Mitigation of Pollutants for Beneficial Use of Stormwater

By

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A Thesis submitted in fulfilment for the degree of

Doctor of Philosophy

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February 2016

CERTIFICATE OF AUTHORSHIP/ ORIGINALITY

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Candidate

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Danious Pratheep Sounthararajah

February 2016.

Acknowledgement

It would not have been possible to achieve this doctorate of philosophy without the help and support of all the people around me. I am highly appreciative to everyone for their help and support during my research.

My first thanks and gratitude goes to my principal supervisor A.Prof. Jaya Kandasamy for the patient guidance and unwearying mentorship and consideration he provided to me, all the way from the start of the PhD degree through to completion of this degree. I would also like to show my thanks and gratitude to my co-supervisors Prof. S. Vigi Vigneswaran and Dr Paripurnanda Loganathan for their tremendous help and support through my whole PhD study. I would also like to thank Drs Prabhu Sivabalan, Vinh Nguyen, Benjamin Kus, Thamer Mohammed and Amit Chanan for their help and support. I would also like to thank my colleagues and lab mates Chung, Kalaruban, Roobavannan, Tanjina, Sukanya, Gayathri, Alex, Sanjeev, Tanh, Hang, Deng, Muna and Jeong, in CTWW. I had a wonderful time with these guys. I would like to give a special mention to my team member and Senior Technical Officer of Environmental Engineering Laboratories, Md Abu Hasan Johir who had always been supportive in sharing his valuable time and ideas for my research. I am also thankful to the academic and technical support of the University of Technology Sydney and its staff, especially Phyllis, Crieg and Kevin for all my academic support and Rami Haddad and David Hooper for their help and support in the environmental and hydraulics laboratories.

I would like to show my gratitude to University of Technology Sydney and CRC Care for their encouragement and financial support of the study. I am thankful to my dear parents and my sister for providing me with great opportunities in life and encouraging me to enter the field of Engineering. I would like to give special thanks to my dear wife and her family for their love and support in latter stage of my PhD. Last but not least, I would also like to thank the rest of my family and friends who have also provided great support during this time.

DEDICATION OF THIS THESIS

TO MY LOVELY PARENTS

Journal articles published

1. Kandasamy J., Sounthararajah D., Sivabalan P., Chanan A., Vigneswaran S. and Sivapalan M. (2014). Socio-hydrologic drivers of the pendulum swing between agricultural development and environmental health: a case study from Murrumbidgee River basin, Australia. *Hydrology and Earth System Sciences* **18**(3), 1027-41.
2. Sounthararajah D. P., Loganathan P., Kandasamy J. and Vigneswaran S. (2015a). Adsorptive removal of heavy metals from water using sodium titanate nanofibres loaded onto GAC in fixed-bed columns. *Journal of Hazardous materials* **287**, 306-16.
3. Sounthararajah D. P., Loganathan P., Kandasamy J. and Vigneswaran S. (2015b). Column studies on the removal of dissolved organic carbon, turbidity and heavy metals from stormwater using granular activated carbon. *Desalination and Water Treatment*, **57**(11), 5045-5055.
4. Sounthararajah D. P., Kandasamy J., Loganathan P. and Vigneswaran S. (2015c). Heavy metals removal by a permeable pavement with zeolite or basalt bedding material and a nano titanate filter. *Journal of Hazardous materials*, Submitted.
5. Sounthararajah D. P., Loganathan P., Kandasamy J. and Vigneswaran S. (2015d). Effects of humic acid and suspended solids on the removal of heavy metals from water by adsorption onto granular activated carbon. *International Journal of Environmental Research and Public Health*, **12**(9), 10475-10489.
6. Kus B., Sountharajah D.P., Kandasamy J., Vigneswaran S., and Moody G., (2015). Quantifying reductions in water demand due to rainwater tank installations at residential properties in Sydney. *Journal Renewable & Sustainable Energy Reviews*. Submitted.

Conference papers and presentation

1. Sounthararajah D. P., Loganathan P., Kandasamy J., Vigneswaran S. (2014) High rate filtration system for stormwater treatment, FEIT Research Showcase 2014, UTS, Sydney, Australia, 4th September, 2014.
2. Sounthararajah D. P., Kandasamy J., Loganathan P., Vigneswaran S. (2014) High rate stormwater treatment system for beneficial use, CRC Communication Conference, Adelaide, South Australia, 10th – 13th September, 2014.
3. Kus B., Sountharajah D.P., Kandasamy J., Vigneswaran S., and Moody G., (2015). Quantifying reductions in water demand due to rainwater tank installations at residential properties in Sydney. 10th Conference on Sustainable Development of Energy, Water and Environment Systems, Dubrovnik, Croatia, 26 Sept-3 Oct 2015.

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NOMENCLATURE

ABS = Australian bureau of statistics

BOM = bureau of methodology

C = the bulk phase concentration (mg/L)

C_0 = initial concentration of adsorbate (mg/L)

C_e = equilibrium concentration of adsorbate (mg/L)

C_o = inlet adsorbate concentration (mg/L)

Cs = the concentration on the external surface (mg/L)

Ct = concentration of adsorbate at time t (mg/L)

DOC = dissolved organic carbon

FTIR = Fourier transform infrared spectroscopy

g = gram

g/L = gram per litre

GAC = granular activated carbon

HA = humic acid

HCl = hydrochloric acid

HFO = iron (iii) oxide

HM = heavy metals

hr/h = hours

K_F = Freundlich constants (mg/g)

K_L = Langmuir constant related to the energy of adsorption (L/mg)

L = litre

M = mass of dry adsorbent (g)

m/h = meter per hour

min = minutes

mL/min = millilitre per minute

n = Freundlich constant

$NaNO_3$ = sodium nitrate

PPS = permeable pavement system

Q = Flow rate (cm^3/s)

Q_e = amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

q_{max} = maximum amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

q_o= equilibrium adsorbate uptake per g of adsorbent (mg/g)

rpm = revolutions per minute

SEM = Scanning electron microscopy

SS = suspended solids

SWC = Sydney water corporation

TNF = sodium nano titanate

TOC = total organic carbon

V = the interstitial velocity (m/s)

V = volume of the solution (L)

XPS = X-ray photoelectron spectroscopy

XRD = X-ray diffraction

ZPC = zero point of charge

ABSTRACT

This thesis examines the efficiency of water demand management techniques throughout Sydney and incorporates possible treatment measures for the removal of the major pollutants of stormwater and their interactions during their removals. After a thorough literature review on the subject in the second chapter, the third chapter discussed the actual reductions in consumption of town water supply due to the widespread installation of rainwater tanks. More specifically it examined the levels of rainwater tank installation in single residential properties in the Sydney metropolitan area and surrounding areas connected to Sydney Water Corporation (SWC) water supply mains. These residential properties' water consumption patterns were based on metered potable water usage between 2002 and 2009. The number of properties in the study database totalled 962,697 single residential dwellings. This was compared against the potable water consumption of residential properties that did install a rainwater tank. By 2009 a total of 52,576 households had registered for a rainwater tank rebate with SWC which represented 5.5% of Sydney's total households. The water usage consumption before and after the installation of the rainwater tank was analysed to quantify the extent to which rainwater tanks reduced mains water consumption. This study showed that the average annual water consumption per household in Sydney's metropolitan area declined from 282 kL/annum (2002) to 200 kL/annum by 2009. The average water consumption fell by 24% over the study period. In many local government authorities (LGAs) in Sydney this reduction was over 28% and up to 33.5%. It may be attributed to effective demand managing techniques such as the Sydney-wide water restrictions, the introduction of water efficient fixtures like taps, dual flush toilets, and efficient shower heads, etc. The average percentage of water savings by installing rainwater tanks across all 44 LGAs was a further 9%. In some

Sydney localities this reduction was up to 15%. On average, a household was able to save around 24 kL of water annually by installing a rainwater tank even without considering other factors that affect water usage. The results were compared against socio-demographic factors using variables such as household size, educational qualifications, taxable income, rented properties, and non-English-speaking background, etc.

Stormwater pollutants have the capacity to damage aquatic environments if they are discharged untreated. Heavy metals constitute some of the most dangerous pollutants of water as they are toxic to humans, animals, and aquatic organisms. These metals are considered to be of major public health concern and therefore need to be removed. Adsorption is a common physico-chemical process used to remove heavy metals. Dissolved organic carbon (DOC) and suspended solids (SS) are associated pollutants in water systems that can interact with heavy metals during the treatment process. In the fourth chapter, the interactions of DOC and SS during the removal of heavy metals by granular activated carbon (GAC) were investigated in batch and fixed-bed column experiments. Batch adsorption studies indicated that Langmuir adsorption maxima for Pb, Cu, Zn, Cd, and Ni at pH 6.5 were 11.9, 11.8, 3.3, 2.0, and 1.8 mg/g, respectively. With the addition of humic acid (HA) (DOC representative), they were 7.5, 3.7, 3.2, 1.6, and 2.5 mg/g, respectively. In the column experiment, no breakthrough (complete removal) was obtained for Pb and Cu but adding HA made a breakthrough in removing these metals. For Zn, Cd and Ni this breakthrough occurred even without HA being added. Adding kaolinite (representative of SS) had no effect on Pb and Cu but it did on the other metals.

In the fifth chapter, study was undertaken to remove Cu, Cd, Ni, Pb and Zn individually (single metal system) and together (mixed metals system) from water by adsorption onto a sodium titanate nanofibrous material. Langmuir adsorption capacities (mg/g) at 10^{-3} M $NaNO_3$ ionic strength in the single metal system were 60, 83, 115 and 149 for Ni, Zn, Cu, and Cd, respectively, at pH 6.5 and 250 for Pb at pH 4.0. In the mixed metals system they decreased at high metals concentrations. In column experiments with 4% titanate material and 96% granular activated carbon (w/w) mixture at pH 5.0, the metals breakthrough times and adsorption capacities (for both single and mixed metals systems) decreased in the order Pb > Cd, Cu > Zn > Ni within 266 bed volumes. The amounts adsorbed were up to 82 times higher depending on the metal in the GAC + titanate column than in the GAC column. The study showed that the titanate material has high potential for removing heavy metals from polluted water when used with GAC at a very low proportion in fixed-bed columns.

In the sixth chapter, suspended solids (turbidity) dissolved organic carbon (DOC) and heavy metals removals from stormwater were investigated in batch and fixed-bed column experiments. Field studies revealed that turbidity and DOC in stormwater were effectively removed at filtration velocities of 5, 10 and 11.5 m/h using a 100 cm height GAC filter column. At the higher filtration velocities of 10 and 11.5 m/h, adding a pre-treatment 100 cm height anthracite filter column further improved DOC and turbidity removal. Batch and column laboratory adsorption experiments at pH 6.5-7.2 using GAC showed that the order of removal efficiency for solutions containing single and mixed metals was Pb, Cu > Zn > Ni, Cd. This order was related to the solubility product and first hydrolysis constants of these metals' hydroxides. This study confirmed that GAC filter is effective in removing turbidity, DOC and heavy metals from stormwater.

Permeable pavement systems (PPS) constitute a widespread treatment measure used in sustainable stormwater management and groundwater recharge. However, PPS are not especially efficient in removing heavy metals from stormwater. In the seventh chapter, pilot scale study using zeolite or basalt as bed material in PPS removed 41-72%, 67-74%, 38-43%, 61-72%, 63-73% of Cd, Cu, Ni, Pb, and Zn, respectively, from synthetic stormwater (pH 6.5) that passed through the PPS for 80 h. Total volume of stormwater was equivalent to runoff in 10 years of rainfall in Sydney, Australia. Metals concentrations in effluent did not satisfy fresh and marine water quality trigger values contained in the Australian and New Zealand guidelines. However, when a post-treatment of a horizontal filter column containing TNF of weight < 1% of zeolite weight and mixed with granular activated carbon was incorporated into the PPS, 77% Ni and 99-100% of all the other metals were removed. Subsequently the effluent satisfactorily met the required standards of marine waters and just met those concerning fresh waters. Batch adsorption data from solutions of metals mixtures fitted the Langmuir model with adsorption capacities in the following the order, TNF >> zeolite > basalt; Pb > Cu > Cd, Ni, Zn.

CHAPTER 1

UTS

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INTRODUCTION

1 Introduction

1.1 Research background

Australia is the driest inhabited continent on earth. The last and long drought experienced from 2001 to 2009 and the pattern of droughts exacerbates recent concerns about the impact of climate change and predicted population growth in capital cities. These factors will have a major effect on water supply and irrigation and they include: the requirement of large catchment areas to supply, capture and store raw water for urban use; increase in the volume of discharge of wastewater and stormwater to (downstream) receiving waters (rivers, lakes, estuaries and coastal areas); and the significant modification to natural hydrological regimes and associated ecological processes in waterways upstream, within and downstream of the urban areas. A number of solutions can be utilised to save water either by reducing water demand and increasing efficiency of its use or by increasing the available supply.

Of all the possible ways, reducing the demand is the most tangible and sustainable way of securing water supplies (Butler and Memon 2006). Recent developments in water efficient fixtures like shower heads, taps, and dual flush toilets have improved water saving. Water consumption and demand patterns are highly varied across households due to the behaviour changes, climate, socio-demographics, household size, family composition, water appliances, cultural and personal practises, etc. (Juárez-Nájera et al. 2010; Loh and Coghlan 2003; Russell and Fielding 2010).

On the other hand, methods of increasing the available supply of water also seem to be achievable as the government has invested heavily in desalination and wastewater recycling plants. Compared to desalination and wastewater recycling, stormwater can be less polluted and potentially easier to treat. In Australia, water recycling has increasingly becoming a valuable contributor to the supply of water even as stormwater harvesting has not been fully utilised. Harvesting and storing stormwater offers a good alternative source for potable water supply and treated stormwater can also be employed for non-potable uses which account more than 40% of household domestic water demand (Loh and Coghlan 2003). The average annual volume of urban stormwater runoff in Australian cities is almost equal to the average annual urban water usages, of which at least 50% is for non-potable purposes. Stormwater treatment can be less expensive and more acceptable to the public compared with wastewater recycling (Kus et al. 2012).

Urban stormwater carries many pollutants such as heavy metals, dissolved organic carbon (DOC), and suspended solids (SS). These pollutants pose a serious danger to the environment if untreated. Studies on the removal of a single pollutant are extensive but the interactions between different pollutants during their removal have been reported only in very few cases. Heavy metals are generating much concern due to their acute toxicity and long-term accumulation and persistence. Numerous methods are available for removing heavy metals from contaminated water such as chemical precipitation, ion exchange adsorption, membrane filtration and electrochemical technologies (Chen 2012; Nyman and Hobbs 2006; Wang et al. 2013). Of these methods, adsorption is preferred due to its simplicity, efficiency, flexibility in design and low waste production (Hua et al. 2012; Pan et al. 2009; Wang et al. 2013).

The adsorption of pollutants especially heavy metals from stormwater using different adsorbents has been extensively studied. However, there are many issues and drawbacks that have not been addressed. There are not many studies that use a dynamic fixed-column arrangement to treat stormwater which is more practical than the commonly used batch experiments. Therefore, it is useful to carry out adsorption experiments in the column mode System and also pilot-scale testing of stormwater treatment in the field such as field columns and permeable pavements will provide valuable information of actual pollutant removal.Very often, stormwater carries more than one metal and there can be competition for adsorption between metals. However, most studies conducted adsorption of a single metal at a time rather than mixed metals. Information on adsorption of heavy metals in the presence of organic and other contaminants is limited. Therefore, the pollutant removal efficiency of adsorbents needs to be studied in the presence of multi-component pollutants/contaminants. This would provide the information necessary to support the application of adsorbents for the treatment of stormwater in a field context. It is also important to investigate the best method of regenerating adsorbents after their use so that they can be reused for many treatment cycles. This would make the whole process more economical.

1.2 Research questions, and scope

An important challenge of water supply is to meet the demand for drinking water in the future as concerns about climate change, the nature of droughts and population growth makes existing sources of water insufficient. This research will present the information on designing an affordable on-site treatment system for stormwater to improve its water quality to meet the standards for outdoor use.

The main objectives of this research are:

1. Conduct a full water demand study to identify the pattern of water use in the Sydney metropolitan area between January 2000 to December 2009 and to

compare it with socio-demographic factors.

2. Identification of pollutants of concern in Australian stormwater.
3. Study the interactions of pollutants during adsorption.
4. Development of novel adsorbents having high adsorption capacity and selectivity to treat pollutants and investigate the mechanisms of adsorption.
5. Develop a simple on-line treatment for selected pollutants based on adsorption to meet the Australian standards for outdoor use.
6. Incorporation of adsorbents into permeable pavements for effective continuous removal of pollutants from stormwater.
7. Development of mathematical models for the adsorptive treatment processes. The purpose of these models is to simulate the laboratory scale studies at field level.

1.3 Overview of the thesis

In order to meet the above objectives, the experimental work and results are organised into 8 chapters. A summary of each chapter is provided below.

Chapter 1: This chapter provides the introduction to the research. It describes the general background of the research problem, objectives and scope. The specific backgrounds are articulated in Chapters 3 to 8.

Chapter 2: This chapter summarises existing technologies of water sensitive urban design and demand management techniques of potable water. It also discusses the impacts of main pollutants in stormwater and their different removal technologies.

Chapter 3: This chapter analyses the water consumption pattern in the Sydney metropolitan area and surrounding areas that are connected to Sydney Water Corporation's (SWC) potable water supply mains.

Chapter 4: This chapter evaluates the effect of dissolved organic matter and suspended solids (a measure of turbidity) on the removal of heavy metals (Cu, Zn, Pb, Cd and Ni) from stormwater using GAC in batch and fixed-bed columns. It also investigates their interactions during the removal process.

Chapter 5: This chapter aimed to determine the adsorptive removal efficiencies of five heavy metals (Cu, Zn, Pb, Cd and Ni) individually and collectively at different pH from synthetically polluted water using a novel sodium titanate nanofibrous material (TNF) in batch experiments and in fixed-bed column experiments.

Chapter 6: This chapter discusses the removal of a wide range of pollutants from urban stormwater using granular activated carbon (GAC) and anthracite via fixed-bed field and laboratory column filtration.

Chapter 7: This chapter discusses the long-term effectiveness of removing five heavy metals by a permeable pavement system using coarse natural Australian zeolite or basalt as bedding material. It is with and without a filter containing a nano-fibrous sodium titanate material below the zeolite bedding layer in a mini-pilot plant scale experiments.

Chapter 8: The final chapter presents the overall conclusions and recommendations of the study.

CHAPTER 2

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LITERATURE REVIEW

2 Literature Review

This review provides a general overview of the water demand management techniques, current stormwater management practices and possible treatment methods. This review also describes the advantages and shortcomings of each treatment method and incorporates a detailed discussion of the major pollutants of stormwater and their interactions during their removals.

2.1 Water use management

Frequent droughts, population growth, urbanisation and concerns about climate change mean that Australian cities have had to find alternative ways to conserve, harvest and treat sources of water supply and to effectively manage existing water resources. These alternative approaches are outlined in "Water Sensitive Urban Design (WSUD)" which was developed in Australia in the 1990s and Mouritz (1992) is generally considered to be the first reference to it.

Initially WSUD grew out of stormwater management. In recent years several researchers have integrated the WSUD framework around the entire urban water cycle including water supply, sewerage and stormwater management (Mouritz 2006; Wong 2006). It represents a significant shift in the way water and related environmental resources and water infrastructure are considered in the planning and design of cities and towns, at all scales and densities. Having originated in Australia, the term WSUD is now increasingly used internationally, particularly in the UK and New Zealand (Fletcher et al. 2014). WSUD has also inspired a number of related concepts, such as climate sensitive urban design (Coutts et al. 2013). According to Wong (2006), key guiding principles of WSUD are:

1. Reducing the potable water demand through the use of water efficient appliances such as shower heads, and dual flush toilets and finding alternative sources of water such as rainwater, and recycle water.
2. Minimising wastewater generation and treatment of wastewater to meet the effluent standards for re-use opportunities and / or release to receiving water
3. Treating urban stormwater to meet water quality objectives for reuse and/or discharge to surface waters.
4. Using the stormwater in the urban landscape to maximise the visual and recreational amenity of developments.

This integrated stormwater management approach regards stormwater as a resource to be recovered rather than a nuisance. It considers all aspects of runoff within a development, including implementation of water quality/quantity controls, maximizing water reuse, conservation and preservation of amenities and environmental values within the catchment (Figure 2.1) (Singh et al. 2012).

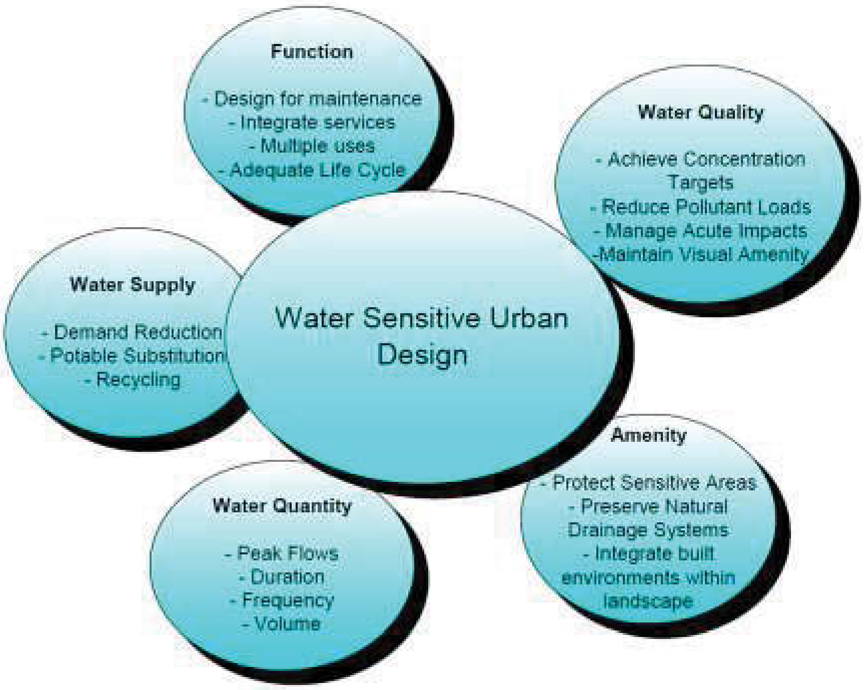

Figure 2.1 WSUD objectives adapted from BMT WBM Pty Ltd (2009)

2.2 Potable water demand reduction techniques

The continuing pattern of droughts and recent concerns about climate change impacts and predicted population growth in capital cities will have a major effect on water supply and irrigation in Australia. There are a number of solutions to save water either by reducing water demand and increasing efficiency of its use or by increasing the available supply. The former include the following: community education; water restrictions; retro-fitment of water fixtures to reduce consumption; and rebate schemes to promote the installation of rainwater tanks. Methods for increasing available supply include employing alternative water supplies such as desalination, recycling, and creating alternative poorer quality supplies from sources such as grey water for local non-potable uses.

Potable water consumption data is highly variable across households due to the behaviour changes, climate, socio-demographics, house size, family composition, water appliances, cultural and personal practises, etc. (Juárez-Nájera et al. 2010; Loh and Coghlan 2003; Russell and Fielding 2010). End use data in combination with such socio-demographic information can facilitate the identification of correlations between potable water usage behaviours and key demographic subsets within a population, for example income, age, gender and family composition (Beal et al. 2013). The following sections will discuss the different potable water demand management techniques employed in Australia.

2.2.1 Water efficient appliances

Efficient water appliances can significantly reduce water consumption and successfully reduce the demand for potable water supplies. They can also significantly reduce the wastewater produced by households and subsequently reduce the wastewater to be treated in treatment plants and the amount discharged into the environment.

Studies in Perth from 1998 to 2001 using smart meters estimated that a dual flush toilet can save 2 to 3 litres less than a single flush toilet (Perth Water Corporation 2010). Based on an average of 10 flushes per day per household, it can save between 7.3 to 11 kL per household per annum when a single flush toilet is replaced by a dual flush toilet. In Australia, the use of water efficient appliances is encouraged and in some states their use is mandatory for new residential properties. Some states provide rebate systems for buying water efficient appliances, for example, the water saving appliances rebates scheme in the Northern Territory.

The national Water Efficiency Labelling and Standards (WELS) scheme and Smart Approved Water Mark (SAWM) scheme provide consumers with information about the water efficiency of products (Figure 2.2). This mandatory WELS scheme was introduced in 2005 by the Alternative Technology Association (ATA) in order to achieve the following objectives: conserve water supplies by reducing water consumption, provide information for purchasers of water-use and water-saving products and promote the adoption of efficient and effective water-use and water-saving technologies (Aither 2015). SAWM is Australia’s outdoor water saving labelling programme for promoting the products and services that help to save water.

Figure 2.2 Water efficient appliances and WELS water rating logo

2.2.2 Water efficient fittings

Water efficient fixtures like showerhead, taps, sprinklers and water timers were found to be effective in reducing the indoor and outdoor water consumption such as gardening, washing, and bathing. These fixtures will also reduce the indoor wastewater flows, subsequently reducing the quantity of wastewater to be treated.

Studies conducted by Perth Water Corporation showed on average a person uses around 23 kL of water a year when showering, which accounts for 22% of overall use (Perth Water Corporation 2010). Previous studies done in Perth (Perth Water Corporation 2002) also suggest a possible water savings of 1-2 L/min can be achieved by using more efficient showerheads without affecting the shower duration (Loh and Coghlan 2003). Some Australian states introduced compulsory regulations in their building codes to use water efficient fixers in new buildings (ex BASIX).

Figure 2.3 Water efficient shower heads/roses

2.2.3 Rainwater tanks

Rainwater tanks have been widely used as an alternative source for many years. In rural Australia where there is no reticulated mains supply, rainwater tanks are still used as the main drinking water supply. In recent years the use of rainwater tanks in cities has risen following a series of severe droughts, restrictions in the potable supply, and active promotion by central and state governments. In WSUD, rainwater plays a more important role in reducing the potable water demand, reducing the stormwater flow from catchments, reducing the pollutant loading of some stormwater pollution, and even reducing the hydraulic loading to downstream stormwater treatment systems.

Figure 2.4 Typical outdoor rainwater tanks

Greater savings can be achieved by connecting the rainwater tanks to the household water uses such as toilet flushing, washing which requires minimum human contact and other uses that pose very little risk to humans. Kuczera (2008) found that rainwater tanks made the most significant contribution to urban water supply drought security. Kuczera (2008) also completed a comparative analysis of complementary centralised and decentralised storage systems to evaluate if rainwater tanks could provide a reliable supply of water, when utilised to complement mains water supply. This author further isolated the conditions where urban rainwater tanks made the most significant contribution to urban water supply drought security. A few key observations from this study are:

- The use of rainwater tanks can improve city-wide drought security for a given centralised reservoir capacity since tanks reduce the chance of crossing storage thresholds associated with imminent collapse of water supply. For a given threshold probability, tanks reduce the required centralised reservoir capacity. Although rainwater tanks draw down at time scales of less than a week and, as a result, may be empty for considerable periods, it is incorrect to conclude they cannot contribute to the drought security of the whole system.

- Rainwater tanks benefit drought security more when a centralised system is more stressed due to high supply variability or high load and when the per-capita household demand is lower.

- As the uptake of installing tanks increase, system drought security also increases. However, any growth in benefits declines when uptake increases.

- The benefits of rainwater tanks were not particularly sensitive to reduced rainfall. This robustness may be an important consideration when facing reduced rainfall due to climate change.

2.2.4 Water restrictions and water use education programs

Community education programs and water restrictions were found to be a more effective way of reducing potable water demand in severe droughts. Large educational programs have been conducted in Australian cities with the purpose of reducing water demand. Due to the prolonged droughts in Sydney mandatory and voluntary restrictions were introduced and some are still active in Sydney (Table 2.1).

Table 2.1 Sydney water restrictions applied to the Sydney water main users from 2003 to the present time (BOM 2015)

Level	**Period**	**Restriction**
Level 1	October 2003 - June 2004	• No hosing of hard surfaces; and no sprinklers or watering systems.
Level 2	June 2004 - June 2005	• No hosing of hard surfaces; • No sprinklers or watering systems; • No hosing of lawns and gardens except hand-held hosing before 9 am and after 5 pm on Wednesdays, Fridays and Sundays; and • No filling of new or renovated pools over 10,000 L except with a permit from Sydney Water.
Level 3	June 2005 - June 2008*	• No hosing of hard surfaces; • No sprinklers or watering systems; • Hosing of lawns and gardens only allowed on Wednesdays and Sundays before 10 am and after 4 pm; • No filling of new or renovated pools over 10,000 L except with a permit from Sydney Water; • No hoses or taps to be left running unattended, except when filling pools or containers; and • Fire hoses used only for fire fighting purposes -

		not for cleaning.
Water Wise Rules	June 2009 - to date	• All hoses must now have a trigger nozzle; • To avoid the heat of the day, watering is allowed before 10 am and after 4 pm; • No hosing of hard surfaces such as paths and driveways. Washing vehicles is allowed; and • Fire hoses must only be used for fire-fighting activities only.

*changes were made to the level 3 restrictions after June 2008 to permit its residential customers to wash cars, boats and caravans at home as well as clean the windows and wall of their house with a hose as long as a trigger nozzle was fitted

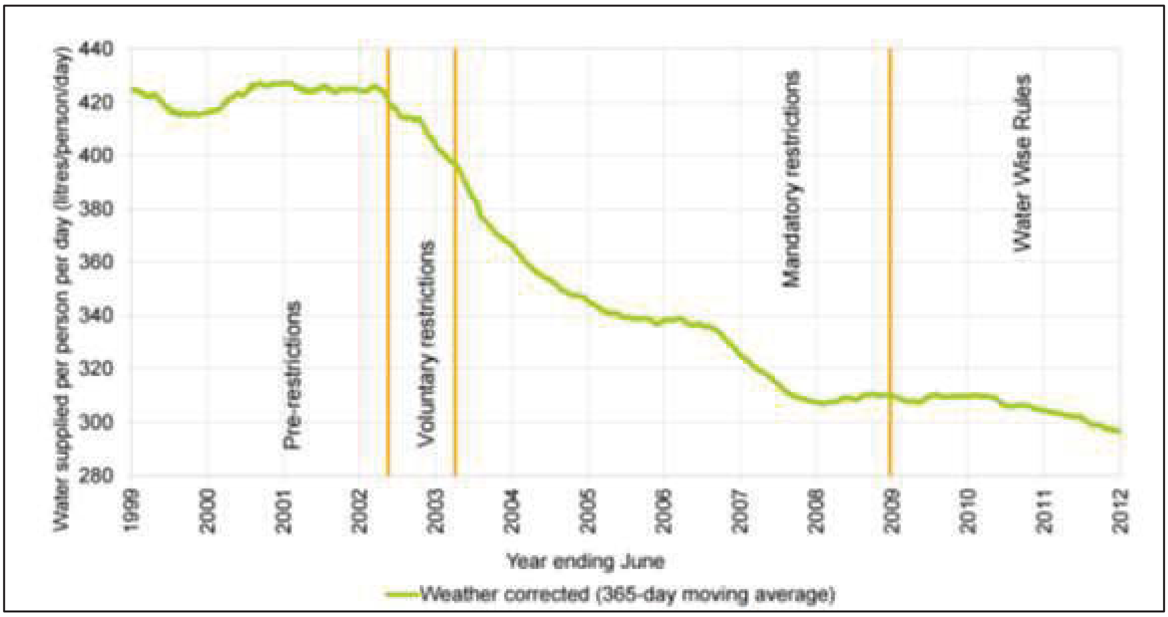

Figure 2.5 Daily water use in greater Sydney adapted from Sydney Water efficiency report 2011/12 (SWC 2012a)

Figure 2.5 illustrates the per capita water demand for the Sydney metropolitan area and it clearly demonstrates a significant decline in water usage from 2002 to 2012. During this 10-year period water usage declined from 420 L/person/day to 297 L/person/day, which amounts to an approximately 30% reduction. This was due to the combined effect of water restrictions and other means although the majority of the reduction was from the former (Sydney Water's Water Conservation Strategy, 2010–15).

2.2.5 Other commons methods

Other common methods to reduce the demand include: stormwater harvesting and reuse; reticulated recycled water; and grey water harvesting and reuse. These alternative supplies can be used mostly for non-potable uses such as toilet flushing, gardening, etc., and can reduce the potable water demand from the reticulated mains.

2.2.5.1 Stormwater harvesting and reuse

The collection and reuse of stormwater is a relatively new technique compared to rainwater tanks but has become more popular in recent years. Stormwater harvesting and reuse can be beneficial in many ways because it can reduce the demand for potable water, reduce the pollution loads to waterways and reduce the stormwater flow. Treated stormwater can serve non-potable applications such as toilet flushing, gardening and car washing, and for residential properties. It can also be used to irrigate public places such as golf courses and gardens. On this theme, potential limitations of stormwater harvesting identified by Department of Environment and Conservation NSW (DEC) (2006) are that they will rely too much on climatic changes and rainfall patterns, potential health risks (which can be minimised through effective treatment), and high relative cost of treated stormwater, although this does not account for multiple environmental benefits (DEC 2006).

2.2.5.2 Reticulated recycled water

In Australia, recycled water refers to the water reclaimed and reused from industrial wastewater, and grey and blackwater sourced from municipal wastewater (Chen et al. 2013). In recent years interest has grown considerably in Australia for using wastewater as the alternative source for potable water. Sydney Water produced 45 GL in 2011-2012 and is expected to increase recycling to 70 GL/year by 2015 (SWC 2012b).

2.2.5.3 Greywater harvesting and reuse

Greywater is generally defined as water from household kitchen sinks, bathroom, showers, hand basins and laundry machines (Chen et al. 2013). Grey water is associated with high levels of turbidity, pathogens and organic matter which pose a potential risk when humans come into contact with it. Without prior treatment it cannot be used for most household applications. This limits greywater applications without pretreatment although it may be used for applications such as toilet flushing which poses no or very minimal risk to humans because there is no direct contact. Benefits of greywater systems are the substantial amounts of reduction in potable demand and sewerage flows. A grey water havesting system can be applied in household lots, in blocks of units, or on a suburban scale (BMT WBM Pty Ltd 2009).

2.3 Treating urban stormwater and reuse

Apart from recycling of wastewater, stormwater can become an alternative source of potable water to mitigate the water shortage problem. As recycled waste water has not yet been fully accepted by the consumers, stormwater treatment has become an important strategy for improving urban water cycle management, given the current and increasing stress on water resources throughout urban centres of Australia, and much of the world. Expanding the use of stormwater to add to the water supply and reducing water pollution are important objectives in the face of the water crisis. Stormwater is now acknowledged as a valuable resource, rather than a nuisance to be disposed of quickly, especially in large urban centres. Harvesting and reusing stormwater offers both a potential alternative water supply for non-potable uses and a means to further reduce stormwater pollution in our waterways.

Studies have shown that a large number of pollutants, both organic and inorganic, may be present in stormwater, both in their dissolved and colloidal forms and associated with particles. Stormwater complements other approaches to sustainable urban water management such as rainwater tanks, the reuse of wastewater and greywater and demand management. Collectively these areas form the basis of developing sustainable water technologies (Kus et al. 2012). Stormwater harvesting provides an alternative water source that can be captured from roads, footpaths, car parks, open space and gardens for use within a city as shown in Figure 2.6. Stormwater can be used for: toilet flushing, garden irrigation and car washing; washing machines; and hot water systems.

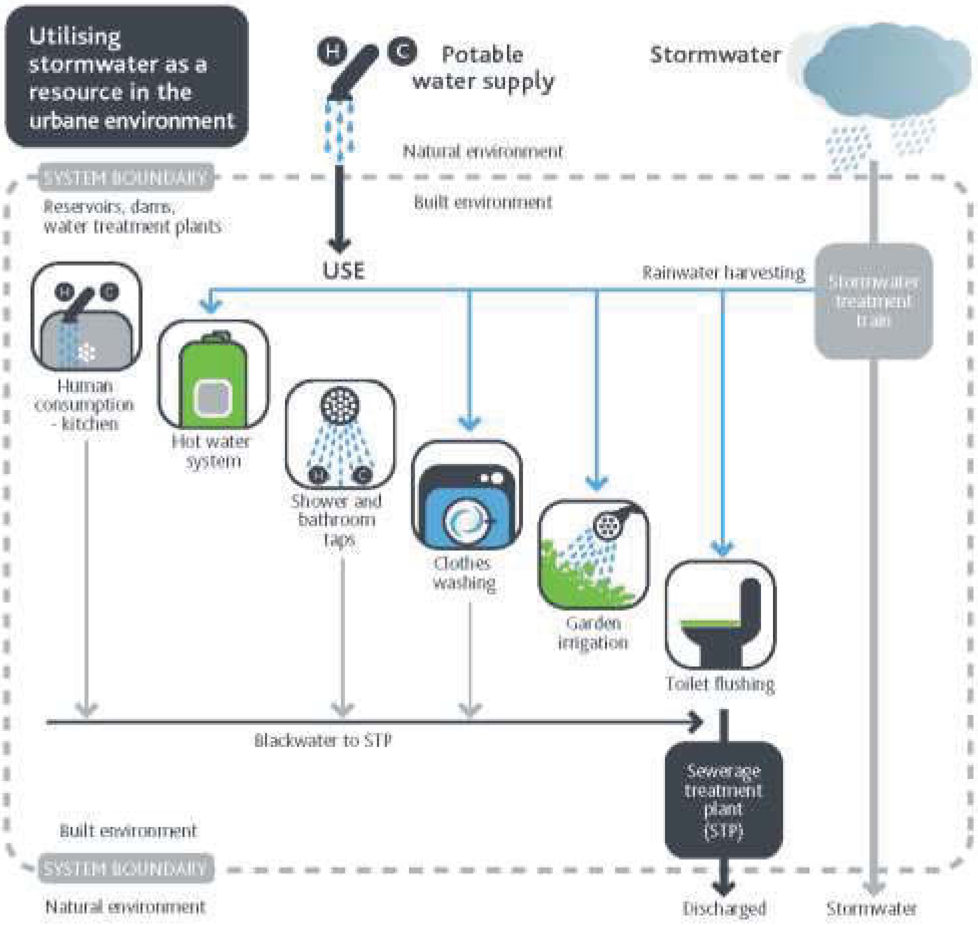

Figure 2.6 Utilising stormwater and rainwater as a resource in the urban environment (Victorian Government 2011)

In Australia, water recycling is increasingly becoming a valuable contributor to the conservation of drinking water although stormwater harvesting has been neglected. The consequences of urbanisation are the increase in impermeable area (roads, carparks, paved areas) leading to more runoff. The average annual volume of urban stormwater runoff in Australian cities is almost equal to the average annual urban water usages, of which at least 50% is for non-potable use. Urban stormwater is perceived to be of better quality than grey water and wastewater, and its reuse has a better public acceptance. The benefits of a successful stormwater harvesting scheme are reductions in: (i) demand for town water; (ii) stormwater pollution loads to downstream waterways and estuaries;

and (iii) stormwater volumes and discharges. Stormwater pollution is a major source of pollution in receiving water. According to Philp et al. (2008), stormwater capture and reuse systems can be considered using their five core components: End Use; Collection; Treatment; Storage; and Distribution. Figure 2.7 illustrates the connection between those components although their positions can vary depending on the purpose and design of different systems.

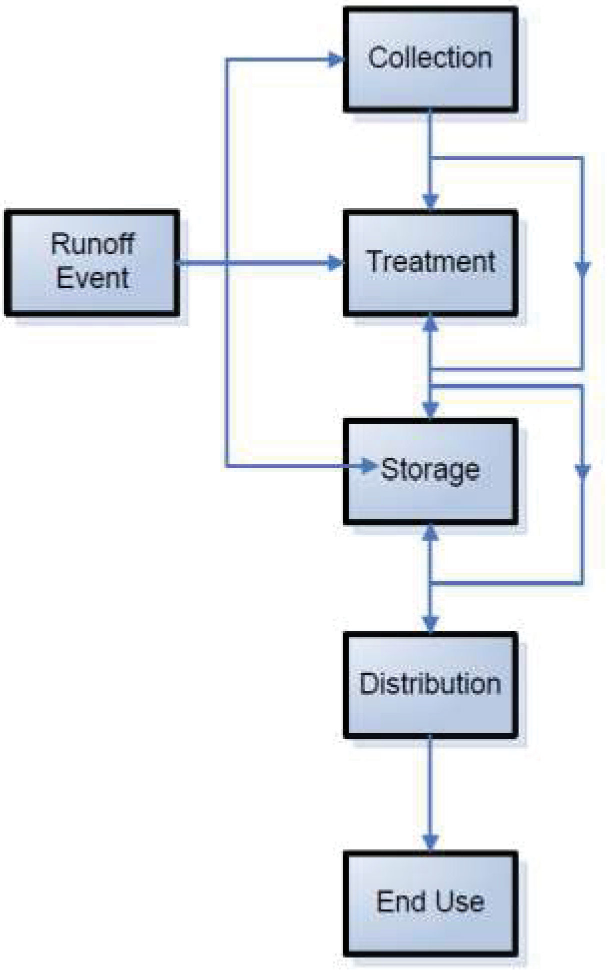

Figure 2.7 Stormwater use components adopted from Philp et al. (2008)

Stormwater capture and recovery has traditionally been undertaken for the purpose of building infrastructure or utilising existing natural features. With the advent and adoption of WSUD techniques, whilst primarily developed for water quality purposes, certain WSUD techniques lend themselves to being extended and refined to allow effective harvesting of treated stormwater and the development of integrated water management systems. Using WSUD approaches in stormwater harvesting systems has the added payback of achieving many benefits such as improved water quality, hydrology, and aesthetics compared to conventional stormwater harvesting infrastructure.

2.3.1 Treatment of stormwater

The treatment of urban stormwater poses numerous technical and operational challenges, particularly due to the intermittent and highly variable nature of hydrologic and pollutant inputs. A significant obstacle to widespread implementation of stormwater use is a lack of reliable and affordable treatment techniques and stormwater managers are seeking technologies that can address the flow and water quality impacts due to urbanisation (Hatt et al. 2007a; Hatt et al. 2007b). At the present time, there is no single process able to adequately treat stormwater, mainly because of the complex nature of the effluents. In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way (Ahmaruzzaman 2011). A treatment train is a sequence of treatments designed to meet the stormwater treatment needs of a particular environment. The concept of a “treatment train” approach is important in treating stormwater because utilising a variety of treatment techniques is needed to treat the water to the level required by the end user. Table 2.2 below summarises the treatment function of each stage of the treatment train and provides possible treatment system combinations to achieve the required water quality for various recycling applications. Treatment trains are not restricted to using methods from any one particular category of treatment technique. A WSUD treatment upstream of an advanced treatment process could be important for the effective functioning of the process (Melbourne Water 2015). This treatment train approach is important when a certain pollutant removal process requires a pre-treatment to remove pollutants that would otherwise impact on its performance. For example, wetlands can be mostly used with other pre-treatment methods such as gross pollutants, litter baskets, etc., in order to remove the gross pollutants that would otherwise clog and hinder the performance of wetlands.

Table 2.2 WSUD application in treatment process (Melbourne Water 2015)

Treatment	Processes	Pollutants	Typical treatment application
Primary treatment	physical screening and rapid sedimentation	gross pollutants and coarse sediment	grassed swales, litter traps and sediment ponds
Secondary treatment	fine particle sedimentation and filtration techniques	fine sediment and attached pollutants	swales, infiltration trenches, porous paving and bio-retention systems
Tertiary treatment	enhanced sedimentation and filtration, biological uptake and adsorption onto sediments	nutrients and dissolved heavy metals	bio-retention/ bio-infiltration systems/ high rate filtration and wetlands

2.3.2 WSUD treatment techniques for stormwater

Water Sensitive Urban Design is used to preserve water and remove pollutants from stormwater before it reaches downstream drainage systems. WSUD is better utilised when it is considered early in a site and building's design. Most of the WUSD elements described below incorporate landscape design. There are many types of WSUD techniques used in managing stormwater and according to Philp et al. (2008), it is categorised into 4 types: physical processes, infiltration methods, biofilters and proprietary devices. These techniques are briefly described in the following sections.

2.3.2.1 Physical processes

These WSUD techniques mainly rely on hydraulic properties to treat stormwater. Physical processes are used in swales, buffer strips, and open water bodies (natural and constructed). These physical processes work on the principle of reducing flow velocities to allow sediments to settle out of the water column. The open water bodies also have the combined benefit of exposure to UV light to provide some level of disinfection (Philp et al. 2008). Physical processes provide important preliminary treatment to reduce pollutants such as sediment loads before subsequent steps in the treatment train. Stormwater from this treatment can be used for on-site irrigation where public access is limited, e.g. at golf courses.

2.3.2.2 Infiltration methods

Infiltration treatment measures use the physical process of infiltration to provide treatment to the collected stormwater (Philp et al. 2008). These processes are used in porous and permeable pavements, infiltration basins and trenches, sand filters and biologically engineered soils. Infiltration devices can also be combined with vegetation to assist with the treatment of the stormwater (refer to Biofilters and Wetlands).

Pervious pavement system is a popular WSUD technology because it allows stormwater runoff to percolate to an underlying reservoir storage or drain to soil and at the same time will treat the stormwater at the site (Huang et al. 2012b). During a storm event, stormwater infiltrates through the pavement surface and is then temporarily stored in the pavement structure before it either further infiltrates to underlying soils or is removed by a subsurface drain. As a result, runoff volume can be significantly reduced and the stormwater pollutants will be trapped and filtered in the structure, thus improving the water quality. Runoff from streets and parking areas with low traffic densities can be infiltrated to support groundwater recharge, recycle water use and reduce the hydraulic stress in the receiving water bodies and treatment plants. However, the use of pervious pavement is somewhat limited because of the concern about the possible migration of pollutants into groundwater. This in turn is due to the ineffective treatment of pollutants when the pervious pavement strategy is applied.

The most widely used permeable pavements today include porous asphalt, porous concrete and concrete paving blocks (or inter-locking pavers). These pavement systems can be used in pathways, driveways, parking lots and access roads. Porous pavements are normally constructed with pervious paver materials where water can percolate through the entire surface area. However, for permeable pavements, the paver material is made out of impervious blocks while the spaces between the paver blocks are filled with coarse grained materials which allow water to pass through. Not many studies have been conducted on water quality improvements with permeable pavements in Australia. According to the small number of studies carried out in Australia

(Beecham et al. 2012; Jayasuriya and Kadurupokune 2010; Myers et al. 2011; Pezzaniti et al. 2009; Yong et al. 2010) the permeable pavements' ability to remove pollutants varies significantly. Table 2.3 summarises the removal of pollutants by permeable pavements.

Sand filtration is another WSUD device that can be used as a component of a treatment train to remove pollutants from stormwater (Kandasamy et al. 2008). Sand filters have been shown to remove pollutants such as suspended solids, nutrients, pathogens, oil and grease from urban runoff (Kandasamy et al. 2008). Birch et al. (2005) tested a field stormwater infiltration basin in Sydney and reported a weighted average reduction of 50% for TSS, and Cu, Pb and Zn by 68%, 93% and 52%, respectively. The removal for total phosphorus (TP) and total Kjeldahl nitrogen (TKN) was 51% and 65%, respectively. Kandasamy et al. (2008) tested an open-topped vertical flow field sand filter in Sydney. The filters showed an average reduction of 32% and 76% for TSS, 41% and 39% for TP, 70% and 70% for TKN and 79% and 83% for Zn for course sand filter and fine sand filter configurations, respectively.

