

Mitigation of Pollutants for Beneficial Use of Stormwater

By

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Doctor of Philosophy



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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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February 2016.

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DEDICATION OF THIS THESIS

TO MY LOVELY PARENTS

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2. Sountharajah 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.
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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)

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

C_t = 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

NaNO₃ = sodium nitrate

PPS = permeable pavement system

Q = Flow rate (cm³/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)

q₀ = 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 $\text{Pb} > \text{Cd}, \text{Cu} > \text{Zn} > \text{Ni}$ 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 $\text{Pb}, \text{Cu} > \text{Zn} > \text{Ni}, \text{Cd}$. 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.