	100%	0%
Lead, Pb	LB066920	mg/kg	1	<1	1%	95%	89%	0%
Nickel, Ni	LB066920	mg/kg	0.5	<0.5	19%	105%	104%	1%
Zinc, Zn	LB066920	mg/kg	2	<2	8%	99%	79%	4%

METHOD

METHODOLOGY SUMMARY

AN002	The test is carried out by drying (at either 40°C or 105°C) a known mass of sample in a weighed evaporating basin. After fully dry the sample is re-weighed. Samples such as sludge and sediment having high percentages of moisture will take some time in a drying oven for complete removal of water.
AN101	pH in Soil Sludge Sediment and Water: pH is measured electrometrically using a combination electrode (glass plus reference electrode) and is calibrated against 3 buffers purchased commercially. For soils, an extract with water (or 0.01M CaCl ₂) is made at a ratio of 1:5 and the pH determined and reported on the extract. Reference APHA 4500-H+.
AN203	The carbon in the sample is oxidised to carbon dioxide gas in a tube furnace using oxygen to aid the oxidation process. The evolved carbon dioxide is measure by an infra red cell. The infra red cell output is calibrated against the value of a known standard sample to provide the total carbon value of the unknown sample.
AN203	The sample is pretreated with hydrochloric acid to remove inorganic carbon/carbonate. The residual non-carbonate carbon is oxidised to carbon dioxide gas in a tube furnace using oxygen to aid the oxidation process. The evolved carbon dioxide is measure by an infra red cell. The infra red cell output is calibrated against the value of a known standard sample to provide the total organic carbon value of the unknown sample.
AN312	Mercury by Cold Vapour AAS In Soils: After digestion with nitric acid, hydrogen peroxide and hydrochloric acid, mercury ions are reduced by stannous chloride reagent in acidic solution to elemental mercury. This mercury vapour is purged by nitrogen into a cold cell in an atomic absorption spectrometer or mercury analyser. Quantification is made by comparing absorbances to those of the calibration standards. Reference APHA 3112/3500
AN320/AN321	Metals by ICP-OES: Samples are preserved with 10% nitric acid for a wide range of metals and some non-metals. This solution is measured by Inductively Coupled Plasma. Solutions are aspirated into an argon plasma at 8000-10000K and emit characteristic energy or light as a result of electron transitions through unique energy levels. The emitted light is focused onto a diffraction grating where it is separated into components.
AN320/AN321	Photomultipliers or CCDs are used to measure the light intensity at specific wavelengths. This intensity is directly proportional to concentration. Corrections are required to compensate for spectral overlap between elements. Reference USEPA3050, USEPA6010C and APHA 3120 B.
AN420	SVOC Compounds: Semi-Volatile Organic Compounds (SVOCs) including OC, OP, PCB, Herbicides, PAH, Phthalates and Speciated Phenols (etc) in soils, sediments and waters are determined by GCMS/ECD technique following appropriate solvent extraction process (Based on USEPA 3500C and 8270D).

FOOTNOTES

IS	Insufficient sample for analysis.	LOR	Limit of Reporting
LNR	Sample listed, but not received.	↑↓	Raised or Lowered Limit of Reporting
*	This analysis is not covered by the scope of accreditation.	QFH	QC result is above the upper tolerance
**	Indicative data, theoretical holding time exceeded.	QFL	QC result is below the lower tolerance
^	Performed by outside laboratory.	-	The sample was not analysed for this analyte
		NVL	Not Validated

Samples analysed as received.
Solid samples expressed on a dry weight basis.

Some totals may not appear to add up because the total is rounded after adding up the raw values.

The QC criteria are subject to internal review according to the SGS QAQC plan and may be provided on request or alternatively can be found here: <http://www.sgs.com.au/pv.sgsv3/~media/Local/Australia/Documents/Technical%20Documents/MP-AU-ENV-QU-022%20QA%20QC%20Plan.pdf>

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