Table 2.3 Summary of pollutant retention by permeable pavements in Australia (Removal percentage (%))

Study	Location	TSS	P/TP	TKN	Cu	Pb	Zn	Cd	Ni
Yong et al. (2010)	Laboratory experiment, Melbourne Victoria	80	35	15	–	–	–	–	–
Jayasuriya and Kadurupokune (2010)	Melbourne, Victoria	88-95	50-63	37-60	0-74	–	76-92	–	–
Pezzaniti et al. (2009)	Laboratory experiment, South Australia	89-97	–	–	–	–	–	–	–
Beecham et al. (2012)	Adelaide, South Australia	0-73	47-60	32-60	7-99	60-86		12-48	
Beecham et al. (2012)	Laboratory experiment, South Australia	38	33	58	3	9	39	–	18
Myers et al. (2011)*	Laboratory experiment, South Australia	–	23-26	4-25	29-37	34-35	61-62	–	–

* After 1h residence time in subsurface storage

2.3.2.3 Biofilters

Biofilters include wetlands (natural and constructed) and they use biological and physical processes to treat stormwater. Biofilters consists of a vegetated soil filter medium and contains a porous collection pipe to convey the filtered water to the receiving waters or downstream storage facilities (Philp et al. 2008). Biofilters have been studied for stormwater treatment extensively in Australia (Bratieres et al. 2008; Hatt et al. 2007b; Read et al. 2008; Scholz et al. 2002; Zinger et al. 2007). Hatt et al. (2007b) conducted laboratory scale experiments on gravel biofilters and found TP, suspended solids and heavy metals were removed effectively but TN was not significantly removed. Read et al. (2008) found biofilters with plant species improved its effectiveness in removing stormwater pollutants, particularly with regard to nitrogen and phosphorus. There was also a difference in performance with different plant species. Bratieres et al. (2008) did experiments with a large-scale column study in Melbourne, Australia, to test the performance of stormwater biofilters for the removal of sediment, nitrogen and phosphorus. They found nutrients (up to 70% for nitrogen and 85% for phosphorus) and suspended solids (consistently over 95%) were removed effectively. These results show biofilters can be effectively used for removing pollutants from stormwater at low hydraulic velocity. Although previous findings suggest biofilters can effectively treat stormwater, extended dry periods may result in re-suspension and flushing of pollutants which can be very harmful to the environment (Baldwin and Mitchell 2000; Scholz et al. 2002).

Constructed wetlands are widely used to control polluted urban stormwater discharges and typically consist of shallow water bodies with extensive amounts of vegetation designed to both treat urban stormwater and control runoff volumes (Greenway 2005). Man-made constructed wetlands have widely been accepted as a stormwater treatment device and this was integrated into WUSD practices (Carleton et al. 2001; Headley and Tanner 2011; Malaviya and Singh 2011; Weiss et al. 2007). The popularity of wetlands is due to their advantages of providing a relatively passive, low-maintenance and operationally simple treatment solution while potentially enhancing habitat, recreational, and aesthetic values within the urban landscape (Headley and Tanner 2011; Malaviya and Singh 2011; Rousseau et al. 2008). However, a number of limitations have emerged with the application of wetlands for stormwater treatment. As with natural wetlands, stormwater wetlands require a continuous base flow or a high water table to support vegetation which is difficult to achieve in dry seasons. They also require a large open area which is not normally available in highly urbanised areas (Headley and Tanner 2011).

Wetland systems with horizontal subsurface flow which are commonly used for wastewater treatment generally have limited application for stormwater treatment due to the hydraulic limitations of the substrate when subjected to high flow velocities. The vegetation in the subsurface flow constructed wetlands can also tolerate only relatively shallow water depths of 30-50 cm and are susceptible to chronic die-back if inundated beyond these depths too frequently or for extensive periods (Davies and Bavor 2000; Greenway et al. 2007; Jenkins and Greenway 2007). Many researchers have shown that wetlands are effective at treating urban stormwater runoff (Birch et al. 2004; Walker and Hurl 2002). Birch et al. (2004) did experiments with constructed wetlands and found 9% of TKN, 12% of TP, 9-46% of TSS, 4% of Cr, 65% of Cu, 65% of Pb, 22% of Ni, and 52% of Zn were removed from urban stormwater from residential areas in Port Jackson, Sydney. Walker and Hurl (2002) found 57% of Zn, 71% of Pb and 48% of Cu were removed from urban stormwater runoff by Barker Inlet wetlands, Adelaide, South Australia.

2.3.2.4 Proprietary devices

There are many types of pollutants, oil and grease, and sediment trap devices available for different applications. These proprietary devices are generally applied at the beginning of the treatment chain which gives a preliminary treatment to the stormwater (Philp et al. 2008). These devices use hydrodynamic vortex separation principles to capture and concentrate sediments and floatables for later periodic removal (Faram et al. 2007). Such systems have been extensively applied and studied especially in the USA to verify their design performance (Faram et al. 2007; Faram et al. 2000; Phipps et al. 2005). Faram et al. (2007) found that sediments from urban runoff were successfully removed by proprietary interceptor devices which prevent them from entering downstream watercourses or further treatment facilities.

Table 2.4 briefly describes the comprehensive studies that implemented different WUSD methods and techniques in Australia. For each stormwater treatment technique their advantages and disadvantages and efficiency in removing pollutants are listed.

Table 2.4 Stormwater treatment methods and techniques and their advantages and, disadvantages (adapted and modified from Begum et al. (2008) and Melbourne Water (2015))

Treatment Measures	Description	Advantages	Disadvantages	Pollutant Trapping Efficiency
Litter Baskets and Pits	A wire or plastic 'basket' installed in a stormwater pit to collect litter from a paved surface (litter basket) or within a piped stormwater system (litter pit).	a) Can be retrofitted in existing areas with high litter loads b) Low downstream maintenance c) Installed underground to minimise visual impacts. d) Litter basket are applicable for small areas (<1–2 ha) and pits can be used for larger catchments (150 ha)	a) Potential for litter pits to aggravate upstream flooding if blocked by litter and vegetation b) Potential for litter baskets to reduce pit inlet capacity if located close to inlet c) Hydraulic head loss occurs for litter pits d) Potential loss of pit inlet capacity due to litter basket on steeper slopes	Litter: M Oxygen demanding material: M Sediment: L Oil and grease: N Nutrient: N Bacteria: N
Trash / Litter Racks	Litter racks (or trash racks) are a series of metal bars located across a channel or	a) Can be used to trap litter upstream of other stormwater treatment measures	a) Racks have a tendency to be blocked by debris b) Collected litter can move	Litter: M Oxygen demanding

Treatment Measures	Description	Advantages	Disadvantages	Pollutant Trapping Efficiency
	pipe to trap litter and debris.	b) Appropriate for retrofitting into existing areas c) Low downstream maintenance d) Applicable for areas between 8 and 20 ha	upstream along a tidal channel due to tidal sway c) Potential odours and health risk to workers when handling litter d) Possible safety risk when installed in channels and difficult to clean/ maintain	material: L Sediment: L Oil and grease: N Nutrient: N Bacteria: N
Catch Basin	A catch basin is a stormwater pit with a depressed base that accumulates sediment.	a) Can be used upstream of other stormwater treatment measures to enhance performance b) Good for retrofitting into existing areas c) Installed below ground and therefore unobtrusive d) Generally can be applied to small catchments (< 1–2 ha)	a) Potential resuspension of sediments b) Potential release of nutrients and heavy metals from sediments c) Needs regular maintenance	Litter: L Oxygen demanding material: L Sediment: L-M Oil and grease: L Nutrient: N Bacteria: N

Treatment Measures	Description	Advantages	Disadvantages	Pollutant Trapping Efficiency
Sediment Trap	Sediment traps (known as sediment basins or sediment fore bays) are designed to trap coarse sediment and can take the form of a formal 'tank' or a less formal pond.	a) Trap coarse sediments upstream such as a wet basin or constructed wetland b) Reduce coarse sediment loads to stormwater systems or receiving waters c) Can be installed underground d) Applicable for areas greater than 5 ha	a) Limited removal of fine sediment, and pollutants can be remobilised b) Above ground sediment traps can be visually unattractive c) Trapping of excessive sediment can result in downstream channel erosion d) Potential for mosquito breeding	Litter: N Oxygen demanding material: L Sediment: H Oil and grease: N Nutrient: N Bacteria: N
Gross Pollutant Trap	Gross pollutants traps are structures that use physical processes to trap solid waste such as litter and coarse sediment in the primary treatment removing mostly large non-	a) GPTs trap coarse sediments before they enter the waterway b) Collect litter at a single location for removal c) Appropriate for retrofitting into existing urban areas d) Traps can be located	a) Litter rack has a tendency for blockage b) Potential to aggravate upstream flooding c) The appearance of the trap and litter can be obtrusive d) Potential odours and health	Litter: M Oxygen demanding material: L Sediment: M-H Oil and grease: N Nutrient: L

Treatment Measures	Description	Advantages	Disadvantages	Pollutant Trapping Efficiency
	biodegradable pollutants	underground, minimising visual impacts e) Suitable for catchments greater than 6–8 ha	risk to workers when handling litter e) Possible safety risk when installed in channels f) Difficult and expensive to clean e) Provide very limited removal of finding and dissolving pollutants	Bacteria: L
Litter Booms	Litter booms are floating booms with mesh skirts placed in channels or creeks to collect floating litter and debris.	a) Used to remove floating litter/debris b) Enhance aesthetic appeal and recreational potential of downstream waterways c) Collects litter at a single location d) No hydraulic head loss	a) Traps floating litter/debris b) Large objects such as branches or boats can reduce boom effectiveness c) Litter can be blown over the boom's collar in wind d) Potential for vandalism e) Possibility of sinking due to	Litter: L Oxygen demanding material: N Sediment: N Oil and grease: L Nutrient: N Bacteria: N

Treatment Measures	Description	Advantages	Disadvantages	Pollutant Trapping Efficiency
		e) Boom can rise and fall with changing level	marine growth f) Low visual amenity	
Infiltration trenches	An infiltration trench is an excavation filled with porous material, which collects runoff. Stormwater infiltrates from the walls and base of the trench into the surrounding soil, while particulate and some dissolved pollutants are retained in the porous material.	a) Replenish ground water and, therefore, dry weather flows to waterways b) Provide a relatively small surface footprint c) Offer water to plants (where vegetated) during dry periods provide a scalable system that can be used at the lot, street and regional level	a) Become clogged with pollutants and sediment unless regularly maintained b) Result in groundwater contamination and low dissolved pollutant removal if soils are coarse c) Cannot be used if contaminated groundwater is present; are ineffective on steep slopes, loose or unstable areas d) Cannot be used in close proximity to buildings, and can cause bogging or damage to	Gross pollutants coarse sediments some nutrient removal dissolved heavy metals

Treatment Measures	Description	Advantages	Disadvantages	Pollutant Trapping Efficiency
			vegetation where car parking occurs	
Rainwater tanks	Rainwater tanks are a traditional source of domestic water supply for isolated properties and small communities. In urban areas, rainwater tanks can significantly reduce demand on potable supplies, as tank water can be used to flush toilets, wash clothes, water the garden and wash the car.	a) Retain water close to source b) Can reduce site runoff and attenuate flood peaks c) Less polluted water	a) Only provide benefits when the tank water is used frequently, allowing each rain event to be more fully exploited	

Treatment Measures	Description	Advantages	Disadvantages	Pollutant Trapping Efficiency
Swales	Swales are linear depression channels that provide stormwater collection and conveyance. They can be grass-lined or more densely vegetated and landscaped	a) Reduce and delay storm runoff b) Retain particulate pollutants close to source c) Are more aesthetically appealing than kerbs and gutters d) Are relatively inexpensive to construct	a) Can only remove a limited amount of fine sediment and dissolved pollutants b) Use more land area than kerb and gutter, and restrict certain activities such as car parking c) Require a sunny aspect for plant growth, which limits their application in shaded areas d) Only suitable for gentle slopes of less than 5% gradient e) Require regular inspections	gross pollutants coarse sediments some nutrient removal
Constructed wetlands	Constructed wetlands are shallow, densely-planted man-made wetlands that regularly fill and drain. Wetlands usually have a	a) Provide high levels of treatment in a relatively small surface footprint b) Improve aesthetics appearance of the site	a) Become clogged with pollutants and sediment unless regularly maintained b) Very low filtration rate c) Take more time to stabilise	gross pollutants coarse sediments nutrients heavy metals

Treatment Measures	Description	Advantages	Disadvantages	Pollutant Trapping Efficiency
	series of planted ponds that help to filter water through physical and biological processes.		d) Require a continuous base flow or a high water table to support the vegetation e) Need a relatively large area	
Bio-retention systems	Bio-retention systems, also known as rain gardens, are vegetated filters that pond stormwater and slowly filter it to provide high levels of stormwater treatment in a relatively small footprint.	a) Can, when unlined, replenish ground water and, therefore, dry weather flows to waterways b) Provide high levels of treatment in a relatively small surface footprint c) Provide a scalable system that can be used at the lot, street and regional level	a) Become clogged with pollutants and sediment unless regularly maintained	gross pollutants coarse sediments nutrients heavy metals
Oil/Grit Separators	Oil/grit separators, also known as water quality inlets, generally consist of three	a) Appropriate for treating stormwater from areas expected to have significant vehicular pollution (e.g. parking)	a) Limited removal of fine or soluble pollutants b) When turbulent stormwater enters the chambers, this action	Litter: L-M Oxygen demanding material: L

Treatment Measures	**Description**	**Advantages**	**Disadvantages**	**Pollutant Trapping Efficiency**
	underground retention chambers designed to remove coarse sediment and hydrocarbons.	b) Can also trap litter c) Can also be used for treating stormwater from areas storing or handling petroleum products d) Can be appropriate for retrofitting into existing areas	may resuspend particulates or entrain floating oil c) Trapped debris is likely to have high concentrations of pollutants, possibly toxicants d) Needs to be regularly cleaned to reduce the safety hazard	Sediment: M Oil and grease: M Nutrient: L Bacteria: L

Efficiency level: H, high efficiency (75–100% removal); M, moderate efficiency (50–75% removal); L, low efficiency (10–50% removal); N, negligible (0–10% removal).

2.3.3 Stormwater pollutants

There are numerous water quality parameters which affect stormwater runoff quality including sediments, nutrients, heavy metals and metalloids; and oxygen demanding substances like organic matter and other toxic substances. These pollutants can originate either from a point source like illegal spilling from industries and mining or from non-point sources such as atmospheric deposition, road dust and soil erosion. Point sources can be controlled by strict regulations and monitored effectively but non-point sources are very challenging to manage as it is difficult to identify their sources. Without appropriate stormwater treatment devices, the resulting impacts of these pollutants on receiving waters can be devastating, not only for aquatic ecosystems but also to community values such as aesthetics, recreation, economics and health of receiving water bodies. Some common pollutants found in urban stormwater runoff are outlined in Table 2.5 (Victorian Stormwater Committee 1999)

Table 2.5 Types, sources, and effects of urban stormwater pollutants (Victorian Stormwater Committee 1999)

Pollutant	Source	Effect
Sediment	• Land surface erosion • Pavement and vehicle wear • Building and construction sites • Spillage, illegal discharge • Organic matter (for example leaf litter, grass) • Car washing • Weathering of buildings/ structures • Atmospheric deposition.	Increased turbidity, clogged waterways, sedimentation, and reduction in bottom living organisms which caused by reduction in sunlight penetration.
Nutrients	• Organic matter • Fertiliser • Sewer overflows, septic tank leaks • Animal faeces • Detergents (car washing) • Atmospheric deposition • Spillage, illegal discharge.	Unwanted growth of algae and undesirable aquatic weeds which leads to *eutrophication.*

Oxygen demanding substances	• Organic matter decay • Atmospheric deposition • Sewer overflows, septic tank leaks • Animal faeces • Spillage, illegal discharges.	Oxygen is used up more quickly than it can diffuse into the water from the atmosphere. The resulting drop in oxygen levels may then be sufficient to kill fish and other aquatic organisms. If all the oxygen in the water is used up, decay of organic matter and unpleasant odours can result.
pH acidity	• Atmospheric deposition • Spillage, illegal discharge • Organic matter decay • Erosion of roofing material.	Increased acidity damages plants and animals
Micro-organisms	• Animal faeces • Sewer overflows, septic tank leaks • Organic matter decay.	Contain very high numbers of bacteria and viruses. Some of these organisms can cause illnesses, including hepatitis and gastroenteritis.
Toxic organics	• Pesticides • Herbicides • Spillage, illegal discharge • Sewer overflows, septic tank leaks.	Can poison living organisms or damage their life processes.
Heavy metals	• Atmospheric deposition • Vehicle wear • Sewer overflows, septic tank leaks • Weathering of buildings, structures • Spillage, illegal discharges.	Can poison living organisms or damage their life processes in some other way. Persists in the environment for a long time.

Gross pollutants (litter and debris)	• Pedestrians and vehicles • Waste collection systems • Leaf-fall from trees • Lawn clippings • Spills and accidents.	Appears unsightly, animals can eat and choke on trapped material, can block the drainage and flow controls.
Oils, detergents and shampoos (surfactants)	• Asphalt pavements • Spillage, illegal discharges • Leaks from vehicles • Car washing • Organic matter.	Highly toxic poison to fish and other aquatic life.
Increased water temperature	• Runoff from impervious surfaces • Removal of riparian vegetation.	High temperatures are lethal to fish and other aquatic organisms. Elevated water temperatures stimulate the growth of nuisance plants and algae. This and other effects can lead to decreased levels of dissolved oxygen which can threaten other aquatic life.

The main pollutants focused on in this study are heavy metals, organics and suspended solids because these are the most common pollutants in urban stormwater along with poly-aromatic hydrocarbons (Aryal et al. 2010).

2.3.3.1 Heavy metals

Of the wide range of pollutants present in urban stormwater, heavy metals and metalloids are growing in importance because of their acute toxicity and long-term accumulation and persistence. Heavy metals are defined as block metals having a specific gravity greater than 5 g/cm^3 (Nies 1999). Metalloids are defined as the elements having properties of both metals and non-metals. In this report metalloids are grouped under heavy metals. Heavy metals such as lead (Pb), mercury (Hg), cadmium (Cd) and metalloids such as arsenic (As) are in the top six hazardous chemicals listed by a US agency for toxic substances and disease registry (ATSDR 2014). Heavy metals at high concentrations may cause neuro-behavioural disorders, retardation, various types of cancers, kidney damages, auto-immunity, and can even cause death when humans are exposed to them at high concentrations (Glover-Kerkvilet 1995; see Table 2.6). If untreated, they can also cause many adverse effects on the environment and aquatic life. Table 2.6 summarises the types of heavy metals mostly found in surface waters and their effect on human health. Some heavy metals are rarely found in high concentrations in Australian stormwaters but they have been reported elsewhere in the world. The presence of heavy metals in surface waters and marine waters poses a significant health threat to aquatic life, the most common being damage done to the gills of fish (Ahmaruzzaman 2011).

Table 2.6 Types of heavy metals and their effect on human health adapted from Singh et al. (2011)

Pollutants	Major Sources	Effect on human health
Arsenic	Pesticides, Fungicides, Metal smelters	Bronchitis, Dermatitis, Poisoning
Cadmium	Welding, Electroplating, Pesticides, fertiliser, cadmium and nickel batteries, Nuclear fission plant	Renal dysfunction, Lung disease, Lung cancer, Bone defects, Increased blood pressure, Kidney damage, Bronchitis, Gastrointestinal disorder, Cancer

Lead	Paint, Pesticide, Smoking, Automobile emission, Mining, Burning of coal	Mental retardation in children, Development delay, Fatal infant encephalopathy, Congenital paralysis, Sensor neural deafness and acute and chronic damage to the nervous system, Epilepsy, liver, kidney, gastrointestinal damage
Zinc	Refineries, Brass manufacture, Zinc metal plating, Plumping	Zinc fumes have a corrosive effect on skin, Cause damage to nervous membrane
Chromium	Mines, Mineral sources,	Cause damage to nervous system, Fatigue, Irritability
Copper	Mining, Pesticide Production, Chemical industry, Metal piping	Anaemia, Liver and kidney damage, Stomach and intestinal irritation

There are many methods used to remove heavy metals from stormwater, namely precipitation as metal hydroxides, coagulation, ion exchange, electrochemical treatments, and adsorption (Table 2.7). According to the abundant literature data in this area, liquid-phase adsorption is the most popular of these methods. The adsorption process is becoming popular due to the high efficiency in removing a wide range of metals, its simple design, and easy handling, less expense involved, and minimum waste production (Ahmaruzzaman 2011; Chen 2012). Metal ions adsorption can be influenced by many factors such as pH, ionic strength, initial metal ion concentrations, temperature, adsorbent type and dosage, and presence of complexing agent and co-ions (Chen 2012). Past studies have shown that pH can greatly influence the removal efficiencies of heavy metals by altering the surface charge of the adsorbent and properties of metals. Ionic strength of the feed solution can also alter the surface charge of the adsorbent and chemical species of the metals leading to changes in adsorption capacity. Influence of temperature can increase (endothermic) or decrease (exothermic) the adsorption capacity. The concentration and type of heavy metals influence the adsorption of each heavy metal generally by competition for adsorption sites.

Table 2.7 Treatment technologies for removing heavy metals from wastewater/ stormwater involving physical or chemical processes, adapted from Ahmaruzzaman (2011)

Methods	**Advantages**	**Disadvantages**
Oxidation	Rapid process for toxic pollutants removal	High energy costs and formation of by-products
Ion-exchange	Wide range of heavy metals can be removed	Selectivity for adsorption poor, adsorbent requires regeneration or disposal
Membrane filtration technologies	High efficiency in removing heavy metals	Concentrated sludge production, expensive
Adsorption	Flexibility and simplicity of design, ease of operation and intensitivity to toxic pollutants	Adsorbents requires regeneration
Coagulation/flocculation	Economically feasible	High sludge production and formation of large particles
Electrochemical treatment	Rapid process and effective for certain metal ions	High energy costs and formation of by-products
Ozonation	Applied in gaseous state: alteration of volume	Short half life
Photochemical	No sludge production	Formation of by-products
Irradiation	Effective at laboratory scale	Required a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production
Fenton's reagents	Effective and capable of treating variety of wastes and no energy input necessary to activate hydrogen peroxide	Sludge generation
Biological treatment	Feasible in removing some metals	Technology yet to be established and commercialised

The process of removing metals from stormwater by adsorption can be carried out by mixing the adsorbent with adsorbate either in a batch-type contact unit operation or a continuous flow packed column bed system. These adsorption processes are further categorised as equilibrium adsorption, adsorption kinetics and fixed bed adsorption. Most studies are conducted on static batch mode of adsorption rather than on the more practical dynamic fixed bed column experiments which are mostly used in water treatment processes. However, batch type experiments are simple and quick to execute and allow many variations in experimental conditions which are harder to conduct in fixed bed scenarios and will still collect much information (Loganathan et al. 2014). Many studies on adsorption investigated the effects of physical and chemical factors influencing adsorption. Some of these factors are pH, concentrations of co-ions, and temperature (Ahmaruzzaman 2011; Babel and Kurniawan 2003; Gupta and Ali 2012).

In equilibrium adsorption studies, the heavy metals adsorption in batch studies have been fitted to models such as Langmuir isotherm, Freundlich isotherm, and Dubinin–Radushkevich isotherm (Chen 2012; Dimirkou and Doula 2008; Doula 2009; Mishra and Patel 2009; Nguyen et al. 2015). Column adsorption data of heavy metals have been modelled using the Thomas model (Han et al. 2009; Nguyen et al. 2015; Nur et al. 2014), Bohart-Adam model (Jusoh et al. 2007), and Yoon-Nelsoon model (Baral et al. 2009; Tabakci and Yilmaz 2008). In adsorption studies, generally the mechanisms of adsorption are investigated using zeta potential (Abdel Salam, Reiad and ElShafei 2011; Nguyen et al. 2015) and spectroscopic (FTIR, EDX) (Doula 2009; Han et al. 2009; Mozgawa 2000; Vidal et al. 2011) measurements.

Stormwater effluents rarely contain a single component and consequently selecting the adsorbent must be based on suitablity for multi-component and multi-metal system. Therefore it is important to study the competitive adsorption behaviour in the presence of different metals and other pollutants such as suspended solids and organic matter (Ahmaruzzaman 2011; Chen 2012). This has rarely been done in past studies. Most studies on pollutants have been conducted in batch experiments on a single metal system (Mohan, Pittman Jr and Steele 2006; Nguyen et al. 2015; Peternele, Winkler-Hechenleitner and Pineda 1999; Zhao et al. 2010). There are, however, not many studies that use a dynamic fixed-column arrangement to treat stormwater.

Many different adsorbents have been employed to remove heavy metals from stormwater, namely: biosorbants such as leaves, fruit peels, agricultural and biological by-products, etc.; industrial by-products such as fly ash, furnace slag, etc.; natural materials such as mud, zeolite, kaolinite, etc.; commercial materials such as ion exchange resins, activated carbon, etc.; metal oxides such as hydrous ferrous oxide, aluminum oxide, titanium oxide, etc.; and finally, novel newly developed nano-materials (Ahmaruzzaman 2011; Chen 2012; Engates and Shipley 2011; Hang et al. 2014; Hua et al. 2012; Liu et al. 2013; Mohammed et al. 2012; Nguyen et al. 2013; Nguyen et al. 2015; Wang, Sun, et al. 2013; Wang, Liu, Xu, et al. 2013). Nano-materials have emerged as one of the most effective adsorbents for removing organic and inorganic pollutants from water and wastewater because of their high surface area leading to high adsorption capacity (Chen 2012). However, because of their fine particle size causing poor hydraulic conditions, it cannot be used directly in fixed-columns. They are often mixed with coarser materials to overcome these problems when used in columns.

Out of these adsorbents, activated carbon for many years has been undoubtedly the most popular and widely used adsorbent in water and wastewater treatment process because of its large surface area and its high degree of surface reactivity (Chen 2012). Activated carbon is known for its high organic removal capacities. It also can remove heavy metals effectively (Chen and Wang 2004; Chen and Wu 2004). Activated carbons can be found in many forms such as powder-activated carbon (PAC), granular-activated carbon (GAC), activated carbon fibrous (ACF), and activated carbon cloth (ACC). Of these, GAC performs better in the column mode adsorption system because of better hydraulic conditions.

2.3.3.2 Organic matter

Natural organic matter (NOM) is an integral part of stormwater as it can be found in all the surface waters. NOM found in stormwater consists of both hydrophobic and hydrophilic components where the largest fraction is generally hydrophobic acids, which makes up approximately 50% of the dissolved organic carbon (DOC) (Parsons et al. 2005). A main component of naturally occurring DOC is humic acid (HA), as it can represent up to 90% of DOC (Chen and Wu 2004). These HAs have good binding properties and electrostatic interactions with heavy metals, leading to the formation of metal-organic complexes. These complexes can affect the adsorption of heavy metals on adsorbents. Heavy metal adsorption in the presence of HA may depend on several factors such as surface charge of the adsorbent and type and abundance of functional groups in HA, concentration of HA, etc. The pH of the water is another important factor which not only influences the surface charge of the adsorbent and type and concentration of metal species but also influences the heavy metal complexation by HA. A schematic illustration of the possible mechanisms of heavy metals adsorption at low and high pH in the presence and absence of HA is presented in Figure 2.8. These mechanisms of adsorption will be used in explaining the results obtained in the laboratory.

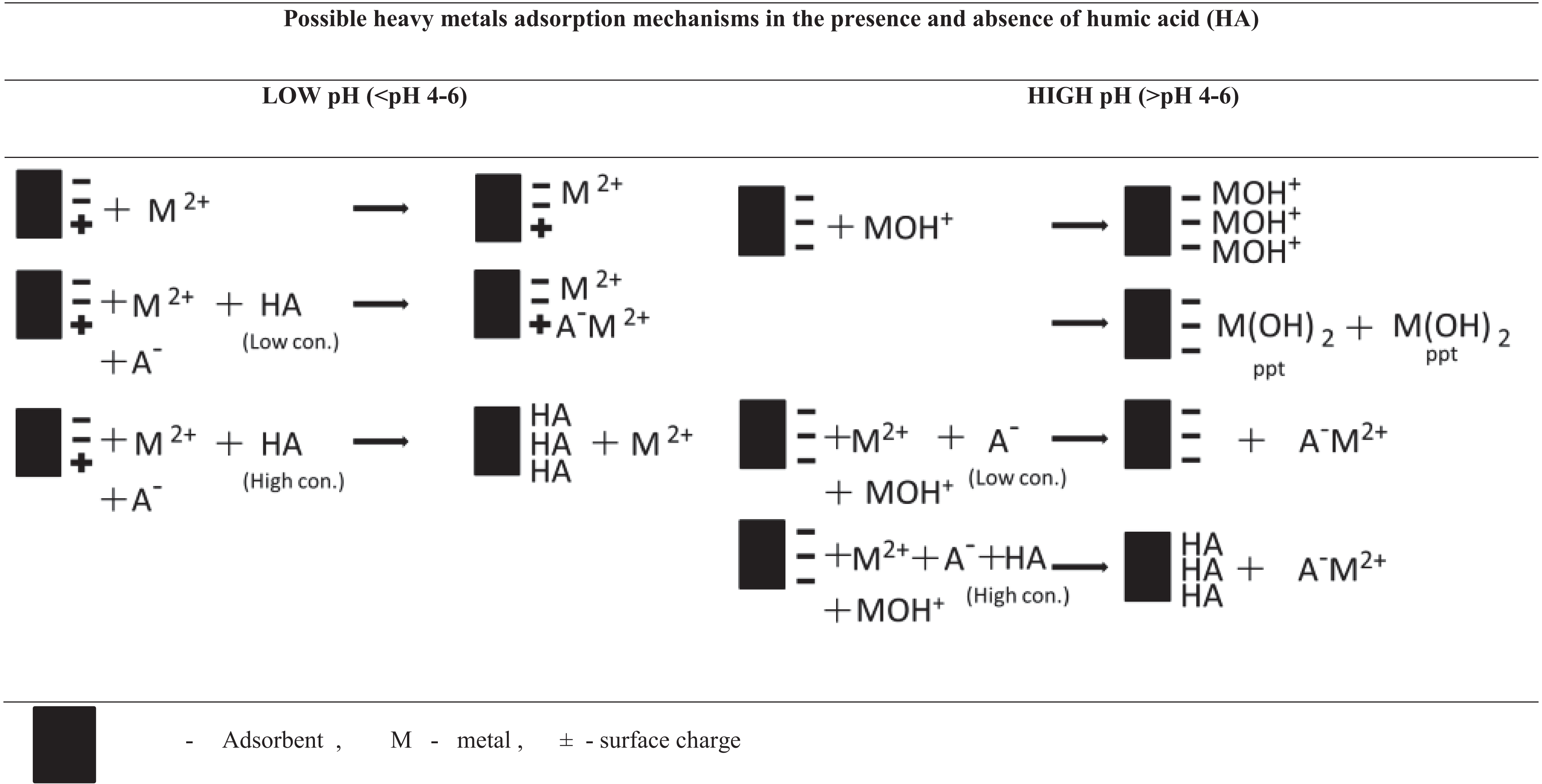

Figure 2.8 A schematic illustration of the different mechanisms of heave metals adsorption at low and high pH in the presence and absence of HA.

Granular activated carbon (GAC) is a common and widely used adsorbent in water treatment because it can remove a range of contaminants such as organic carbon, turbidity and nutrients. GAC was also found to be effective in removing many heavy metals (Chen 2012). GAC is widely known for its large surface area (internal surface area of between 700 and 1,200 m^2/g; (Loganathan et al. 2014) and higher degree of surface reactivity. Powdered GAC is used in waste and potable water treatment, air emission cleaning, chemical processes such as solvent recovery and decolourising, and general domestic applications such as odour removal. Nevertheless, its application fields are restricted due to its high cost. Low cost wastes and agricultural by-products are also now being used to produce activated carbon which provides an economical solution to the high cost of the treatment process (Cimino et al. 2005). Chen (2012) reported that there is limited knowledge available on the effect of the presence of HA on heavy metals adsorption by GAC. Chen also found that the feed solution's pH of is an important factor which can affect the removal efficiency of metals by GAC.

2.3.4 Guidelines and standards applied to stormwater

The water quality of treated stormwater for public use should meet certain health and safety criteria and it should have a high level of uniformity and certainty to meet end-use requirements. The level of treatment required is largely determined by both the catchment properties (which influence the type and level of pollutants) and the intended end-use (Philp et al. 2008). The following guidelines can be applied for different types of end-use (i.e. potable, non-potable uses such as gardening toilet flushing, etc.)

Australian Drinking Water Guidelines (ADWG)

These guidelines provide a framework for managing drinking water supplies to ensure safety and aesthetic quality at the point of use. The latest version of these guidelines was released in 2011.

National Guidelines for Water Recycling (Phase 1, Phase 2)

Phase 1 Managing Health and Environmental Risks deal primarily with greywater and sewage reuse. Phase 2 of the guidelines includes modules on stormwater reuse and augmenting drinking water supplies.

ANZECC Guidelines for Fresh and Marine Water Quality (2000)

These guidelines were formulated to protect environmental values of water resources in line with the community needs. The guidelines consider five environmental values, these being ecosystem protection (both freshwater and marine) including protection of waters used for shellfish and fish production and by wildlife; recreation and aesthetics, raw water for drinking water supply, agricultural water; and industrial water. Table 2.8 summarises the permissible limits of major pollutants found in stormwater with different end use requirements and environmental protection.

Table 2.8 Australian guidelines on permissible levels of target pollutants for different end uses and environmental protection

Pollutants	Unit	Marine water Ecosystems [1,a]	Freshwater Ecosystems [1,a]	Irrigation [1]		Drinking Water [2]	Aesthetic [1]
				Long-term	Short-term		
pH		-	-	6.5-8.5	6.5-8.5	6.5-8.5	-
TSS	mg/L	-	-	-	-	500	-
Turbidity	NTU	-	-	-	-	5	-
Aluminium	mg/L	-	0.08	5	20	-	-
Arsenic	mg/L	-	0.042	0.1	2	0.01	-
Cadmium	mg/L	0.0014	0.0004	0.01	0.05	0.002	-
Chromium	mg/L		0.00001	0.1	1	0.05	-
Copper	mg/L	0.003	0.0018	0.5	5	2	-
Iron	mg/L			0.2	10	-	0.3
Lead	mg/L	0.0066	0.0056	2	5	0.01	-
Mercury	mg/L	0.0007	0.0019	0.002	0.002	0.001	-
Nickel	mg/L	0.2	0.013	0.2	2	0.02	-
Zinc	mg/L	0.023	0.015	2	5	-	3

[1] ANZECC and ARMCANZ (2000)

[2] NHMRC (2011)

[a] Values are reported for 90% of species protection

2.4 Conclusions

Water consumption data is highly variable across households due to the behaviour changes, climate, socio-demographics, household size, family composition, water appliances, cultural and personal practises, etc. (Juárez-Nájera, Rivera-Martínez and Hafkamp 2010; Loh and Coghlan 2003; Russell and Fielding 2010). End-use data in combination with such socio-demographic information can help to identify correlations between water behaviours and key demographic subsets within a population, for instance income, age, gender and family composition (Beal, Stewart and Fielding 2013). A comprehensive demand analysis of end-users in Sydney has not been done previously. It is important to know the effect of different demand management techniques on a larger scale, interpreted together with socio-demographic information. This will provide valuable information for future demand management strategies.

WSUD treatment devices such as wetlands, bio-retention, and permeable pavement are widely used in stormwater management. Current WSUD devices used in Australia for stormwater pollution control do not reliably provide the water quality necessary for water recycling due to their varying removal efficiency for a range of inflow conditions and pollutants. Furthermore, to adequately remove pollutants using these treatment devices, a large surface area (or footprint) is needed which is very rarely available in urban areas. Stormwater discharge is relatively high and therefore needs to be treated intensively at a high rate. Treatment systems such as fibre filters, deep bed filters and biofilters treat at a high rate and have been used successfully in water and wastewater treatment.

Pervious pavement system is a popular WSUD technology as it allows stormwater runoff to percolate to an underlying reservoir storage or drain into the soil and at the same time treat the stormwater on-site. However, the use of pervious pavement is somewhat limited because of the concern about the possible migration of pollutants into groundwater due to ineffective treatment of pollutants by pervious pavement. It is therefore critical to improve the quality of water coming through the pervious pavement by introducing novel materials which have high adsorption capacity for specific pollutants.

The adsorption of pollutants especially heavy metals from stormwater using different adsorbents has been extensively studied. However, there are many issues and drawbacks that need to be addressed. Not many studies use a dynamic fixed-column arrangement to treat stormwater which is more practical than the commonly used batch experiments. Therefore, it is useful to carry out the adsorption experiments in column mode trials in the laboratory. Very often stormwater carries more than one metal and there can be competition for adsorption between metals. However, most studies conducted adsorption of a single metal and not mixed metals. Information on the adsorption of heavy metals in the presence of organics and other pollutants is limited. Therefore, the suitability of an adsorbent to remove heavy metals in the presence of multi-component pollutants needs to be examined. This would provide the information necessary to support the application of adsorbents for the treatment of stormwater in the field. Finally it is also important to study the possibility of regenerating adsorbents following its use so that the adsorbent can be repeatedly used in many treatment cycles, thus making the process economical.

CHAPTER 3

University of Technology, Sydney

Water consumption patterns in the Sydney metropolitan area and surrounding areas[1]

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[1] This chapter reports a study conducted jointly by Benjamin Kus and Danious Southararajah. The results of this study was reported in

- Benjamin Kus (2014) Cost Effective Filtration System to Improve the Water Quality in Rainwater Tanks, PhD Thesis, University of Technology Sydney.
- B. Kus, D.P. Sountharajah, J. Kandasamy, S. Vigneswaran, G. Moody, (2015). Quantifying reductions in water demand due to rainwater tank installations at residential properties in Sydney. **10th Conference on Sustainable Development of Energy, Water and Environment Systems, Dubrovnik, Croatia, 26 Sept-3 Oct 2015.**

3 Water consumption patterns in the Sydney metropolitan area and surrounding areas[1]

3.1 Introduction

In Australia potable water demand is expected to increase above the current available water supplies due to the predicted population increases in capital cities, and the reoccurrence of the recent drought exacerbated by climate change. This has forced governments to look at ways of securing alternative water supplies. A number of solutions can be utilised to save water either by reducing demand, increasing efficiency or by increasing the available supply. The former include community education, water restrictions, retrofitting water fixtures to reduce consumption, and rebate schemes to promote the installation of rainwater tanks. Methods for increasing available supply include alternative water supplies such as: firstly, desalination and recycling; and secondly, creating alternative but poorer quality supplies from sources such as grey water for local non-potable uses.

Moy (2012) undertook a post-installation analysis of a group of rainwater tanks installed between 2005 and 2007 in the Wollongong and Shellharbour LGAs, towns south of Sydney and their effects on mains water consumption. The study aimed to determine the average mains water reductions achieved in households with rainwater tanks. The results reveal that households with rainwater tanks in Wollongong and Shellharbour reduced their consumption during 2005-2007 by approximately 10.3%. However, these towns were not analysed separately and given that this was a relatively short period the analysis did not adjust the data for the overall reduction of water consumption in the wider community. The total residential water consumption for

Wollongong and Shellharbour LGAs during 2005-2007 indicated that water consumption fell by 3.3% and 0%, respectively.

Knights et al. (2012) present data from a rainwater tank incentive scheme in Marrickville LGA where pre- and post-rainwater tank installation water usage was examined. The study included real-time metering of mains water and rainwater use of some individual households participating in the program. The results showed that rainwater tanks can reduce water consumption on average by 110 L/d ranging from 7 L/day to 390 L/day. This equates to a reduction in water consumption of 25%. The data was not adjusted for the overall reduction of water consumption that occurred in the wider community. It was not possible to assess this since the time period over which the analysis took place was not given.

Households in Sydney account for about 70% of the total drinking water consumption. The uses of water in and around the home are: 23% for lawn and garden watering; 4% for pools, hosing down and car washing; 25% for showers; 17% for washing machines; 16% for kitchen, laundry and bathroom taps; 14% for toilets; and 1% for dishwashers (NSW Government, 2013). Rainwater tanks may replace potable water used for lawn and garden watering, hosing down and car washing, and laundry and toilet flushing. Indeed Sydney Water provided a higher rebate if the rainwater tank was plumbed for the toilet and laundry. These imply that, if available, nearly 60% of household water uses could be provided by rainwater tanks and there is a large potential to reduce water use in Sydney. By 2010, 11.1% of the Sydney households had rainwater tanks (ABS, 2010).

The aim of this chapter is to analyse the water consumption pattern in the Sydney metropolitan area and surrounding areas (Illawarra and Blue Mountains) that are connected to SWC potable water supply mains. This was based on the metered potable water usage of all single dwelling residential properties between 2002 and 2009. Additionally this paper compares the potable water consumption in residential properties within the greater Sydney metropolitan area against the residential properties that installed a rainwater tank and received a rebate from SWC. The water usage consumption before and after rainwater tank's installation was analysed to quantify the amount by which rainwater tanks reduce water consumption. The results were then compared against socio-demographic factors to explain why they had occurred.

3.2 Background and data

3.2.1 Climate

The average rainfall in Sydney from 1913 to 1998 was 1203 mm/yr. The year is sub-divided into quarters that approximately follow the seasons: Q1 from November to January; Q2 from February to April; Q3 from May to July; and Q4 from August to October. The wettest period of the year is generally in the second quarter (Q2) while the driest is the fourth quarter (Q4). The average quarterly and yearly rainfall patterns over the study period (2002 to 2009) vary greatly from year to year. The driest year was 2005 with a total annual rainfall of only 808 mm and the wettest year was 2007 with 1325 mm of rainfall. In fact 2005 was the third hottest summer recorded in NSW (Randolph and Troy, 2007). Some notable phases during the study period include the fourth quarter of 2002 (Q4-2002) and first quarter of 2003 (Q1-2003) where a total of only 47 mm and 120 mm of rainfall occurred respectively; and the third quarter of 2007 (Q3-2007) where a total of 588 mm of rainfall occurred. This was almost three quarters of the total rainfall that occurred in 2005 and well above the quarterly average.

High average temperatures can be a leading factor for increased water consumption due to the need for additional watering of gardens and lawns and higher overall consumption. The quarterly and annual average temperature were 25.6 (Q1), 25.2 (Q2), 19.1 (Q3), 21.7 (Q4), and the annual average was 22.9. The hottest part of the year is generally in the first and second quarter (November through to April) while the coldest part of the year is the third quarter (May through to July).

3.2.2 Water restrictions

SWC implemented various water restrictions over the past decade due to the declining water levels in dams that supply the Sydney metropolitan area (SWC 2012a). Voluntary restriction commenced in Sydney in October 2002. SWC introduced Level 1 restrictions in October 2003 when dam levels dropped below 60% (Sydney Water, 2013). Dam levels continued to decline due to the lack of rainfall in the dams' catchment and by June 2004 were below 50% when SWC implemented Level 2 restrictions (Sydney Water, 2013). In June 2005 the dam levels had dropped further to below 40%, resulting in Level 3 restrictions (Sydney Water, 2013). Level 3 restrictions remained in place for a number of years. In June 2008, SWC eased Level 3 restrictions to permit its residential customers to wash cars, boats and caravans at home as well as to clean the windows and walls of their house with a hose as long as a trigger nozzle was fitted. By June 2009 water levels in the dam had been steady at around 60% for 12 months. Level 3 restrictions ceased and SWC brought in new 'Water Wise Rules' (Sydney Water, 2013) which are still in effect despite dam water levels currently at 100%. Detail description of water restrictions is given in section 2.2.4.

3.2.3 SWC rainwater tank rebate

In October 2002, SWC introduced a rainwater tank rebate scheme in an effort to promote the installation of rainwater tanks so that water consumption could be better managed. The scheme provided various rebates (monetary refunds) for their installation. $150 was provided for the installation of rainwater tanks with a capacity of between 2,000 to 3,999 L, $400 for 4,000 to 6,999 L and $500 for more than 7,000 L. Additionally; further monetary incentives ($150) were provided to connect the rainwater tank to the household toilet system and/or laundry systems. This rose to $300 from October 2006. In July 2007, $500 was given for a rainwater tank connected to the household toilet system and/or $500 to the laundry systems. This scheme ended in June 2011.

3.2.4 SWC database

SWC supplies water to properties located in Sydney's metropolitan area. A database of water bills, which are issued quarterly and include the amount of water used at a property, was used to undertake a statistical analysis of residential water usage in Sydney. The database covered the period spanning from November 2001 (Q1-02) to October 2009 (Q4-09). The quarters approximately follow the seasons: Q1 from November to January; Q2 from February to April; Q3 from May to July; and Q4 from August to October. The first quarter in the dataset (Q1) covered the period November 2001 to February 2002. The total number of properties in the database totalled 1,207,359, of which 962,697 were categorised as 'Residential - Single Dwelling'. By 2009, a total of 52,576 households had registered for a rainwater tank rebate with SWC which represented a 5.5% of all residential single dwellings supplied by SWC. The average quarterly consumption for these properties with and without rainwater tanks for each local government authority (LGA) was provided. Data was released in this restricted form to comply with Sydney Water's privacy restrictions which prohibits releasing any information pertaining to their individual customers.

The SWC database covers a large data set of various property types, land sizes and water usages. A subset was created - Conditional Data Set – Residential Properties (CDSR) - to remove data not used in this study. The CDSR was separated into individual LGAs to provide a location-based investigation and further isolated properties to the following conditions: single dwelling residential properties only; properties with a lot area greater then 100m^2 and no larger than 2000 m^2 as larger properties are not typically urban residential; and properties with typical water usage between 10 kL to 500 kL per quarter (typically 100 L to 5000 L per day). Subsequent to creating the CDSR, a second data set was created with these same conditions and including only those properties with a registered rainwater tank rebate (CDSRT).

3.2.5 Standardisation of data set

To ensure that the data set contains consistent data making it possible to compare water usage before and after a rainwater tank has been installed, the CDSRT had to be standardised. To standardise the data, individual LGA CDSR were graphed to observe the typical water usage trend over the study period (Q1-02 to Q4-09) to determine the impact of factors that led to changes in water usage other than the rainwater tank. These factors include the effects of Sydney Water's restrictions on water usage, seasonal and climate variations, and the changes in consumers' water usage patterns (e.g. as a result of public education campaigns).

The CDSR data was grouped by LGAs. For each LGA a factor was determined for each quarter based on the average of the respective quarterly water usage compared to the average of each LGAs water usage over the study period (Q1-02 to Q4-09). Subsequently, these factors were applied to the respective individual quarterly water bills of the CDSRT. The data set with factors applied is called the Standardised

Conditional Data Set with rainwater tanks (S-CDSRT). The outcome of applying the factors to the CDSRT allowed a comparison between water usage, before and after the rainwater tanks were installed with any of the other effects discussed above removed. The reduction in water consumption was calculated for rainwater tanks over a period of at least two years (8 quarters) before and at least two years after the installation. There were 32,276 properties with rainwater tanks or 61.4% of the total number of properties with rainwater tanks meeting this criterion. The proportion of rainwater tanks meeting this criterion was over 50% in all but 6 LGAs. Any decline in the average water usage trend after the installation of the rainwater tank would confirm that it led to a reduction in potable water usage.

3.3 Results and discussions

3.3.1 Water consumption for residential single dwellings

Figure 3.1 shows the reduction in water consumption in Sydney and in various LGAs over the period leading up to and including the water restrictions. The overall trend in the data in terms of the times when water consumption rises, falls and plateaus is similar. Water consumption sharply fell during the period of voluntary restriction and reflects: firstly, the community education and publicity campaign to save water; and secondly, the falling of dam storage to critical levels over that period. The saving was so large that the reduction in water consumption level during periods of level 1, 2 and 3 restrictions actually levelled off even when they became increasingly severe. Savings in water consumption became harder to achieve once practices and habits in the community that were easier to change were accomplished. The average reduction in water consumption from 2002 to 2009 was about 24%. Not all the saving in water consumption can be attributed to the water restrictions program. Concurrently, during this period other measures were implemented to reduce water consumption. This included the installation of water savings devices such as water efficient shower heads and dual flush toilets, and implementing the Building Sustainability Index (BASIX) for new and refurbished buildings which aimed to deliver effective water reductions in Sydney and across New South Wales. Another objective was to continually replace water appliances with new and more efficient ones.

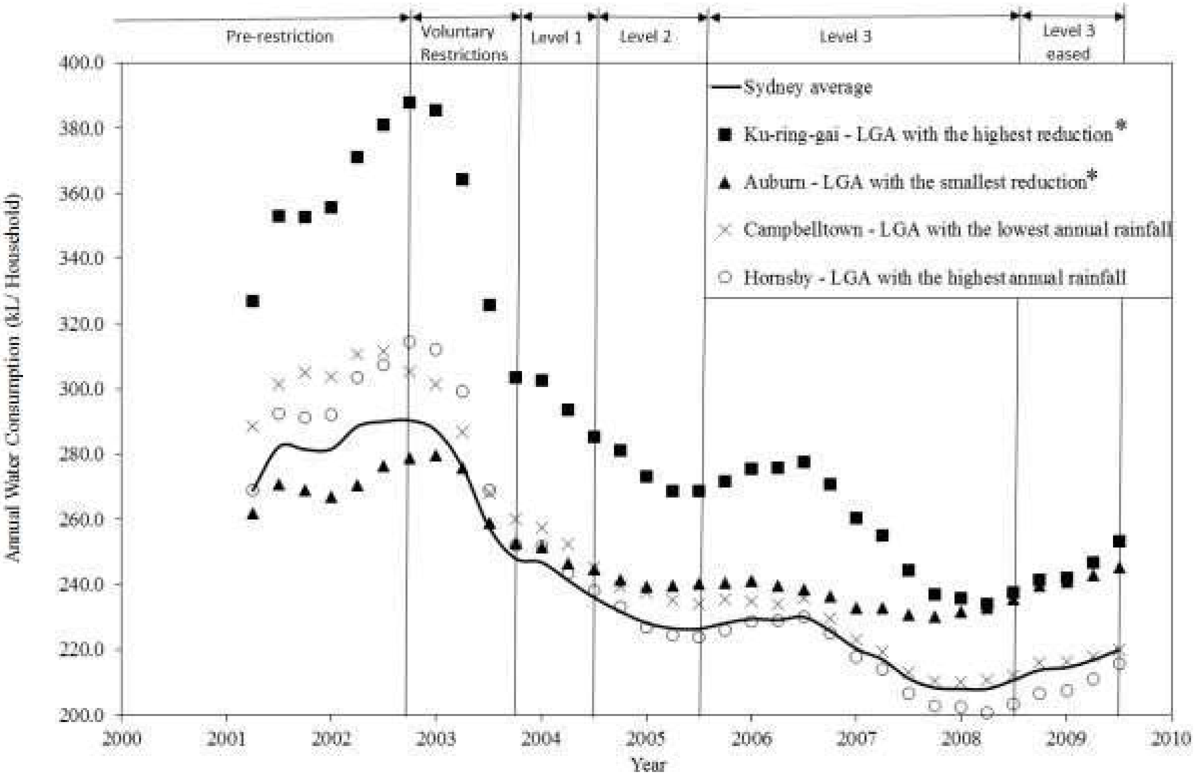
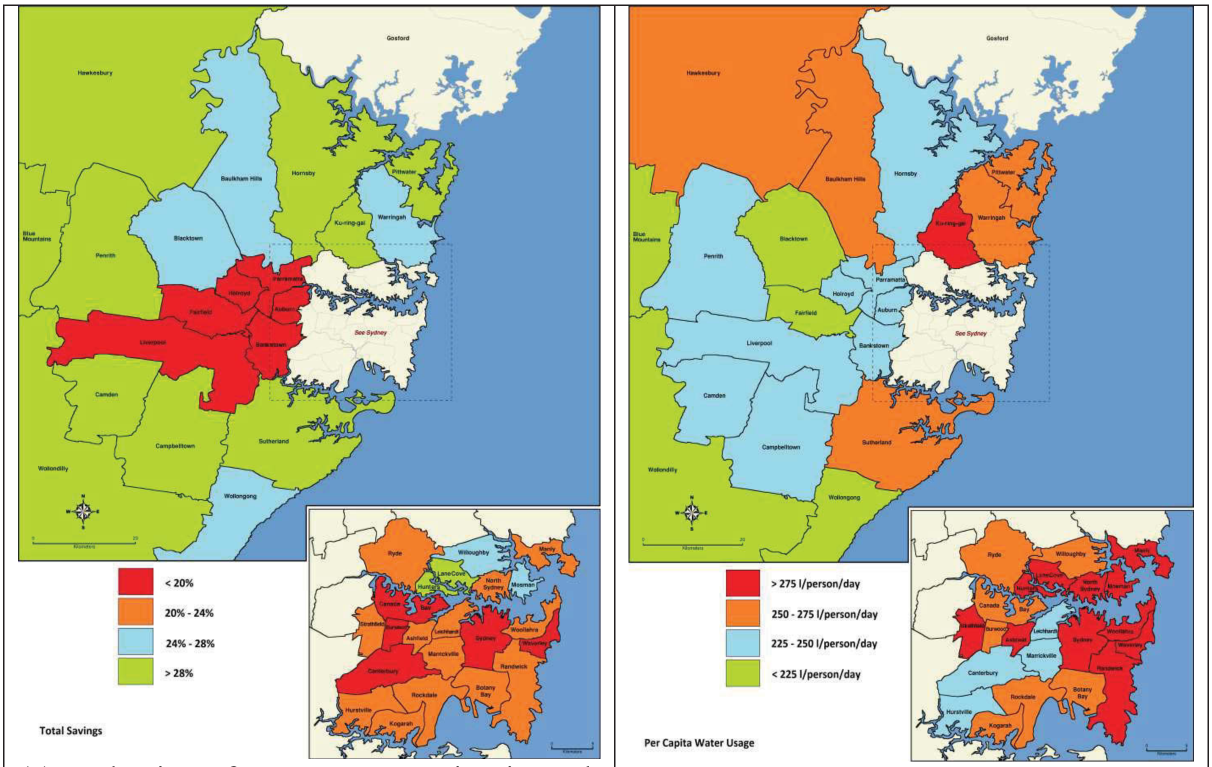


Figure 3.1 Variation in average water consumption in Sydney and its LGAs.

Figure 3.1 shows the variation in water demand in Campbelltown and Hornsby which have the lowest and highest rainfall, respectively. The annual rainfall in Hornsby is approximately double that in Campbelltown. Both suburbs are similar in character with predominantly single dwelling houses and large gardens. Income levels in both suburbs (ABS, 2009) are also similar and reasonably close to the Australian average

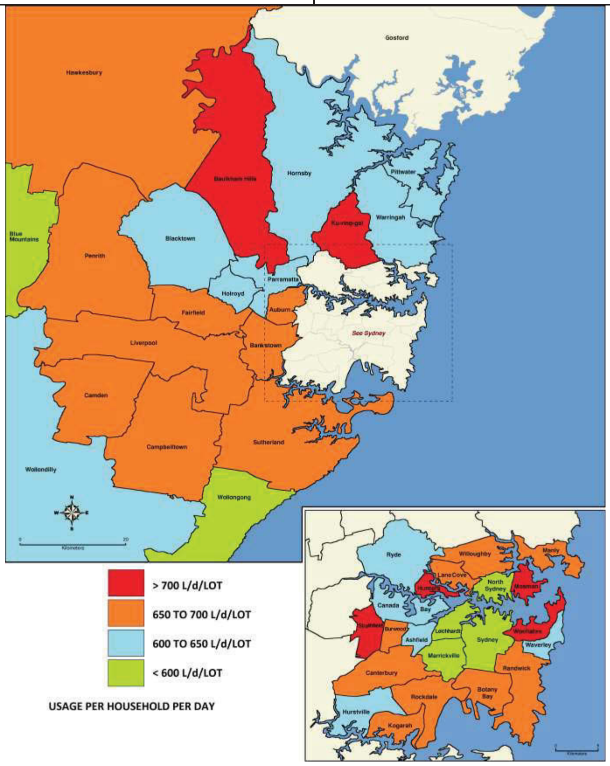
(ABS, 2009). While the difference in water consumption between the two LGAs is not large (<5%), Hornsby had a slightly lower consumption. The plot also shows the LGAs with the largest (Ku-ring-gai) and smallest (Auburn) reduction in water consumption during the water restrictions period. The former is a wealthy leafy suburb with predominantly single dwelling houses with large gardens while Auburn is a suburb located near the geographical centre of Sydney (20 km from the CBD) with mainly smaller lot areas and smaller outdoor/garden areas. While there was a tangible reduction in both suburbs, the reduction in Ku-ring-gai was substantial. Both Ku-ring-gai and Auburn had similar water consumption patterns at the end of the monitoring period and this was about 10% larger than the Sydney average.

Figures 3.2 to 3.5 presents an overview of water consumption in Sydney together with various socio-economic indicators which were prepared from the SWC database together with data from the Australian Bureau of Statistic (ABS, 2006; ABS, 2007), and the Bureau of Meteorology (BOM, 2012). The data across Sydney is presented by LGAs. For clarity, the overarching map containing most of the LGAs is referred to as the ‘outer Sydney area’ and the smaller insert is referred to as the ‘inner Sydney area’. **High resolution large size images are attached in the Appendix for further clear reference (Appendix A).**



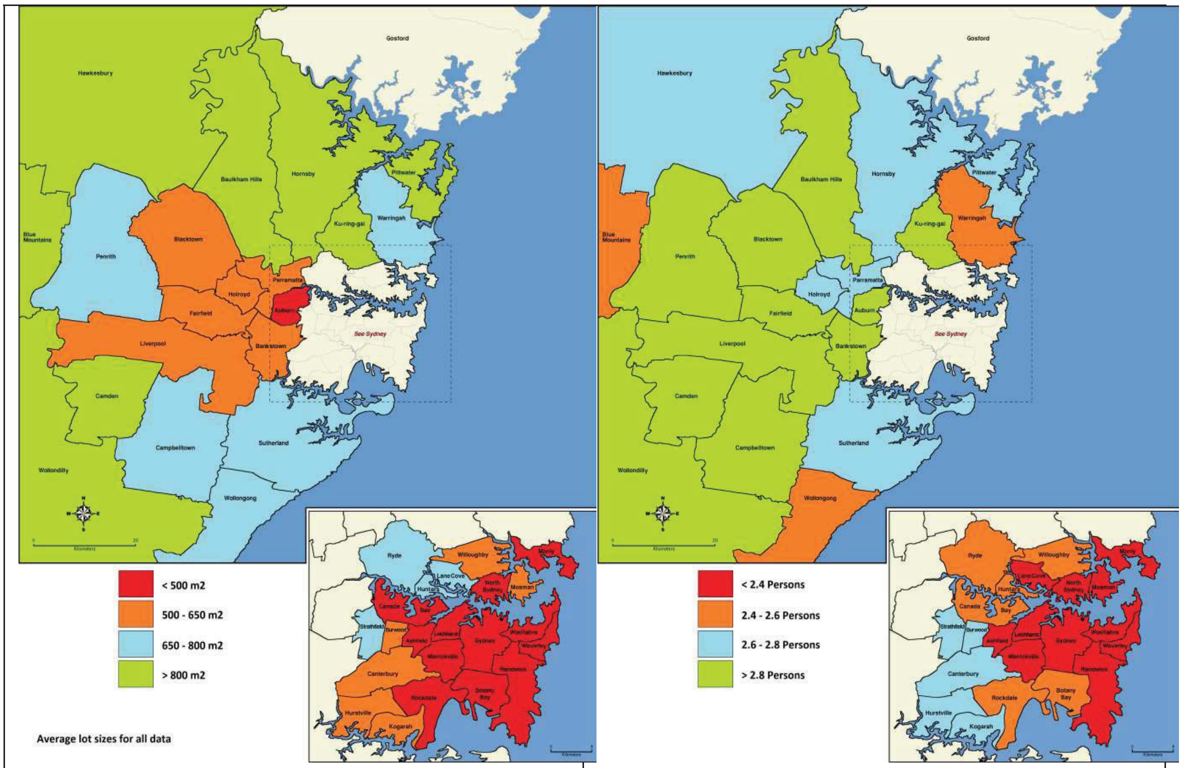
(a) Reduction of water consumption in each LGA over the study period.

(b) Average daily per capita water usage.



(c) Average daily household water usage.

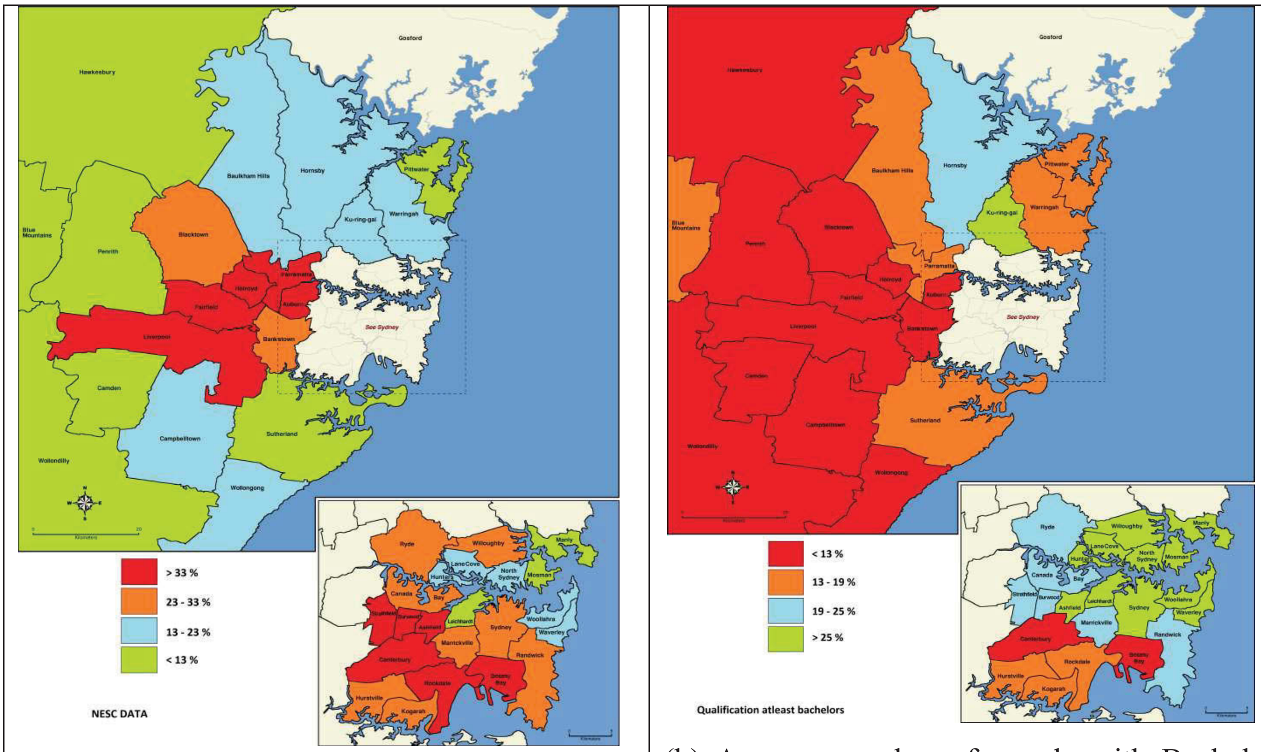
Figure 3.2 Water consumption for single households in the Sydney metropolitan area



(a) Average lot sizes.

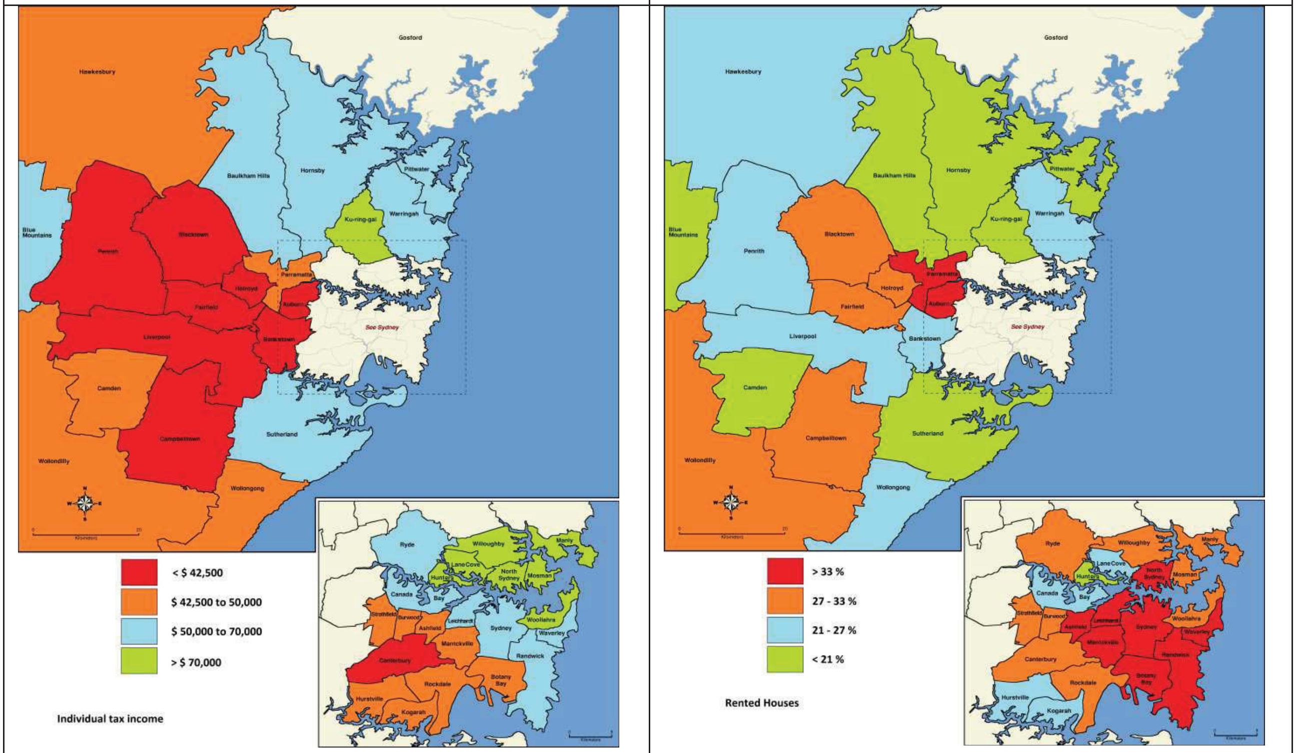
(b) Average number of persons per household

Figure 3.3 Average single dwelling property area and average number of persons per household in Sydney



(a) Percentage of residents born in non-English speaking countries

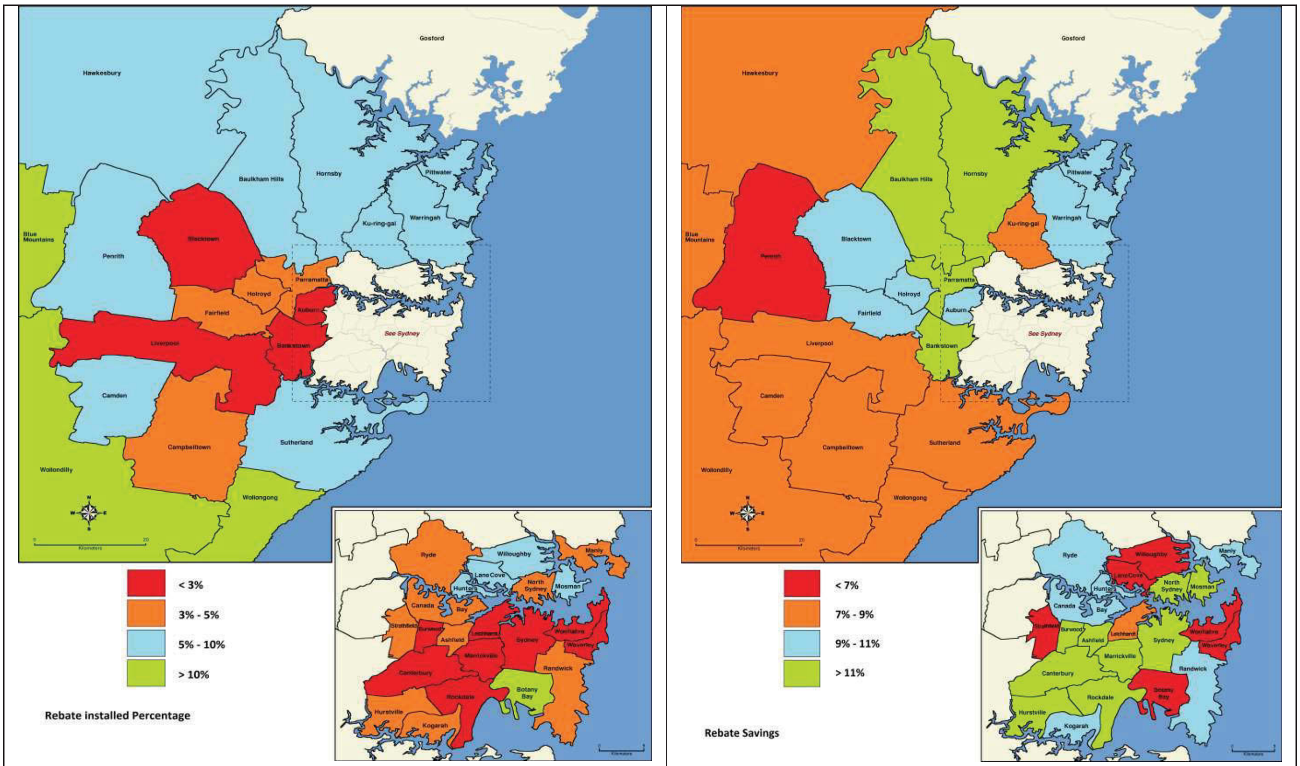
(b) Average number of people with Bachelor qualifications or higher



(c) Mean taxable income

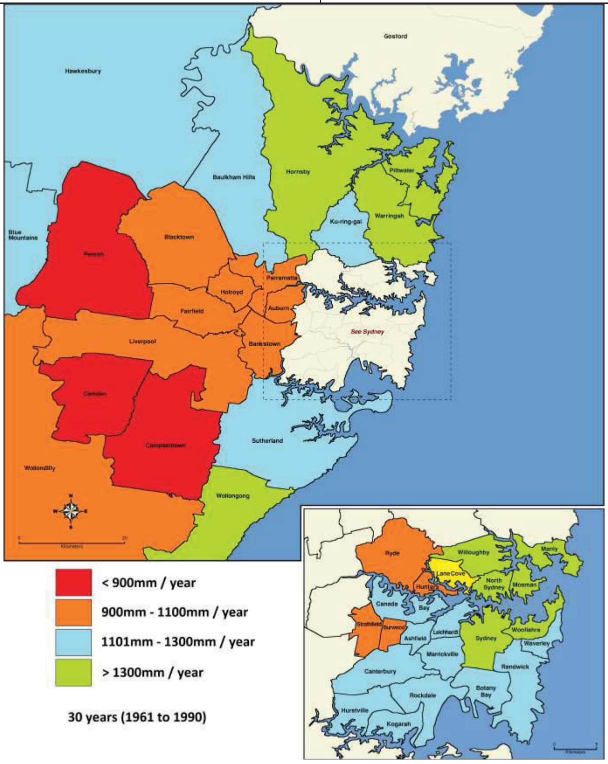
(d) Percentage of houses that are not owner occupied (rented)

Figure 3.4 Socio economic indicators in the Sydney metropolitan area



(a) Percentage of rebated rainwater tanks installed.

(b) Average percentage of water savings from rebated rainwater tanks.



(c) Sydney Metropolitan area long term average rainfall by LGA from 1961 to 1990

Figure 3.5 Average percentages of water savings from rebated rainwater tanks in the Sydney metropolitan area

The SWC data shows that the average annual water consumption per household in Sydney's metropolitan area during the study period (Q1-02 to Q4-09) declined from 282 kL/annum in 2002 to 200 kL/annum in 2009. Even without including the impact of rainwater tanks (discussed in the next section) the average water consumption fell by 24% over the study period. Table 3.1 summarises the reduction in water savings in all 44 LGAs. These reductions can be attributed to effective demand management techniques such as the Sydney-wide water restrictions between 2003 and 2009 (Sydney Water, 2013) and the introduction of water efficient fixtures like taps, dual flush toilets and efficient shower heads. SWC installed these free of charge or at subsidised prices. Other factors included the implementation of BASIX for new and refurbished buildings, and the installation of new water efficient water appliances. It may also be due to lot sizes becoming smaller in part due to sub-division of existing residential lots which leads to smaller gardens (Troy et al. 2005).

Table 3.1 Percentage of water saved by installing a rainwater tank for LGAs in Sydney

LGA	Annual Water Usage +/- Std Deviation* (kL/Household)	Reduction in Water Consumption (%)	Further reduction due to Rainwater Tanks (%)	Portion of Rainwater Tanks Installed (%)
Ashfield	233 ± 24	22	12	3.7
Auburn	246 ± 19	11	11	1.9
Bankstown	237 ± 22	19	10	2.8
Blacktown	233 ± 28	24	10	2.8
Blue Mountains	181 ± 31	32	9	12.2
Botany Bay	254 ± 24	22	6	15.2
Burwood	250 ± 22	19	8	2.1
Camden	248 ± 40	29	7	6.8
Campbelltown	242 ± 34	29	9	3.6

Canada Bay	225 ± 22	19	11	3.6
Canterbury	243 ± 21	19	10	2.3
Fairfield	253 ± 24	19	9	3.1
Hawkesbury	251 ± 47	32	8	7.0
Holroyd	226 ± 19	17	9	4.1
Hornsby	237 ± 39	30	11	7.0
Hunters Hill	284 ± 47	31	12	7.9
Hurstville	230 ± 24	21	12	4.0
Kiama	172 ± 21	25	10	15.7
Kogarah	244 ± 27	22	10	4.2
Ku-ring gai	284 ± 53	34	11	7.5
Lane Cove	249 ± 37	30	12	5.6
Leichhardt	175 ± 17	20	9	2.0
Liverpool	249 ± 25	19	7	2.8
Manly	239 ± 31	22	10	4.7
Marrickville	196 ± 19	22	11	1.8
Mosman	284 ± 38	26	16	5.3
North Sydney	215 ± 27	24	12	3.2
Parramatta	230 ± 25	19	11	3.6
Penrith	244 ± 37	29	7	5.2
Pittwater	237 ± 36	30	12	7.5
Randwick	242 ± 26	24	10	3.5
Rockdale	242 ± 22	24	10	2.0
Ryde	229 ± 25	22	11	4.2
Shellharbour	206 ± 22	24	7	17.0
Strathfield	279 ± 35	21	7	3.0
Sutherland	242 ± 16	29	9	7.4
Sydney CDB	184 ± 101	20	9	0.7
The Hills Shire	276 ± 46	27	12	5.2
Warringah	237 ± 30	24	11	5.5
Waverly	232 ± 20	18	8	2.3
Willoughby	239 ± 30	26	8	5.9
Wollondilly	233 ± 40	29	9	12.0

Wollongong	196 ± 22	25	8	16.4
Woollahra	280 ± 35	23	9	2.3
Average	236 ± 31	24	9 +/- 1.9	5.5

Average over the period 2002-2009 ± Standard Deviation

When comparing the reduction in the level of water consumption between the various LGAs (Figure 3.2a) it is evident that water reductions are smaller for properties with smaller lot areas (Figure 3.3a). The majority of LGAs in inner Sydney which have small lot areas had about 20% to less than 20% reductions in water usage. Most of the LGAs in the outer Sydney area with some exceptions (Liverpool, Fairfield, Holroyd, Parramatta, Auburn and Blacktown), had significant reductions, most of which were greater than 28%.

A relationship exists between the water consumption in terms of per capita daily demand (L/p/d) compared to the number of people per household (ABS, 2005; SWC, 2012b). Figure 3b shows that as the number of people per household increases, water consumption (in per capita terms) (Figure 3.2b) generally decreases. This is true for most LGAs in the inner Sydney area (except Leichardt and Marrickville) which have less people per household and higher per capita usage compared to most LGAs in the outer Sydney area (except Pittwater, Baulkham Hills, Hawkesbury, Wollongong and Sutherland). These areas have more people per household and lower per capita usage. The trend between water consumption is not completely explained by the house lot area and number of people per household. Socio-economic factors must also be considered and they are explored in more detail below to assess their impact on water consumption.

3.3.2 Socio-economic Aspects

Figure 3.4 (a-d) shows the distribution of socio-economic aspects such as levels of educational qualifications, mean taxable incomes, portion of rental properties and portion of residents born in non-English-speaking countries (NESC) (ABS, 2007).

Educational qualification and mean taxable income: Troy et al. (2005) suggested that people with higher education qualifications and higher incomes generally consume more resources including water. Figure 3.4a shows that the education qualifications of people are much higher in the inner Sydney LGAs (ABS, 2007). More than 1 in 4 people who live in harbour-side LGAs (Sydney, Woollahra, Waverley, Leichhardt, Ashfield, Hunters Hill, Lane Cove, North Sydney, Mosman, Willoughby and Manly) have a Bachelor degree or higher. This ratio is less than 1 in 7 in most of the LGAs west of the inner Sydney area. A larger proportion of people with higher educational qualifications in an LGA (Figure 3.4a) also corresponds to higher than average individual taxable income (Figure 3.4b) (ABS, 2007). Further, it appears most of the LGAs with higher levels of educational qualifications (Figure 3.4a) generally had households with fewer occupants (Figure 3.3b). These suburbs generally had a higher per-capita water consumption pattern (Figure 3.2b). This is true for most LGAs in the Sydney metropolitan area except for Sutherland, Baulkham Hills and the Blue Mountains where there are less people with higher educational qualifications but they still have a fairly high individual taxable income. On the other hand, Ashfield which has more than 1 in 4 people with a Bachelor degree or higher, has an average individual taxable income similar to those LGAs with people who had low education qualifications. This may be due to the high number of students and recently arrived migrants.

LGAs that are an exception to this trend are Leichhardt and Marrickville. Based on election returns, these two LGAs contain a higher number of supporters of environmentally aligned political parties compared to other LGAs. They also have large numbers of people with Bachelor degrees or higher qualifications. Leichhardt also has reasonably high income levels in-line with nearby suburbs (CBD Sydney, Randwick and Waverley). However, these LGAs have low water consumption levels in terms of daily household consumption and daily per-capita household consumption.

Rented properties: Figure 3.4c shows that in most inner Sydney LGAs more than 1 in 3 properties were rented while in the remaining inner Sydney LGAs the ratio was at least 1 in 4 properties. This is very different to most outer Sydney LGAs where less than 1 in 4 properties were rented. There seems to be no relationship between per-capita daily household water consumption to the proportion of rental properties in an LGA (Figures 3.2b and 3.4c). Although some inner Sydney LGAs with more rental properties have higher per-capita water consumption levels (Figures 3.2b and 3.4c), others with a high per-capita water consumption level have fewer rental properties.

People born in non-English-speaking countries (NESC): There appears to be a relationship between the level of water consumption and the various LGAs (Figure 3.2b) where many people born in NESC live (Figure 3.4d). LGAs comprising a higher proportion of people born in NESC were LGAs south of Sydney (Botany Bay and Rockdale) and LGAs west of Sydney (Canterbury, Ashfield, Burwood, Strathfield, Auburn, Parramatta, Holroyd, Fairfield and Liverpool) (Figure 3.4d) (ABS, 2007). These areas are generally the same areas which have less people with at least a Bachelor degree and lower than average individual taxable income (Figure 3.4a and b). With the exception of Strathfield and Ashfield, these areas generally have average or below average levels of per-capita water consumption (Figure 3.2b). Figure 3.2c shows that Strathfield had a very high level of household consumption whereas Ashfield was slightly below average. The remaining LGAs, with higher numbers of people born in NESC, generally had average levels of household consumption.

The LGAs with a higher proportion of people born in NESC generally had reduced levels of water consumption between 2001 and 2009, (Figure 3.2a). Other LGAs such as Campbelltown, Camden, Penrith and Hornsby, which have much less people born in NESC, had similar low average per-capita water consumption levels (Figure 3.2b) yet all had the biggest reductions in water consumption between 2001 and 2009 of more than 28% (Figure 3.2a). This could be due to the communication/education barriers faced by people born in NESC who did not fully benefit from the education programs in water restriction regulations and water saving incentives that were run when these programs were implemented.

3.3.3 Rainwater Tanks

Table 3.1 also provides the percentage of water savings by installing rainwater tanks. The average distribution of reduction in water savings across all 44 LGAs is 9% +/- 1.9%. The statistical significance in the reduction of the mean water usage (P) is extremely small (1.9E-143) due to the very large data set of properties on the SWC database. On average a household could save around 24 kL of water annually by installing a rainwater tank. This level of savings was compared to the findings of other studies undertaken on individual LGAs in Sydney's metropolitan area and surrounding LGAs that received SWC water. Moy (2012) revealed households that installed rainwater tanks in Wollongong and Shellharbour reduced their water consumption by approximately 10.3% although this data was not adjusted for the overall reduction of water consumption that occurred in the wider community.

Furthermore the reduction in water consumption was not individually reported for Wollongong LGA and Shellharbour LGA. Table 3.1 shows the reduction in water consumption due to rainwater tanks for Wollongong and Shellharbour was 7% and 8%, respectively in this study. Knights et al. (2012) present data from the rainwater tank incentive scheme in Marrickville LGA indicating that rainwater tanks can reduce residential water consumption on average by 25%. Again this data was not adjusted for the overall reduction of water consumption that occurred in the wider community. A comparison of the methods of analysis between the studies is difficult without knowing the full extent of the data sets selected and whether specific conditions were placed on removing any data (e.g. as was carried out in this study, and outlined in the 'SWC Database' section of this paper).

Figure 3.5a shows the level of uptake of the rainwater tank rebate in LGAs, and demonstrates that the largest adopters were Wollongong, Wollondilly and the Blue Mountains in the outer Sydney area, and Botany Bay in the inner Sydney area, with more than 10% of houses having received a rainwater tank rebate. Other outer Sydney LGAs with high levels (5 to 10%) were Sutherland, Camden and Penrith, along with all northern LGAs from the Hawkesbury through to Pittwater and the inner Sydney LGAs of Hunters Hill, Lane Cove, Willoughby and Mosman. The remaining inner Sydney areas were evenly split between lower uptakes of 3 to 5% or less than 3%. This could be due to the general lack of space for a rainwater tank in residential backyards in the inner Sydney locations (Figure 3.3a). Also a higher proportion of the houses were rented compared to the outer Sydney LGAs (Figure 3.4c). LGAs located in the outer Sydney area with more people born in NESC had lower levels of rainwater rebate uptake (between 3 to 5% or less than 3%).

Figure 3.5b shows the level of reduction in water consumption attributable only to installed rainwater tanks. The reduction in water consumption was calculated for rainwater tanks over a period of at least two years before and at least two years after their installation. The results indicate that most properties within inner Sydney with a rainwater tank achieved at least a 9 to 11% additional reduction in water usage, with more than half of those LGAs achieving more than 11% additional reductions. These same levels of water usage reductions were also observed for most of the northern and central LGAs in the outer Sydney area.

A reason for this large reduction in water consumption in the inner Sydney LGAs as compared to southern and western outer Sydney LGAs (Figure 3.5b), could be explained by the smaller lot areas (Figure 3.3a) in the former. It is estimated that the sizes of the rainwater tanks would not differ all too much in inner and outer Sydney LGAs, as compared to the difference in lot sizes. In inner Sydney LGAs, there would be a higher yield of collected rainwater relative to the area of garden. A rainwater tank in the inner Sydney LGAs would likely contain enough yield for most if not all outdoor watering requirements, and perhaps completely replace the potable water needed for outdoor/garden use. In outer Sydney LGAs, with much larger outdoor and/or garden areas, rainwater can only supplement potable water supplies rather than replace it.

People born in NESC: Those central LGAs with more people born in NESC also experienced less water consumption reductions from 2002 to 2009. Generally they had a lower uptake of the rainwater rebate but nonetheless actually achieved high water usage reduction following the installation of rainwater tanks. This could be due to the fact that the few people who received the grant in these LGAs were strongly motivated and recognised the great potential in saving water for gardening and other outdoor requirements.

Lot size: An analysis of the average lot size of properties that received rainwater tank rebates shows a bias to large properties. This is likely due to people with larger properties having larger gardens and being able to better utilise and warrant a rainwater tank.

Influence of rainfall: The typical rainfall patterns show that the coastal and elevated areas of the Sydney Basin (Blue Mountains, Hawkesbury and Baulkham Hills) generally have higher levels of rainfall compared to other LGAs located away from the coastline. There appears to be some relationship between the average total annual rainfall (Figure 3.5c) for each LGA compared to the level of water usage reductions from installing a rainwater tank (Figure 3.5b). A few of the LGAs (Sydney, Marrickville, North Sydney, Mosman, Baulkham Hills and Hornsby) that had high levels of rainfall experienced higher levels of water usage reductions. Western and south-western LGAs in outer Sydney (from Parramatta to Penrith down to Wollondilly) that received less rainfall achieved lower water usage reduction levels. While this is true for some LGAs, there are also a significant number of LGAs (Botany Bay, Waverley, Woollahra, Leichhardt, Lane Cove, and Willoughby) that received high levels of rainfall but did not achieve large reductions in water usage and vice versa (Ryde, Strathfield and Burwood).

3.4 Conclusions

The SWC data shows that the average annual water consumption per household in Sydney metropolitan areas during the study period (2002 to 2009) declined from 282 kL/annum to 200 kL/annum. Even without including the impact of rainwater tanks the average water consumption decreased by 24% over the study period. In many LGAs in Sydney the reduction in water consumption was over 28% and up to 33.5%. These reductions were due to the effective "demand management" techniques such as the Sydney-wide water restrictions and the introduction of water efficient fixtures like taps, dual flush toilets and efficient shower heads. The average percentage of water savings by installing rainwater tanks across all 44 LGAs was a further reduction of 9%. In some LGAs the decline in water consumption due to rainwater tanks was up to 15%. On average, a household could be expected to save around 24 kL of water annually by installing a rainwater tank controlling for the effects of other factors that influenced water usage.

CHAPTER 4

UTS

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EFFECTS OF HUMIC ACID AND SUSPENDED SOLIDS ON THE REMOVAL OF HEAVY METALS FROM WATER USING GRANULAR ACTIVATED CARBON

The major part of this chapter was published in Sounthararajah D. P., Loganathan P., Kandasamy J. and Vigneswaran S. (2015d). Effects of humic acid and suspended solids on the removal of heavy metals from water by adsorption onto granular activated carbon. ***International Journal of Environmental Research and Public Health*, 12(9), 10475-10489**.

4 Effects of humic acid and suspended solids on the removal of heavy metals from water using granular activated carbon

4.1 Introduction

Heavy metals, dissolved organic carbon (DOC), and suspended solids (SS) are serious pollutants of stormwater. Of these, heavy metals are generating much concern due to their acute toxicity and long-term accumulation and persistence. The toxic effects of heavy metals on humans, animals and aquatic organisms were discussed in Chapter 2.

There is a broad range of treatment practices to remove pollutants from wastewaters. Among them, bed filtration using adsorbents has been widely employed as an effective treatment strategy for removing organic and inorganic pollutants from stormwater (Chen 2012; Gupta and Ali 2012). Granular activated carbon (GAC) is a widely used versatile adsorbent in the water treatment process because it can remove a wide range of contaminants such as organic carbon, turbidity, and nutrients (Kim and Jung 2008; Pollard et al. 1992; Thiruvenkatachari et al. 2008; Yin et al. 2007). GAC has also proved to be effective in removing many heavy metals (Chen 2012; Goel et al. 2005). The efficiency of GAC in removing pollutants using the adsorption process is due to its exceptionally high surface area (500-1500 m^2/g), highly developed internal microporosity, the presence of a range of functional groups, low cost, and easy availability (Chingombe et al. 2005; Cougnaud et al. 2005; Yin et al. 2007). Through GAC can remove heavy metals, the removal efficiency may depend on the concentrations of other pollutants; such as SS and DOC in the water. These effects, however, have been seldom investigated (Chen 2012).

A major component of naturally occurring DOC is humic acid (HA), as it can represent up to 90% of DOC (Chen 2012; Chen and Wang 2004). Humic acid has great binding properties and electrostatic interactions with heavy metals, leading to metal-organic complexes. These complexes can affect the adsorption of heavy metals on GAC. Heavy metal adsorption in the presence of HA may depend on several factors such as surface charge of the adsorbent and type and abundance of functional groups in HA, concentration of HA, etc. In addition to GAC, SS can also adsorb heavy metals and HA and their complexes. Therefore, studies on the adsorptive removal of pollutants from water need to consider all these factors simultaneously and not in isolation. The novelty of the current study is the simultaneous consideration of these factors during the removal of heavy metals by adsorption in fixed-bed columns, especially their interactions which were not previously reported. Evaluating the removal mechanism using zeta potential data and chemistry of adsorption and metal complexation with HA is an additional innovation of this study.

The aims of this study were: firstly, to determine the effect of DOC and SS (a measure of turbidity) on the removal of heavy metals (Cu, Zn, Pb, Cd and Ni) from stormwater using GAC fixed-bed columns; and secondly, to investigate their interactions during the removal process. The reason for studying Cu, Zn, Pb, Cd, and Ni was that these metals are widespread environmental pollutants that have aroused serious concerns. They can exist at high concentrations in urban and industrial stormwater throughout the world (Tayler et al. 2009 ; Loganathan et al. 2013b). GAC was mainly used as an adsorbent medium in this study as this is a common adsorbent used to remove many pollutants of water. HA was used as a representative for naturally occurring DOC (Divakaran and Pillai 2001; Lin et al. 2006) and kaolinite as a representative of turbidity (Chen 2012; Chen and Wu 2004).

4.2 Experimental methodology

4.2.1 GAC

Granular activated carbon used in the study was obtained from James Cummins P/L, Australia. It is a wood-based activated carbon with a nominal size of 0.3-2.4 mm and BET surface area of 750 m^2/g. The physical properties of GAC are given in Table 4.1. Zeta potential which is related to the surface charge was measured on GAC suspensions using a zetasizer nano instrument (Nano ZS Zne 3600, Malvern, UK). For each sample, the instrument automatically made triplicate measurements and a mean value was produced. Zeta potential was measured by adjusting the pH of GAC suspensions in deionised water (0.1 g/L) to pH 3-10 and equilibrating for 6 h.

Table 4.1 Physical properties of GAC

Properties	GAC	Reference
Nominal size (mm)	0.3-2.38	a, b
Bulk density (kg/m^3)	748	a
Iodine number (mg /g.min)	800	a
BET surface area (m^2/g)	750	a
Maximum Moisture content (%)	5	a

a Kus et al. (2012)

b Mohammed et al. (2011)

4.2.2 Humic acid, kaolinite and chemicals

Humic acid and kaolinite used in the study were obtained from Sigma Aldrich (USA). The approximate molecular weight of HA was 1000 g/mol (as determined by LC-OCD analysis). Analar Grade nitrate salts of heavy metals (Cu, Zn, Pb, Cd, Ni) were used in the study. These salts were also obtained from Sigma Aldrich (USA). Zeta potential of kaolinite was determined by a method similar to the one used for GAC.

4.2.3 Batch experiments

Batch adsorption experiments were conducted to determine the adsorptive properties of each of the heavy metals on the GAC. The experiments had initial metal concentrations of 5 mg/L and GAC doses of 0.1 to 7.5 g/L. Similar experiments were also conducted on the adsorption of heavy metals in the presence of HA at a concentration of 10 mg/L. Initial pH of the suspensions was maintained at 6.5 ± 0.1 to simulate pH to approximately the same as that of Australian stormwaters which is 6.68-7.28 (Mohammed et al. 2012). The adsorption experiments were carried out in a flat shaker using 200 mL Pyrex vessels containing 100 ml metal solutions and specified adsorbent dose and agitated at 120 rpm for 24 h at room temperature ($24\pm1^{o}C$). The background ionic strength was kept at 0.001 M $NaNO_3$. After 6 h of agitation the pH was adjusted back to the initial pH of 6.5 using 0.1 M NaOH or 0.1 M HNO_3, in order to eliminate the possibility of any major pH changes during adsorption (Chen 2012; Chen et al. 2003). After 24 h of agitation the suspensions were filtered using filter disks with 0.45 µm openings and heavy metals concentrations in the filtrate were analysed using a Microwave Plasma-Atomic Emission Spectrometer (Agilent 4100 *MP-AES).* The amount of heavy metals adsorption at equilibrium was calculated by subtracting the amounts of metals in the filtrate from the amounts of metals initially added to the suspensions.

4.2.4 Fixed-bed column experiments

Initially, the GAC was washed thoroughly with deionised water in a basin to remove any fine and floating particles. The washed GAC was packed within an acrylic fibre column (2-cm internal diameter) to a height of 90 cm. The amount of GAC used was 100 g. Deionised water was passed upwards through the column at a velocity of 5 m/h for 5 min to expel the air in the particle pores. Experiments were then conducted by filtration of tap water spiked with Zn, Pb, Cu, Ni, and Cd at the same velocity in the downward direction using peristaltic pumps. The solution's flow rate was 26.4 ml/min. One pump was installed before the water entered the column and the other when the water left the column. The empty bed contact time (EBCT) at this filtration velocity was 10.8 min. The concentrations of Zn, Pb, Cu, Ni, and Cd in the influent water were 2.0, 1.0, 0.6, 0.06, 0.04 mg/L, respectively. These concentrations were approximately twice the maximum concentrations reported for Australian stormwaters (Wong et al. 2000). High concentrations of heavy metals were used to simulate the high concentrations normally observed in the first flush after long dry periods (Aryal and Lee 2009; Nie et al. 2008) and in industrial spills. Australian guideline limits for Cd, Cu, Pb, Ni, and Zn in water for long-term irrigation use are 0.01, 0.5, 2, 0.2, and 2 mg/L, respectively (ANZECC and ARMCANZ 2000). Their corresponding values for marine water ecosystems are 0.0014, 0.003, 0.0066, 0.2, and 0.023, also respectively (ANZECC and ARMCANZ 2000). Samples were collected at 10 min, 30 min, and thereafter every hour and analysed for heavy metals, DOC and turbidity. A Hach Model 2100P Turbidimeter was used to measure the turbidity levels followed by samples that were filtered through 0.45 μm disks and DOC was measured in the filtrate using Multi N/C 2000 analyzer (Analytik Jena AG). Heavy metals concentrations in the filtrate were measured using a Microwave Plasma-Atomic Emission Spectrometer (Agilent 4100 MP-AES).

In the experiments on the effect of DOC and SS on heavy metals removal by GAC, tap water spiked with heavy metals with and without the addition of HA (representing DOC) and kaolinite (representing SS) was utilised. An initial concentration of 10 mg/L, each of HA and kaolinite was used as this concentration produced a DOC concentration of 5 mg/L and turbidity level of 12 NTU, which were approximately the same as those found in the stormwater collected from Carlton, Sydney. Filtration experiments were run continuously for 80 h and samples were collected more frequently at the initial stages and less frequently after 24 h. The effluent samples were analysed for DOC, heavy metals, pH and turbidity.

4.3 Results and discussion

4.3.1 Zeta potential of GAC and kaolinite

Zeta potential of GAC decreased when pH increased. The pH at which the zeta potential is zero is called the zero point of charge (ZPC). Figure 4.1 shows that the ZPC of GAC tested was 5.3. Faust and Aly (1987) reported a ZPC range of 4.75 to 7.10 for five types of activated carbons tested. At pHs less than the ZPC, GAC carries predominantly positive surface charges and at pH above the ZPC, it carries predominantly negative charges. GAC had more negative charges at the pH of 6.5 tested in the experiment indicating that GAC has a high affinity for adsorbing heavy metals that are present as cations. The effect of pH on the kaolinite’s zeta potential was similar to that of GAC but the ZPC of kaolinite was much lower (pH 2.8) (Figure 4.1). Zeta potential of kaolinite was more negative than that of GAC at all pH levels. The difference in the zeta potentials ranged from 20 mV to 50 mV and at pH 6.5 where the heavy metals adsorption studies were conducted it was 35 mV.

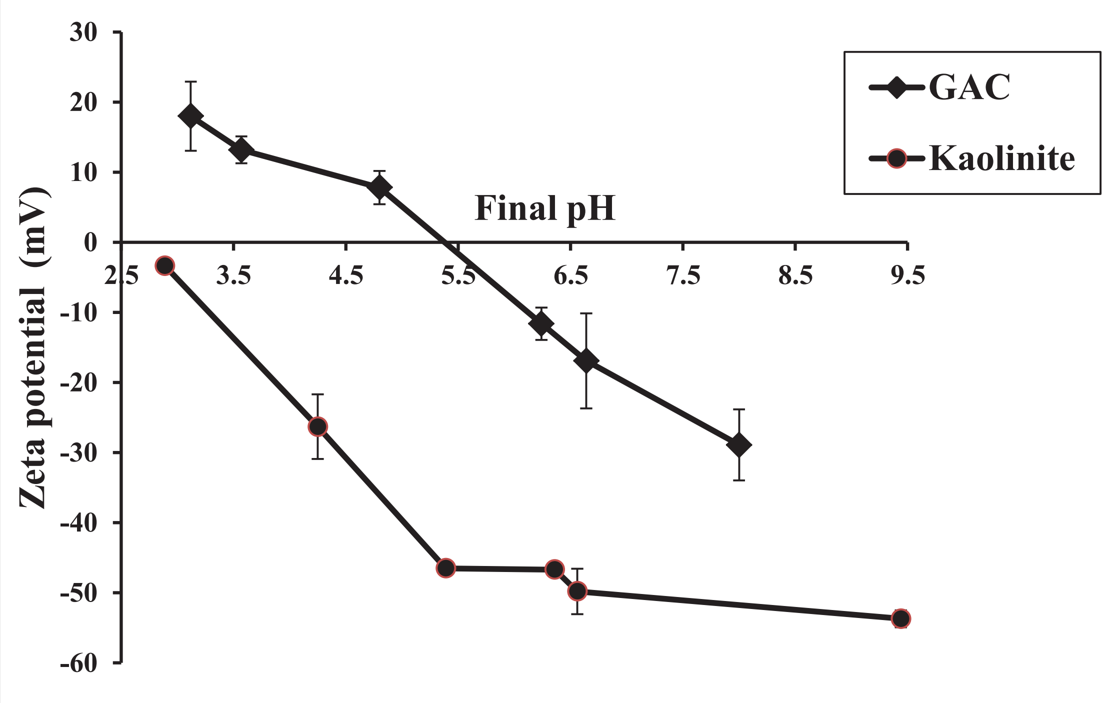


Figure 4.1 Zeta potential values of GAC and kaolinite at different pH values in 0.001 M $NaNO_3$ after 6 h of agitation with standard deviations (GAC and kaolinite doses of 0.1 g/L and 0.2 g/L, respectively).

4.3.2 Heavy metals adsorption on GAC in batch experiments

The adsorption of heavy metals by GAC from solutions in the absence and presence of HA was conducted at pH 6.5. The adsorption data fitted satisfactorily to the Langmuir adsorption isotherm model described below (Nur et al. 2014) ($R^2 = 0.75$-0.99, number of data points 6-7, Table 4.2).

$$Q_e = \frac{q_{max} K_L C_e}{1+K_L C_e} \qquad \text{Eq (1)}$$

where, q_{max} = the maximum amount of the heavy metals adsorbed per unit weight of the GAC (mg/g) and K_L = Langmuir adsorption constant (L/mg).

This model can be linearized as follows:

$$\frac{C_e}{Q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \qquad \text{Eq (2)}$$

From the inverse of the slope of the graph of C_e/Q_e vs C_e, q_{max} was calculated.

The Langmuir adsorption maximum for GAC in the absence of HA decreased in the following order: Pb, Cu > Zn > Ni, Cd (Table 1). This order is similar to that of the solubility product of the metal hydroxide ($M(OH)_2$) precipitate (pK_{sp} for Pb, Cu, Zn, Ni, and Cd hydroxides). These were 19.9, 19.3, 16.5, 15.2, 14.4, respectively (Rao 2011; Walker et al. 2012)). The adsorption maxima also followed the reverse order of the metals' first hydrolysis constant (MOH^+ formation) (pK_1 of hydroxyl complexes of Pb, Cu, Zn, Ni, and Cd are 7.7, 7.7, 9.0, 9.9, and 10.1, respectively (Pohlmeier 2004). The higher the pK_{sp} the more likely metal hydroxides precipitation would occur, whereas a lower pK_1 value made it easier for the metal to produce the soluble hydroxyl complex. The higher adsorption capacity of the metals having higher pK_{sp} values is due to these metals forming precipitation on the adsorbent surface (Loganathan et al. 2014). Precipitation on the adsorbent surface can occur at pH levels less than those at which precipitation occurs in solution. This is due to the adsorbent providing a nucleus promoting precipitation. The metals which easily form hydroxyl complexes (lower pK_1 values, e.g. Pb and Cu) had larger adsorption capacities because these complexes have higher affinity for adsorption than divalent metal ions.

Table 4.2 Langmuir maximum adsorption capacity (q_{max} mg/g), coefficients of determination of Langmuir isotherm fit to data (R^2) and adsorption capacity at an equilibrium metal concentrations equivalent to the influent concentrations (Zn 1.80, Cu 0.99, Cd 0.11, Ni 0.12, Pb 1.03) used in column study(Q_e mg/g) for heavy metal adsorption on GAC at pH 6.5.

	GAC					**GAC + HA**				
Metals	q_{max} mg/g	K_L L/mg	R^2	n	Q_e mg/g	q_{max} mg/g	K_L L/mg	R^2	n	Q_e mg/g
Cu	11.8	42.0	0.99	6	11.0	3.7	67.2	0.99	6	3.5
Pb	11.9	1.8	0.91	6	8.1	7.5	1.7	0.75	7	4.0
Zn	3.3	6.1	0.94	5	2.8	3.2	5.7	0.96	7	2.6
Ni	1.8	15.3	0.98	6	1.3	2.5	19.9	0.98	6	2.0
Cd	2.0	4.4	0.95	7	0.9	1.6	8.7	0.99	6	0.9

* n = no of data points

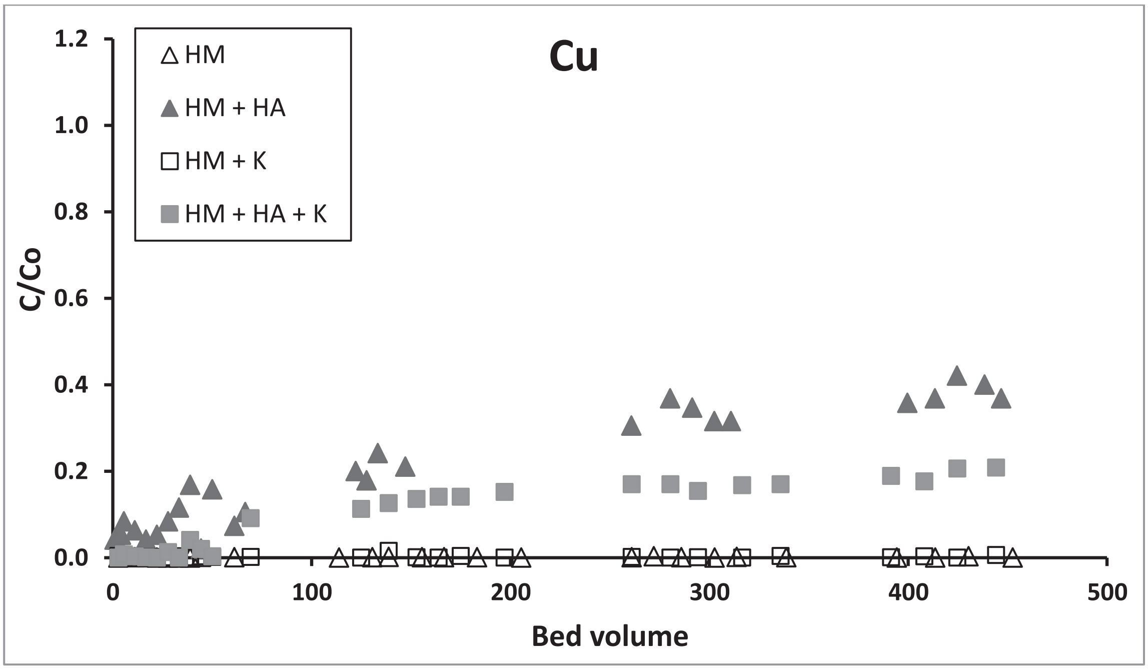
In the presence of HA the Langmuir adsorption capacity of Cu and Pb drastically decreased (Table 4.2). The reason for this is probably that these two metals form strong complexes with HA in solution, thus they are not precipitated on the GAC surface. Sholkovitz and Copland (1981) also found that adding fulvic acid to clay suspensions containing metal ions at high pH values (> 6.5) prevented Pb, Cu, and Cd from forming hydroxide precipitates. Pandey et al. (2000) reported that the stability constants for the metal-HA complex followed the order, Cu > Pb > Ni > Cd, Zn. HA exerted little effect on the adsorption capacity of Zn, Ni, and Cd because they have low stability constants.

4.3.3 Heavy metals removal in column experiments in the absence of HA and kaolinite

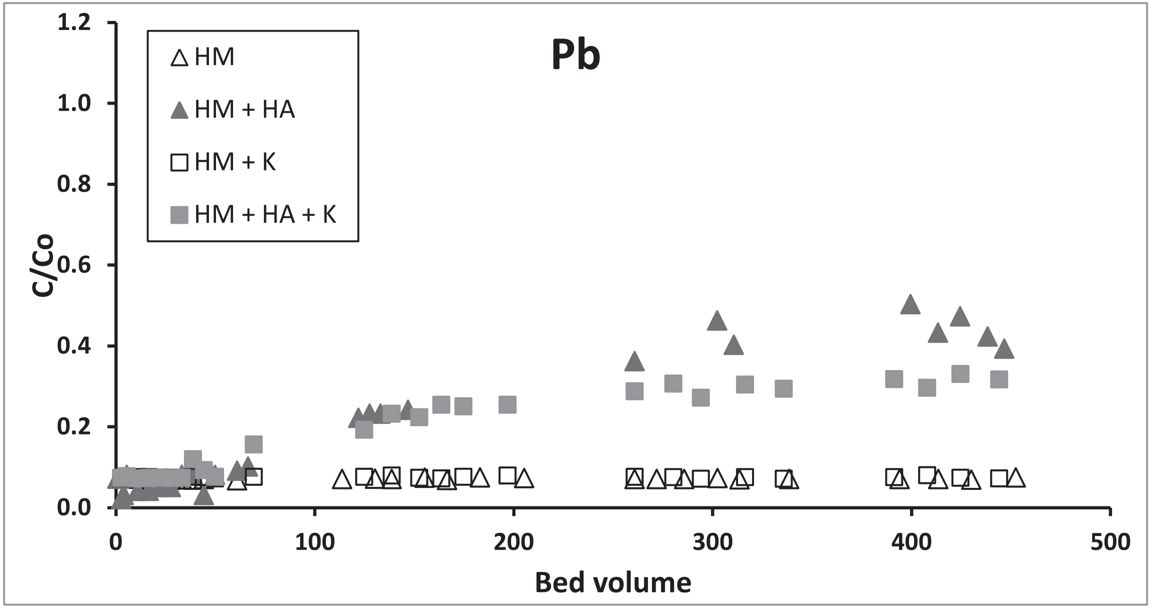
Column experimental results showed that no breakthrough was achieved for Cu and Pb up to 450 bed volumes (BV) (Figure 4.2). However, for Cd, Zn and Ni a breakthrough commenced at 50 BV and was nearly completed when 130 BV was reached (Figure 4.3). The absence of breakthrough for Cu and Pb is probably because these metals have formed surface precipitation on GAC at the pH of 6.5 used in the influent in addition to forming $Cu(OH)^+$ and $Pb(OH)^+$, which had a stronger adsorption tendency than Cu^{2+} and Pb^{2+} onto GAC, unlike the other metals as discussed previously under batch experiments. Almost all Zn would have precipitated up to 50 BV because of solution's elevated pH in the adsorbent during this period (Figure 4.4). Others have also reported this initial rise in pH followed by a decrease reaching the pH of the influent pH in fixed-column adsorption studies (Chen and Wang 2004; Reed et al. 1994). The increase in the pH was explained as being due to initial adsorption of hydrogen ions from the solution and dissolution of basic impurities from the GAC (Chen and Wang 2004). A large proportion of Ni and Cd may have also precipitated or been adsorbed, resulting in the low breakthrough of these metals during the first 50 BV. These metals have lower K_{sp} and lower concentration than Zn and therefore might have not completely precipitated or formed hydroxylated species.

Table 4.3 shows the cumulative percentage removal of heavymetals after 80 h (450 BV). Heavy metals adsorption of metals in column follows an order of Cu, Pb > Zn > Cd, Ni which is similar to the batch adsorption results shown in Table 4.2. In addition to the reasons given for this trend in the batch studies the metal concentration differences in the influent solution can also explain the adsorption differences. Cd and Ni adsorption was low compared to the other metals considered in the column study because of: firstly, the relatively low concentrations of these metals in the influent water; and secondly, low adsorption capacities obtained in the batch adsorption results.

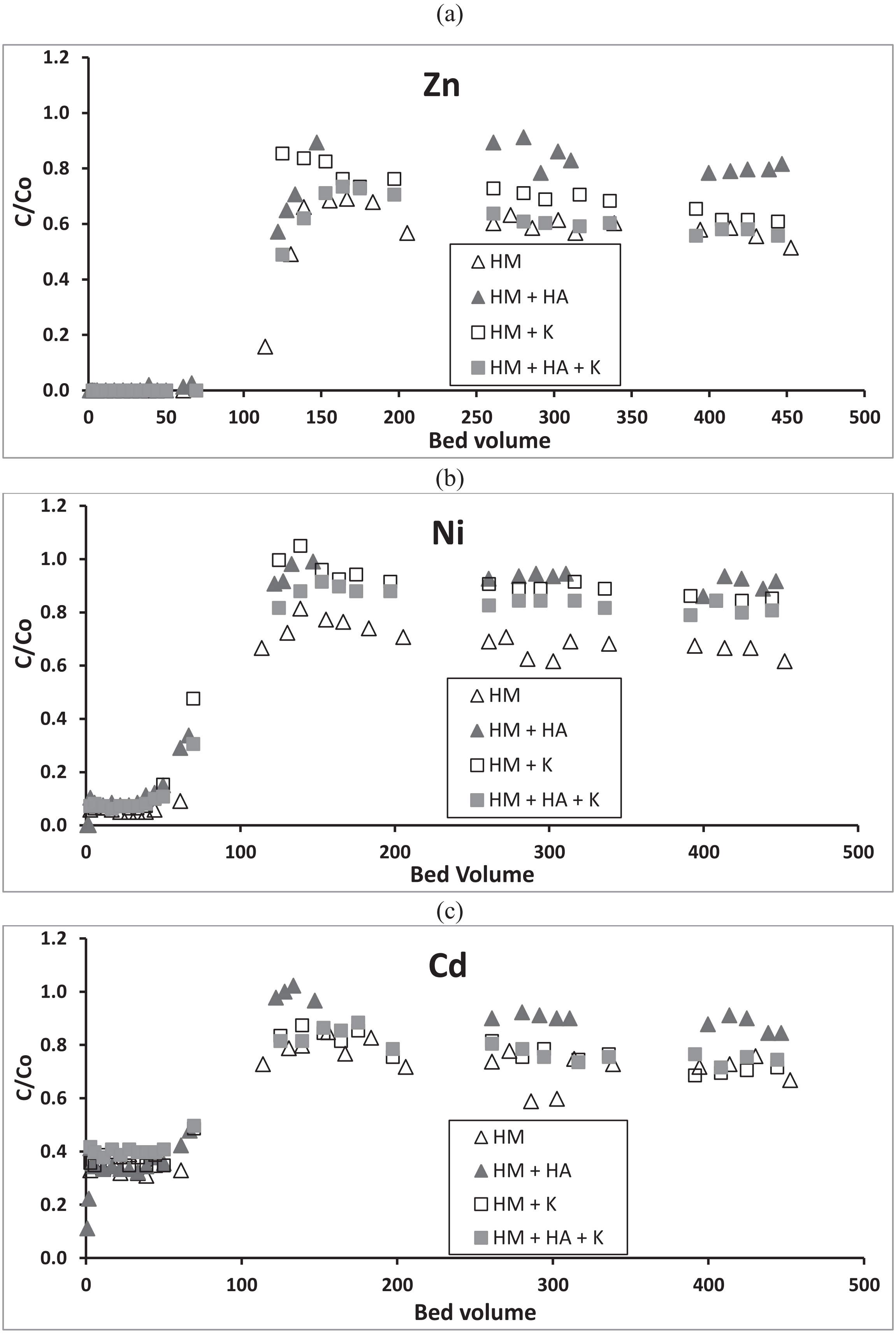
(a)



(b)



Figures 4.2 Breakthrough plots of (a) Cu and (b) Pb in the laboratory column study (HM - heavy metals, HA - humic acid, K - kaolinite).



Figures 4.3 Breakthrough plots of (a) Zn, (b) Ni, and (c) Cd in the laboratory column study (HM - heavy metals, HA - humic acid, K - kaolinite).

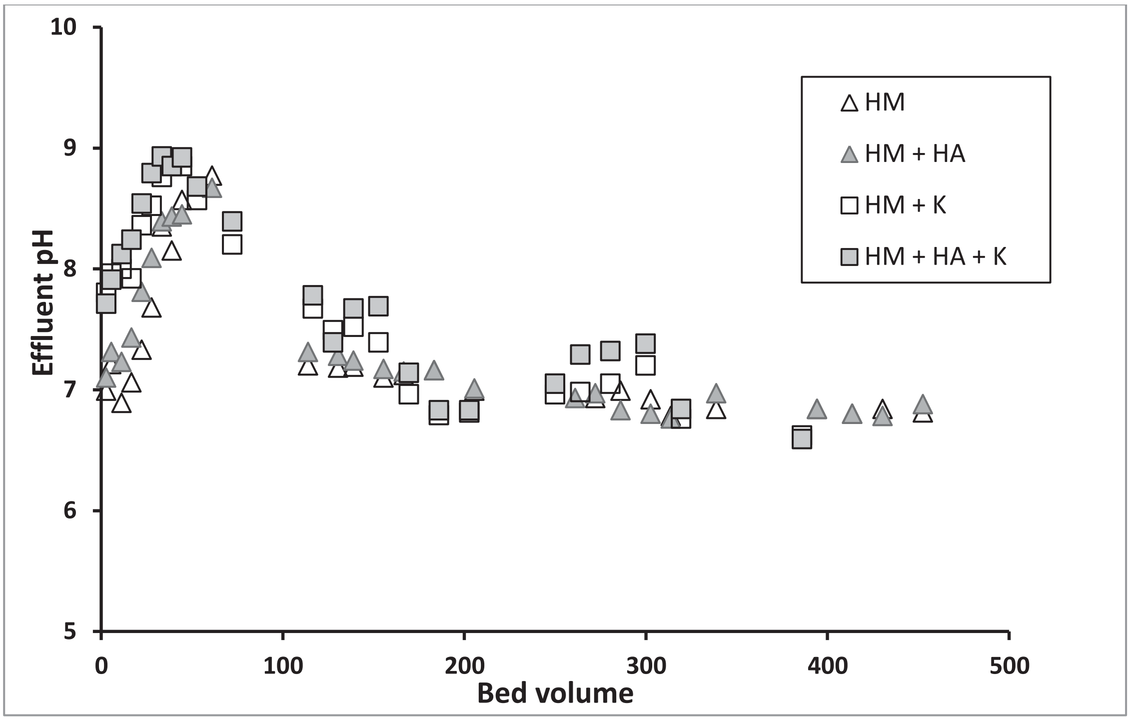


Figure 4.4 Effluent pH variation with time in the laboratory column study (HM - heavy metals, HA - humic acid, K - kaolinite).

Table 4.3 Effects of humic acid (HA) and kaolinite (K) on the percentages* of cumulative removals of heavy metals (HM) by GAC (Influent concentrations (mg/L): Zn 1.80, Cu 0.99, Cd 0.11, Ni 0.12, Pb 1.03)

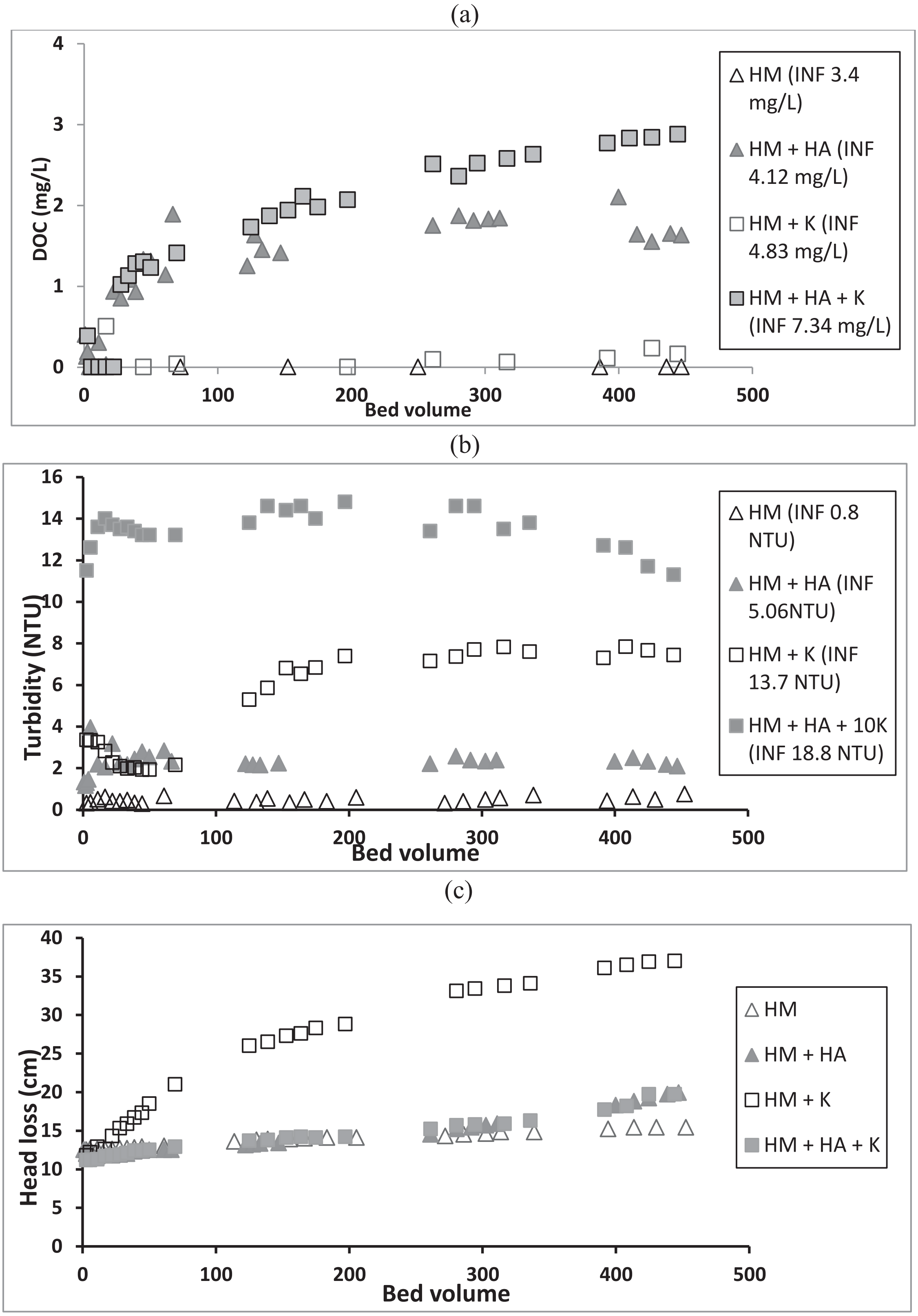
	Zn	Cu	Cd	Ni	Pb
HM only	53.7	99.9	36.7	39.9	93.0
HM + HA	29.4	72.1	15.2	17.6	59.8
HM + HA + K	48.6	84.3	26.6	24.8	70.5
HM + K	39.2	98.0	28.1	18.1	86.7

*Percentage of cumulative metal removal = (cumulative metal added – cumulative metal in effluent) / cumulative metal added

4.3.4 Effect of HA on heavy metals removal in column experiments

Addition of HA to the metal solution significantly reduced all heavy metals adsorption on GAC (Table 4.3, Figure 4.5), with the highest reduction being that for Cu and Pb. This is because the heavy metals formed heavy metal-HA complexes in the solution which prevented the metals from adsorbing or precipitating on GAC surfaces. Thus, a significant percentage of all heavy metals transported with HA into the effluent. A significant amount of HA movement into the effluent is supported by the decline in DOC from the influent to the effluent (Fig. 4.5).

Batch adsorption of the metals at an equilibrium metal concentration equivalent to the influent concentrations used in the column study (Q_e mg/g) revealed that there was a marked reduction of adsorption of Cu and Pb in the presence of HA (Table 1). This was observed in the column study but had little effect on the adsorption of other metals unlike the column study results. The difference in the results between the static batch and dynamic column studies is explained by the fact that equilibrium between the solution phase metals and adsorbed phase metals had not been reached in the column study. This was due to the short residence time of metals in the column, especially at the high flow rate used, unlike in the batch study (Akbour et.al 2002). The adsorption capacities for Cu, Pb, Zn, Ni, and Cd in the column study were 1.25, 1.21, 1.22, 0.06, and 0.05 mg/g, respectively. In the presence of HA, these values fell to 0.90, 0.78, 0.67, 0.03, and 0.02 mg/g, also respectively. These values are lower than the values obtained in the batch study for solution metal concentrations same as those in the column study (Table 1). However, the column study is closer to the operational conditions in the real full-scale treatment system and consequently the results from this study are more applicable to real practical conditions.



Figures 4.5 Simultaneous removal of (a) DOC, (b) turbidity and (c) head loss generated in the GAC column in the laboratory study (HM - heavy metals, K – Kaolinite, INF - influent).

4.3.5 Effect of kaolinite on heavy metals removal in column experiments

Adding kaolinite to the heavy metals solution significantly reduced the adsorption of Zn, Cd and Ni on GAC (Table 4.3, Figure 4.3). This is probably due to these positively charged metals adsorbing onto the negatively charged surfaces of the finer sized kaolinite by Coulombic forces (Figure 4.1) and passing through the column along with the kaolinite to the effluent. High turbidity in the effluent of the column (Fig. 5) confirms that significant amounts of kaolinite passed through the column into the effluent. The reason for these metals adsorbing more on kaolinite than on GAC is due to kaolinite having much a higher negative zeta potential and therefore higher number of negative charges than GAC (Fig. 4.1). In contrast to Zn, Cd, and Ni, the adsorption of Pb and Cu was not significantly affected by the presence of kaolinite (Table 4.3, Fig. 4.2). This may be due to the high removal of Pb and Cu by surface precipitation onto GAC and kaolinite. Pb and Cu precipitated on the surface of kaolinite were probably retained in the column pores and this affected the flow of the solution. The large head loss observed in the column when kaolinite was present (Fig. 4.5) is due to this precipitation and blockage of the pores.

4.3.6 Effect of HA and kaolinite together on heavy metals removal in column experiments

The addition of both HA and kaolinite to the metal solution reduced the metal adsorption compared to that from the metal solution alone. However, the reduction in adsorption was less than when HA only was added to the metal solution (Table 4.3, Figure 4.2 and 4.3). This is probably because part of the HA added was adsorbed to the kaolinite particles and retained in the column, leaving a smaller amount of HA to complex with heavy metals and move down the column into the effluent. Though both HA and kaolinite have net negative charges at the pH 6.5 used in the experiment, some of the HA might have adsorbed to the positive charges on the edges of the kaolinite (Akbour et al. 2002).

4.4 Conclusions

Fixed-bed column containing GAC effectively removed heavy metals from water. At the normal pH of stormwaters (pH 6.5), removal of heavy metals by GAC column followed the decreasing order of Cu, Pb > Zn > Cd, Ni, which was consistent with the metals' adsorption capacity as assessed by Langmuir adsorption isotherm.

The presence of DOC and turbidity (SS) in stormwater of pH 6.5, as simulated by spiking aqueous solutions with HA and kaolinite, respectively, had different degrees of influence on the removal of heavy metals. Adding HA reduced the removal efficiency of Cu and Pb very strongly but that of the other metals only marginally. Kaolinite addition had no effect on the removal of Pb and Cu but it reduced the removal of the other metals. Kaolinite and HA together reduced the removal of all metals but the effect was less than the addition of HA alone. Overall, the study demonstrated the strong influence effects of HA and kaolinite on the removal of heavy metals from stormwater, which varied with the type of heavy metals.

CHAPTER 5

University of Technology, Sydney

ADSORPTIVE REMOVAL OF HEAVY METALS FROM WATER USING SODIUM TITANATE NANOFIBRES LOADED ONTO GAC IN FIXED-BED COLUMNS

The major part of this chapter was published in Sounthararajah D. P., Loganathan P., Kandasamy J. and Vigneswaran S. (2015a). Adsorptive removal of heavy metals from water using sodium titanate nanofibres loaded onto GAC in fixed-bed columns. ***Journal of Hazardous Materials*** **287, 306-16.**

5 Adsorptive removal of heavy metals from water using sodium titanate nanofibres loaded onto GAC in fixed-bed columns

5.1 Introduction

In the adsorbent group, nano-sized metal oxides are growing in importance due to their unique properties and use in many applications. Nano-sized metal oxides have promising metal removal capacities, partly due to their large surface areas and high activities in size-quantisation effect (El-Sayed 2001; Henglein 1989). However, these nano-sized particles are unusable as they are in fixed-bed columns where they cause excessive pressure drop and have poor mechanical strength (Cumbal and SenGupta 2005; Hua et al. 2012; Pan et al. 2009). To overcome this problem, nano-sized particles are commonly impregnated into coarse-sized porous material such as granular activated carbon (GAC) (Jang et al. 2008; Kikuchi et al. 2006; Vaughan Jr and Reed 2005; Zhuang et al. 2008) and used in fixed-bed columns.

Titanium-based adsorbents show robustness under harsh chemical conditions and are effective in a variety of media such as acidic, basic and neutral pH and high and low ionic strengths (Nyman and Hobbs 2006). Mesoporous titanate nanostructures have been synthesised from TiO_2 using a variety of technologies and used to remove pollutants including heavy metals (El Saliby et al. 2011; Liu et al. 2009; Nyman and Hobbs 2006). For example, Hang et al. (2014) reported that titanate whiskers prepared using an alkaline hydrothermal method starting from hydrous metatitanic acid and KOH had a Langmuir maximum adsorption capacity of 144 and 385 mg/g for Cu and Pb, repectively in a batch study. Sheng and Hu (2013) found that titanate nanotubes prepared using a similar hydrothermal method with titanium oxide and NaOH had a Langmuir adsorption capacity of 51 mg/g for Th(IV). However, simultaneous removal of several heavy metals from their mixtures in both batch (Engates and Shipley 2011; Huang et al. 2012a) and column adsorption conditions is rare. The simultaneous removal of several heavy metals is important as most wastewaters contain more than one heavy metal and there can be competition for adsorption between metals.

This chapter aimed to determine the adsorptive removal efficiencies of five heavy metals (Cu, Zn, Pb, Cd and Ni) individually and together from synthetically polluted water using a sodium titanate nanofibrous material (TNF) in batch experiments and mixed with a wood-based GAC in fixed-bed column experiments.

5.2 Experimental methodology

5.2.1 Preparation of TNF

A commercial titanium dioxide (P-25, Degussa AG, Germany) was used as a precursor for preparing the sodium form of titanate microspheres (TNF). P-25 is a non-porous, crystalline structure with 70% anatase, 30% rutile composition and a BET surface area of 50 m^2/g with a mean particle size of about 30 nm (El Saliby et al. 2011). TNF was prepared using a modified hydrothermal method similar to that described by El Saliby et al. (El Saliby et al. 2011). In this method, 12 g of NaOH pellets were weighed into a Teflon cell containing 6 g of the TiO_2 powder. To this container which was kept in a water bath at room temperature (24 ± 1^oC), 36 ml of H_2O_2 (50% V/V) was added drop-wise and the mixture was mechanically stirred for 5 min at 300 rpm. The resultant slurry was kept in a water bath for 24 h at 80^oC without any vigorous agitation. The precipitate obtained was washed repeatedly with Milli Q water; pH neutralised to 7.0 using 2 N HCl, and dried at 100^oC. The resultant nanotitanate had a pale yellow colour characteristic of peroxotitanate materials precipitated under alkaline conditions (Nyman and Hobbs 2006).

5.2.2 GAC

The granular activated carbon (GAC) used in Chapter 4 was sieved to a particle size range of 0.3-0.6 mm and used in the study. The GAC had a BET surface area of 950 m^2/g.

5.2.3 Characterisation of TNF

X-ray diffraction (XRD) was conducted using a XRD Shimadzu S6000 (Japan) diffractometer on powder samples of TNF. The X-ray diffraction unit (Theta/2Theta) was equipped with a Cu target operated at 40 kV and 30 mA with a setting of 5–45° 2-theta, step time 2° 1/min. Scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, surface area, and porosity measurements were also conducted on TNF. For the SEM analysis, samples were imaged, uncoated, in a Zeiss Evo LS15 SEM using its variable pressure mode and an accelerating voltage of 15 kV. FTIR pattern was recorded in a Nicolet 6700 FTIR Spectrometer equipped with a room temperature DLaTGS detector and a Nicolet FT-IR Smart System with Smart Accessories using a Diamond crystal HATR. Surface area and porosity were determined by nitrogen-sorption measurements carried out at 77 K with a Micromeritics 3Flex surface characterisation analyser.

5.2.4 Zeta potential

Zeta potential which is linked to the surface charge was measured at different pHs on GAC and TNF suspensions using a zetasizer nano instrument (Nano ZS Zne 3600, Malvern, UK). For each sample, the instrument automatically made triplicate measurements and a mean value was produced. Zeta potential was measured at pH 3 to

9, after adjusting the pH of 100 ml suspension of TNF in deionised water with background ionic strength of 10^{-3} M $NaNO_3$ (0.5 g/L dose of TNF) and agitating it at 120 rpm for 24 h.

5.2.5 Batch adsorption experiments

For the laboratory batch experiments, Milli Q water was spiked with individual heavy metals (Cu, Zn, Pb, Cd, and Ni) using their nitrate salts at a concentration of 5 mg/L. Different doses of TNF (0.01 to 0.09 g/L) were added to 100 ml of these metal solutions, and the suspensions were agitated at 120 rpm for 24 h at room temperature ($24\pm1^{o}C$) and different suspension pHs. The background ionic strength was kept at 10^{-3} M $NaNO_3$. After 2 h of agitating the suspensions, pH was adjusted back to the initial pH using 0.1 M NaOH or 0.1 M HNO_3, in order to eliminate the possibility of any major pH changes during adsorption. Buffered solutions were not used to keep the pH constant because the buffer components may have interfered with metals adsorption by forming metals complexes and competing with metals for adsorption. After a further 20 h of agitation the suspensions were filtered using filter disks with 1.2 µm openings and heavy metal concentrations in the filtrate were analysed using a Microwave Plasma-Atomic Emission Spectrometer (Agilent 4100 *MP-AES)*. The experiments were repeated utilising a mixture of heavy metals with a concentration of 15 mg/L each and TNF doses of 0.05-0.5 g/L. The amount of heavy metal adsorption at equilibrium, Q_e (mg/g), was calculated using equation (1):

$$Q_e = \frac{(C_0 - C_e)V}{M} \qquad \text{Eq (3)}$$

Where, C_0 = initial concentration of the heavy metal (mg/L); C_e = equilibrium concentration of the heavy metal (mg/L); V = volume of the solution (L); and M = mass of TNF (g).

5.2.6 Batch desorption and TNF regeneration experiment

To use an absorbent economically and effectively it should be reutilized many times. This requires complete desorption of the previously adsorbed metals and regeneration of the adsorbent to its original adsorption capacity. An experiment was conducted where Ni, Zn, Cd, Cu, and Pb were adsorbed by 2 g TNF from a 1.5 L solution containing 20 mg/L of each metal at pH 5.0, after shaking the suspensions for 3 h and filtering these suspensions. The adsorbed metals were desorbed by shaking the residues with 1.5 L of 0.1 M $NaNO_3$, or 0.1 M HNO_3 for 3 h. 0.1 M $NaNO_3$ was selected because it provided large amounts of a cation that could displace the adsorbed metals. 0.1 M HNO_3 was chosen to produce low pH where the adsorption of metals is low (Figure 5.5). Following the metals' desorption the TNF was again tested for its adsorption capacity. A portion of the TNF, after desorption with 0.1 M $HNO_{3,}$ was treated with 0.2 M NaOH for 3 h to introduce the lost Na into the TNF structure (Wang et al. 2013c) and the adsorption of metals was resumed.

5.2.7 Fixed-bed column experiments

Using TNF alone as the filter media to remove heavy metals from water in the fixed-bed column is not practical because it causes poor hydraulic conductivity giving rise to large head loss. Therefore a mixture of TNF (75-150 μm) and GAC (0.3-0.6 mm), a material commonly used in fixed-bed columns to remove pollutants, at a weight ratio of 25:1 (GAC: TNF) was used in this study. To determine the effect of TNF alone, two columns - one with GAC alone and the other with GAC + TNF - were used. TNF's removal of heavy metals was calculated by subtracting the amounts of heavy metals removed by GAC from those removed by GAC + TNF.

The GAC used was initially washed thoroughly with deionised water to remove any fine and floating particles. Then 39g of the washed GAC or 37.5g GAC + 1.5g TNF was packed into a 2 cm internal diameter transparent acrylic fibre column to 30 cm height. Tap water at pH 5.0 was passed through the column in a gravity flow mode at a velocity of 5 m/h for 24 h to eliminate the pH increase normally expected when using unwashed GAC as an adsorbent (Chen et al. 2003). The tap water was spiked with heavy metals, one at a time, at a concentration of 5 mg/L each, at pH 5.0. Tap water (ionic strength of 95.1 mg/L) was utilised instead of distilled water at the ionic strength of 10^{-3} M $NaNO_3$ as in the batch study because large volumes of distilled water that were required for the long-term column study were not available. Concentrations of heavy metals larger than those normally observed in stormwater and wastewater were used to simulate metals concentrations normally observed in the first flush of stormwater after long dry periods (Aryal and Lee 2009; Nie et al. 2008) and in industrial spills in water and wastewater. Experiments were then conducted by filtrating metals-spiked tap water at a velocity of 5 m/h in the gravity flow mode with two peristaltic pumps; one before the water enters the column and the other when the water leaves the column. The empty bed contact time (EBCT) at this filtration velocity was 3.6 min. Samples were collected at 30 min and thereafter every hour and analysed for pH and heavy metals concentrations. The experiments were repeated with a mixture of heavy metals with each metal at a concentration of 1 mg/L.

The maximum column adsorption capacity, q_{total} (mg) for a given feed concentration is equal to the area under the plot of the adsorbed metal concentration, C_{ad} ($C_{ad} = C_o - C$) (mg/L) versus time (t, min) and was calculated manually from the breakthrough curves using Microsoft Excel spreadsheet according to equation (2) where Q is the flow rate of the solution (L/min):

$$q_{\,total} = \frac{Q}{1000}\int_{t=0}^{t=16h} C_{ad}\ dt \qquad \text{Eq (4)}$$

5.3 Results and Discussion

5.3.1 Characterisation of TNF

Scanning electron microscopic images revealed that TNF had a nanofibrous appearance (Figure 5.1) similar to that observed for materials prepared by others using similar methods (Huang et al. 2009; Nyman and Hobbs 2006; Yada et al. 2006). The exact appearance of the nanomaterials depends on the duration and temperature of the NaOH reaction in their preparations. For example, Yada et al. (2006) reported that at 20 h and 100-120^{o}C NaOH reaction conditions, short nanofibres were evident, but when the reaction time was increased to 72 h, a clear long fibrous material was observed.

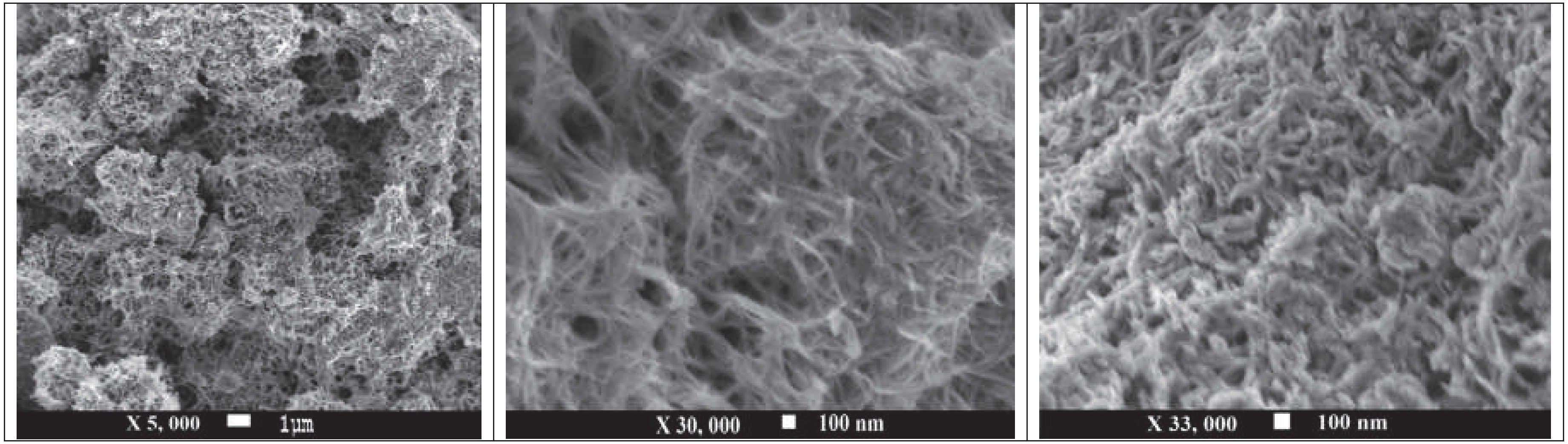


Figure 5.1. SEM images of TNF (magnifications 5,000X (left), 30,000X (middle) and 33000X (right)).

X-ray diffraction pattern of the TNF sample had peaks corresponding to anatase, rutile and sodium titanate (Figure 5.2). The peaks at 2-theta of 25.5, 38 and 48.5 are characteristics of the presence of anatase (El Saliby et al. 2011; Seo et al. 2005). Those at 2-theta of 27.5 and 63 are characteristic of rutile (El Saliby et al. 2011; Wang et al. 2013b) and those of 9.5, 24.5, 28.5 and 48.5 are typical of sodium titanate (Huang et al. 2008; Wang et al. 2013b; Yang et al. 2003; Zárate et al. 2008). The peak at 48.5 is common for both anatase and sodium titanate as also found by Wang et al. (2013b). The anatase and rutile peaks observed in the XRD pattern are those of the unreacted Degussa P-25 used to prepare the nanotitanate material. The major peaks observed in the XRD pattern in the current study are the same as those reported for the titanate nanorods, nanoflowers and nanosheets synthesised by the hydrothermal treatment of anatase using 10 M NaOH (Huang et al. 2008).

Four FTIR transmittance bands, centred at 3390, 1635, 1347, and 450 cm^{-1}, similar to those reported for sodium titanate nanofibres (Yada et al. 2006) and nanotubes (Chen et al. 2010), were obtained for TNF (Figure 5.3). Kubo and Nakahira (2008) also reported similar FTIR bands, one at 3400 cm^{-1} and another at 1630 cm^{-1} for a nanotubular titanate material and assigned them to O-H stretching mode of interlayer water, oxonium ions, and hydroxyl groups, and H-O-H bending of water, respectively. Huang et al. (2010) also assigned the 1630 cm^{-1} band obtained for their titanate nanotubes and nanowires to H-O-H deformation mode. The band at 450 cm^{-1} is probably due to Ti-O-Ti vibrations in TiO_6 octahectrons (Chen et al. 2010; Huang et al. 2010). The band at 1347 cm^{-1} is probably due to Na-O vibration as reported for a titanate nanotube material prepared by an alkaline hydrothermal method where a band appeared at 1400 cm^{-1} (Chen et al. 2010).

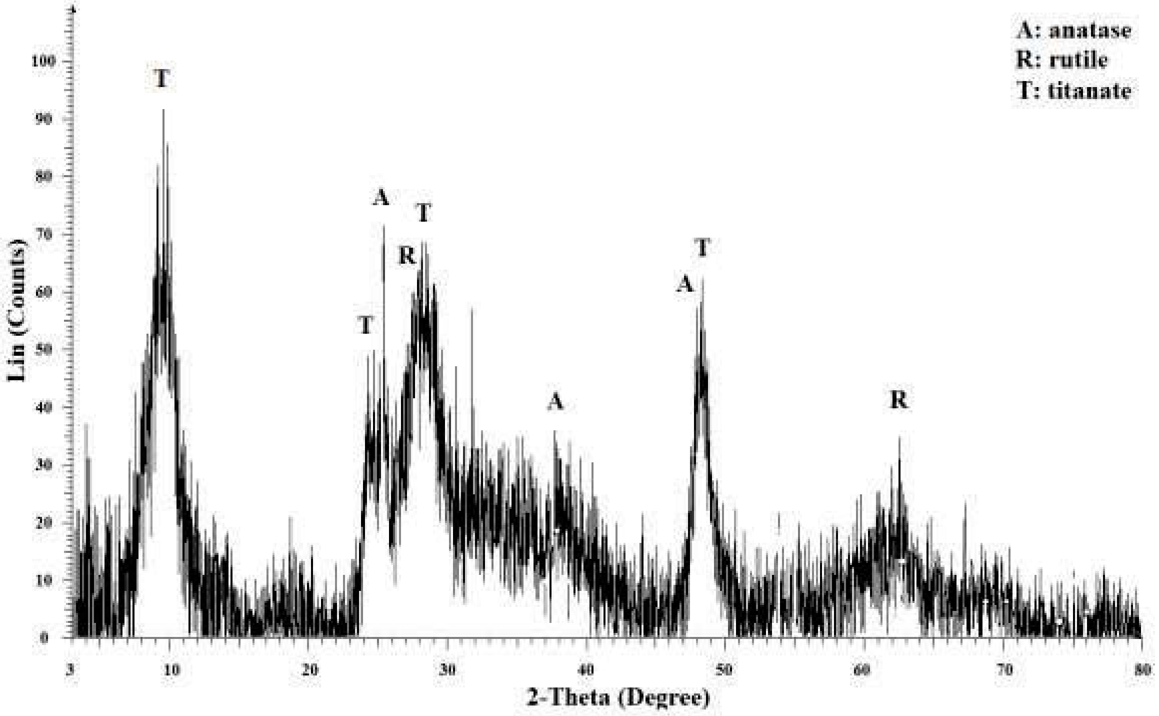


Figure 5.2 XRD pattern of TNF (A- anatase, R- rutile, T- sodium titanate).

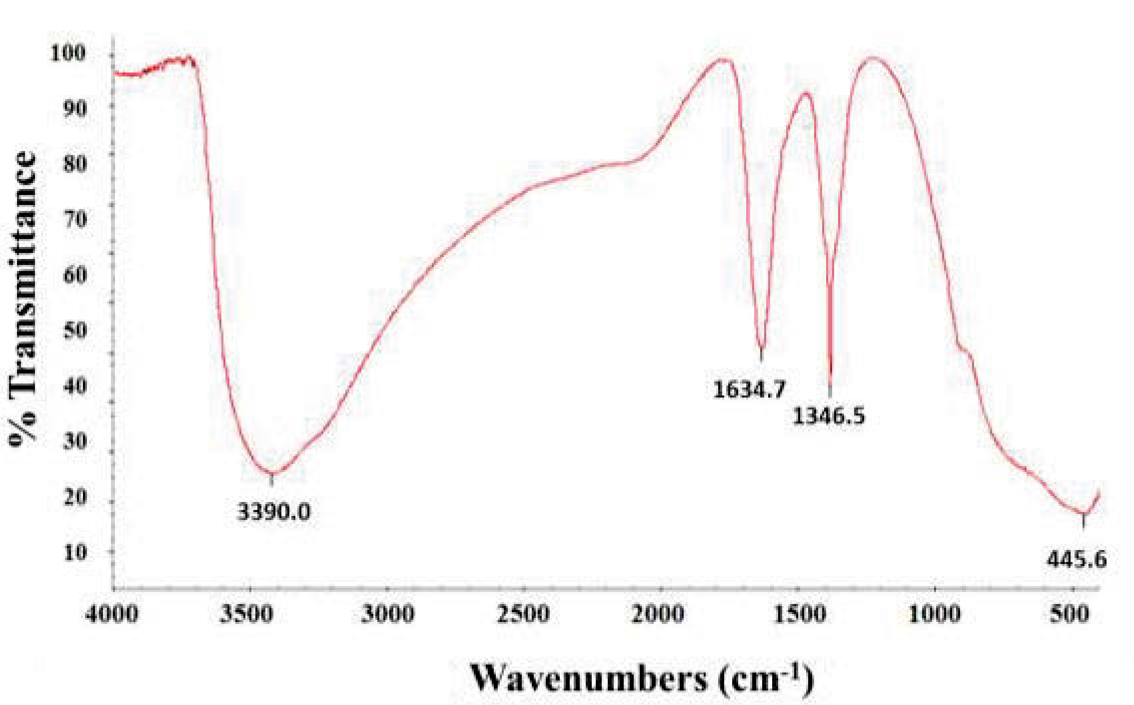


Figure 5.3 FTIR pattern of TNF.

The BET surface area and total pore volume of TNF were 58.6 m^2/g and 0.142 cm^3/g, respectively. These values are comparable to those of 64.8 m^2/g and 0.25 cm^3/g, respectively, as reported by El Saliby et al. (2011).

The zeta potential data at different pHs showed that a rise of pH increased the negative zeta potential of GAC and TNF (Figure 5.4). TNF had higher negative zeta potential than GAC at all pHs. The zero point of charge (ZPC, i.e. the pH at which the net surface charge is zero) of TNF and GAC were 3.2 and 5.5, respectively, suggesting that at the normal pH of 6-7 of most wastewaters the net surface charge on these materials is negative. This favours the adsorption of the positively charged heavy metal cations. The ZPC of 5.5 obtained for GAC is within the range of 4.75-7.00 reported for five types of activated carbons by Faust and Aly (1987). The ZPC of TNF of 3.2 agrees well with the ZPC values of 3.16- 3.55 reported by Chen et al. (2010) for sodium titanate nanomaterials.

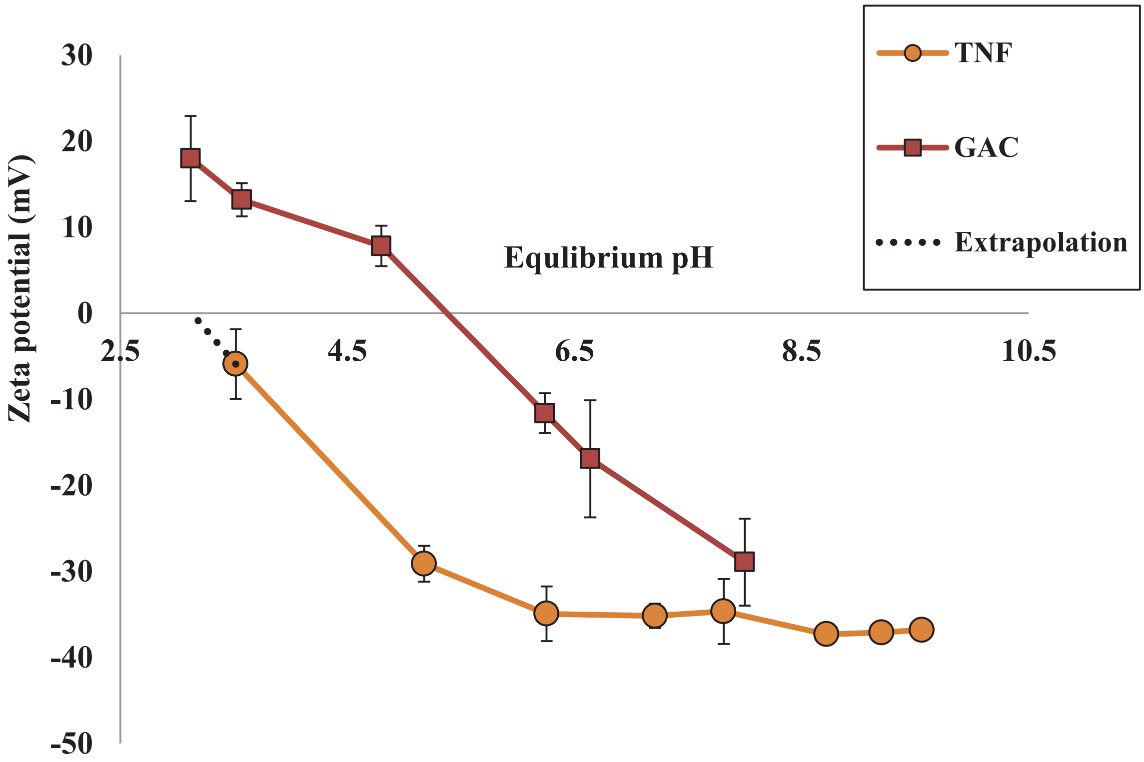


Figure 5.4 Zeta potential of TNF and GAC (ionic strength 10^{-3} M $NaNO_3$).

5.3.2 Batch adsorption

5.3.2.1 pH effect

The adsorption of all the heavy metals continued to increase when equilibrium pH rose from 3 to 7.5 (Figure 5.5). There are many reasons for this increased adsorption. Firstly, at low pHs the adsorption is low because there are less negative charges on the TNF surface (Figure 5.4) for adsorbing the positively charged heavy metal cations (M^{2+}) by coulombic forces. Secondly, the abundant protons (H^+) compete with the metal cations for adsorption. Thirdly, as the pH increases the concentrations of the metal hydroxyl complexes (MOH^+), which have higher affinity to metal oxides and hydroxides surfaces, become significant and this causes an abrupt increase in metal adsorption (Huang and Fuerstenau 2001). Fourthly, when the pH further increases the metal initially precipitates on the TNF surface before precipitation occurs in solution (Erdemoğlu and Sarıkaya 2006; Loganathan et al. 2014). The abrupt increase in the adsorption occurred at pH 3-4 for Pb, 4-6 for Cu and Cd and 5-7 for Zn and Ni. This abrupt elevation in the adsorption of metals is due to the large increase in concentration of metal hydroxide complex species in solution, or degree of surface precipitation within a narrow pH increases as observed for heavy metal adsorption on many other adsorbents (Huang and Fuerstenau 2001; Loganathan et al. 1977; Lv et al. 2004).

The degree of metal adsorption at pH 6.5 was in the order Pb > Cu > Cd > Zn > Ni, which follows the order of the ease of metal precipitation (pK_{sp})/or metal hydroxide complex formation (pK_1) except Cd (Table 5.1). At pH < 6.5 the order changed to Pb > Cd > Cu > Zn > Ni. This is probably because at low pH, instead of metals forming significant amounts of hydroxyl complexes they exist as hydrated divalent ions where the tendency for adsorption depends on the hydrated ionic radius and hydration energy.

Ions with smaller hydrated ionic radius are able to move closer to the adsorbent surface as well as easily enter the channels in the adsorbent for preferential adsorption. Ions with low hydration energies can easily become dehydrated and shrink in size for greater adsorption (Lv et al. 2004). On this basis, Pb with the lowest hydrated radius and hydration energy has produced the highest degree of adsorption, followed by Cd, Cu, Zn, and Ni in that order. Similar orders of adsorption were observed by others for Pb, Cu, Cd, and Zn on a titanosilicate at pH 5 (Lv et al. 2004) and Pb, Cd, and Zn on a zeolite and granular activated carbon ((Minceva et al. 2007), pH not reported), and Pb, Cd, Cu, and Cr on a titanate nanotube at pH 5 (Liu et al. 2013).

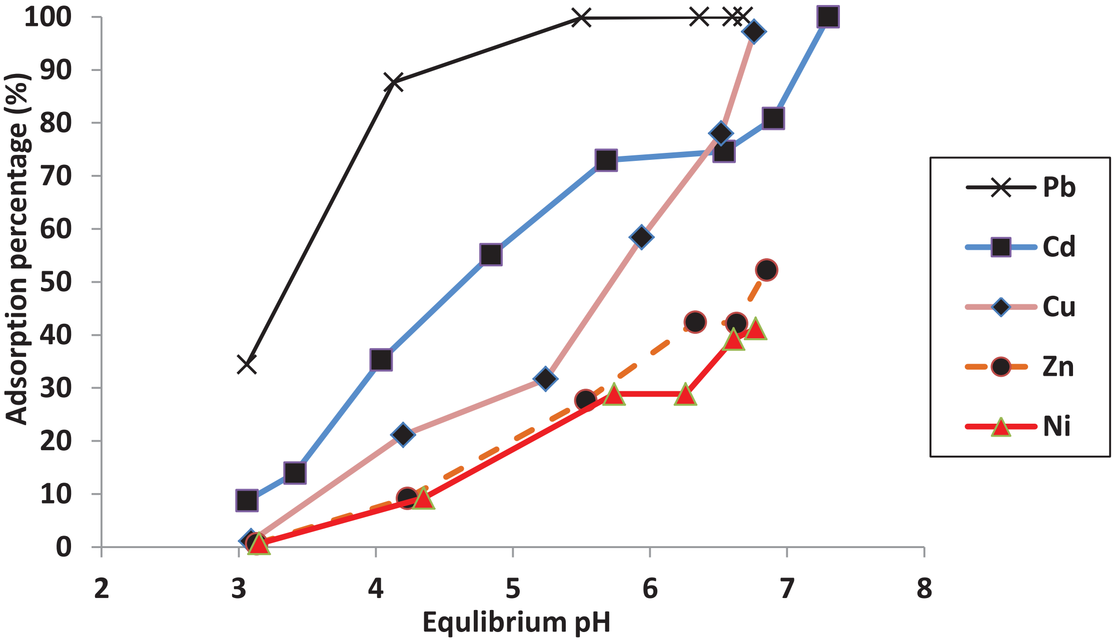


Figure 5.5 Effect of equilibrium pH on heavy metal adsorption from single metal solutions by TNF (ionic strength 10^{-3} M $NaNO_3$. Adsorption percentage (%) = metals adsorbed (mg) / metals initially present (mg) x 100).

Table 5.1 Characteristics of heavy metal ions.

Metal	Hydrated radius (nm)[1]	Hydrated energy (kJ/mol)[2]	Solubility of hydroxides (pK_{sp})[3]	First hydrolysis constants (pK_1)[4]
Ni	0.302	-2005	15.2	9.86
Zn	0.295	-1880	16.5	8.96
Cu	0.297	-1920	19.3	7.96
Cd	0.275	-1575	14.4	10.08
Pb	0.261	-1345	19.9	7.71

[1.2] Marcus (1991)

[3] Rao (2011) and Walker et al. (2012)

[4] Baes and Mesmer (1976) and Barnum (1983)

5.3.2.2 Adsorption model

The batch adsorption data were analysed using the Langmuir, Freundlich and Dubinin–Radushkevick models.

Langmuir isotherm model

Langmuir adsorption model can be described by equation (5)

$$Q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad \text{Eq (5)}$$

where, q_{max} = the maximum amount of the heavy metals adsorbed per unit weight of the adsorbent (mg/g) and K_L = Langmuir adsorption constant (L/mg).

This model can be linearized as follows:

$$\frac{C_e}{Q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \qquad \text{Eq (6)}$$

From the inverse of the slope of the graph of C_e/Q_e vs C_e, q_{max} was calculated.

Plots of C_e/Q_e vs C_e indicated significant linear relationships for all metals at all pHs (Figure 5.6; Table 5.2, $R^2 = 0.955$-0.998), demonstrating that the adsorption data fitted satisfactorily to the Langmuir adsorption model. This suggests that the adsorption sites on TNF were homogeneous with monolayer adsorption coverage.

Freundlich isotherm model

Freundlich adsorption model can be described by equation (7)

$$Q_e = K_F \, C_e^{1/n} \qquad \text{Eq (7)}$$

Where C_e = the equilibrium concentration of the adsorbate (mg/L); q_e = the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g); K_F and n = Freundlich constants.

This model can be linearized as follows:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad \text{Eq (8)}$$

From the plots of lnq_e vs $\ln C_e$ the K_F and n were calculated and the values are presented in Table 5.3.

Dubinin–Radushkevick isotherm model

The Dubinin–Radushkevick adsorption model can be described by equation (9)

$$Q_e = q_m \exp(-\beta \varepsilon^2) \qquad \text{Eq (9)}$$

Where q_e = the amount of heavy metal adsorbed per unit dosage of the adsorbent (mg/g); q_m = the monolayer capacity, and β is the activity coefficient related to mean sorption energy and ε is the Palanyi potential described as: $\varepsilon = RTln[1 + (\frac{1}{C_e})]$.

This model can be linearized as follows:

$$\ln(Q_e) = \ln(q_m) - \beta\varepsilon^2 \qquad \text{Eq (10)}$$

From the plots of ln (Q_e) versus ε^2 the values of β and q_m were determined and the values are presented in Table 5.4

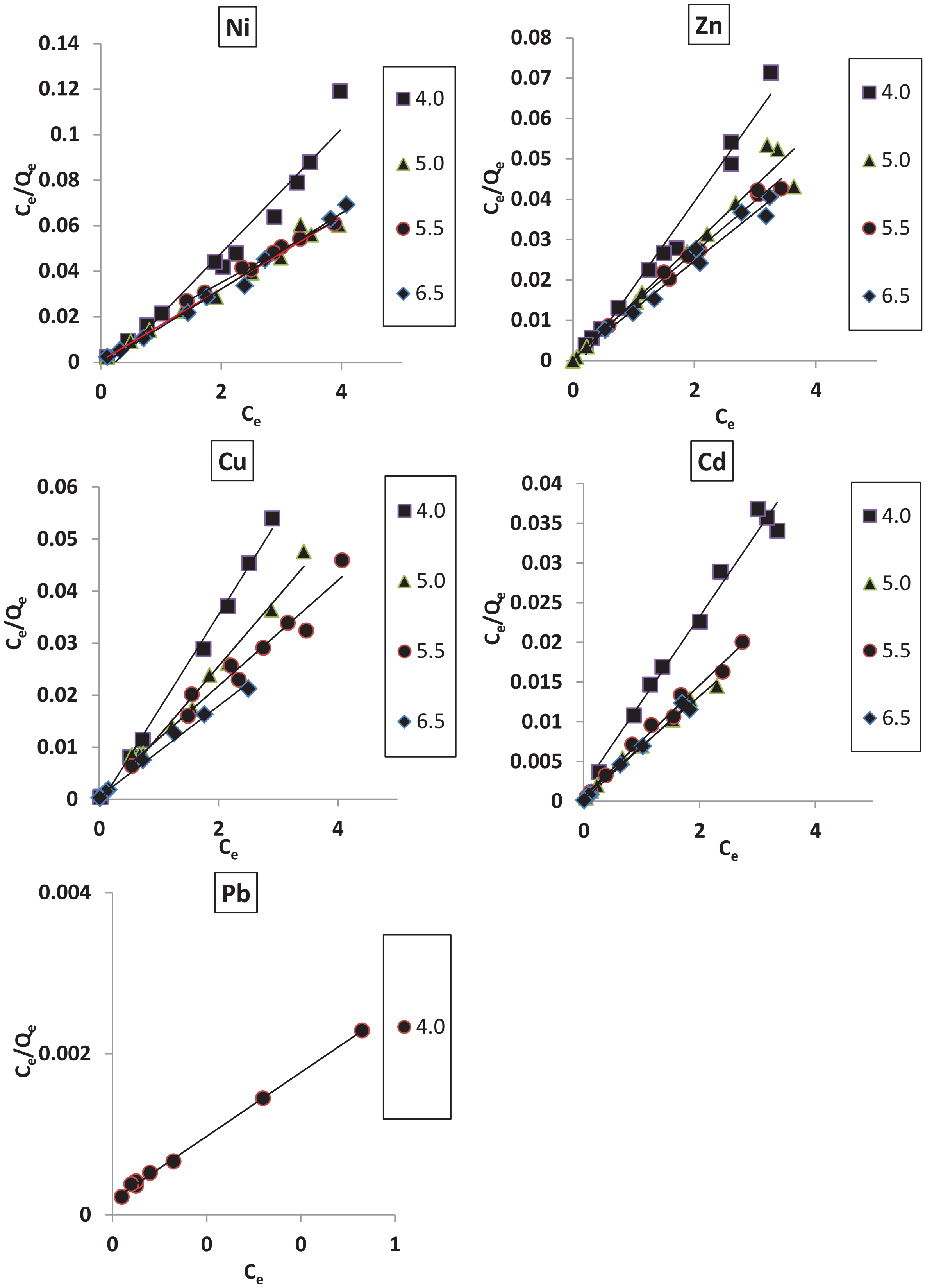


Figure 5.6 Langmuir plots for metals adsorption on TNF from single metal solutions at different pHs.

Table 5.2 Langmuir parameters for individual heavy metals adsorption on TNF (ionic strength 10^{-3} M $NaNO_3$) and coefficients of determination for the Langmuir plots (R^2).

	pH 4.0				pH 5.0				pH 5.5				pH 6.5			
Metals	q_{max} (mg/g)	q_{max} (mmol/g)	K_L (L/mg)	R^2	q_{max} (mg/g)	q_{max} (mmol/g)	K_L (L/mg)	R^2	q_{max} (mg/g)	q_{max} (mmol/g)	K_L (L/mg)	R^2	q_{max} (mg/g)	q_{max} (mmol/g)	K_L (L/mg)	R^2
Ni	37	0.62	4.6	0.960	63	1.08	26.3	0.982	69	1.19	2.2	0.992	60	1.02	13.9	0.992
Zn	47	0.72	13.0	0.981	70	1.07	71.5	0.961	79	1.21	9.1	0.985	83	1.26	24.2	0.972
Cu	54	0.85	18.5	0.996	75	1.17	10.3	0.983	99	1.56	6.7	0.955	115	1.81	17.4	0.993
Cd	93	0.83	5.9	0.978	159	1.41	10.5	0.994	143	1.27	11.7	0.988	149	1.33	10.5	0.992
Pb	250	1.21	20.0	0.998	-	-	-	-	-	-	-	-	-	-	-	-

Table 5.3 Freundlich isotherm model parameters for the adsorption of heavy metals on TNF from solutions containing mixed metals at an ionic strength of 10^{-3} M $NaNO_3$ for two pHs and coefficients of determination for the Freundlich isotherm fit to data (R^2).

Data separated into low (L) and high (H) metal concentrations

	Low metal concentration				**High metal concentration**			
	pH 5.0 (L)				pH 5.0 (H)			
Metals	K_F (mg/g) (L/mg)$^{1/n}$	n	R^2	N	K_F (mg/g) (L/mg)$^{1/n}$	n	R^2	N
Ni	15.9	-34.0	0.1486	8	4136.9	-0.4	0.8314	8
Zn	17.6	93.5	0.0382	9	915.8	-0.6	0.7715	7
Cd	27.1	13.4	0.6574	6	186.0	-1.1	0.8354	5
Cu	30.9	7.2	0.8728	6	85.4	-2.6	0.7236	5
Pb	-	-	-	-	-	-	-	-
	pH 6.5 (L)				pH 6.5 (H)			
Metals	K_F (mg/g) (L/mg)$^{1/n}$	n	R^2	N	K_F (mg/g) (L/mg)$^{1/n}$	n	R^2	N
Ni	22.2	-6.5	0.7098	5	477.4	-0.59	0.9140	5
Zn	22.9	-41.2	0.1577	5	1649.1	-0.45	0.7575	5
Cd	34.2	8.5	0.8806	5	44.6	-5.36	0.7003	5
Cu	42.0	8.0	0.9028	5	42.0	-57.80	0.0237	5
Pb	-	-	-	-	-	-	-	-

N- Number of data points

Table 5.4 The Dubinin–Radushkevick isotherm model parameters for the adsorption of heavy metals (15 mg/L) on TNF from solutions containing mixed metals at an ionic strength of 10^{-3} M $NaNO_3$ for two pHs and coefficients of determination for the Langmuir isotherm fit to data (R^2).

Data separated into low (L) and high (H) metal concentrations

	Low metal concentration				**High metal concentration**			
	pH 5.0 (L)				pH 5.0 (H)			
Metals	q_m (mg/g)	β (mol^2/kJ^2)	R^2	N	q_m (mg/g)	β (mol^2/kJ^2)	R^2	N
Ni	2.2	-3×10^{-5}	0.7996	7	15.8	-4×10^{-10}	0.0018	9
Zn	4.3	-2×10^{-5}	0.7285	8	18.4	3×10^{-9}	0.2651	8
Cd	15.6	-8×10^{-6}	0.7766	5	30.8	5×10^{-8}	0.9117	6
Cu	28.8	-3×10^{-6}	0.6427	5	38.0	7×10^{-8}	0.9436	6
Pb	-	-	-	-	-	-	-	-
	pH 6.5 (L)				pH 6.5 (H)			
Metals	q_m (mg/g)	β (mol^2/kJ^2)	R^2	N	q_m (mg/g)	β (mol^2/kJ^2)	R^2	N
Ni	4.0	-5×10^{-8}	0.3893	5	17.4	-2×10^{-5}	0.9154	5
Zn	3.4	-2×10^{-5}	0.7217	5	22.5	-3×10^{-9}	0.0253	5
Cd	29.7	-3×10^{-7}	0.4451	5	35.1	8×10^{-9}	0.9365	5
Cu	41.1	2×10^{-8}	0.0161	5	39.3	5×10^{-9}	0.9313	5
Pb	-	-	-	-	-	-	-	-

N- Number of data points

As the data fit was best for Langmuir model compared to the other two models, only the results of Langmuir model are discussed in the rest of the chapter

(a) Single metal adsorption

The Langmuir adsorption maxima calculated from the slope of the linear plots of C_e/Q_e vs C_e for the metals at different pHs followed the order Pb > Cd > Cu > Zn > Ni when the adsorption capacities were expressed as mg/g and Pb > Cu > Cd > Zn > Ni when they are expressed as mmol/g (Table 5.2). The difference in the adsorption capacity between Cu and Cd changed in favour of Cu when: firstly, the data were expressed as mmole/g; and secondly, when the pH increased for the reasons presented in the previous section. When pH increased, all the metals revealed an increase in the maximum adsorption capacities up to pH 5 and remained nearly the same beyond pH 5 up to 6.5. Lead adsorption capacity is presented only for pH 4.0. The adsorption data for Pb at higher pHs could not be described using the Langmuir adsorption model because nearly all the Pb from the solutions were adsorbed or precipitated.

The Langmuir adsorption maxima (mg/g) of 60, 83, 115, and 149 at pH 6.5 for Ni, Zn, Cu, and Cd, respectively, and 250 for Pb at pH 4.0 (Table 5.2) are higher than the corresponding values at pH 5.0-7.0 of several carbon nanotubes adsorbents. These values are 7-48, 10-44, 24, 1-11 and 1-97, and agricultural and industrial wastes adsorbents of 3-26, 3-18, 6-109, 5-60, and 11-267 for Ni, Zn, Cu, Cd, and Pb, respectively (Rao et al. 2007). The Langmuir adsorption maxima of TNF are also higher than the values reported for the commercial ion exchange resins, Amberlite IR-120 (Langmuir adsorption maxima (mg/g) of 48, 85, 22, 100, and 84 for Ni, Zn, Cu, Cd, and Pb, respectively, pH not reported) (Demirbas et al. 2005) and Lewatit CNP 80 (Langmuir adsorption maxima (mg/g) of 19, 20, 10, 5, and 73 for Ni, Zn, Cu, Cd, and Pb, respectively, pH 8.0) (Pehlivan and Altun 2007). The adsorption capacities of TNF improve on those reported for a similar titanate material (microporous titanosilicate) (11, 27, 41, and 170 mg/g for Zn, Cu, Cd, and Pb, respectively, pH 5.0) (Lv et al. 2004).

(b) Mixed metals adsorption

The data for the adsorption of metals from solutions containing mixed metals showed that at equilibrium concentrations greater than 2-4 mg/L, the adsorption of all metals except Pb decreased at both low and high pHs (Figure 5.7). The reason for this decrease is that at high concentrations of the metals, these metals competed for adsorption on the limited number of unoccupied adsorption sites on the TNF surface. The weakly adsorbed metals, Ni and Zn, showed a greater reduction in adsorption than the other metals.

Table 5.5 Langmuir parameters for heavy metals adsorption on TNF from mixed metals solutions (ionic strength 10^{-3} M $NaNO_3$) and coefficients of determination for the Langmuir plots (R^2) (n denotes number of data points).

Data for all metal concentrations

Metals	pH 5.0				pH 6.5			
	q_{max} (mg/g)	q_{max} (mmol/g)	R^2	n	q_{max} (mg/g)	q_{max} (mmol/g)	R^2	n
Ni	6.5	0.11	0.828	16	7.5	0.13	0.899	9
Zn	9.5	0.15	0.884	16	7.0	0.10	0.772	9
Cd	22.0	0.20	0.950	11	29.0	0.25	0.984	9
Cu	34.0	0.53	0.981	11	39.0	0.62	0.992	9
Pb	322.5	1.56	0.938	15	333.5	1.61	0.953	13

Data separated into low (L) and high (H) metal concentrations

Metals	pH 5.0 (L)				pH 5.0 (H)			
	q_{max} (mg/g)	q_{max} (mmol/g)	R^2	n	q_{max} (mg/g)	q_{max} (mmol/g)	R^2	n
Ni	13.5	0.23	0.989	8	2.0	0.03	0.802	8
Zn	16.0	0.25	0.987	9	3.5	0.05	0.812	7
Cd	31.0	0.27	0.999	6	12.0	0.11	0.936	5
Cu	40.0	0.63	0.995	6	24.0	0.38	0.960	5
Pb	322.5	1.56	0.938	15	-	-	-	-

Metals	pH 6.5 (L)				pH 6.5 (H)			
	q_{max} (mg/g)	q_{max} (mmol/g)	R^2	n	q_{max} (mg/g)	q_{max} (mmol/g)	R^2	n
Ni	14.0	0.24	0.982	5	3.5	0.06	0.946	5
Zn	21.5	0.33	0.988	5	3.0	0.05	0.698	5
Cd	36.0	0.32	0.997	5	25.5	0.23	0.974	5
Cu	39.5	0.62	0.998	5	37.0	0.58	0.981	5
Pb	333.5	1.61	0.953	13	-	-	-	-

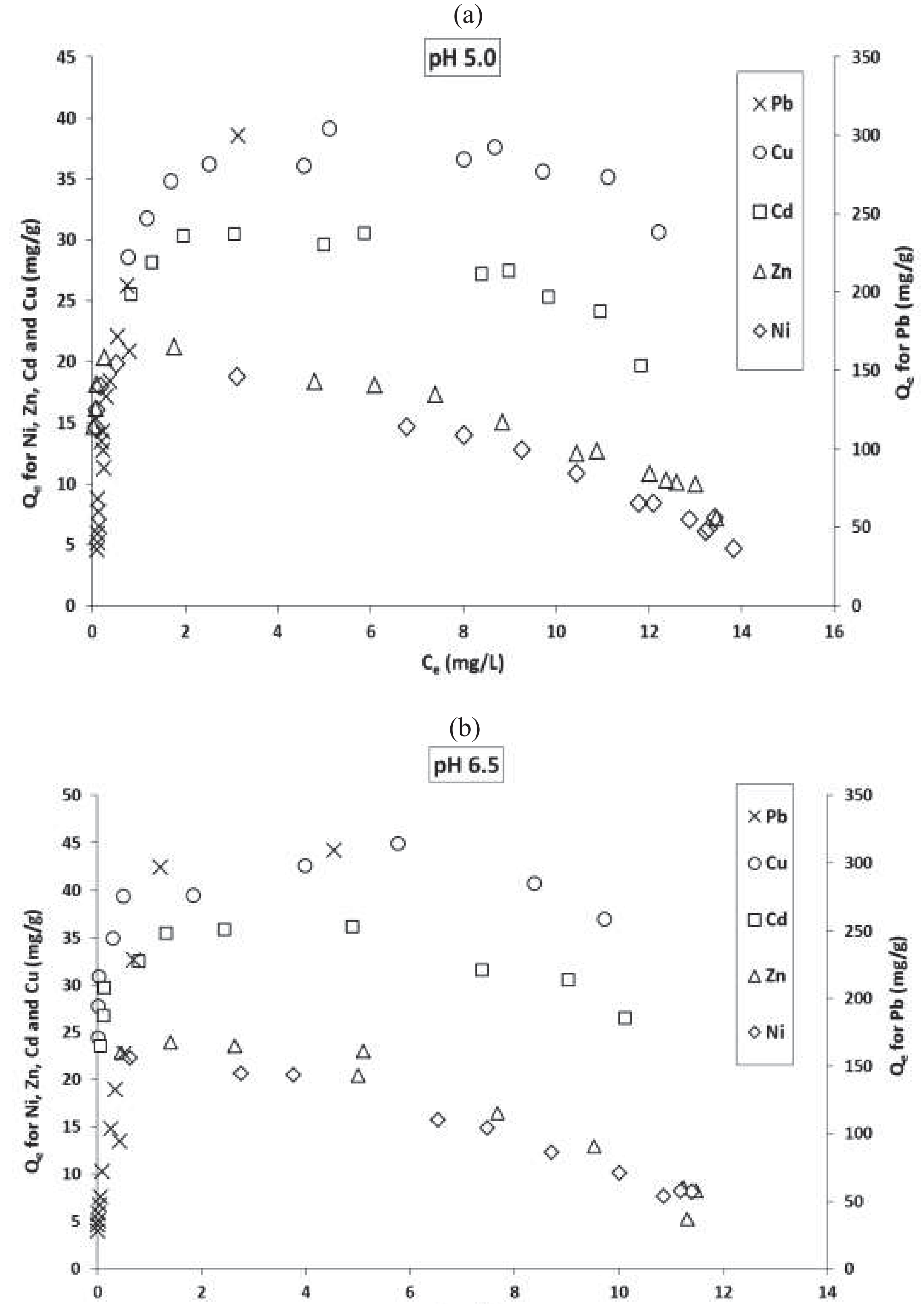


Figure 5.7 Metals adsorption by TNF from mixed metals solution at (a) pH 5.0, (b) pH 6.5 (ionic strength 10^{-3} M $NaNO_3$).

Since greater competition for adsorption of metals occurred at high solution metal concentrations, the adsorption data were divided into two groups: one at solution concentrations of 0-3 mg/L; and the other at > 3 mg/L. When the data were fitted to the Langmuir adsorption model, results showed that both groups of data satisfactorily fitted to the model (Table 5.3; R^2 = 0.935-0.999 low concentrations; R^2 = 0.698-0.981 high concentrations, Figures 5.8 and 5.9). However, the fits were better at low solution concentrations than at high ones and when the entire concentration ranges were considered for all metals except Pb (R^2 = 0.772-0.992, Table 5.3, Figure 5.10). For Pb, the whole concentration range was less than 3 mg/L, probably due to significant surface precipitation of $Pb(OH)_2$ above this concentration range, and therefore the above comparison was not possible. Langmuir adsorption maxima for all metals except Pb were higher at lower solution metal concentrations than for the entire concentration range. As explained earlier this is due to greater competition between metals for adsorption at higher concentrations. The adsorption maxima followed the order Cu > Cd > Zn > Ni at low metal concentration ranges and at the entire concentration ranges whether they were expressed as mg/g or mmol/g (Table 5.3).

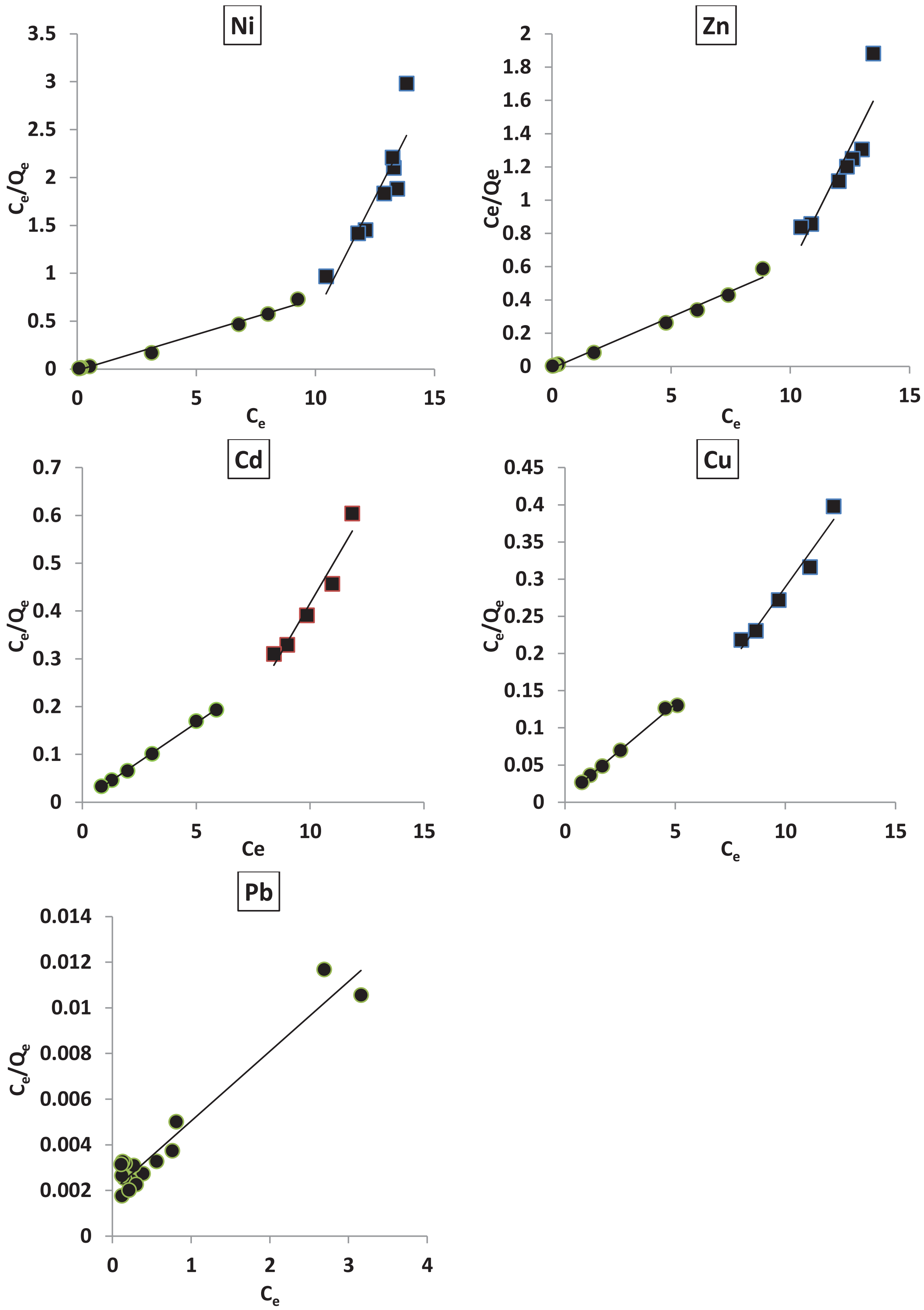


Figure 5.8 Langmuir plots for adsorption of metals on TNF from solutions containing mixed metals at low and high metal concentrations at pH 5.

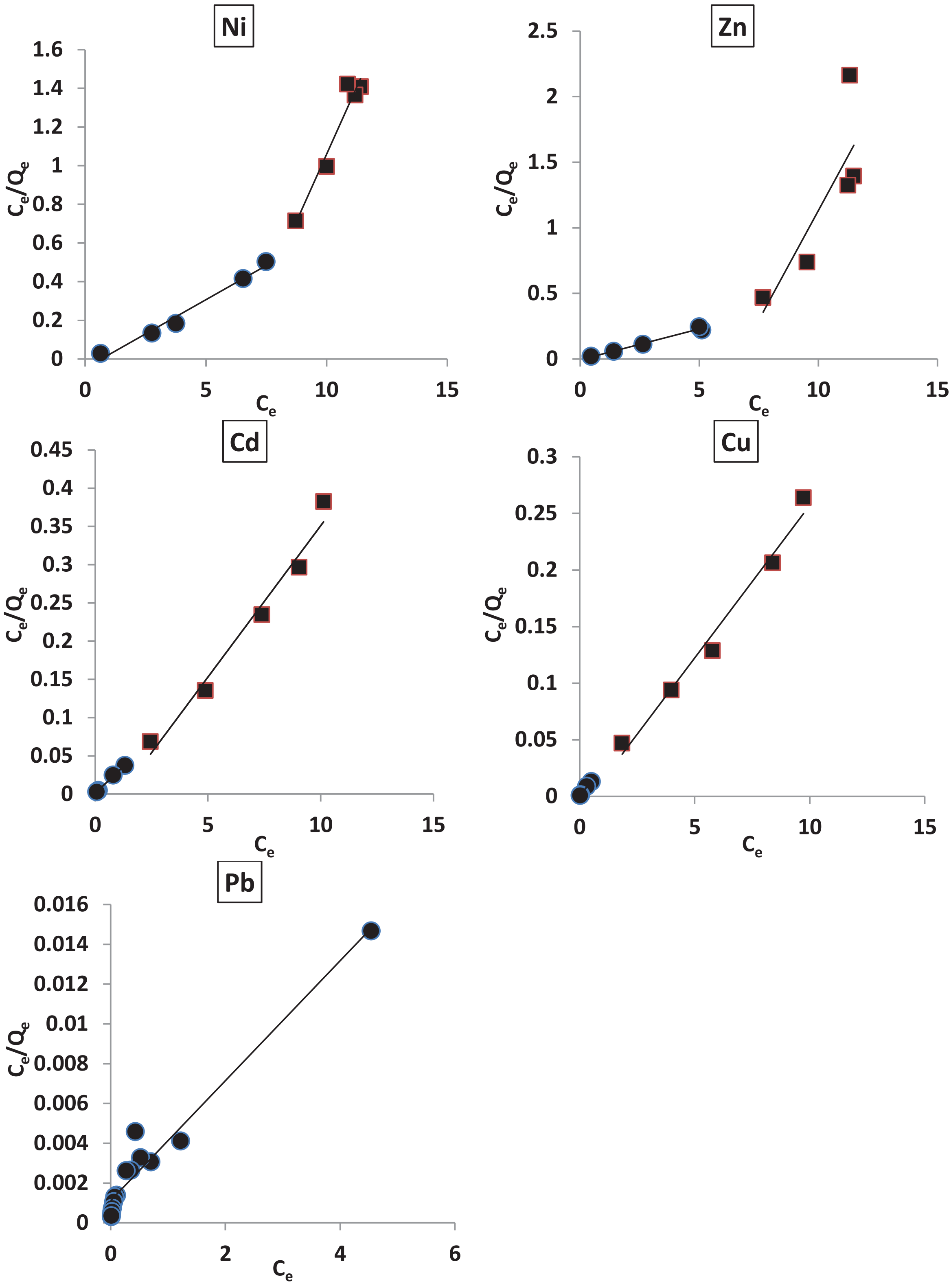


Figure 5.9 Langmuir plots for adsorption of metals on TNF from solutions containing mixed metals at low and high metal concentrations at pH 6.5.

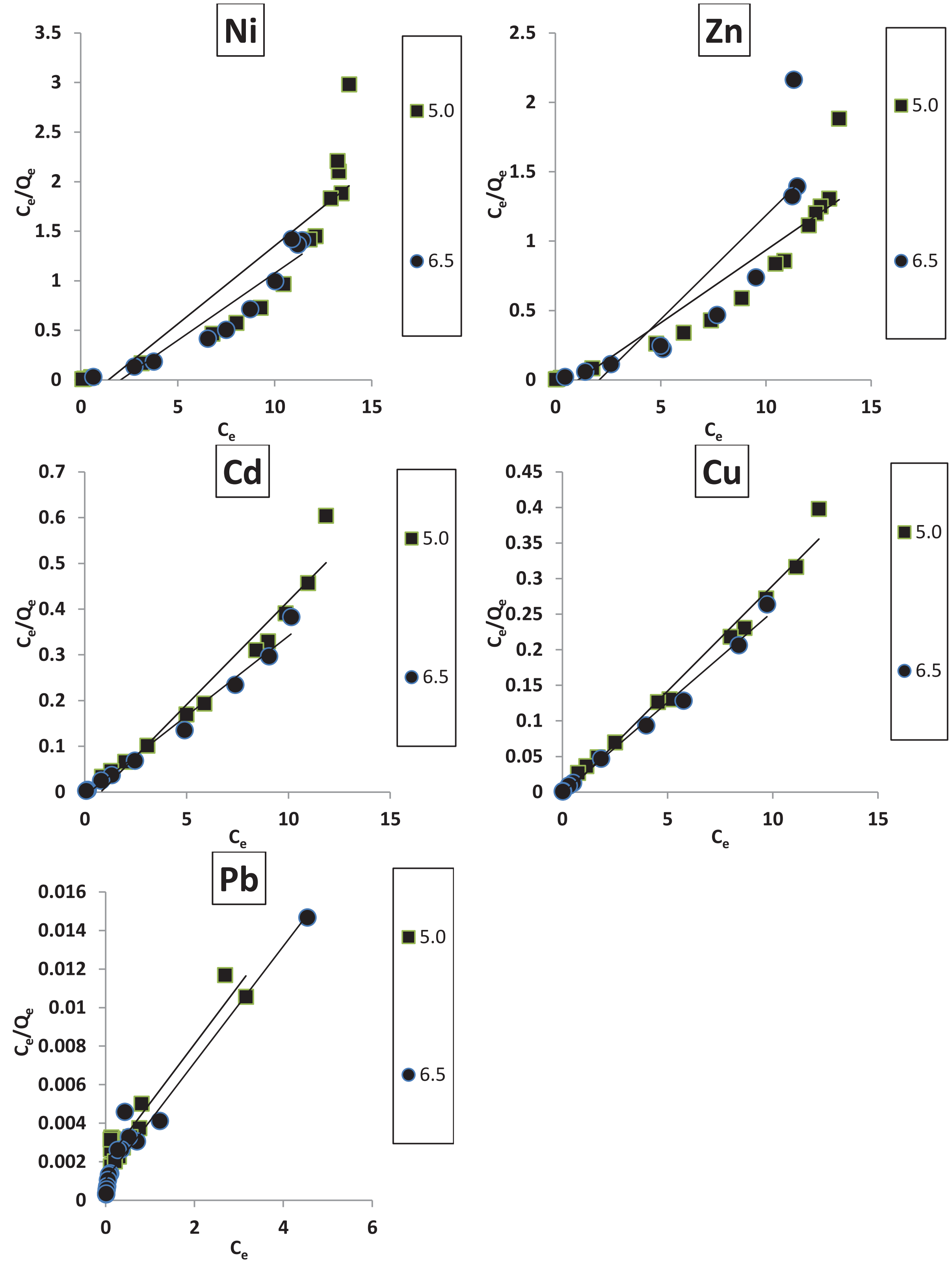


Figure 5.10 Langmuir plots for adsorption of metals on TNF from solutions containing mixed metals at different pHs (not divided into two regions).

5.3.2.3 Metals desorption and TNF regeneration

The data on adsorption/desorption of metals showed that 0.1 M HNO_3 desorbed nearly 100% of the adsorbed Zn, Cd, Cu, and Ni but only 12% of Pb (Table 5.6). However, desorption of all the metals using 0.1M $NaNO_3$ was poor (0.7-35%). The adsorption capacities after the desorption process were very much reduced for many metals, especially after desorption with 0.1 M HNO_3. In contrast to desorption using these two reagents, when the metals were desorbed using 0.1 M HNO_3 and TNF was regenerated by adding 0.1 M NaOH, the TNF almost regained its original adsorption capacity for all metals. Wang et al. (2013c) also reported that this method was effective in regenerating titanate nanotubes (TNT) adsorbent. They stated that during metals desorption using acid the TNT's structure and morphology changed due to losing Na from the structure. This in turn reduced the adsorption capacity but adding NaOH neutralized the acid and introduced Na so that the adsorption capacity was restored.

Table 5.6 Adsorption/desorption of metals on TNF (mg/g)

	Ni	Zn	Cd	Cu	Pb
Amount adsorbed in original TNF	14.0	14.6	14.4	15.4	19.2
Amount desorbed using 0.1 M $NaNO_3$	4.9	1.7	0.1	0.5	4.0
Amount desorbed using 0.1 M HNO_3	14.2	14.8	14.4	15.1	2.4
Amount adsorbed after desorption with 0.1 M $NaNO_3$	0.0	1.7	12.1	13.8	21.3
Amount adsorbed after desorption with 0.1 M HNO_3	0.6	1.0	2.4	3.6	19.4
Amount adsorbed after desorption with 0.1 M HNO_3 and TNF regeneration with 0.2 M NaOH	11.9	12.8	13.9	15.1	19.1

5.3.2.4 Fixed-bed column experiments

(a) Single Metals

In columns packed with only GAC the metals' breakthrough occurred faster and the breakthrough curves were steeper for Ni, Zn, and Cd whereas the breakthrough was the slowest and the curves were least steep for Pb (Figure 5.11). The characteristic of the curve for Cu was in between Pb and the other metals. The patterns of the breakthrough curves are reflected in the order of the cumulative adsorption of the metals on GAC: Pb > Cu > Cd > Zn > Ni (Table 5.7).

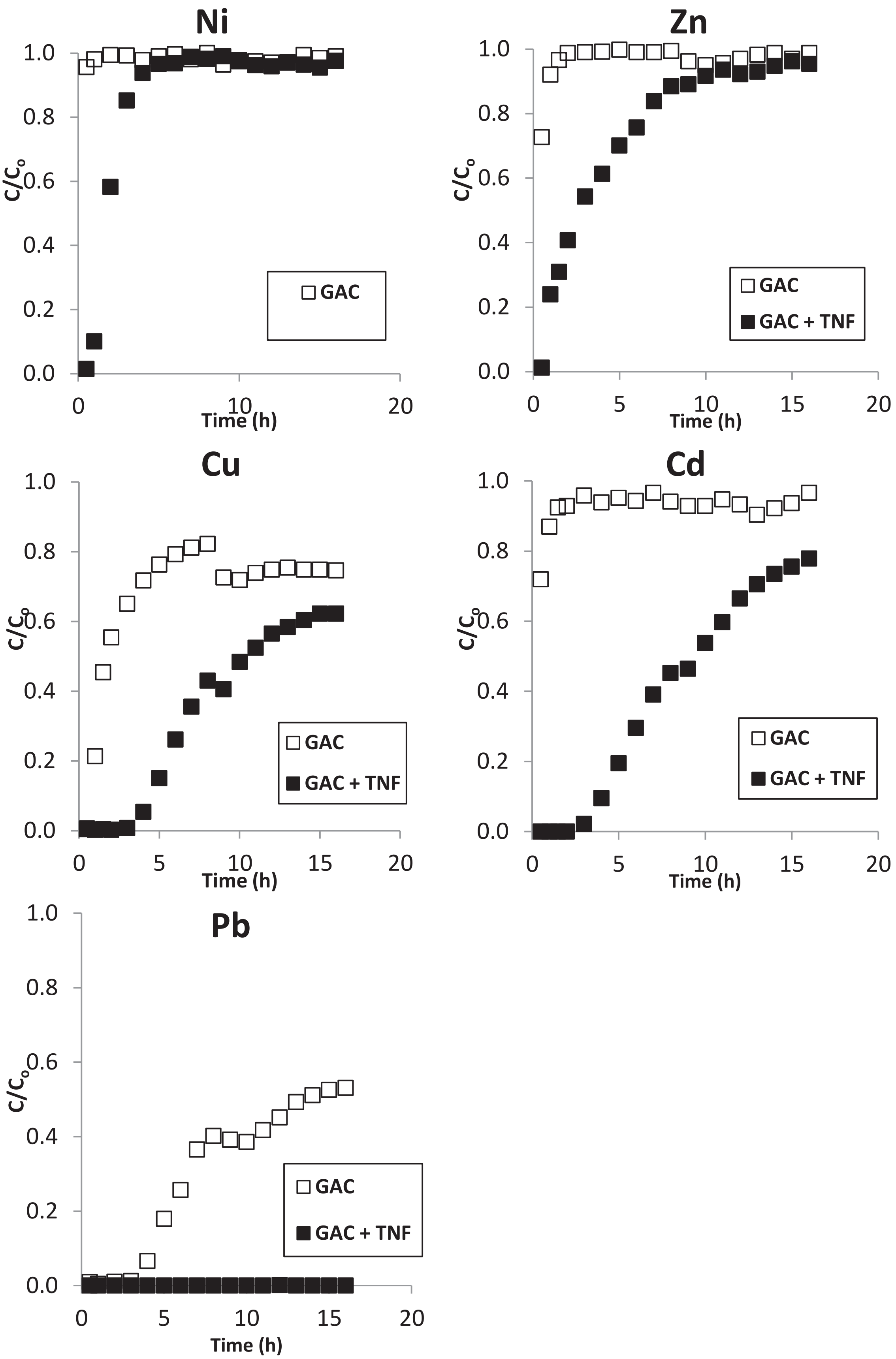


Figure 5.11 Breakthrough plots of (a) Ni, (b) Zn, (c) Cu, (d) Cd and (e) Pb in GAC and GAC + TNF column study for single metals.

Table 5.7 Cumulative adsorption of heavy metals by GAC and GAC + TNF from single metals and mixed metals solutions after 16 h (266 BV) at pH 5.0.

	Column media	**Units**	**Ni**	**Zn**	**Cu**	**Cd**	**Pb**
Single metals Experiments	GAC, q_{total}	mg	2.5	5.0	44.0	9.0	85.0
	GAC + TNF, q_{total}	mg	15.5	29.5	88.5	70.0	123.0
	TNF, q_{total} [a]	mg	13.0	24.5	44.5	61.0	38.0
	GAC [b]	(%)	2.0	4.0	32.0	8.0	69.0
	GAC + TNF [b]	(%)	12.0	23.5	64.5	58.0	100.0
Mixed metals Experiments	GAC, q_{total}	mg	0.25	1.75	14.25	0.25	26.25
	GAC + TNF, q_{total}	mg	2.50	8.00	27.25	20.50	29.50
	TNF, q_{total} [a]	mg	2.25	6.25	13.00	20.25	3.25
	GAC [b]	(%)	1.0	6.5	46.0	1.5	86.0
	GAC + TNF [b]	(%)	9.5	29.5	87.0	79.5	96.0

[a] adsorption on TNF = adsorption on GAC + TNF minus adsorption on GAC

[b] percentage of cumulative metal adsorption = (cumulative metal added – cumulative metal in effluent) / cumulative metal added

The breakthrough curves for all the metals were less steep and the breakthroughs were slower when TNF was added to GAC in the column (Figure 5.6) because of the much greater adsorption capacity of TNF compared to GAC. The adsorption capacity of TNF in the presence of GAC was calculated to be 10-20 times higher than that of GAC (Table 5.6). However, the order of the cumulative adsorption of metals on GAC + TNF remained the same as in the GAC-only column (Pb > Cu > Cd > Zn > > Ni). The contribution of TNF to adsorption in the GAC + TNF column was assessed by subtracting the cumulative adsorption by GAC from that of GAC + TNF. The results showed that TNF strongly influenced the removal of Cd. This is consistent with the results of the batch adsorption study where the Langmuir adsorption capacity of TNF followed the order Pb > Cd > Cu > Zn > Ni at low pHs (Table 5.2). Adsorption capacity of TNF for Pb obtained by the above calculation is low because of the high adsorption capacity of Pb on GAC (Table 5.7).

(b) Simultaneous removal of metals

The patterns of metals breakthrough from solutions containing mixed metals (Figure 5.12) were similar to those of solutions containing single metals (Figure 5.11). The steepness of the breakthrough curves followed the order Ni > Zn > Cd > Cu > Pb in both the GAC and GAC + TNF columns as observed in the single metals experiment. The cumulative amounts of each metal adsorbed up to 16 h (266 bed volumes) (Table 5.7) were smaller than the respective metal adsorption in the single metals experiment (Table 5.7) due to the lower influent concentration of the metals in the mixed metals system. The order of the cumulative amounts adsorbed was Pb > Cu > Zn > Cd > Ni in the GAC column but it was Pb > Cu > Cd > Zn > Ni in GAC + TNF column. This indicates that GAC has less adsorption preference for Cd than Zn in a competitive adsorption system whereas the opposite occurred on TNF. The cumulative amounts of metals adsorbed in the GAC + TNF column were larger than those in the GAC column for all metals, thus indicating the higher adsorptive capacity of TNF. In the case of Cd the amount adsorbed was nearly 80 times larger in the GAC + TNF column.

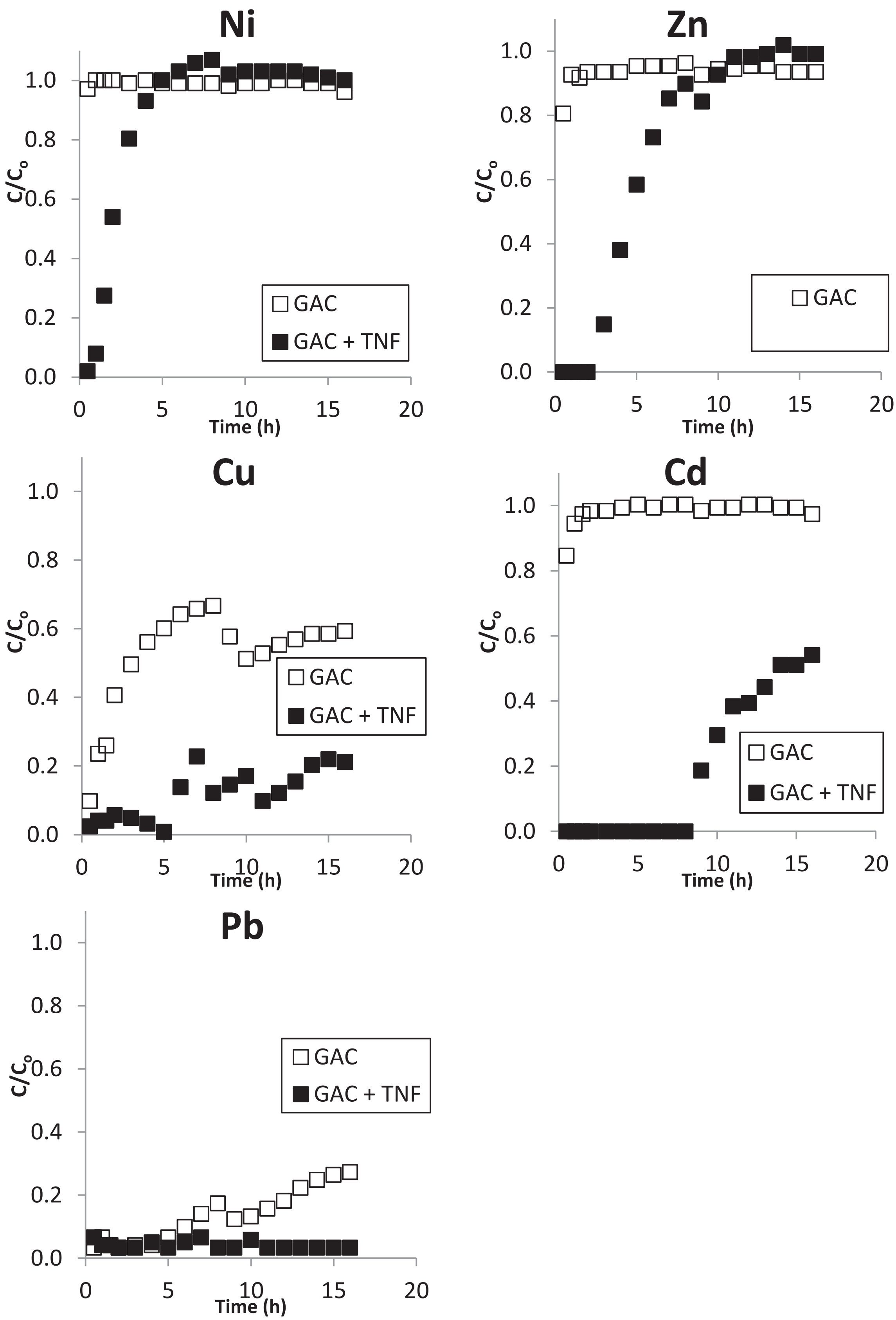


Figure 5.12 Breakthrough plots of (a) Ni, (b) Zn, (c) Cu, (d) Cd and (e) Pb in GAC and GAC + TNF column study for mixed metals.

5.4 Conclusions

Batch experiments on heavy metals adsorption on TNF (zero point of charge 3.2) from solutions containing single or mixed metals showed that elevated pH increased the adsorption of Pb, Cd, Cu, Zn and Ni. Adsorption data at pH 4.0, 5.0, 5.5 and 6.5 for the single metal system fitted satisfactorily to the Langmuir isotherm model for Cd, Cu, Zn and Ni. The Langmuir adsorption maxima at pH 6.5, which is the pH of most natural and waste waters, for these metals were 149, 115, 83 and 60 mg/g, respectively. For Pb, because TNF removed all solution Pb above pH 4.0, only the data for pH 4.0 fitted to the Langmuir isotherm model which gave an adsorption maximum of 250 mg/g. For the mixed metal systems, the adsorption of all metals except Pb decreased at high solution concentration, especially for weakly adsorbed Ni and Zn, due to the competition between metals for adsorption. Most waters contaminated from diffuse sources of metals have metal concentrations less than 3 mg/L and therefore their competition for adsorption on TNF is unlikely. The Langmuir adsorption capacities for Cd, Cu, Zn, Ni, and Pb in mixed metals system at pH 6.5 were lower than the respective values in the single metal system. For the repeated use of TNF the adsorbed metals need to be desorbed and TNF regenerated. Desorption using 0.1 M HNO_3 followed by regeneration of the TNF by the addition of 0.1 M NaOH appeared to be an efficient method.

Column experiments on TNF (4%) mixed with GAC (96%) in both single and mixed metal systems showed that the metals removed by adsorption varied widely and up to 80 times greater than in the column with only GAC. Metal breakthrough times decreased in the same order as the adsorption capacities in batch studies. The study showed that TNF can potentially remove a large percentage of heavy metals from polluted water. Because TNF is finer in size, it can be mixed with GAC to provide better hydraulic properties, and at the same time it can effectively remove heavy metals.

CHAPTER 6

University of Technology, Sydney

COLUMN STUDIES ON THE REMOVAL OF DISSOLVED ORGANIC CARBON, TURBIDITY AND HEAVY METALS FROM STORMWATER USING GRANULAR ACTIVATED CARBON

The major part of this chapter was published in Sounthararajah D. P., Loganathan P., Kandasamy J. and Vigneswaran S. (2015b). Column studies on the removal of dissolved organic carbon, turbidity and heavy metals from stormwater using granular activated carbon. ***Desalination and Water Treatment***, **57**(11), 5045-5055.

6 Column studies on the removal of dissolved organic carbon, turbidity and heavy metals from stormwater using granular activated carbon

6.1 Introduction

Urban stormwater is the main source of pollution in water bodies such as lakes and rivers in Australia (Kus et al. 2012; Lawrence and Breen 1998; Lee et al. 2007). The stormwater carries a large number of organic and inorganic pollutants in colloidal and dissolved forms such as heavy metals, suspended solids (SS), and dissolved organic carbon (DOC) (Aryal et al. 2010). These pollutants can have adverse effects on the environment when discharged in untreated form into receiving water bodies. Studies on heavy metals effects on environment and their removal from water were presented in Chapters 2, 4 and 5.

Suspended solids contribute to the water's turbidity, cause temperature changes and lessen sunlight penetration, which can reduce the resulting activity and growth of photosynthetic organisms. This leads to aesthetic issues, higher cost of water treatment, declining fish resources, serious ecological degradation of aquatic life, reduced navigability of channels and decreased longevity of dams and reservoirs (Aryal et al. 2010; Bilottaa and Brazier 2008). Suspended solids also work as carriers of pollution because the finer sediments carry pollutants such as heavy metals, pesticides, nutrients and organic matter in particulate form and release them into the environment (Bilottaa and Brazier 2008).

Dissolved organic carbon causes oxygen deficiency in water and subsequently leads to the death of aquatic organisms (Committee 1999; Ryan 1991). It also creates an unpleasant taste and odour in water and acts as a substrate to microbial growth. Furthermore, DOC can reduce the effectiveness of water treatment processes (Matilainen et al. 2010; Treatment 2005), increase coagulant and disinfection demands, and foul membrane filters (Fabris et al. 2008; Zularisam et al. 2006).

The purpose of this study was to investigate the efficiency in removing a wide range of pollutants from urban stormwater using granular activated carbon (GAC) and anthracite by fixed-bed field and laboratory column filtration, thereby preventing the contaminant loading to waterways and increasing the likelihood of recycle and reuse of stormwater. The specific contaminants studied in this paper are DOC, SS and heavy metals (Cu, Zn, Pb, Cd and Ni). Other contaminants, such as polycyclic aromatic hydrocarbons (PAHs) in stormwater were not studied as their concentrations were very low (water sediment concentrations, 0.49-5.29 µg/g (Nguyen et al. 2014)). In field experiments, natural stormwater served in the analysis of removing DOC and SS using anthracite and GAC columns in series with different filtration velocities. The removal of heavy metals was not studied in the field because their concentrations in natural stormwater are extremely small. In laboratory studies, tap water was spiked with heavy metals and kaolinite to test the ability of heavy metals, turbidity and DOC removals using GAC.

6.2 Experimental methodology

6.2.1 GAC and anthracite

Granular activated carbon and anthracite used in the study were obtained from James Cummins P/L, Australia. Selected properties of the anthracite are summarised in Table 6.1 and GAC properties were tabulated in Table 4.1 in section 4.2.1. Zeta potential which is related to the surface charge of the adsorbent was measured in GAC suspensions using a zetasizer nano-instrument (Nano ZS Zne 3600, Malvern, UK) as mentioned in section 4.2.1.

6.2.2 Stormwater

The stormwater used in field studies was predominantly from the base flow in a stormwater harvesting plant located at Lower West Street Reserve, Carlton in Sydney (S 33.979972, E 151.115360), which constantly flowed in the stormwater canal between rainfall events. Rainfall on 1st, 2nd and 3rd day of the field experiment was 19, 13, 84 mm measured at a weather station close to the site. The stormwater was drained by gravity through a sump pit in the floor of the stormwater canal to an adjacent wet well. It was then pumped through a control valve pit to a collection tap, from which point the stormwater was continuously fed directly to the fixed-bed absorbent columns at a velocity controlled by valves before and after the filter columns. Table 6.2 presents the stormwater characteristics. For laboratory experiments, synthetic stormwater was prepared using tap water to produce a mix of heavy metals and kaolinite which had the specified required concentrations of metals and turbidity.

Table 6.1 Physical properties of anthracite

Properties	Anthracite	Reference
Nominal size (mm)	1.0-1.1	a, b
Bulk density (kg/m^3)	660-720	a
Iodine number (mg /g.min)	-	a
BET surface area (m^2/g)	-	a
Maximum Moisture content (%)	-	a
Uniformity coefficient	1.30	a, b
Acid solubility (%)	1	a, b
Specific gravity	1.45	a

a Kus et al. (2012)

b Mohammed et al. (2011)

Table 6.2 General characteristics of stormwater collected in Carlton, Sydney (Mohammed et al. 2011)

Parameter	Unit	Value
Physical and chemical properties		
pH	–	6.68–7.28
TOC	mg/L	4.25–8.96
Turbidity	NTU	1.5–370
True Colour	PtCo	18–270
Bicarbonate	mg/L $CaCO_3$ equivalent	30–95
Water Hardness	mg/L $CaCO_3$ equivalent	22–145
Metals		
Al	mg/L	0.028–0.188
As	mg/L	0.001–0.005
Cd	mg/L	0.0009–0.001
Cr	mg/L	0.002–0.002
Cu	mg/L	0.008–0.049
Fe	mg/L	0.05–2.55
Mn	mg/L	0.001–0.024
Ni	mg/L	0.003–0.10
Pb	mg/L	0.001–0.022
Se	mg/L	0.001–0.004

6.2.3 Kaolinite and chemicals

Kaolinite (aluminium silicate CAS no. 1302-93-8) used in the study was obtained from Sigma Aldrich (USA). Analar grade nitrate salts of heavy metals (Cu, Zn, Pb, Cd, and Ni, CAS No's 10031-43-3, 10196-18-6, 10099-74-8, 10022-68-1 and 13478-00-7, respectively) were utilised in the study.

6.2.4 Field fixed-bed column experiments

A schematic diagram of the different media filters set-up in the field is shown in Figure 6.1(a). The media used in the experiments conducted in dynamic adsorption conditions were anthracite and GAC. Field experiments were conducted using 10 cm internal diameter PVC columns, one packed with anthracite and two with GAC to a height of 100 cm. As shown in Figure 6.1(a), two filtration set-ups were used: i) an anthracite filter column followed by a GAC column; and ii) a single GAC filter column. The anthracite filter column was used before the GAC filter to test the necessity of pre-treatment at different hydraulic loadings. High SS loading to the GAC filter may hinder its ability to effectively remove other pollutants such as organics from stormwater by clogging its active pores. Anthracite was chosen as a pre-treatment filter material due to cost considerations and its ability to effectively remove suspended solids (Johir et al. 2009; Mohammed et al. 2011; Templeton et al. 2007). The flow rates of stormwater through the columns were 5 m/h, 10 m/h and 11.5 m/h, for 1-2 d, 3-4 d, and 5-6 d, respectively. At these flow rates the empty bed contact times (EBCT) were 12, 6, and 5.2 min, respectively. At the end of each day of operation of 4-6 h filtration, the columns were backwashed with tap water for 1 min and kept in a moist state overnight (18 h) until the filtration experiments re-commenced the following day.

Influent and effluent samples from each column were collected at 5, 10, 15, and 30 min intervals, and afterwards every hour. Turbidity in a portion of each sample was measured using a Hach Model 2100P Turbidimeter. Samples were then filtered through 0.45 µm filter disks and DOC in the filtrate was measured using a Multi N/C 2000 analyzer (Analytik Jena AG).

6.2.5 Laboratory batch experiments

Batch adsorption experiments were conducted under static condition in a closed system to obtain information on the adsorptive properties of each of the heavy metals on GAC. Anthracite was not tested because its properties tend to be inert toward heavy metals compared to GAC (Mohammed et al. 2012). Initial metal concentration used in these experiments was 5 mg/L. Doses of adsorbent ranging from 0.1 to 7.5 g/L served to provide a range (low to high values) of equilibrium concentrations and adsorption capacities of metals. Initial pH was kept at 6.5 ± 0.1 to simulate a pH close to that of natural stormwater (Table 6.2).

In the adsorption experiments, 100 ml metal solutions were mixed with specified adsorbent dose and agitated at 120 rpm in a flat shaker for 24 h at room temperature ($24\pm0.5^{o}C$). The solution ionic strength was kept at 10^{-3} M $NaNO_3$. The suspensions were then filtered using filter disks with 0.45 µm pore opening and heavy metal concentrations in the filtrate were analysed. Heavy metals were measured using an atomic absorption spectrophotometer (AAS) (ContraAA 300). The amount of heavy metal absorption at equilibrium, Q_e (mg/g) was calculated by subtracting the amount of metals in the solution at equilibrium from the amount of metals added using the equation 3 at section 5.2.5. The efficiency in removing heavy metals was calculated using the following formula:

$$Removal\ Efficiency(\%) = \frac{(C_o - C_e)}{C_o} \qquad \text{Eq (11)}$$

The experiments were repeated for multi-metals adsorption in order to determine the effect of co-existing heavy metal ions on each metal being removed. The concentrations of Zn, Cd, Ni, Pb, and Cu were 10.0, 0.2, 0.3, 5.0, 3.0 mg/L, respectively. The heavy metal concentrations used were approximately ten times the maximum concentrations reported for Australian stormwater (Wong et al. 2000). Doses of adsorbent used varied from 0.5 to 10 g/L.

6.2.6 Laboratory fixed-bed column experiments

A schematic diagram of the GAC filtration unit set-up in the laboratory is shown in Figure 6.1(b). Initially, the GAC was packed into a 2-cm internal diameter transparent acrylic fibre column to 90 cm height (100 g of GAC) and deionised water was passed upwards through the column for 5 min to expel air within the pores of the particles. Filtration experiments were then conducted using synthetic stormwater at a filtration velocity of 5 m/h in the gravity flow mode using two peristaltic pumps; one before the water enters to the column and the other when the water leaves the column. The empty bed contact time (EBCT) at this filtration velocity was 10.8 min.

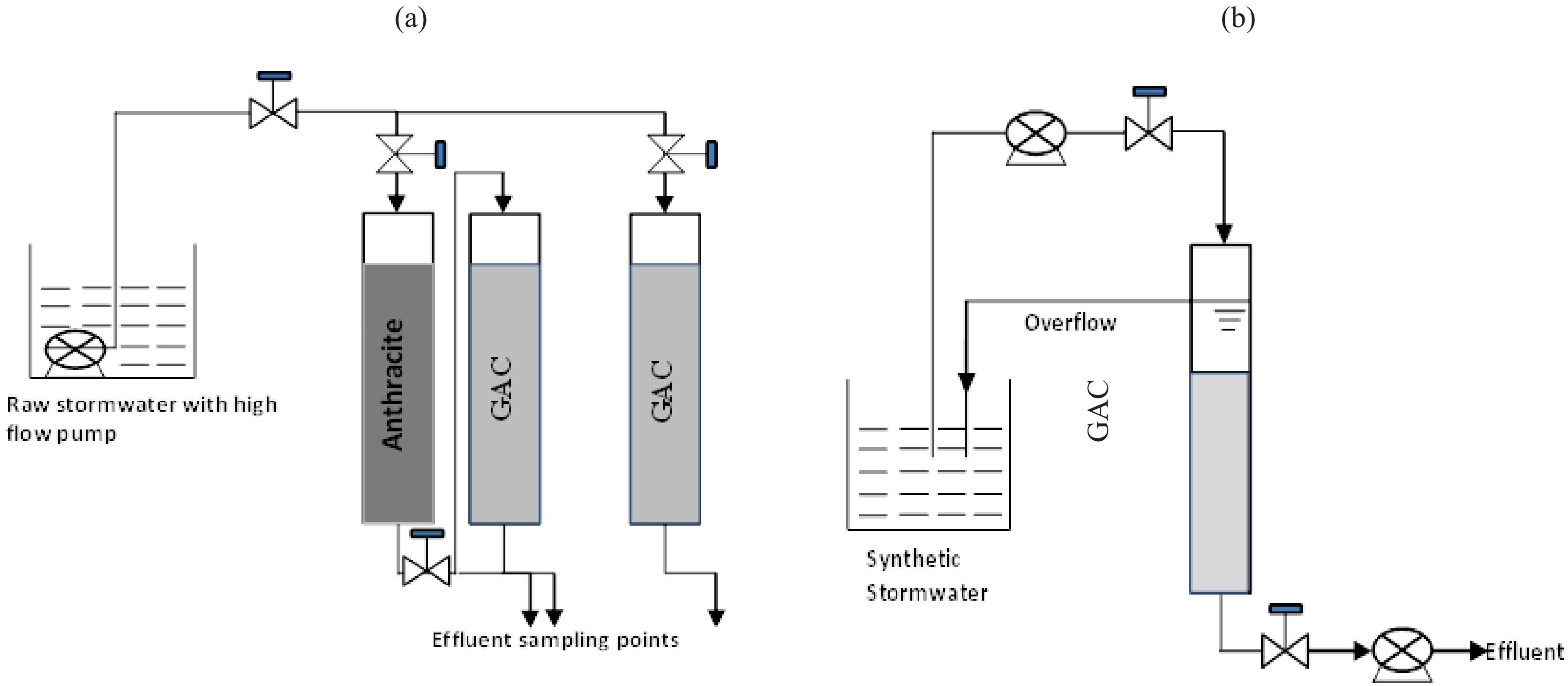


Figure 6.1 Schematic diagrams of GAC filtration set-up used in the (a) field study and (b) laboratory study (diagrams not to scale).

Heavy metal concentrations in the influent natural stormwater were extremely low (Table 6.2) compared to the average concentrations found in stormwater reported across Australia (Wong et al. 2000). Therefore, in the experiments on removing heavy metals with GAC, tap water was spiked with heavy metals to produce the required concentrations of heavy metals. The concentrations of the heavy metals Zn, Cd, Ni, Pb and Cu used in this study were 2.0, 0.04, 0.06, 1.0, 0.6 mg/L, respectively. These concentrations were approximately twice the maximum concentrations reported for Australian stormwaters (Wong et al. 2000). To simulate turbidity in the water, the tap water was also spiked with kaolinite at a concentration of 7 mg/L. This produced a desired turbidity which is an average of the values for the stormwater at Carlton (Table 6.2). The tap water was not spiked with any organics since it already contained a DOC level of 5.1 mg/L which was close to the DOC levels found in the field (Table 6.2). Samples were collected at 10 min and 30 min, thereafter every hour for 8 h and then less frequently for up to 120 h. The effluent samples were analysed for DOC, heavy metals, pH and turbidity.

The cumulative column adsorption capacity, q_{total} (mg), for a given feed concentration and filtration velocity is equal to the area under the plot of the adsorbed metal concentration, C_{ad} ($C_{ad} = C_o - C_e$) (mg/L) with time (t, min). It was calculated from the breakthrough curves according to equation (5) where Q is the flow rate of the solution (L/min):

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=120\,h} C_{ad}\, dt \qquad \text{Eq (12)}$$

6.3 Results and discussion

6.3.1 Zeta potential of GAC

Zeta potentials of GAC were +18.0, +13.2, +7.8, -11.6, -16.9, and -28.9 mV at the final suspension pHs of 3.12, 3.57, 4.80, 6.24, 6.64, and 8.00, respectively. Therefore the zero point of charge (ZPC, pH at which zeta potential is zero) of GAC tested was 4.8-6.2. This agrees with the ZPC values of 5.4 and 5.5 reported by Sepúlveda et al. (2014) and Wei et al. (2012) for GAC, respectively. At pH less than the ZPC, GAC carries a net positive surface charge and at pH above the ZPC, it carries predominantly negative charges. Therefore, in our experiments, GAC had more negative charges at the pH of 6.5 which indicates that GAC had a high affinity for adsorbing heavy metals that are present as cations.

6.3.2 Field fixed-bed column experiments

6.3.2.1 DOC and turbidity removal

Field experiments were conducted in order to test the removal efficiency of DOC and turbidity by GAC filter column operated at different filtration velocities and the possibility of improving the turbidity removal by using a pre-treatment of anthracite filtration before GAC filtration. Figure 6.3 presents the temporal variation of turbidity and DOC removal by GAC filter column operating intermittently in the field over a period of six days. The turbidity and DOC levels of the influent raw stormwater during the experiment varied in the range of 3-343 NTU and 4.3-16.6 mg/L, respectively. The large variation in turbidity and DOC levels is due to the storm events that had occurred in the days prior to the experiment. Regardless of the huge variation in the influent turbidity and DOC of the stormwater, GAC filter and anthracite filter + GAC filter performed well in removing up to 98.5% of turbidity for both filter arrangements and up to 96.0% and 97.5% of turbidity, respectively during the six days of intermittent operation. On average, the single GAC filter and the anthracite filter followed by GAC filter removed 71% and 78% of DOC, respectively, and 65.5% and 75% of turbidity, respectively.

The anthracite filter removed a small fraction of DOC (7%) but 67% of turbidity when it operated in a series as a pre-treatment strategy before GAC. The DOC and turbidity of the effluent from the GAC filter were 0.2-3.9 mg/L, and 1.9-13.0 NTU, respectively. The corresponding values for the effluent from the anthracite filter followed by GAC filter were 0.3-3.5 mg/L and, 1.0-8.0 NTU, respectively. This demonstrates that a single GAC filter and anthracite followed by GAC filter effectively removed turbidity and DOC. Adding a pre-treatment of an anthracite filter significantly reduced turbidity and the suspended solids loading to the subsequent GAC column. A negligible improvement was observed in the removal of DOC by anthracite pre-treatment because of the inert adsorption properties of anthracite compared to GAC. Kus et al. (2012) also discovered that on average, an anthracite column with the same column height of 100 cm and filtration rate of 10 m/h could remove only 11% of total organic carbon (TOC) from an influent TOC concentration of 3.9-9.7 mg/L during 3 days of filtration. However, for an influent turbidity of 14.5-48.5 NTU, the average effluent turbidity was 8 NTU. The pre-treatment with anthracite could provide a screening barrier to the GAC filter column, so clogging of GAC can be reduced to improve the performance of the GAC filter.

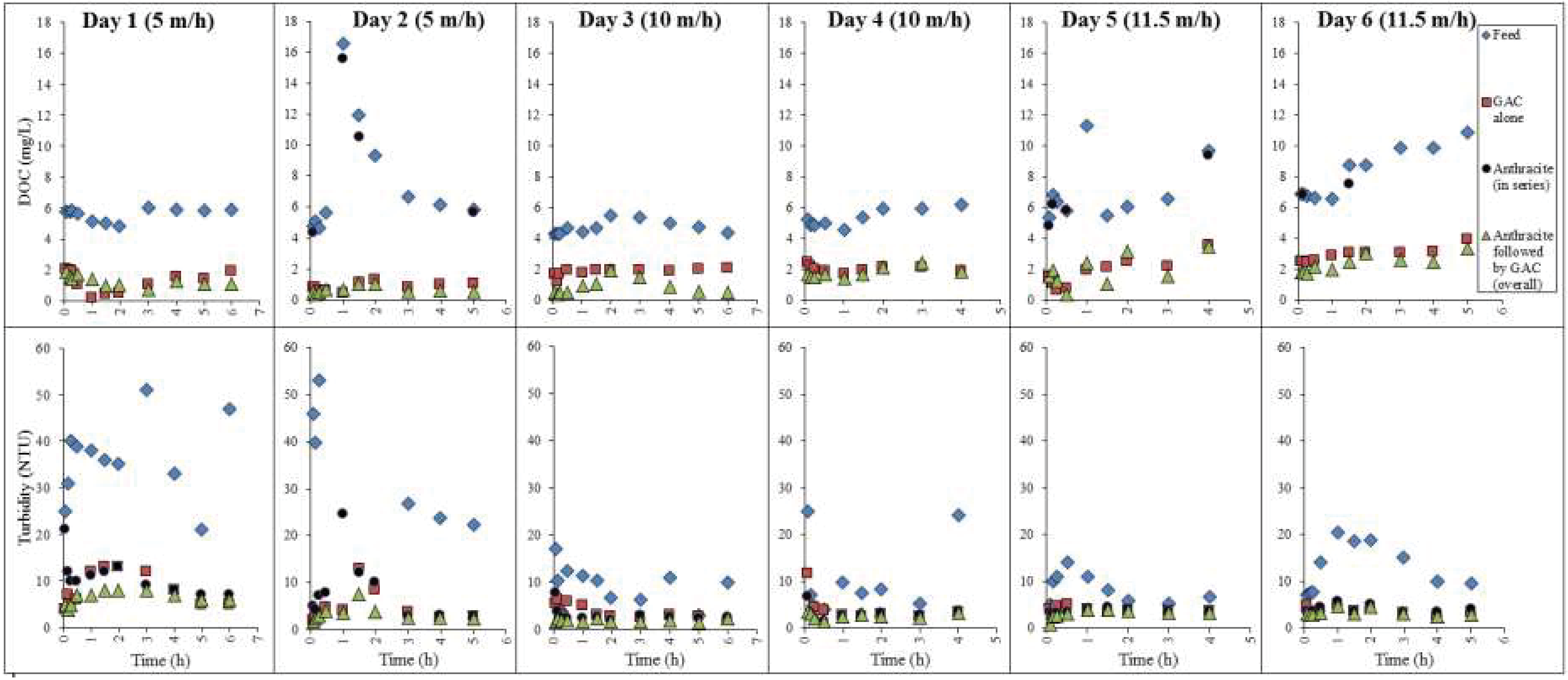


Figure 6.2 (a) DOC and (b) turbidity removals from stormwater by GAC, and anthracite + GAC columns at velocities of 5, 10, and 11.5 m/h for days 1-2, 3-4, and 5-6, respectively in the field (column height 1 m).

Table 6.3 DOC and turbidity levels in influent and effluent water (based on 9-11 samples taken daily for 6 consecutive days)

Treatment Chain	**DOC (mg/L)**		**Turbidity (NTU)**	
	Influent[1]	**Effluent**[1]	**Influent**[1]	**Effluent**[1]
Single GAC filter	6.4 ± 0.3	1.8 ± 0.6	26.1 ± 4.8	4.8 ± 0.4
Anthracite only (in series)	6.4 ± 0.3	6.3 ± 0.5*	26.1 ± 4.8	5.6 ± 0.6
Anthracite + GAC (overall)	6.4 ± 0.3	1.4 ± 0.1	26.1 ± 4.8	3.5 ± 0.2

*Only eight effluent samples were analysed for the removal of DOC by anthracite because the removals in the samples analysed were extremely low.

[1] Mean ± standard error

The mechanism used to remove DOC was mainly adsorption onto surface functional groups of GAC by hydrogen bonding and van der Waals forces (Loganathan et al. 2012). Xing et al. (2008) reported that the removal of DOC by GAC in the early stages was governed by adsorption but once the GAC was saturated with adsorption, after a week, microbes started to develop on the GAC and it functioned as a biofilter. Growth of microbes within 6 days of intermittent usage in the current study is unlikely and therefore the removal of DOC is ascribed mainly to adsorption. GAC's removal of turbidity occurred predominantly through physical retention.

Table 6.4 Effect of flow velocity on DOC and turbidity removals (based on 9-11 samples taken daily for 2 consecutive days for each velocity)

Velocity (m/h)	**Influent DOC (mg/L)**[1]	**Removal efficiency of DOC (%)**		**Influent turbidity (NTU)**[1]	**Removal efficiency of turbidity (%)**	
		GAC[1]	anthracite + GAC[1]		GAC[1]	anthracite + GAC[1]
5	6.6 ± 0.6	82.6 ± 2.1	83.7 ± 1.9	55.2 ± 11.2	83.8 ± 2.3	87.1 ± 1.6
10	5.0 ± 0.1	61.8 ± 1.1	76.0 ± 2.4	9.9 ± 1.5	50.7 ± 7.0	69.5 ± 5.6
11.5	7.6 ± 0.4	68.9 ± 2.3	72.5 ± 2.1	10.9 ± 1.1	58.6 ± 4.3	65.9 ± 3.5

[1] Mean ± standard error

Table 6.4 shows the effect of filtration velocity on the removal of DOC and turbidity using GAC and anthracite + GAC filter columns. At a filtration velocity of 5 m/h, both filtration systems showed higher removal efficiency of DOC and turbidity compared to the 10 and 11.5 m/h filtration velocities. Increases in the filtration velocity reduced the efficiency of the single GAC column system more than that of anthracite and GAC filters in series for the removal of both DOC and turbidity. The anthracite + GAC filter system always performed better in removing DOC and turbidity at all velocities studied. These results indicate that high removal efficiencies can be achieved by single GAC without pre-treatment for lower velocities but at higher velocities pre-treatment is necessary to achieve high efficiency in removing DOC and turbidity.

6.3.3 Laboratory batch experiments

6.3.3.1 Heavy metal adsorption by GAC

a) Individual metals

Figure 6.3 illustrates the removal efficiencies of all metals studied which followed the order of Pb, Cu > Zn > Ni, Cd at pH 6.5. This is the same order as the solubility product constant of metal hydroxide ($M(OH)_2$) precipitate (pK_{sp} of metal hydroxides for Pb, Cu, Zn, Ni, and Cd are 19.9, 19.3, 16.5, 15.2, and 14.4, respectively (Rao 2011; Walker et al. 2012)). It is also in the reverse order as the first hydrolysis constant of the metals (MOH^+ formation) (pK_1 of metal hydroxyl complexes for Pb, Cu, Zn, Ni, and Cd are 7.7, 7.9, 9.0, 9.9, and 10.1, respectively (Malandrino et al. 2006; Pagnanelli et al. 2003; Pohlmeier 2004)). The higher the pK_{sp} value the greater the metal's tendency to precipitate as the metal hydroxide, while a lower pK_1 value reveals that the metal produces a soluble metal hydroxyl complex more easily. The higher adsorption capacity of the metals with a high pK_{sp} values is due to these metals forming surface precipitation on the adsorbent (Loganathan et al. 2013a). Surface precipitation can occur at pHs lower than those at which precipitation occurs in solution because the adsorbent provides a nucleus to induce precipitation. Metal hydroxyl complexes have higher affinity for adsorption than divalent metal ions. Therefore metals which readily form hydroxyl complexes (lower pK_1 values, e.g. Cu and Pb) had higher adsorption capacities. Similar results were obtained in Chapter 4 and pK_1 of metals hydrolysis and pKs of metal hydroxide precipitate were used to explain the results.

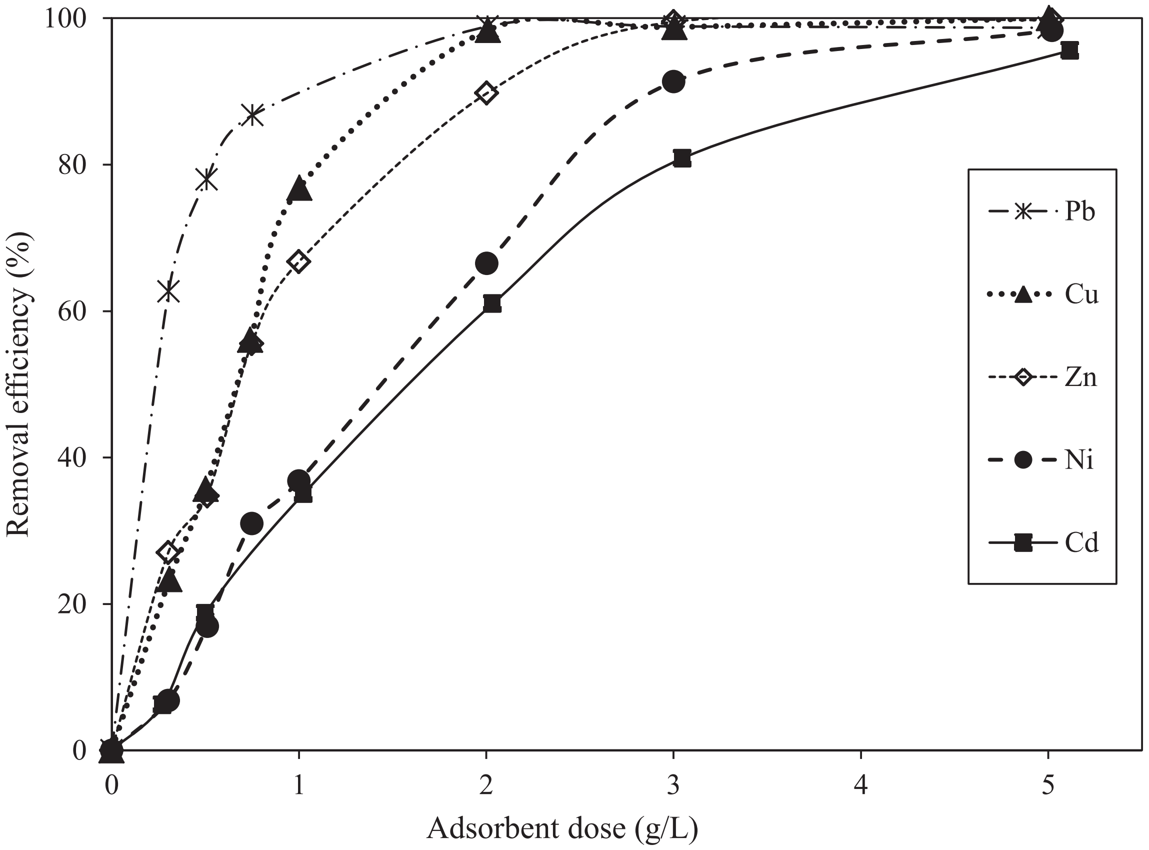


Figure 6.3 Removal efficiencies of single metals adsorption on GAC at pH 6.5 in laboratory batch experiments (initial metal concentration 5 mg/L, adsorbent doses 0.1-7.5 g/L, 24 h shaking).

b) Mixed metals

Figure 6.4 shows the removal efficiencies of mixed metals at various concentrations. The heavy metals used in this study were Zn, Cd, Ni, Pb and Cu and their concentrations were 10.0, 0.2, 0.3, 5.0, 3.0 mg/L, respectively. This initial concentration of metals followed an order of Zn > Pb > Cu > Ni > Cd but the removal efficiencies of metals followed the order of Pb, Cu > Zn > Ni, Cd. The latter order is similar to single metal adsorption despite the huge differences in the initial concentrations. This may be because the adsorption of metals is more governed by mechanisms of adsorption discussed earlier than the initial concentrations in the mixture that were used (Pagnanelli et al. 2003).

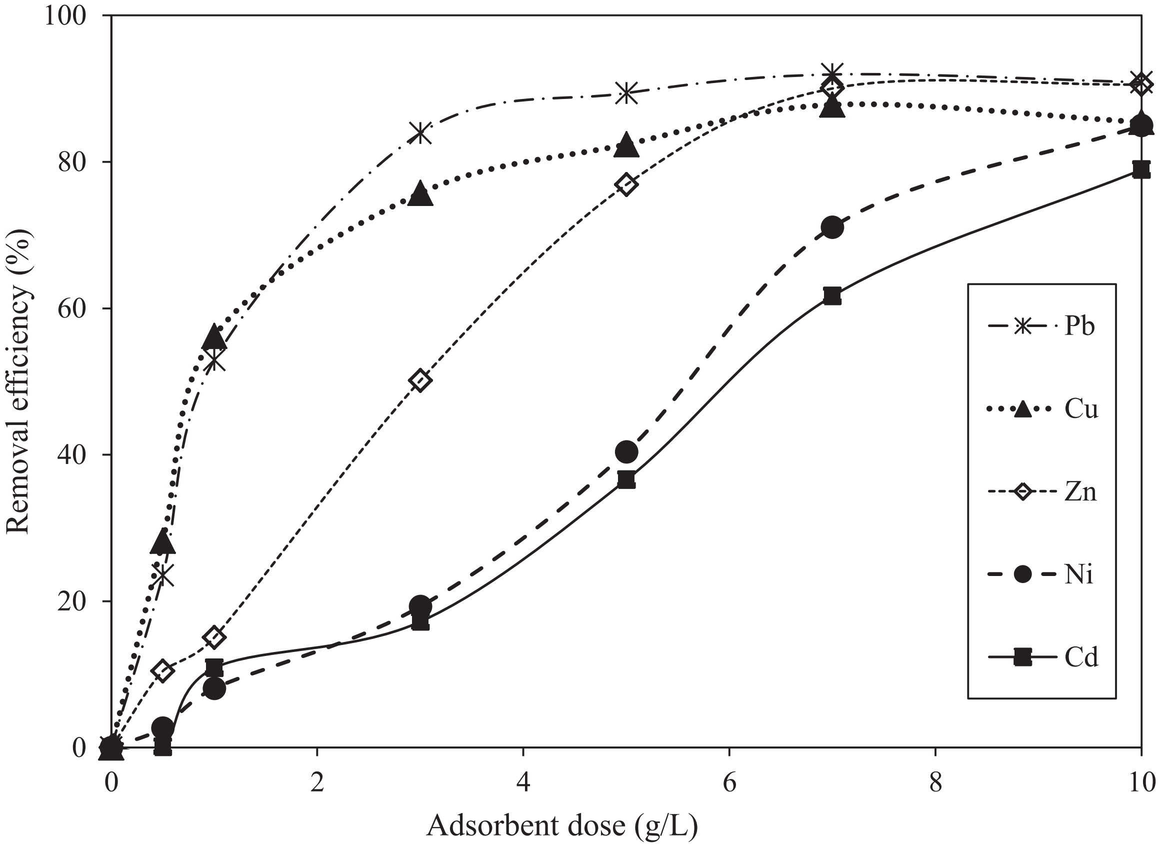


Figure 6.4 Removal efficiencies of mixed metals on GAC at pH 6.5 in laboratory batch experiments (initial metal concentrations (mg/L): Zn 10.0, Cd 0.2, Ni 0.3, Pb 5.0, and Cu 3.0, adsorbent doses 0.5-10 g/L, 24 h shaking).

6.3.4 Laboratory fixed-bed column experiments

6.3.4.1 Heavy metal removal

Column breakthrough curves for all metals tested are presented in Figure 6.5. The breakthrough for Cu was achieved after 24 h (133 BV) but the exhaustion point did not occur until 120 h (666 BV). For Pb, no clear breakthrough occurred in the 120 h of filter operation. However, for Cd, Zn and Ni a breakthrough commenced as early as 8 h (45

BV) and exhaustion was nearly completed for Ni, Cd within 24 h (133 BV) of operation. Zn breakthrough was nearly completed after 120 h. These results agree with those of others reported in literature for other adsorbents and to the results achieved in Chapter 4 section 4.3.3. In Chapter 4, the results of experiments showed that Cd, Zn and Ni adsorption breakthrough commenced at 50 BV and was nearly completed when 130 BV was reached which are very much comparable to the values of 45 BV and 133 BV achieved in this section. Apiratikul and Pavasant (2008) reported that the breakthrough time of metals at pH 5 in dried green algae fixed-bed columns was longest for Pb followed by Cu and Cd. They also stated that the average adsorption capacity calculated from the breakthrough curves followed the order of Pb > Cu > Cd. Similarly, Jeon et al. (2012) reported that the time taken for the effluent concentration of metals to reach the influent concentrations ($C_e/C_o = 1$) was longer for Cu than Cd when the metal solutions at pH 3 were passed through zeolite and iron oxide coated zeolite columns. During the entire experiment, no Pb was detected in the effluent of any of the columns.

The steepness of the breakthrough curves followed an order of Pb, Cu > Zn > Ni, Cd in GAC columns which is similar to that of single metal and mixed metals batch adsorption results. The cumulative removal of heavy metals and the cumulative percentage of metals removed after 120 h (666 BV) of operation also followed the same order. Pagnanelli et al. (2003) cited many references in the literature for the adsorption of heavy metals on several inorganic and organic adsorbents in both batch and column studies where the order of adsorption was similar to the currect study. In addition to the reasons given for this trend earlier, when discussing the batch studies, such as solubility products of metal hydroxide precipitate and hydrolysis constants of the metals, the differences in concentration of metals in the influent solution can also explain the adsorption differences between metals. Cd and Ni adsorption was low compared to the other metals considered in the column study because: firstly, these metals had relatively low concentrations of these metals in the influent water; and secondly, the low adsorption capacities of these metals on GAC as found in single metal batch adsorption results.

6.3.4.2 Turbidity and DOC removal

Figure 6.6 shows the influent and effluent values of DOC and turbidity of laboratory GAC column using synthetic stormwater. Influent DOC and turbidity levels were 5.1 mg/L and 15.4 NTU, respectively, and the corresponding effluent values were 0-0.3 mg/L DOC and 1.6-4.5 NTU turbidity for 120 h of continuous operation. On average, GAC removed 98% of DOC and 80% of turbidity from the stormwater at a filtration velocity of 5 m/h which is comparable to the results obtained in the field. In the field 83% of DOC and 84 % of turbidity were removed by GAC columns of approximately the same height at the same filtration velocity. The mechanism for removing turbidity involves physical screening, whereas that for DOC removal is mainly through chemical adsorption which is governed by H-bonding and Van der Waals forces as explained earlier in the paper.

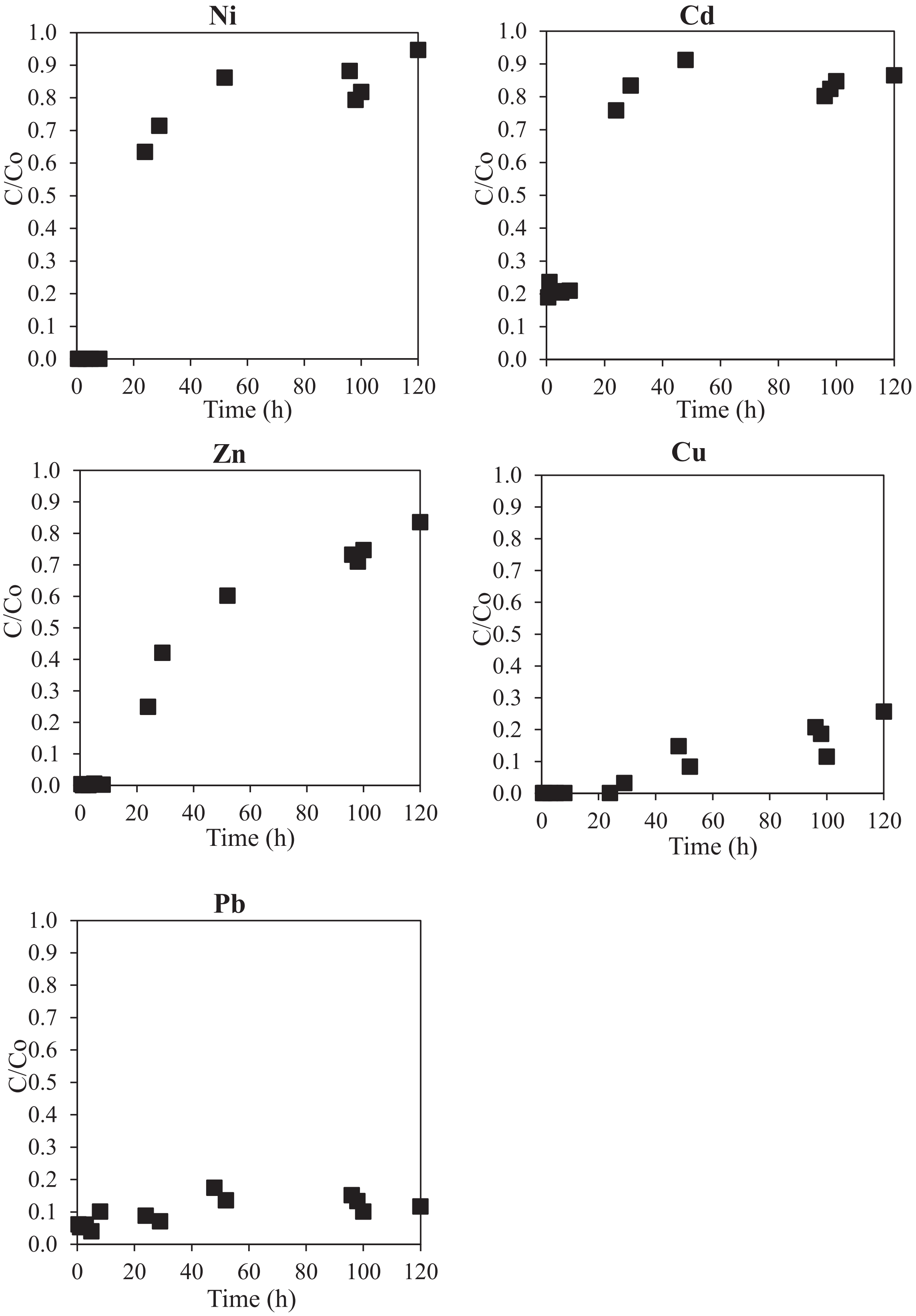


Figure 6.5 Breakthrough plots of (a) Ni, (b) Cd, (c) Zn, (d) Cu and (e) Pb in GAC column in the laboratory for mixed metals (column height 0.9 m, filtration velocity 5 m/h, influent pH 6.9-7.2, initial metal concentrations (mg/L): Zn 2.0, Cd 0.04, Ni 0.06,

Pb 1.0, and Cu 0.6).

Table 6.5 Percentage* of cumulative removals of heavy metals by GAC after 120 h (666 BV) at pH 6.9-7.2 (Influent concentrations (mg/L): Zn 1.99, Cu 0.87, Cd 0.06, Ni 0.08, Pb 0.90)

	Units	**Ni**	**Cd**	**Zn**	**Cu**	**Pb**
Total metals added	mg	15	12	388	168	174
Metals removed by GAC, q_{total}	mg	3	2	147	143	151
Metals removed by GAC*	(%)	20	21	38	85	87

*Percentage of cumulative metal removal = (cumulative metal added – cumulative metal in effluent) / cumulative metal added

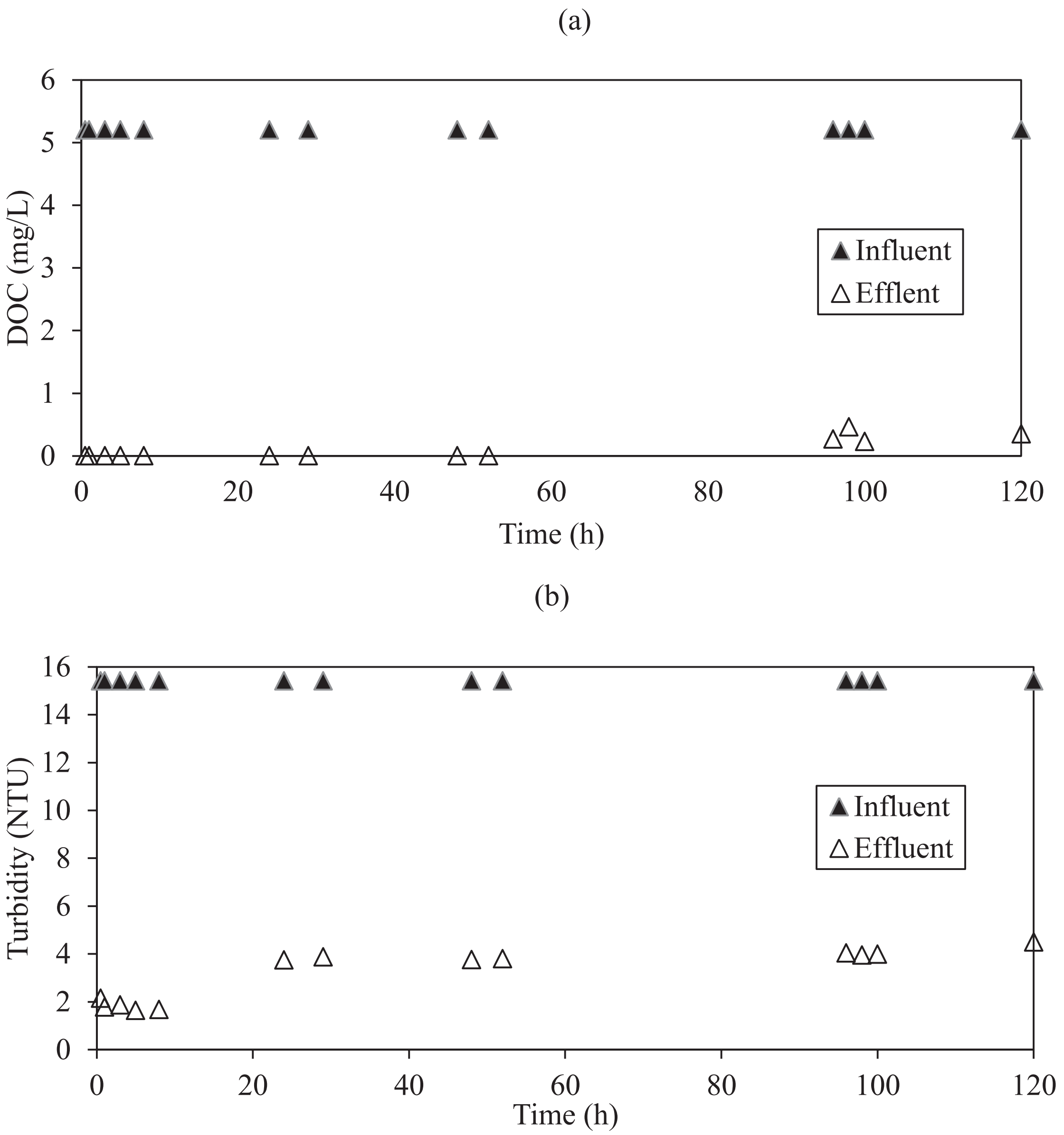


Figure 6.6 Influent and effluent values of (a) DOC and (b) turbidity in GAC column in the laboratory using synthetic stormwater (column height 0.9 m, filtration velocity 5 m/h, influent pH 6.9-7.2).

6.4 Feasibility study and optimum conditions

The batch and column studies showed that pollutants from urban stormwater such as DOC, turbidity and heavy metals can be effectively removed by single 100 cm height GAC column at a filtration velocity of 5 m/h. At the higher filtration velocities of 10 and 11.5 m/h, DOC and turbidity removal efficiencies fell, but a pre-treatment column with anthracite before GAC treatment improved the performance of the GAC column system. Depending on the levels of pollutants at the specific site, suitable operational conditions may change. Therefore, a series of experiments similar to the current study need to be conducted at different concentrations of pollutants, filtration velocities and column height to determine the optimum conditions for various scenarios. There is no single optimum condition for the operation because it will vary depending on the water pollutants and column characteristics.

6.5 Conclusions

A GAC fixed-bed filter column and a series of anthracite filter followed by GAC filter effectively removed DOC and turbidity from stormwater. A single GAC filter column operating at a lower filtration velocity of 5 m/h was able to remove most of the DOC and turbidity. At higher filtration velocities of 10 m/h and 11.5 m/h, an additional pre-treatment of anthracite filter to the GAC filter enhanced the overall effectiveness. At natural pHs of stormwater (6.9-7.2), the GAC filter column showed high absorptive removal for Pb, and Cu. GAC adsorption of Zn, Cd and Ni over 120 h of continuous operation at a filtration velocity of 5 m/h was moderate. Batch adsorption of single and mixed metals had the same removal order as in column studies. The removal of metals followed the order of Pb, Cu > Zn > Ni, Cd which can be explained by the solubility product and first hydrolysis constants of these metal hydroxides.

CHAPTER 7

University of Technology, Sydney

HEAVY METALS REMOVAL BY A PERMEABLE PAVEMENT WITH ZEOLITE OR BASALT BEDDING MATERIAL AND A NANO TITANATE FILTER

The major part of chapter is submitted to Sounthararajah D.P., Kandasamy J., Loganathan P. and Vigneswaran S. (2015c). Heavy metals removal by a permeable pavement with zeolite or basalt bedding material and a nano titanate filter. ***Journal of Hazardous materials*****, Submitted.**

7 Heavy metals removal by a permeable pavement with zeolite or basalt bedding material and a nano titanate filter

7.1 Introduction

Frequent droughts, growing populations, urbanisation and concerns about climate change have forced many communities to find alternative ways to conserve, harvest and treat sources of water supply and effectively manage them. Unlike impervious pavements, permeable pavement systems (PPS) incorporate a reservoir in the voids of porous materials and offer the possibility of a decentralised source control measure that can reduce pollutant loads and stormwater flows (Brattebo and Booth 2003; Dierkes et al. 2002). It can be a useful treatment measure in sustainable stormwater management. Runoff from urban streets and parking areas can infiltrate through PPS to support groundwater recharge, recycle water use and reduce hydraulic stress in receiving water bodies. To date, utilising PPS has been somewhat limited because of concerns about pollutants migrating into groundwater due to the ineffective treatment of these pollutants by the PPS (Scholz and Grabowiecki 2007). Urban stormwater carries many pollutants broadly classified as heavy metals, hydrocarbons and nutrients that can endanger soil and environment (Scholz and Grabowiecki 2007). Of these, heavy metals are growing in concern because of their acute toxicity and long-term accumulation and persistence.

PPS have not always been efficient in completely trapping dissolved heavy metals in surface runoff over an extended period of time. Many studies have provided a ‘snapshot’ performance of heavy metals removal by PPS while focusing more on hydraulic aspects of the water (Ahiablame et al. 2012; Dietz 2007; Imran et al. 2013).

For example, Beecham et al. (2012) tested the water quality of effluents from PPS made up of 20-mm gravel sub-base that was 280 mm height, in four different locations in Adelaide, South Australia. They found that 7-99% Cu, 60-86% Pb and 12-48% Cd were removed from stormwater. They also found that in laboratory experiments conducted using similarly arranged PPS using field stormwater with higher metals concentrations, the removal efficiency was 2.9%, 9.4%, 38.9%, and 18.2% for Cu, Pb, Zn, and Ni, respectively. Pagotto et al. (2000) investigated a porous asphalt PPS performance in a French highway and found that 20% Cu, 59% Zn, 62% Cd and 74% Pb were removed from stormwater. Dierkes et al. (2002) tested the performance of four different sub-base materials, specifically, limestone, basalt, sandstone, and gravel in laboratory experiments and found that these materials removed 89-98% Pb, 74-98% Cd, 89-96% Cu, and 72-97% Zn, respectively, from synthetic stormwater. However, these studies used low rainfall intensities and deep sub-base material (390 mm) which are not common in typical PPS installations. Myers et al. (2011) also conducted laboratory studies on PPS with very deep (380 mm) base materials, namely quartzite and dolomite. They concluded that 99% Zn, 99% Pb, 94-97% Cu were removed from synthetic stormwater after 144 h of retention in the base course. However, during the initial stages (1 h residence time) smaller percentages of metals (i.e. 61-62% Zn, 34-35% Pb, and 29-37% Cu) were removed.

The degree of heavy metals removed from stormwater depends on the type and amount of bedding materials used in PPS, influent metal concentrations and infiltration rate. Pavements with large amounts of conventional adsorbents/bedding materials are not efficient and practical due to their cost considerations and practical difficulties in their installation. Recently, several adsorbents having very high adsorption capacities such as carbon nanotubes (Hua et al. 2012; Rao et al. 2007; Wang et al. 2013a; chapter

5) ion exchange resins (Demirbas et al. 2005; Pehlivan and Altun 2007), titanium nano materials (Lv et al. 2004) have been developed and tested for their heavy metals removal in batch and column studies but their application in PPS has not been investigated.

The objective of this study was to evaluate the long-term effectiveness of two pilot scale PPS that used coarse natural Australian zeolite as bedding material in one PPS and basalt in the other PPS to remove five heavy metals. A second experiment incorporated a post-treatment of a filter containing a nano-fibrous sodium titanate material material used in the study reported in Chapter 5 into the PPS with zeolite bed material.

7.2 Materials and methods

7.2.1 Materials

Basalt and natural zeolite were used as bedding material in the PPS. Basalt was selected because it has a demonstrated ability to remove heavy metals (Dierkes et al. 2002) and and is used commercially in PPS (HydroCon 2015). Dierkes et al. (2002) tested four different sub-base materials, namely limestone, basalt, sandstone, and gravel and found that basalt removed the largest amounts of Pb, Cd, Cu and Zn from synthetic solutions. Basalt used in the study was supplied by HydroCon Australasia Pty Ltd. Zeolite used in the study is a locally available low cost material which exhibits a good adsorption capacity towards heavy metals (Nguyen et al. 2015; Wang and Peng 2010). The zeolite was sourced from a natural deposit at Werris Creek, New South Wales and supplied by Zeolite Australia Pty Ltd., Australia.

The sodium form of titanate nano fibrous (TNF) material used in the study reported in Chapter 5 was selected for use in the PPS, because of the very high adsorption capacities of this material towards heavy metals. Analar Grade nitrate salts of heavy metals (Cu, Zn, Pb, Cd and Ni) were used in the study to prepare the heavy metals solution. These salts were obtained from Sigma Aldrich (USA).

7.2.2 Materials characteristics

The BET surface area and total pore volume of TNF were 58.6 m^2/g and 0.142 cm^3/g, respectively. The surface area (BET) of zeolite was 15.4 g/m^2 (Nguyen et al. 2015). This shows TNF has higher surface area to adsorb more metals on the surface than zeolite. The zero point of charge (ZPC, the pH at which the net surface charge is zero) of TNF and zeolite were 3.2 (Chapter 5) and 2.2 (Nguyen et al. 2015), respectively, suggesting that at the pH of most stormwaters (which is 6-7) the net surface charge on these materials is negative and favourable for adsorption of positively charged metals. The zeta potential values of TNF and zeolite were -35 and -17 mv at pH 6.5, respectively. This also shows that TNF potentially has a higher affinity for adsorbing heavy metals than zeolite at pH 6.5.

7.2.3 Batch experiments

Laboratory batch experiments were done to understand the basalt and zeolite bed and TNF filter materials' efficiency in removing heavy metals. The batch experiment data was used to obtain these materials' batch adsorption isotherm. In these experiments, Milli Q water was spiked with a mixture of heavy metals (Ni, Cd, Zn, Cu, and Pb) at a concentration of 10 mg/L each, and shaken with different doses of zeolite, basalt or TNF in 100 ml solutions. The suspensions were agitated at 120 rpm for 24 h at room temperature (24±1^{o}C) and at pH 6.5. The background ionic strength was kept at 10^{-3} M $NaNO_3$. The suspensions were filtered using filter disks with 1.2 μm openings and heavy metal concentrations in the filtrate were analysed using a Microwave Plasma-Atomic Emission Spectrometer (Agilent 4100 *MP-AES).* The amount of heavy metal adsorption at equilibrium, Q_e (mg/g), was calculated using equation 3 in section 5.2.5.

7.2.4 Pilot-scale experiments

Two PPS were constructed side by side with perspex, each with a dimension of 0.4 m length x 0.195 m width x 0.8 m height (Figure 7.1). One PPS had basalt as the bedding material and the other had zeolite as the bedding material. Each PPS was made by packing 12.7 kg of 7 mm size crushed stones as base course at the bottom of the container to a height of 200 mm. Above this layer, a basalt bedding layer of 4.5 kg (2-3 mm nominal size) was placed to a height of 30 mm in one PPS and a zeolite bedding layer of 2.4 kg (2-3 mm nominal size) in the other PPS. Geofabrics were omitted in the PPS unlike some previous studies (Beecham et al. 2012; Pezzaniti et al. 2009) because recent concerns have emerged about installation problems and the creation of a potential slip plane when geofabrics were laid below the bedding materials (Mullaney and Lucke 2014). Pervious HydroSTON 80 pavers (210 mm x 140 mm x 80 mm (height) nominal size) were placed over the bedding layers. These pavers are being used in car parks, parking bays, driveways, laneways, and residential and low traffic volume roads (HydroCon 2015). All the materials were washed with clean water to remove any adhering dusts and silts before being used in the experiments. Outlets were placed at the bottom of the PPS to collect water samples.

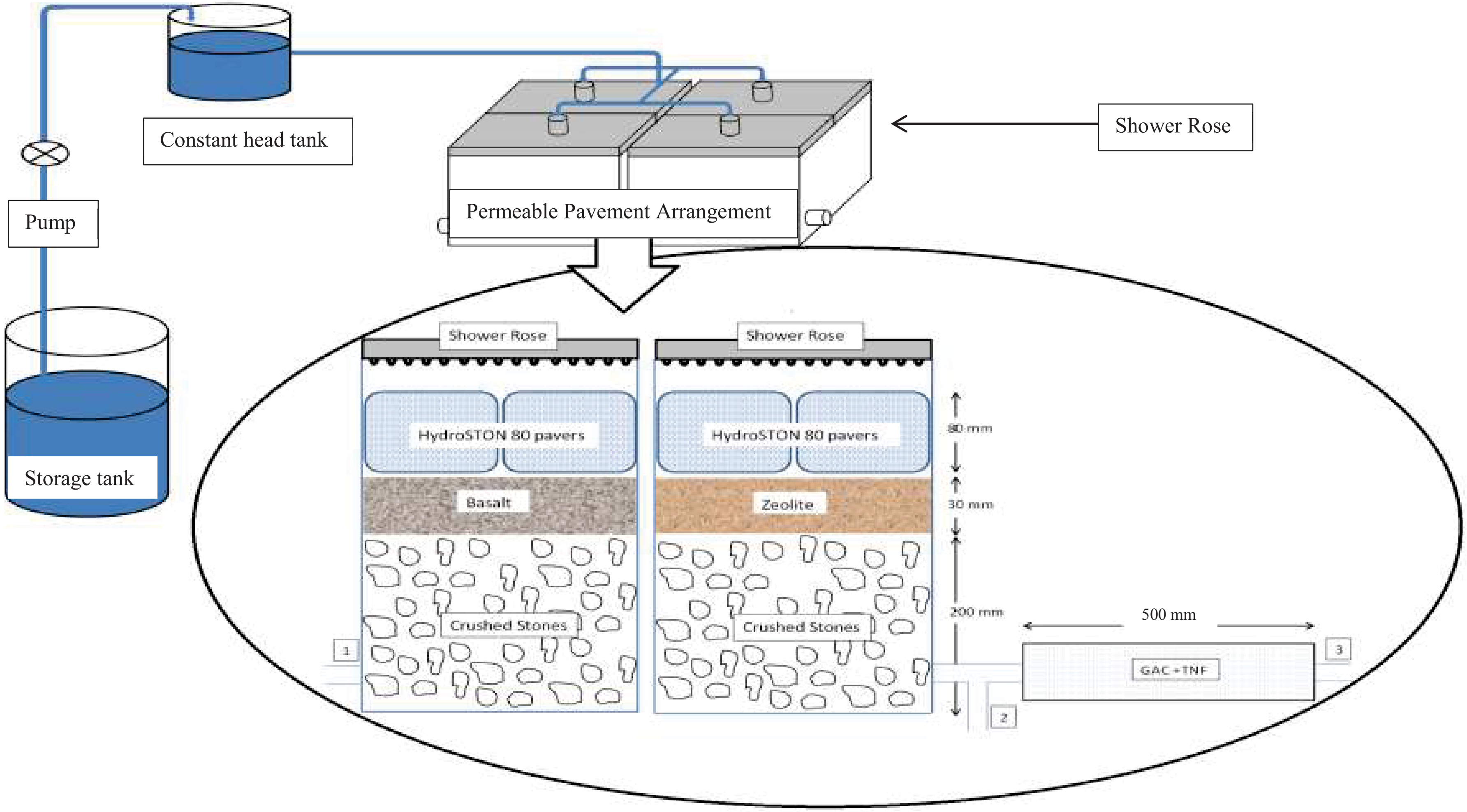


Figure 7.1 Permeable pavement bedding and sub-base arrangement used in the laboratory experiment (not to scale). Sampling points are marked 1, 2, and 3.

The outlet from the PPS containing the zeolite bedding layer was connected to a horizontal filter column (50 mm internal diameter) filled with TNF mixed with granular activated carbon (GAC) to further remove the heavy metals. Using TNF alone as the filter media to remove heavy metals from stormwater is not practical because of its poor hydraulic conductivity. Therefore a mixture of TNF (75-150 µm) and GAC (0.3-0.6 mm), a material commonly used in fixed-bed filter columns to remove pollutants, at a weight ratio of 25:1 (GAC: TNF) was used as done in the study reported in Chapter 5. The horizontal filter column had 480 g GAC + 20 g TNF which was packed into polyvinyl chloride (PVC) column to a 500 mm length and sealed at both ends with inlet and outlet openings. Before commencing the experiments, tap water was passed through the column in a horizontal flow mode at a velocity of 6.4 m/h for 4.7 min to expel trapped air and any impurities in the column. A peristaltic pump was connected to the column's outlet to drain the water at a flow rate of 6.4 m/h, which proved to be adequate in removing the filtered water from the system without emptying the voids in the PPS bed layers. The empty bed contact time (EBCT) at this filtration velocity was 10 min. Samples of filtered water were collected at frequent intervals (hourly).

To ensure a consistent water quality throughout the experiments, tap water was spiked with different concentrations of heavy metals (Ni, Cd, Zn, Cu and Pb) and pH adjusted to 6.5. The concentrations of Ni, Cd, Zn, Cu and Pb were 0.06, 0.04, 2.0, 0.6, 1.0 mg/L, respectively, and they are approximately twice the maximum concentrations reported for Australian stormwater (Wong et al. 2000). Concentrations of heavy metals higher than those normally observed in stormwater were used to simulate the high concentrations of metals normally observed in the first flush of stormwater after long dry periods (Aryal and Lee 2009) and in industrial spills in stormwater. The pH 6.5 was chosen as the pH of stormwater in field is generally 6 to 7.

A uniform distribution of rainfall was simulated using square shower roses connected to a constant head tank suspended 1.5 m above the pavement system (Figure 7.1). The total volume of water that passed through the PPS during one experiment was equivalent to the total rainfall that occurred during an accelerated time scale of 10 years in Sydney, Australia. In the experiments, the rainfall simulation over the PPS incorporated intermittent dry periods. The average annual rainfall in Sydney is approximately 1300 mm/year (Whetton 2011). The tests were carried out with continuous rain at an intensity of 163 mm/h lasting 8 h each day for 10 days. The rate of stormwater inflow to each PPS was 212 ml/min (0.195 m x 0.4 m surface area x 0.163 m/h rain intensity x 10^6 cm^3/m^3/ 60 min/h). This is equivalent to 13,000 mm (1300 mm x 10 years) of total rainfall over 10 days.

Samples were collected every two hours when rain was applied for the entire 10-day period from three outlets, the zeolite compartment outlet, basalt compartment outlet and horizontal column outlet (sampling points 1, 2, 3 in Figure 7.1). Collected samples were acidified before filtration and the filtrates were analysed for heavy metals.

7.3 Results and Discussions

7.3.1 Batch adsorption of metals

The batch adsorption data (Figure 7.2) were analysed using Langmuir and Freundlich models.

The Langmuir adsorption model is described by equation (1, 2) in section 4.3.2.

Plots of C_e/Q_e vs C_e for the adsorption data indicated significant linear relationships for all metals on these adsorbents (Table 7.1, R^2 = 0.7711-0.9975), demonstrating that the adsorption data fitted satisfactorily to the Langmuir adsorption model. This suggests that the adsorption sites on these adsorbents were homogeneous with monolayer adsorption coverage.

The Freundlich adsorption model is described by equation (5, 6) in section 5.3.2.3.

Plots of ln Q_e vs ln c_e for the adsorption data indicated significant linear relationships for all metals only for zeolite and basalt (Table 7.1, R^2 = 0.7775-0.9873), demonstrating that the adsorption data fitted satisfactorily to this model. However, the model fit to data was generally better with Langmuir model than the Freundlich model, especially for basalt. The data fit to Freundlich model for TNF was poor for Ni, Cd, and Zn.

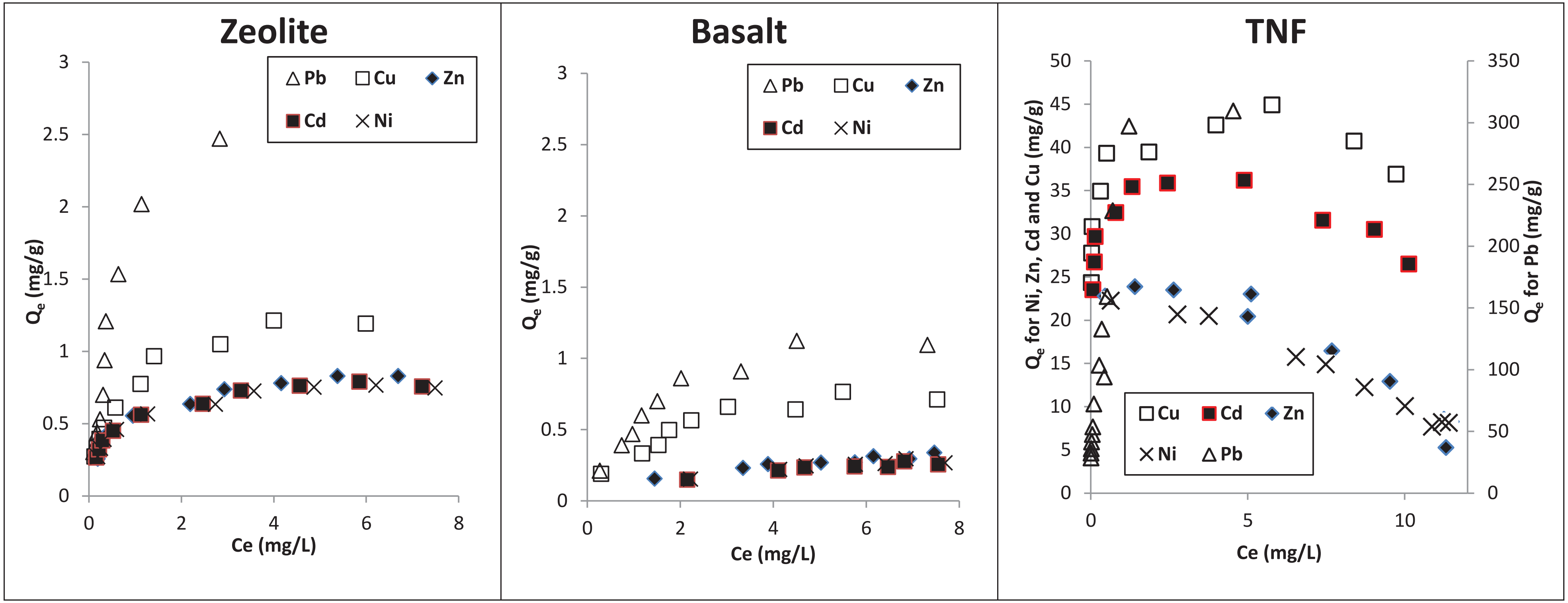


Figure 7.2 Adsorption isotherms of mixed metals at pH 6.5 and an ionic strength of 10^{-3} M $NaNO_3$ for basalt, zeolite and TNF (Note that the scale of y-axis of TNF is very different from those of others).

The Langmuir adsorption maxima calculated from the slopes of the linear plots of Ce/Qe vs Ce for the mix of metals followed the order of Pb > Cu > Zn, Cd, Ni for all three adsorbents (Table 7.1, Figure 7.2). The adsorption capacities of the three adsorbents followed the order of TNF >> zeolite > basalt. This indicates that TNF is a much better adsorbent than the other two and zeolite is slightly better than basalt.

The reason for Pb and Cu having higher adsorption capacities than the other metals can be explained by: firstly, the first hydrolysis constant of the metals (MOH^+ formation where M represents metal); and secondly, the solubility product of the metal hydroxides. Of all the metals, Pb has the lowest first hydrolysis constant followed by Cu. $Pb(OH)_2$ has the highest solubility product followed by $Cu(OH)_2$ (Barnum 1983; Walker et al. 2012) . The lower the first hydrolysis constant, the greater the proportion of MOH^+ which has stronger adsorption affinity than M^{2+} among the various metal species in solution. High solubility product favours precipitation of metals, especially on the surface of adsorbents which can occur at a pH lower than the pH of precipitation in solutions (Loganathan et al. 2012). Nguyen et al. (2015) also found that the order of adsorption capacity of heavy metals onto natural Australian zeolite in single metal and mixed metals systems at pH 6.5 was highest for Pb followed by Cu while the capacities for Cd and Zn were the lowest.

Table 7.1 Langmuir and Freundlich models parameters for heavy metals adsorption on basalt, zeolite and TNF from mixed metal solutions (pH 6.5, ionic strength 10^{-3} M $NaNO_3$) and coefficients of determination (R^2).

Material	Metals	**Langmuir**			**Freundlich**		
		q_{max} (mg/g)	**R^2**	**K_L** (L/mg)	**K_F** (mg/g) $(L/mg)^{1/n}$	n	**R^2**
Basalt	Ni	0.35	0.8991	0.4	2.56	9.8	0.9387
	Cd	0.33	0.9121	0.3	2.18	11.4	0.7775
	Zn	0.45	0.9555	0.3	2.19	12.6	0.7858
	Cu	0.88	0.9698	0.7	2.50	5.3	0.9145
	Pb	1.37	0.9821	0.6	2.59	3.3	0.9514
Zeolite	Ni	0.80	0.9975	2.4	1.74	1.8	0.9873
	Cd	0.81	0.9969	2.5	1.68	1.9	0.9833
	Zn	0.88	0.9960	2.0	1.71	1.9	0.9856
	Cu	1.32	0.9957	1.7	2.20	1.3	0.9819
	Pb	3.55	0.9280	0.9	5.88	0.6	0.9598
TNF	Ni	7.5	0.8991	0.5	25.1	-2.6	0.6759
	Cd	29.0	0.9838	4.4	30.3	26.9	0.2378
	Zn	7.0	0.7717	0.5	25.7	-2.7	0.5113
	Cu	39.0	0.9916	15.1	36.7	13.7	0.7963
	Pb	333.5	0.9529	2.7	195.6	2.3	0.9498

7.3.2 PPS removal of metals

Figure 7.3 shows the breakthrough curves over 80 h for all metals studied. The results indicated that the cumulative removal of heavy metals by zeolite (43-74%) is slightly higher than that of basalt (38-67%) (Table 7.2). This is expected as the Langmuir adsorption capacity of zeolite is higher (Table 7.1), despite nearly twice the weight of basalt used. However, these degrees of removal are not sufficient because the concentrations of metals in the effluent were still high enough to impact adversely on the aquatic organisms/plants/humans that use this water (ANZECC and ARMCANZ 2000). The addition of a post-treatment of horizontal filter column filled with TNF removed more of the metals (76-99%). The increased removal of the metals caused by TNF with <1% of the weight of zeolite and basalt is remarkable. This is due to the very high adsorption capacity of TNF (Langmuir adsorption capacities of 7.5, 7.0, 29, 39, and 333.5 mg/g for Ni, Zn, Cd, Cu, and Pb, respectively (Table 7.1) compared to zeolite and basalt). TNF had an adsorption capacity that was 8-100 times higher than zeolite and 15-250 times higher than basalt.

The breakthrough of metals for PPS packed with only basalt occurred faster for all metals and especially for Cd than where PPS contained only zeolite. This is because zeolite has a higher adsorption capacity for metals than basalt (Table 7.1). The PPS (basalt) had a complete breakthrough for only Cd as a result of reaching adsorption saturation. This is because of basalt's low adsorption capacity for Cd and Cd which in turn have the lowest influent concentration of all the metals. When a TNF filter was installed as a post-treatment to the PPS with zeolite bedding course no breakthrough was observed for any of the metals except Ni. This is due to the superior Langmuir adsorption capacity of TNF.

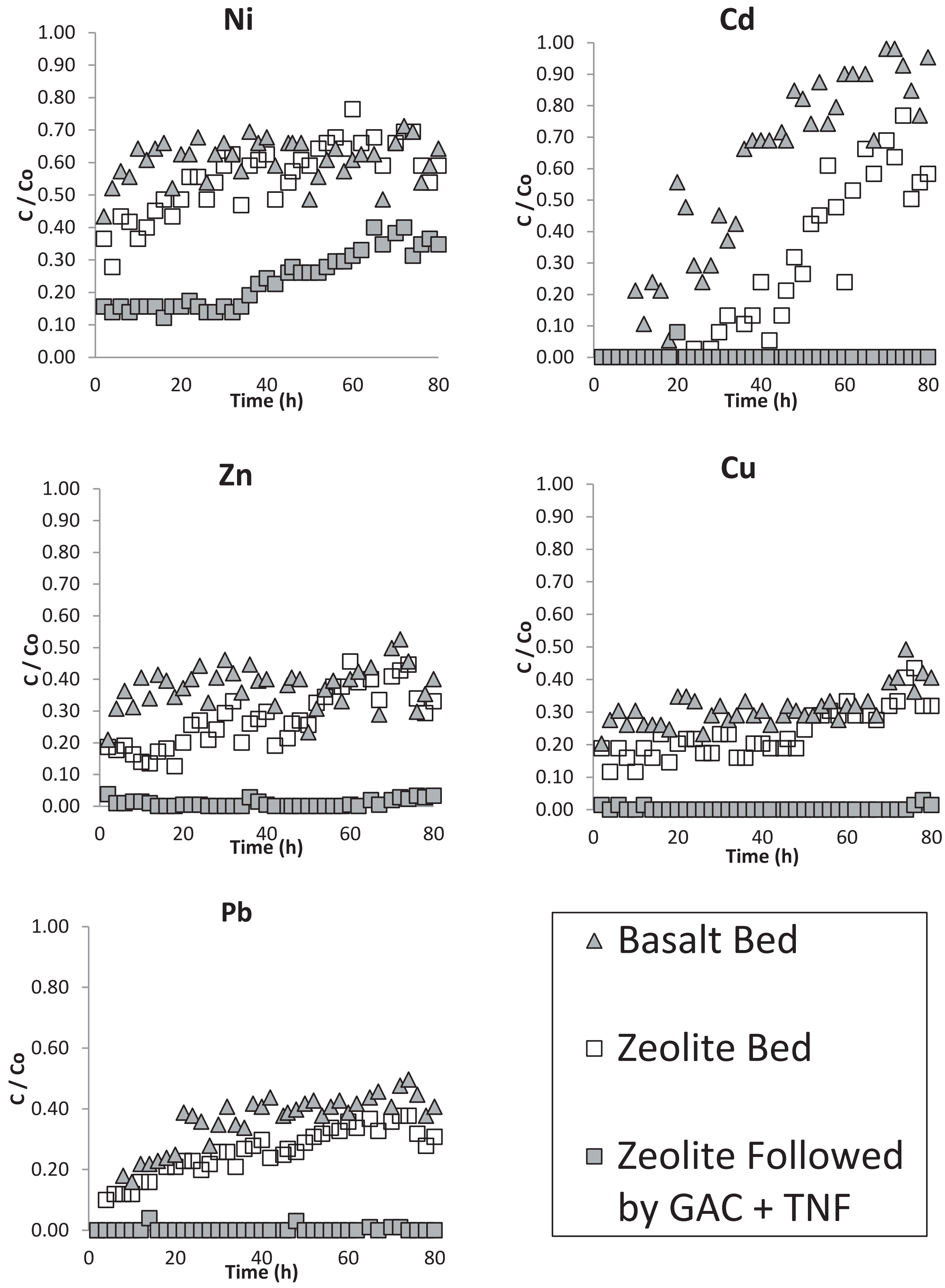


Figure 7.3 Breakthrough plots of Ni, Cd, Zn, Cu, and Pb in basalt, zeolite and zeolite followed by GAC + TNF. Influent concentrations (C_o) of Ni, Cd, Zn, Cu, and Pb were 0.06, 0.04, 2, 0.6 and 1 mg/L, respectively; C represents effluent concentrations (mg/L).

Table 7.2 Cumulative adsorption of heavy metals (q_{total})

PPS media	**Units**	**Ni**	**Cd**	**Zn**	**Cu**	**Pb**
Measured influent concentration	mg/L	0.06	0.04	2.15	0.69	1.01
Total added	mg	57.5	37.7	2147	690	1007
Basalt bed, q_{total}	mg	21.6	15.4	1343	461	617
Zeolite bed, q_{total}	mg	24.6	27.3	1564	512	721
Zeolite bed followed by GAC + TNF, q_{total}	mg	42.6	36.7	2125	671	880
Basalt bed [a]	(%)	37.6	40.8	62.5	66.8	61.3
Zeolite bed [a]	(%)	42.7	72.3	72.8	74.3	71.6
Zeolite bed followed by GAC + TNF [a]	(%)	76.6	99.8	99.1	99.8	99.8

[a] percentage of cumulative metal adsorption = (cumulative metal added – cumulative metal in effluent) / cumulative metal added

Table 7.3 Average effluent metals concentrations[a] (mg/L) and their trigger values[b] (mg/L)

	Ni	**Cd**	**Zn**	**Cu**	**Pb**
Basalt Bed [a]	0.035	0.021	0.812	0.215	0.366
Zeolite Bed [a]	0.032	0.009	0.592	0.163	0.263
Zeolite bed followed by GAC + TNF [a]	0.014	0.000	0.019	0.002	0.003
ANZECC(2000) freshwater [b]	0.013	0.0004	0.015	0.0018	0.0056
ANZECC(2000) marine [b]	0.200	0.0140	0.023	0.0030	0.0066

[a] Average concentration of metals during 80 h of operation

[b] ANZECC (2000) trigger values for 90% protection of species

ANZECC trigger values for freshwater and marine water estuaries were used to indicate whether the heavy metal concentration in the effluent of the PPS could be safely discharged to natural water bodies (ANZECC and ARMCANZ 2000). The results of the study reveal that PPS with zeolite and with basalt bedding layers were not able to reduce heavy metal concentrations to below trigger values for fresh water or marine water. The PPS with zeolite bedding layer followed by post-treatment of GAC + TNF filter reduced the heavy metal concentrations to levels below the trigger values of marine waters (Table 7.3). It could just meet the requirements of fresh water. Of the metals, despite Ni and Zn demonstrating the poorest removal efficiency in the combined PPS and TNF filter system, their trigger values are relatively high and therefore do not require high removal efficiency to satisfy their trigger values.

7.4 Conclusions

The study showed that using zeolite or basalt as bedding layer in a PPS did not remove sufficient levels of Cd, Cu, Ni, Pb, and Zn from a synthetic stormwater (pH 6.5) that passed through the PPS over 80 h. In this time, the total volume of synthetic stormwater that passed through the PPS was equivalent to 10 years of simulated rainfall over Sydney, Australia. The concentrations of metals in the effluent did not satisfy the water quality standards of fresh and marine waters. However, incorporating a post-treatment of a horizontal filter column containing TNF (< 1% of zeolite weight) mixed with GAC removed 77% Ni and 99-100% of all the other metals and satisfactorily met the required metals standards of marine waters and just met those concerning fresh waters. These results were explained by how well the metals adsorb onto the two different PPS bedding layers and onto the TNF. The concentration differences of the metals in the influent water also contributed to the metals' adsorption efficiencies. The Langmuir adsorption capacities for the metals followed the order: TNF >> zeolite > basalt; Pb > Cu > Cd, Ni, Zn.

CHAPTER 8

UTS

University of Technology, Sydney

CONCLUSIONS AND RECOMMENDATIONS

8 Conclusions and Recommendations

8.1 Conclusions

The first objective of this research was to provide a complete water demand analysis in Sydney in a large scale together with socio-demographic information. This will provide valuable information for future demand management strategies. This research also examined the possible ways of recycle stormwater in a cost effective way to reduce the scarcity of water in dry periods. The second objective was to investigate reduction in the pollutant loads in stormwater by adsorptive removal of the pollutants.

8.1.1 Water demand

Water consumption data is highly variable across households due to the behaviour changes, climate, socio-demographics, household size, family composition, water appliances, cultural and personal practises, etc. (Juárez-Nájera et al. 2010; Loh and Coghlan 2003; Russell and Fielding 2010). End-use data in combination with such socio-demographic information can facilitate the identification of correlations between water behaviours and key demographical subsets within a population (e.g. income, age, gender and family composition) (Beal et al. 2013). A comprehensive demand analysis of end-users in Sydney has not been studied previously. It is important to know the effect of different water demand management techniques in large scale, interpreted together with socio-demographic information. This will provide valuable information for future water demand management strategies.

Water consumption pattern in the Sydney metropolitan area and surrounding areas that are connected to Sydney Water Corporation (SWC) potable water supply mains were analysed. This was based on the metered potable water usage of all single dwelling residential properties between 2002 and 2009. Additionally this thesis compared the potable water consumption in residential properties within the greater Sydney metropolitan area against the residential properties that installed a rainwater tank and received a rebate from SWC The SWC data showed that the average annual water consumption per household in Sydney metropolitan areas during the study period (2002 to 2009) declined from 282 kL/annum to 200 kL/annum. Even without including the impact of rainwater tanks the average water consumption decreased by 24% over the study period. In many LGAs in Sydney the reduction in water consumption was over 28% and up to 33.5%. These reductions were due to the effective "demand management" techniques such as the Sydney-wide water restrictions and the introduction of water efficient fixtures like taps, dual flush toilets and efficient shower heads. The average percentage of water savings by installing rainwater tanks across all 44 LGAs was a further reduction of 9%. In some LGAs the decline in water consumption due to rainwater tanks was up to 15%. On average, a household could be expected to save around 24 kL of water annually by installing a rainwater tank.

8.1.2 Interactions of pollutions in stormwater

Stormwater carries different types of pollutants such as heavy metals, DOC and turbidity. Of these, heavy metals constitute some of the most dangerous pollutants of water as they are toxic to humans, animals, and aquatic organisms. Adsorptive process is an attractive method of removal of these pollutants. However, there is little data available for the adsorption of one pollutant in the presence of other pollutants. Therefore, the suitability of an adsorbent needs to be studied in solutions containing multi-component pollutants/contaminants. Laboratory experiments were designed to investigate interactions during the removal of organic matter and suspended solids (SS) (a measure of turbidity) on the removal of heavy metals (Cu, Zn, Pb, Cd and Ni) from stormwater using GAC in batch and fixed-bed columns. Fixed-bed column containing GAC effectively removed heavy metals from water. At the normal pH of stormwaters (pH 6.5), removal of heavy metals by GAC column followed the decreasing order of Cu, Pb > Zn > Cd, Ni, which was consistent with the metals' adsorption capacity as assessed by Langmuir adsorption isotherm.

The presence of DOC and turbidity (SS) in stormwater of pH 6.5, as simulated by spiking humic acid (HA) and kaolinite, respectively, had different degrees of influences on the removal of heavy metals. Adding HA reduced the removal efficiency of Cu and Pb very strongly but that of the other metals only marginally. Kaolinite addition had no effect on the removal of Pb and Cu but it reduced the removal of the other metals. Kaolinite and HA together reduced the removal of all metals but the effect was less than the addition of HA alone. Overall, the study demonstrated the strong influence effects of HA and kaolinite on the removal of heavy metals from stormwater, which varied with the type of heavy metals.

8.1.3 Novel adsorbent

Nano size materials are growing in importance in environmental applications due to their high porosity, small size, and active surface, nano-adsorbents not only are capable of sequestering contaminants with varying molecular size, hydrophobicity, and speciation behaviour but also they enable the manufacturing processes as raw materials are utilized efficiently without releasing their toxic payload. A novel sodium titanate nanofibrous material (TNF) was synthesized and tested in batch experiments and mixed with a wood-based GAC in fixed-bed column experiments to determine the adsorptive removal efficiencies of five heavy metals (Cu, Zn, Pb, Cd and Ni) individually and together at different pH.

Batch experiments on heavy metals adsorption on TNF (zero point of charge 3.2) from solutions containing single or mixed metals showed that elevated pH increased the adsorption of Pb, Cd, Cu, Zn and Ni. Adsorption data at pH 4.0, 5.0, 5.5 and 6.5 for the single metal system fitted satisfactorily to the Langmuir isotherm model for Cd, Cu, Zn and Ni. The Langmuir adsorption maxima at pH 6.5, which is the pH of most natural and waste waters, for these metals were 149, 115, 83 and 60 mg/g, respectively. For Pb, because TNF removed all solution Pb above pH 4.0, only the data for pH 4.0 fitted to the Langmuir isotherm model which gave an adsorption maximum of 250 mg/g. For the mixed metal systems, the adsorption of all metals except Pb decreased at high solution concentration, especially for weakly adsorbed Ni and Zn, due to the competition between metals for adsorption. Most waters contaminated from diffuse sources of metals have metal concentrations less than 3 mg/L and therefore their competition for adsorption on TNF is unlikely. The Langmuir adsorption capacities for Cd, Cu, Zn, Ni, and Pb in mixed metals system at pH 6.5 were lower than the respective values in the single metal system. For the repeated use of TNF the adsorbed metals need to be desorbed and TNF regenerated. Desorption using 0.1 M HNO_3 followed by regeneration of the TNF by the addition of 0.1 M NaOH appeared to be an efficient method.

Column experiments on TNF (4%) mixed with GAC (96%) in both single and mixed metal systems showed that the metals removed by adsorption varied widely and up to 80 times greater than in the column with only GAC. Metal breakthrough times decreased in the same order as the adsorption capacities in batch studies. The study showed that TNF can potentially remove a large percentage of heavy metals from polluted water. Because TNF is finer in size, it can be mixed with GAC to provide better hydraulic properties, and at the same time it can effectively remove heavy metals.

8.1.4 Field experiment and pilot scale testing

Stormwater discharge amounts are relatively high and therefore need to be treated at a high-rate. Treatment systems such as fibre filters, deep bed filters and biofilters treat at a high rate and have been used successfully in water and wastewater treatment. Following high rate treatment the stormwater can be stored and distributed to different end-users. This research discusses the efficiency in removing a wide range of pollutants from urban stormwater using GAC and anthracite by fixed-bed field and laboratory column filtration. A GAC fixed-bed filter column and a series of anthracite filter followed by GAC filter effectively removed DOC and turbidity from stormwater. A single GAC filter column operating at a lower filtration velocity of 5 m/h in the laboratory was able to remove most of the DOC and turbidity. At higher filtration velocities of 10 m/h and 11.5 m/h, an additional pre-treatment of anthracite filter to the GAC filter enhanced the overall effectiveness. At natural pHs of stormwater (6.9-7.2), the GAC filter column in the laboratory also showed high absorptive removal for Pb, and Cu. GAC adsorption of Zn, Cd and Ni over 120 h of continuous operation at a filtration velocity of 5 m/h was moderate. The removal of metals followed the order of Pb, Cu > Zn > Ni, Cd which can be explained by the solubility product of these metal hydroxides and first hydrolysis constants of the metals

Pervious pavement system (PPS) is a popular WSUD technology as it allows stormwater runoff to percolate to an underlying reservoir storage or drain into the soil and at the same time will treat the stormwater on-site. However, the use of pervious pavement is somewhat limited because of the concern about the possible migration of pollutants into groundwater due to ineffective treatment of pollutants by pervious pavement. A study was designed to evaluate the long-term effectiveness of five heavy metals removal by a PPS using a coarse natural Australian zeolite or basalt as bedding material and their removal improvement by incorporation of a filter containing TNF below the zeolite bedding layer in a mini-pilot plant scale experiment. The results showed that using zeolite or basalt as bedding layer in a PPS did not remove sufficient levels of Cd, Cu, Ni, Pb, and Zn from a synthetic stormwater (pH 6.5) that passed through the PPS over 80 h. In this time, the total volume of synthetic stormwater that passed through the PPS was equivalent to 10 years of simulated rainfall over Sydney, Australia. The concentrations of metals in the effluent did not satisfy the water quality standards of fresh and marine waters. However, incorporating a post-treatment of a horizontal filter column containing TNF (< 1% of zeolite weight) mixed with GAC removed 77% Ni and 99-100% of all the other metals and satisfactorily met the required metals standards of marine waters and just met those concerning fresh waters. These results were explained by how well the metals adsorb onto the two different PPS bedding layers and onto the TNF. The concentration differences of the metals in the influent water also contributed to the metals' adsorption efficiencies. The Langmuir adsorption capacities for the metals followed the order: TNF >> zeolite > basalt; Pb > Cu > Cd, Ni, Zn.

8.2 Recommendations for future studies

The following recommendations are made for any future study on this important topic:

- The interactions of different pollutants in stormwater on heavy metal removal should be expanded not only to organic matters and suspended solids but also to other pollutants such as nutrients and specialised organics (polycyclic aromatic carbons). The study used fixed concentrations of heavy metals and humic acid. More research is required to investigate the effect of varying concentrations of these pollutants.
- The treatment system developed in this study was focussed mainly on heavy metals. It should be augmented for other types of stormwater pollutants and a detail long term monitoring of water quality is needed for high quality water uses.
- Majority of studies were conducted for short term on synthetic stormwater with limited pollutants. These experiments should to be extended to long term experiments with real stormwaters in the field to further optimise the operating conditions.
- The novel PPS used in the thesis was found to be efficient for heavy metals removal from stormwater. This PPS design can be modified by changing the adsorbents to suit the removal of other pollutants and tested both in laboratory and field.

Appendix

Large size high resolution colour images are provided here.

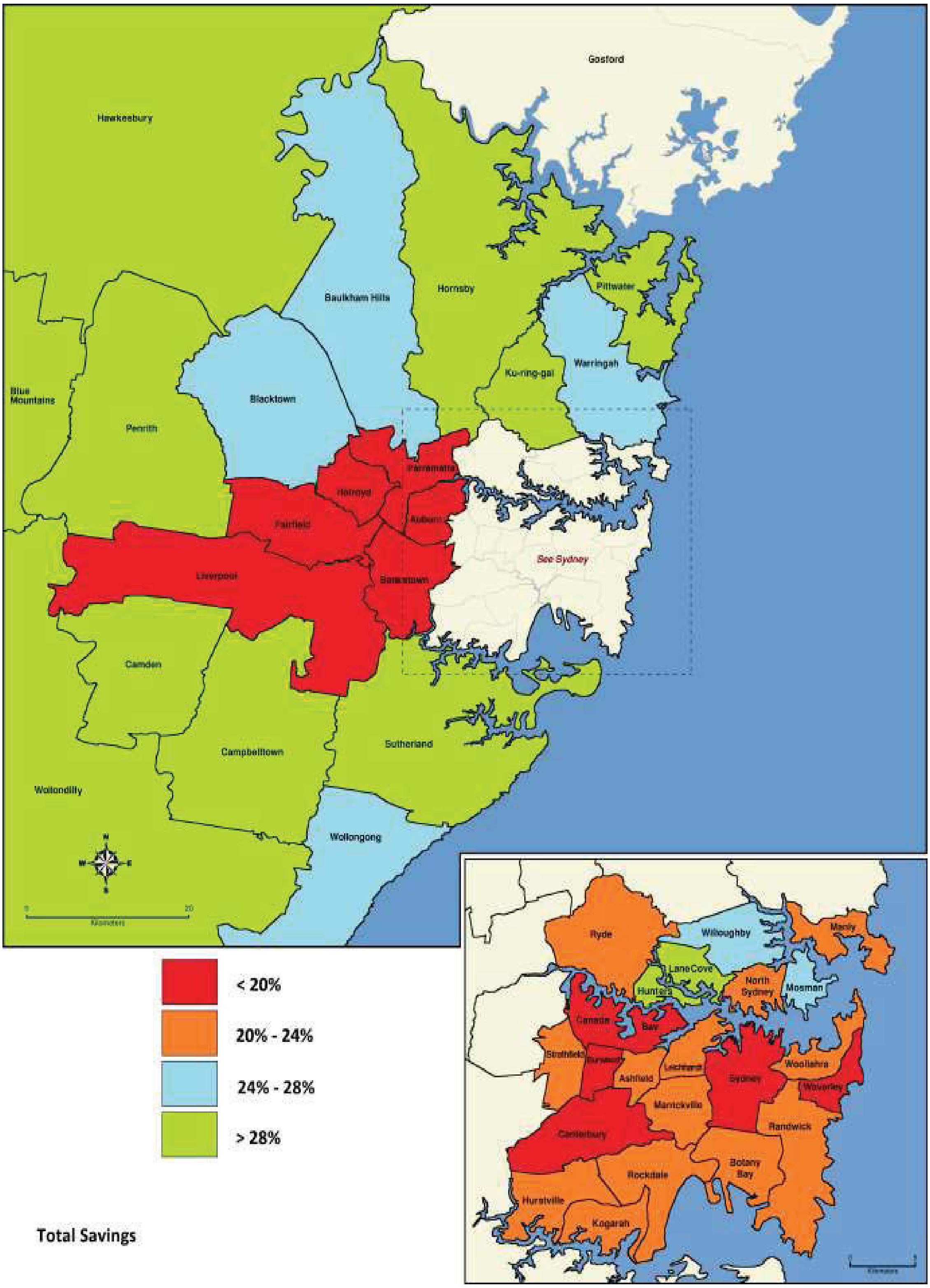


Figure 3.2(a) Reduction of water consumption in each LGA over the study period.

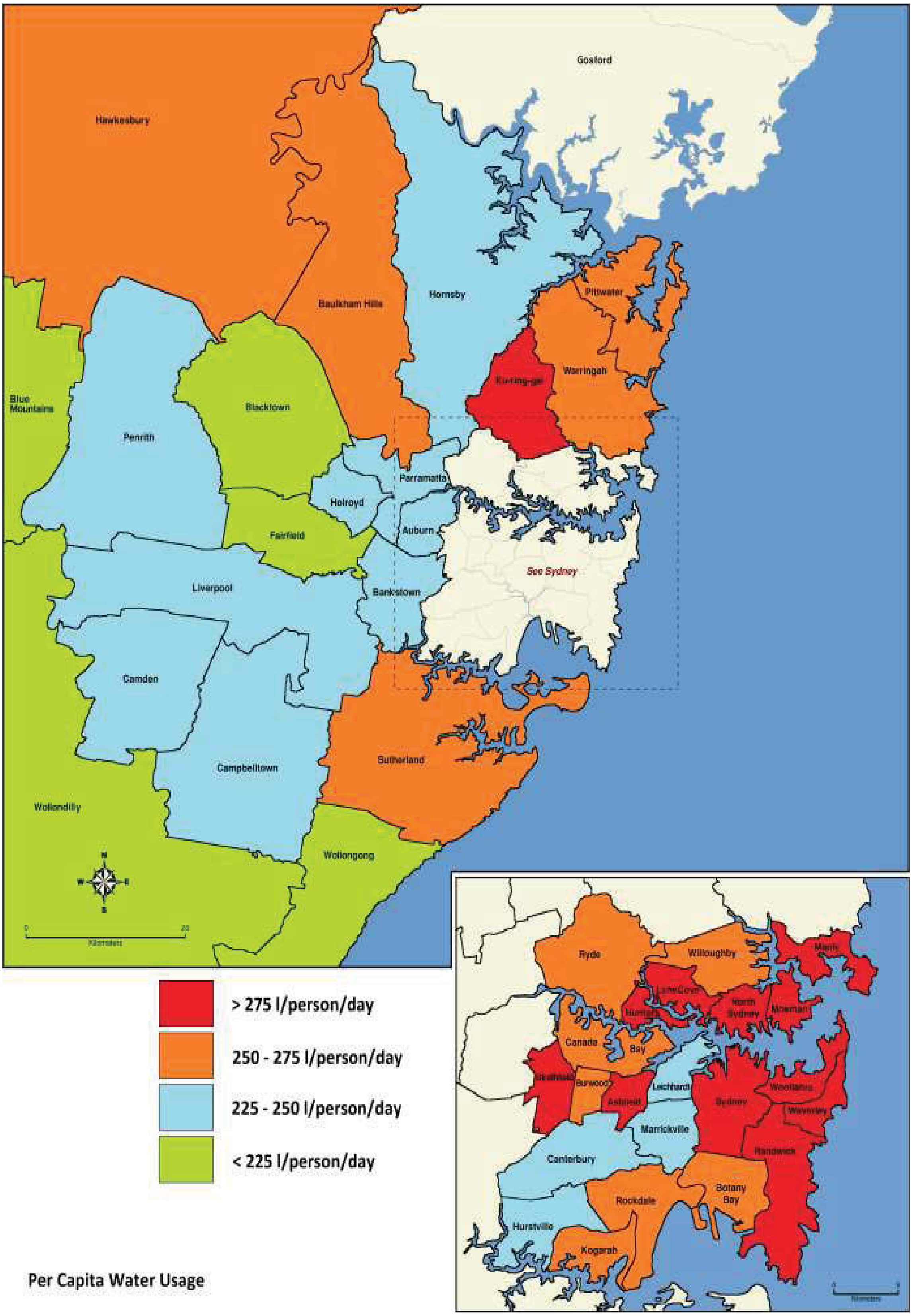


Figure 3.2(b) Average daily per capita water usage.

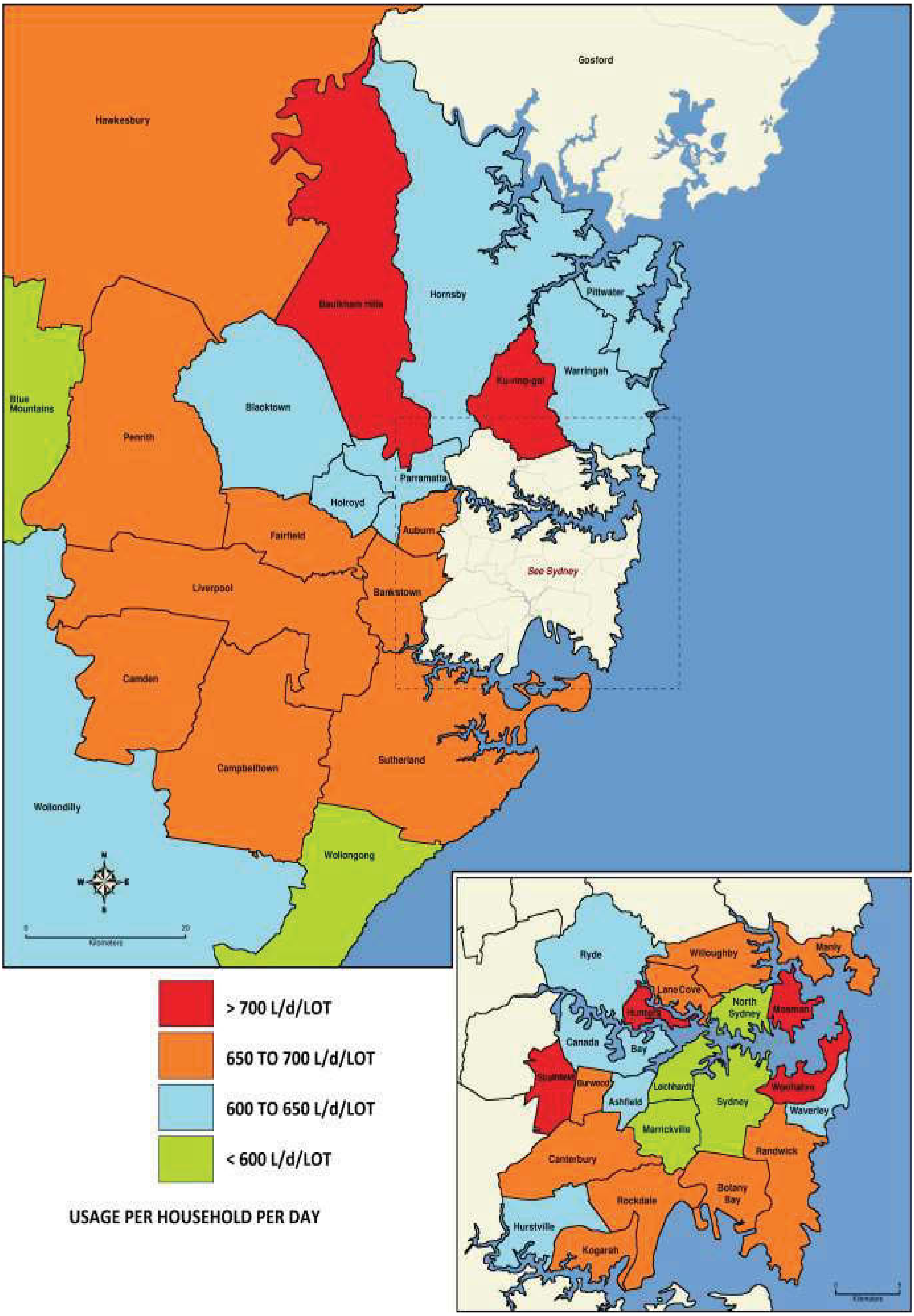


Figure 3.2(c) Average daily household water usage.

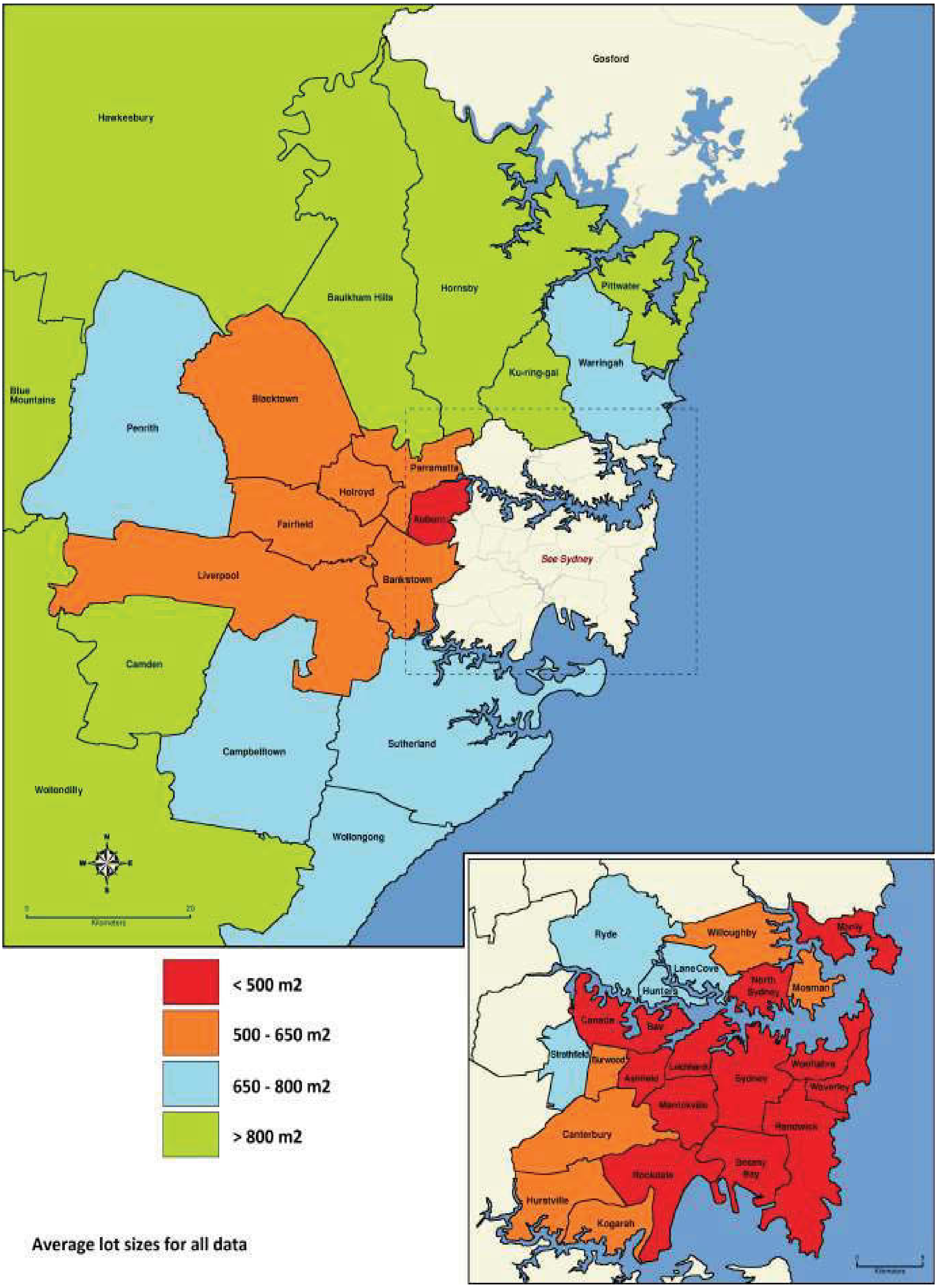


Figure 3.3(a) Average lot sizes

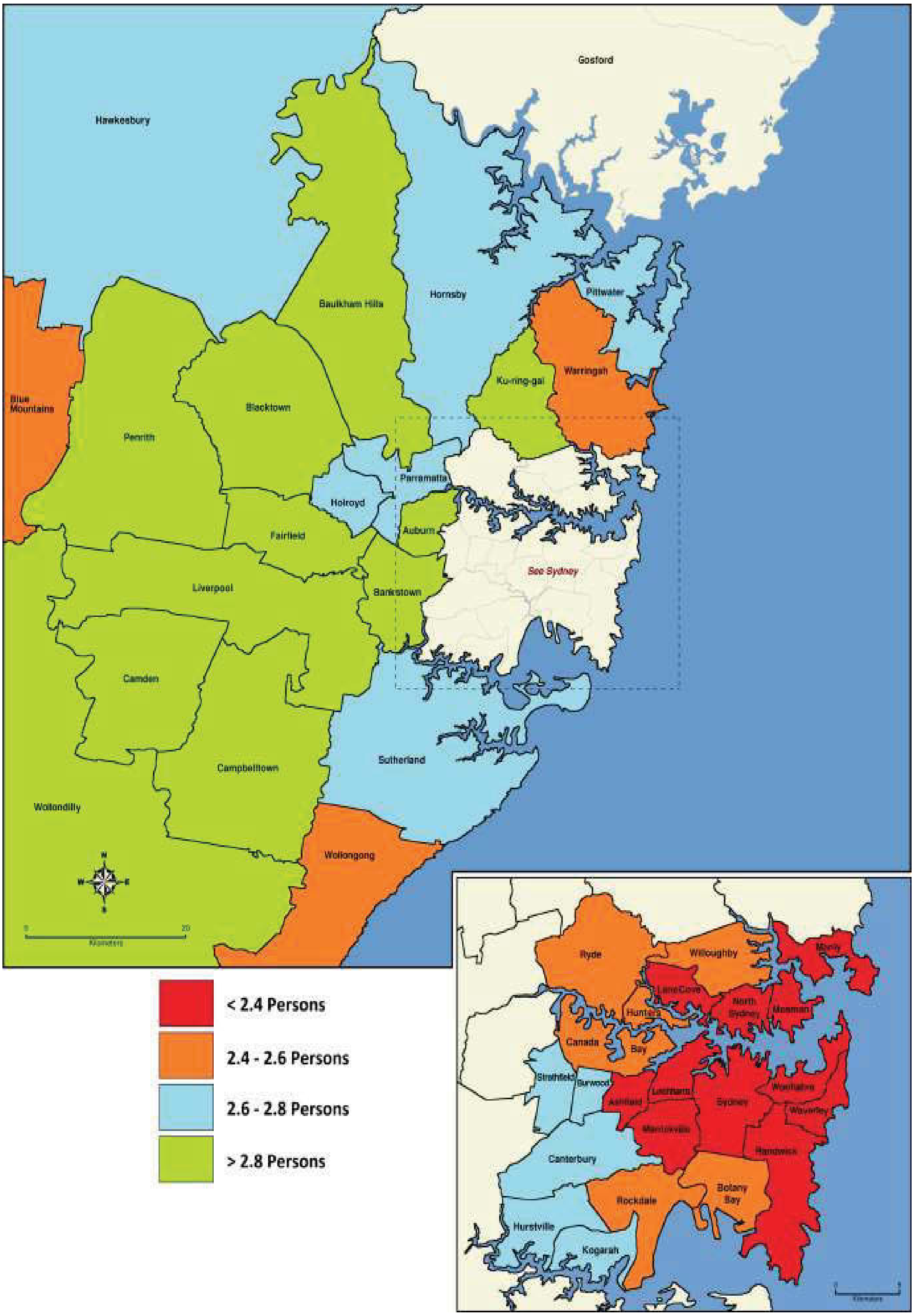


Figure 3.3(b) Average number of persons per household

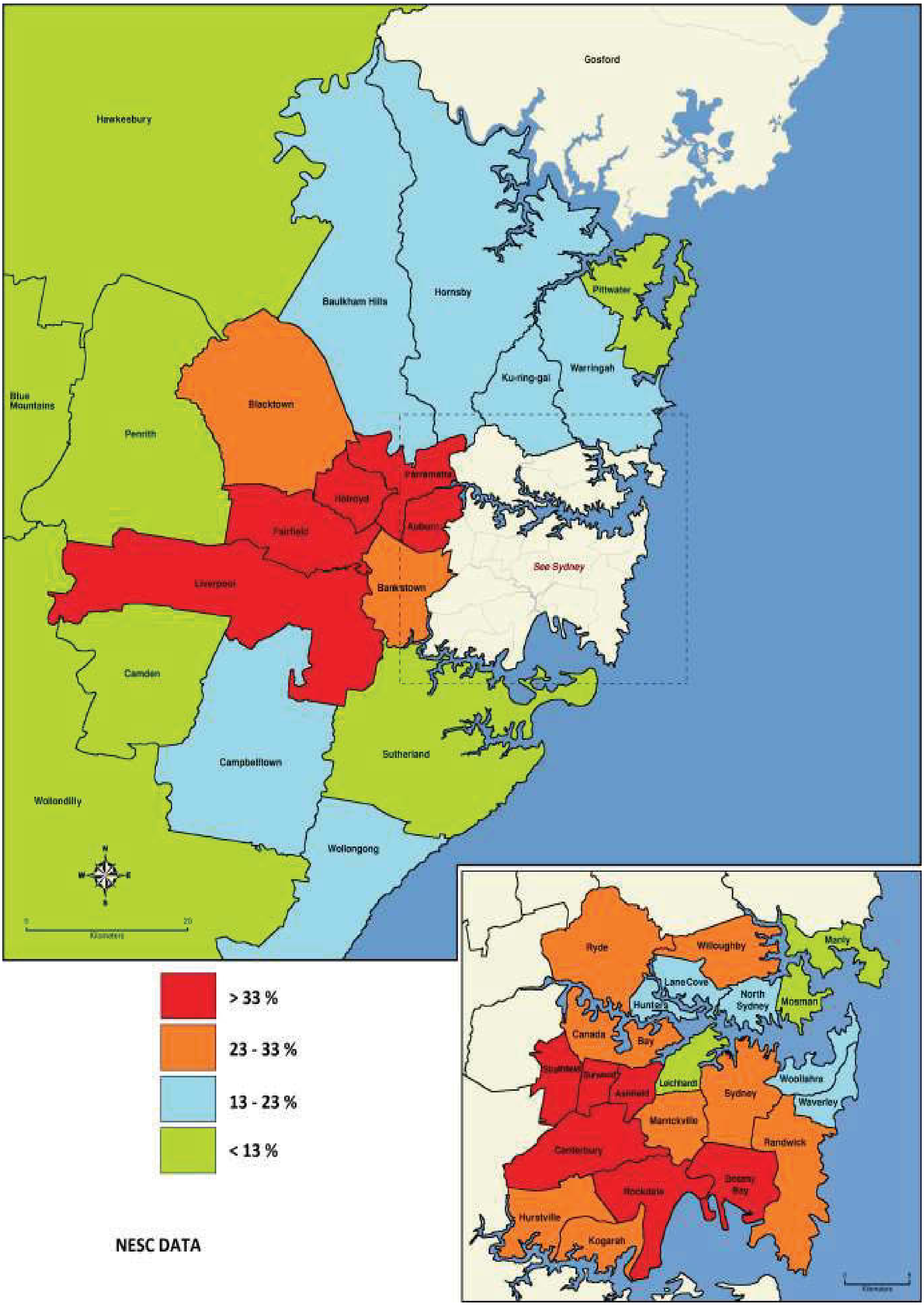


Figure 3.4(a) Percentage of residents born in non-English speaking countries

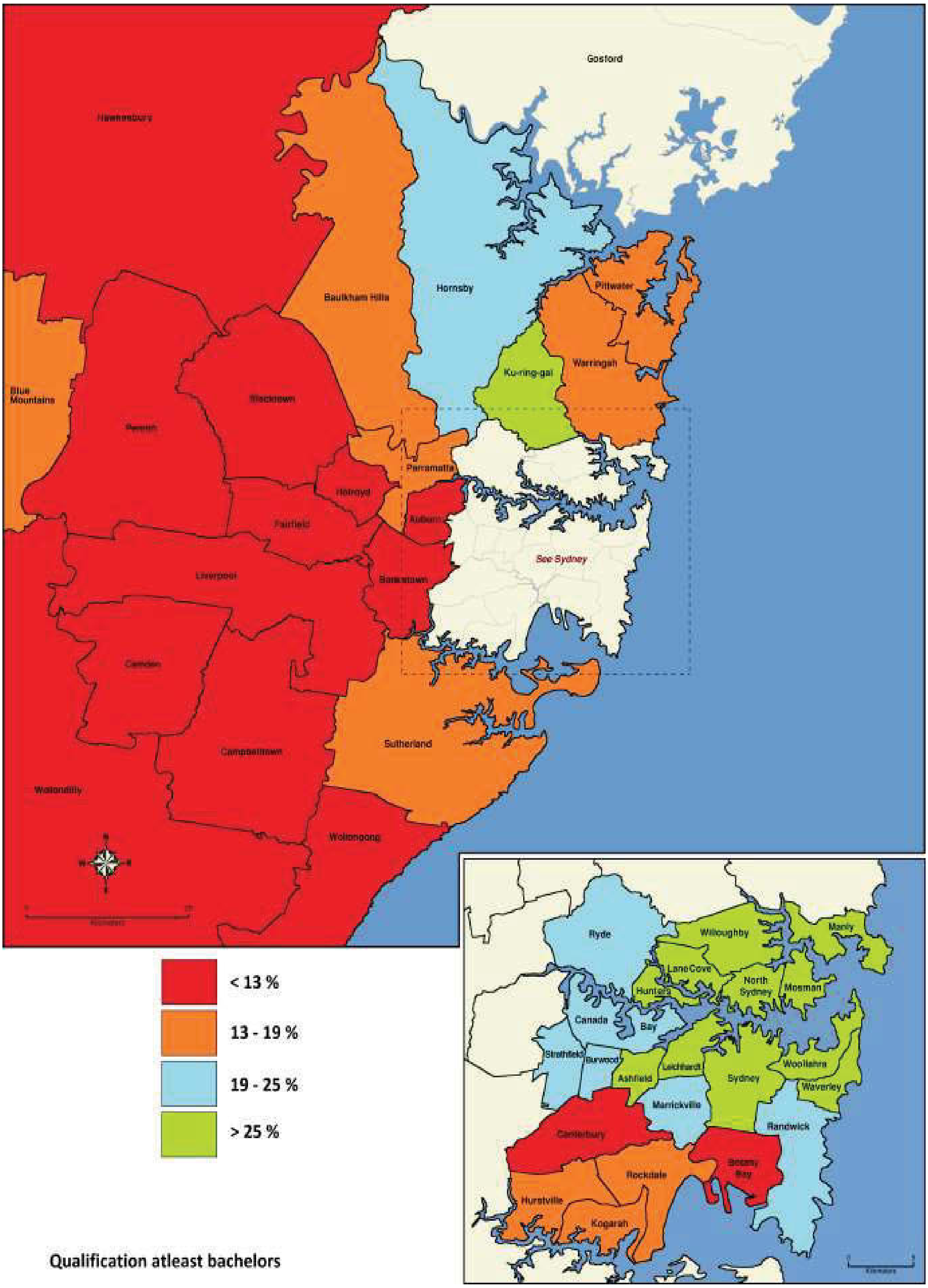


Figure 3.4(b) Average number of people with Bachelor qualifications or higher

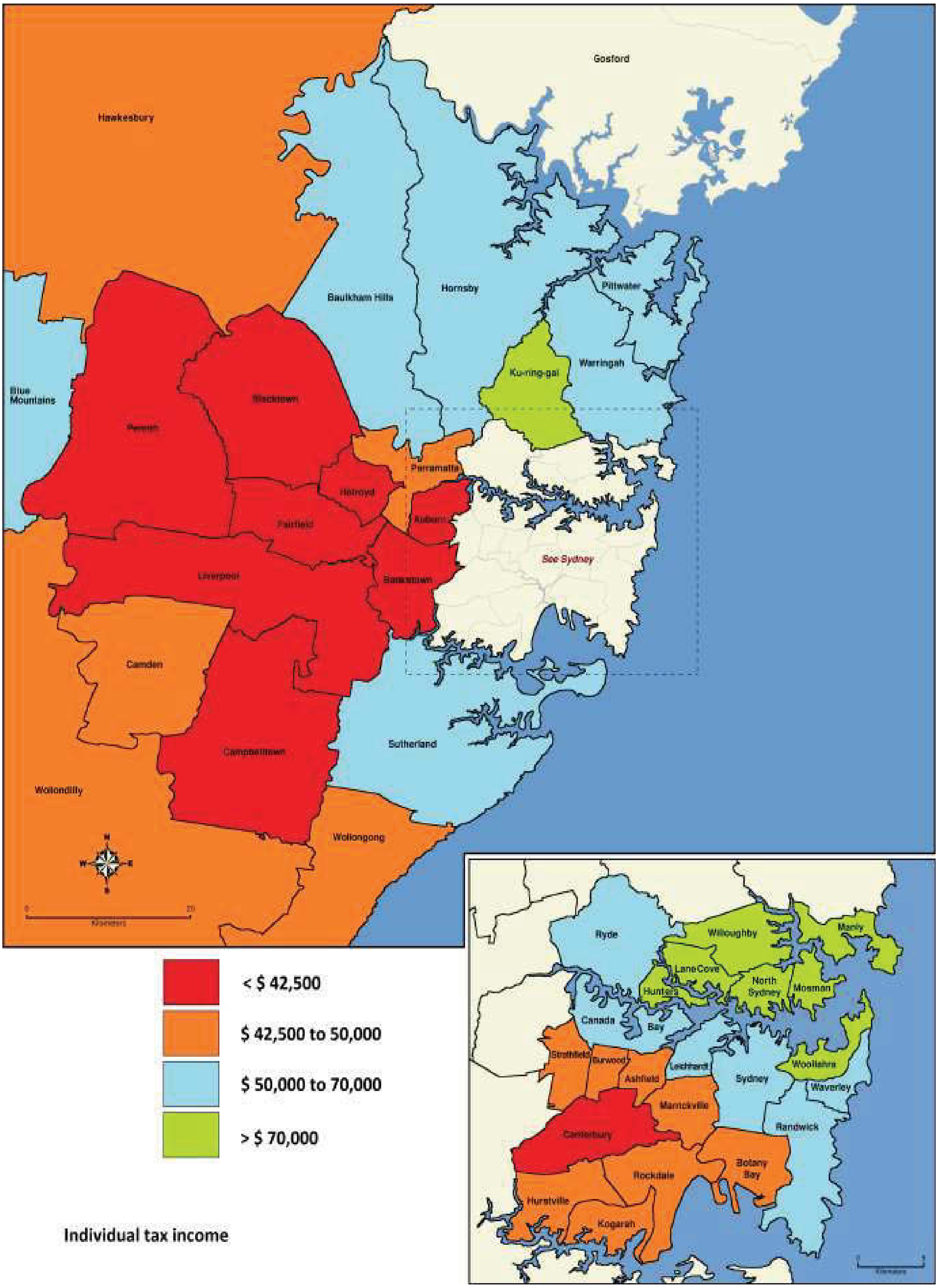


Figure 3.4(c) Mean taxable incomes

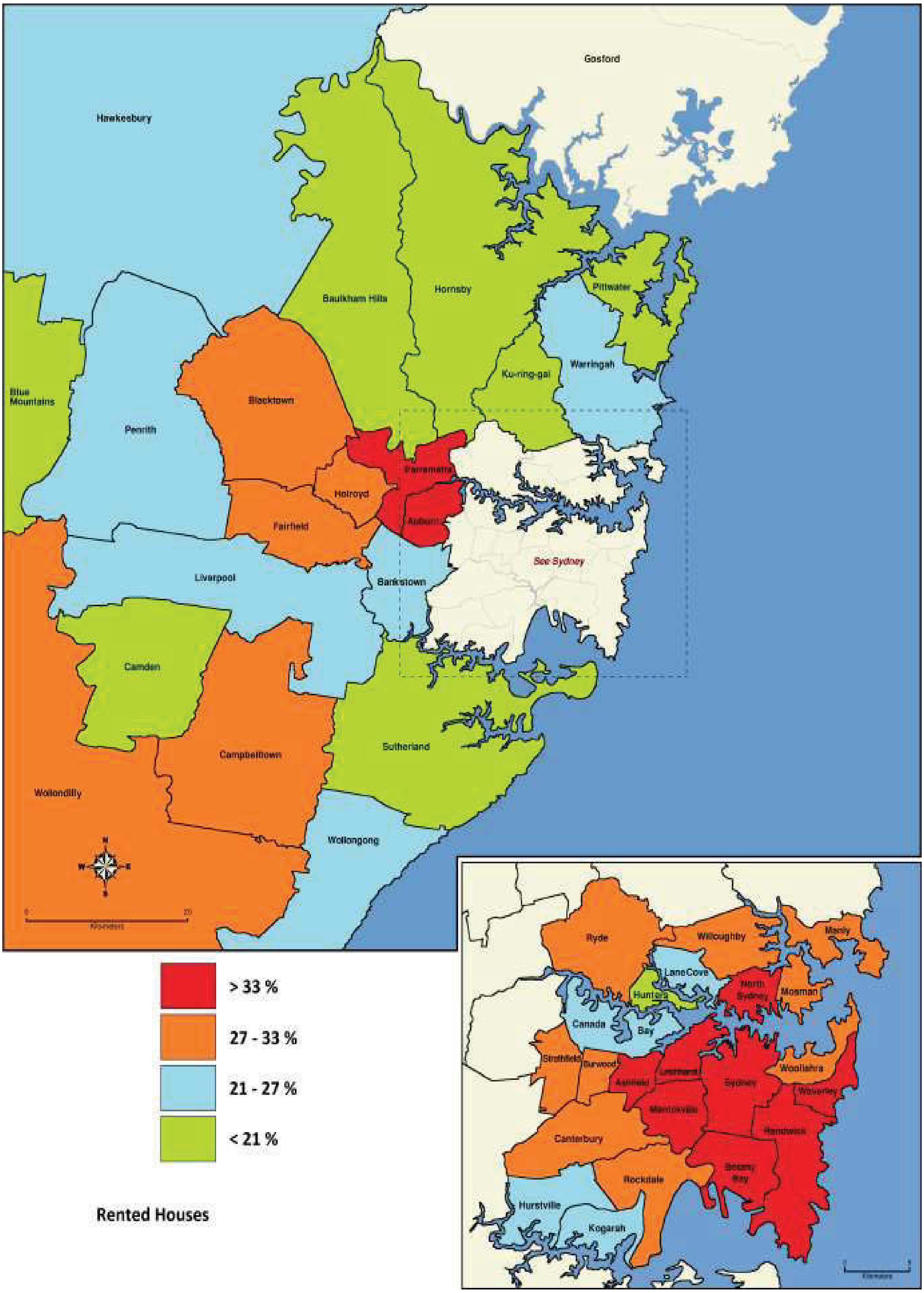


Figure 3.4(d) Percentage of houses that are not owner occupied (rented)

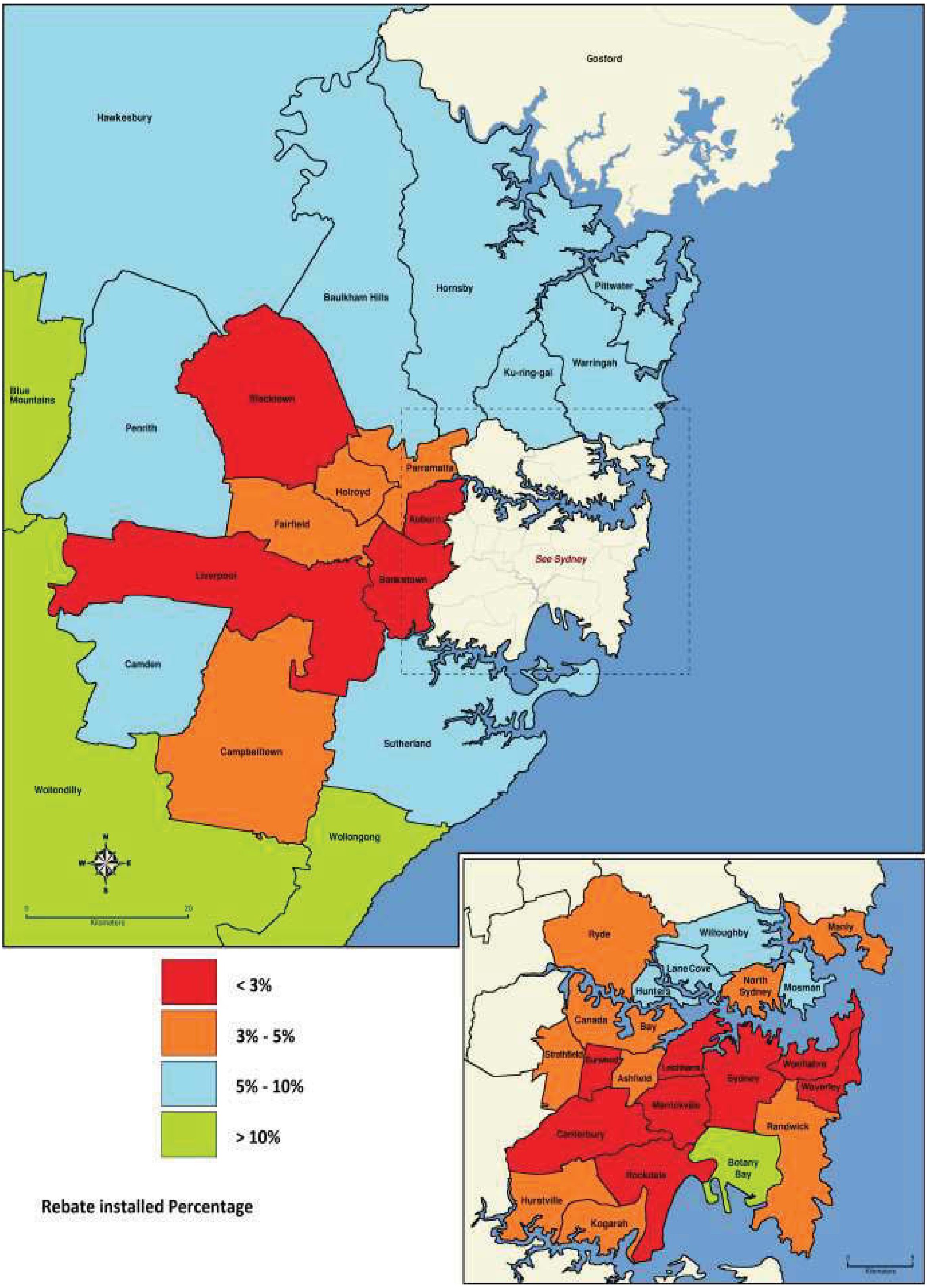


Figure 3.5(a) Percentage of rebated rainwater tanks installed.

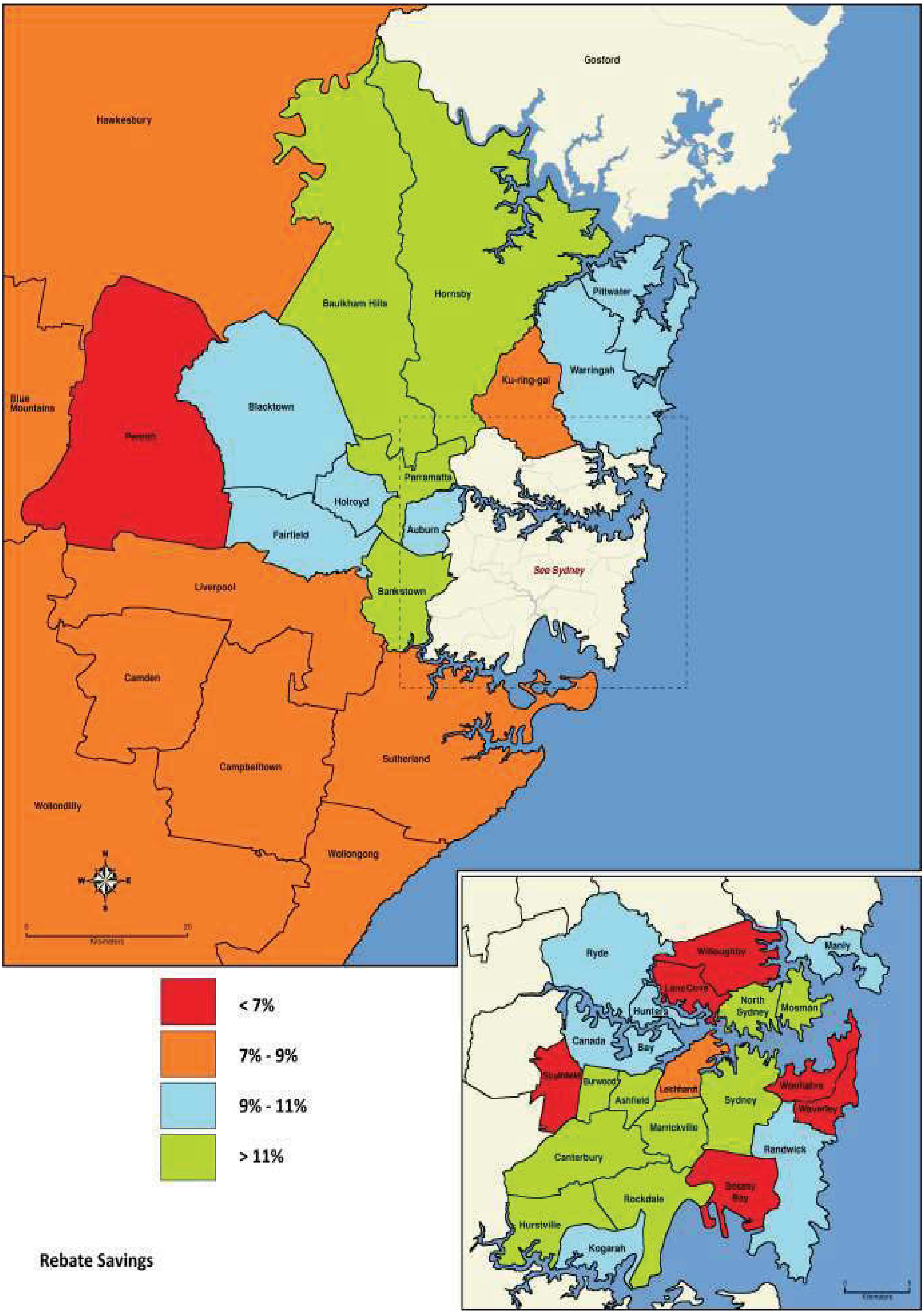


Figure 3.5(b) Average percentage of water savings from rebated rainwater tanks.

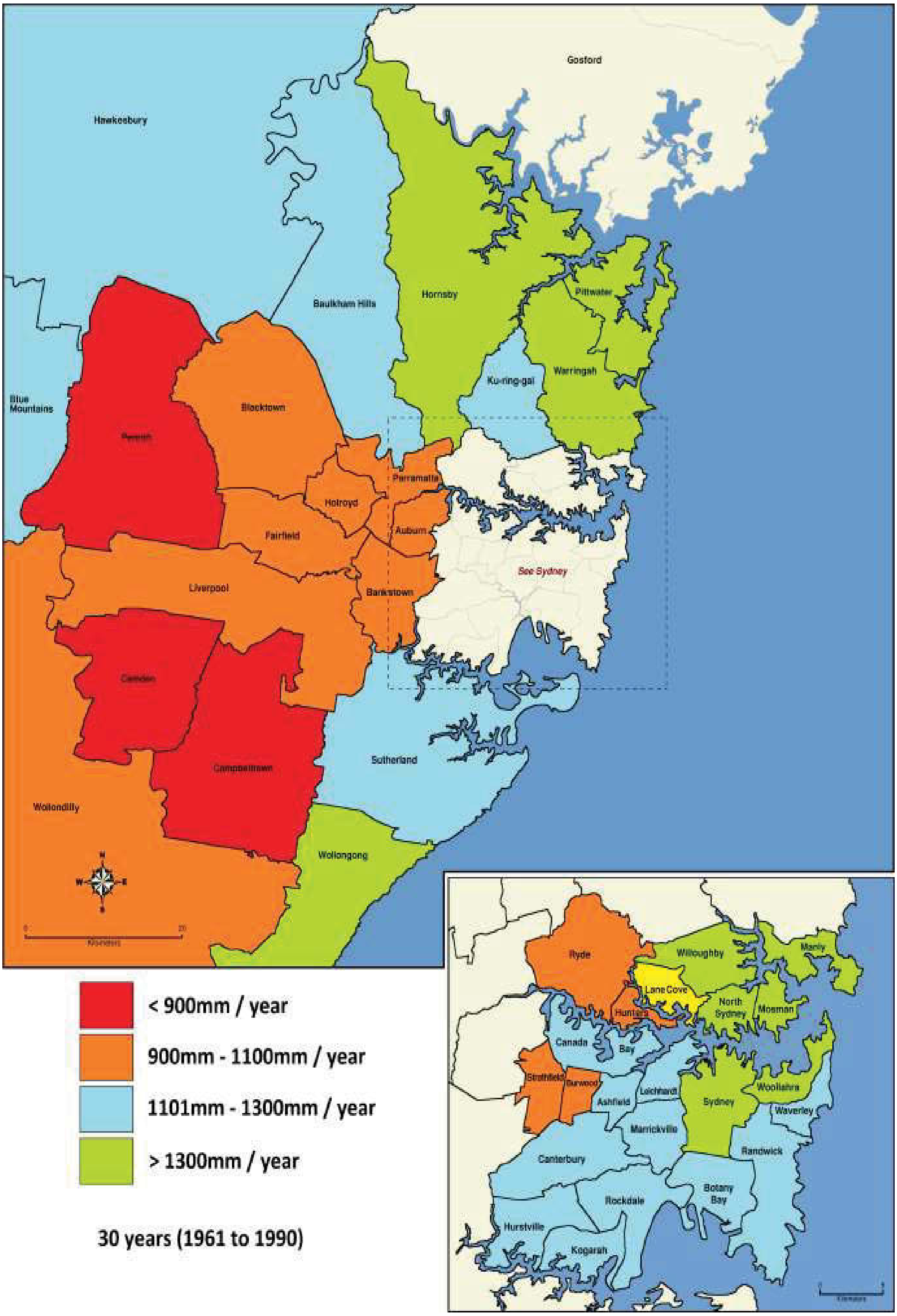


Figure 3.5(c) Sydney Metropolitan area long term average rainfall by LGA from 1961 to 1990

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