New developments in stormwater characterization and remediation for water reuse

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Under the supervision of Prof. Saravanamuthu Vigneswaran

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Certificate of authorship/ originality

I, *Dinushika Ekanayake* declare that this thesis, is submitted in fulfilment of the requirements for the award of *doctor of philosophy* , in the *School of Civil and Environmental Engineering, Faculty of Engineering and Information Technology* at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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DEDICATION OF THIS THESIS

TO MY LOVING PARENTS AND HUSBAND

Research outcome summary

Publications arising from this work

Eeshwarasinghe, D., Loganathan, P., Kalaruban, M. *et al.* 2018, Removing polycyclic aromatic hydrocarbons from water using granular activated carbon: kinetic and equilibrium adsorption studies. *Environ Sci Pollut Res* **25,** 13511–13524.

Eeshwarasinghe, D., Loganathan, P. & Vigneswaran, S. 2019, 'Simultaneous removal of polycyclic aromatic hydrocarbons and heavy metals from water using granular activated carbon', *Chemosphere*, vol. 223, pp. 616-27.

Ekanayake, D., Aryal, R., Johir, M.A.H., Loganathan, P., Bush, C., Kandasamy, J. & Vigneswaran, S. 2019, 'Interrelationship among the pollutants in stormwater in an urban catchment and first flush identification using UV spectroscopy', *Chemosphere*, vol. 233, pp. 245-51.

Ekanayake, D., Loganathan, P., Johir, M.A.H. *et al.* Enhanced Removal of Nutrients, Heavy Metals, and PAH from Synthetic Stormwater by Incorporating Different Adsorbents into a Filter Media. *Water Air Soil Pollut* **232,** 96 (2021).

Conference papers

D. Eeshwarasinghe[1], C. Bush[2], P. Loganathan[1], J. Kandasamy[1], S. Vigneswaran[1] 2017, The importance of determining pollutant loads from varying rainfall events for stormwater harvesting and reuse schemes, NSW Stormwater Conference September 2017

Eeshwarasinghe, D., Loganathan. P., Kalaruban. M., Southararajah. D.P., Kandasamy, J., Vigneswaran, S. 2017, Polycyclic aromatic hydrocarbons in water: simple analytical method and removal technique. International Conference in Waste Water and Waste Management for Extractive Industries. October 23-24, 2017, Nusa Dua, Bali, Indonesia, Book of Abstract page 68.

Conferences

Presented at International Conference in Waste Water and Waste Management for Extractive Industries, October 23-24, 2017, Nusa Dua, Bali, Indonesia.

Presented at Stormwater NSW Conference which was held at the Newcastle Exhibition & Convention Centre on Wednesday, 6th and Thursday, 7th September, 2017

Presented at 11^{TH} CESE conference, Sukosol, 4-8 November 2018, Bangkok, Thailand

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AC= Activated Carbons

$(NH4)_2NO_3$ = ammonium sulphate

AET = apparent effects threshold

Barrett-Joyner-Hanlenda (BJH)

Brunauer = Emmett-Teller (BET)

$Ca(OH)_2$ = Calcium hydroxide

Ca^{2+} = Calcium

Ce = equilibrium concentration of adsorbate (mg/L)

Co = initial concentration of adsorbate (mg/L)

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

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

DOC = dissolved organic carbon

Dw = dry weight

FTIR = Fourier transform infrared spectroscopy

G = gram

g/L = gram per litre

GAC = Granular activated carbon

GSMS =Gas chromatography–mass spectrometry

HA = humic acid

HCl = hydrochloric acid

HCO3 = bicarbonates

HPLC =High-performance liquid chromatography

hr = hours

hr/h = hours

k1 = equilibrium rate constant of pseudo-first-order sorption (1/min)

k2 = equilibrium rate constant of pseudo-second-order (1/min)

k_{AB} = kinetic constant, (L/mg.min)

KCl = Potassium chloride

KF = Freundlich constants (mg/g)

kf = the external mass transfer coefficient (m/s)

KH_2PO_4 = Monopotassium phosphate

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

KNO_3 = Potassium nitrate

K_{ow} = Octanol-water partition coefficient

L = litre

M = mass of dry adsorbent (g)

m/h = meter per hour

mg/L = miligram per litre

$MgCl2.6H_2O$ = Magnesium Chloride Hexahydrate

μg/L = Micrograms per litter

min = minutes

mL/min = millilitre per minute

MQ = Milli-Q water MW = Molecular weight

n = Freundlich constant

Na_2CO_3 = sodium carbonate

$NaCl$ = sodium chloride

$NaHCO_3$ = sodium bicarbonate

$NaNO_3$ = sodium nitrate

NaOH = Sodium hydroxide

PAH = Polynuclear aromatic hydrocarbon

PCB = Polychlorinated biphenyl

Q = Flow rate (cm3/s)

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

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

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

rpm = revolutions per minute

SEM = Scanning Electron Microscopy

SS = suspended solids

t = filtration time (min).

TEF = Toxic equivalency factor

TEQ = toxicity equivalent quotient

TOC = total organic carbon

UV /VIS spectrum= Ultraviolet–visible spectroscopy

V = the interstitial velocity (m/s)

WHO = World Health Organization

USEPA = United States Environmental Protection Agency

WUSD = Water Sensitive Urban Design

Abstract

Water scarcity due to persistent drought is forcing many countries around the world to explore alternative freshwater resources. Australia is the world's driest inhabited continent, and has one of the most variable rainfall intensities. This has encouraged the harvesting of stormwater and reuse of water in order to reduce the demand placed on municipal water supplies. Urban and industrial stormwater runoff has high potential as a reusable water resource for agricultural irrigation, irrigation of parks and sportsgrounds, and toilet flushing. However, stormwater contains many pollutants which can have dire effect on plants, animals, aquatic organisms and humans and for this reason they should be removed before the water is used for these beneficial purposes.

Assessing urban stormwater quality by investigation and characterisation of pollutants is a prerequisite for its effective management, for reuse and safe discharge. The stochastic nature of rainfall, dry weather periods, topology, human activities and climatic conditions generate and wash-off pollutants differently from event to event. Therefore, a study was commenced to investigate the major physico-chemical pollutants in stormwater runoff collected from an urban catchment system after several rainfall events over a period of three years. Correlation analysis and principal component analysis (PCA) were done to identify the possible relationships among measured pollutants. Although correlation analysis revealed some relationships between pollutants, PCA biplots suggested a few group-related pollutants and revealed that a two-component model could explain nearly 72% of the variability between pollutants. Pollutants in the group that included dissolved organic carbon (DOC) behaved in a similar manner. Most of the pollutants were washed off during an early stage of an event giving rise to the first flush phenomenon. UV spectroscopy was applied to identify the first flush by comparing the recorded spectrum of consecutive samples that were collected in an event. Analysis of the spectra was able to isolate the point when first flush ends for DOC and pollutants that behaved similar to it.

The second part of the thesis dealt with remediation of stormwater by removing important organic and inorganic pollutants. Organic pollutants and heavy metal concentrations in stormwater are expected to increase and reach toxic levels in the near future because of rapid urbanisation leading to increasing density of motor

vehicles. Polycyclic aromatic hydrocarbons are a group of highly persistent, toxic and widespread environmental micropollutants that are increasingly found in water. A study was conducted in removing five PAHs, namely naphthalene, acenaphthylene, acenaphthene, fluorene and phenanthrene from water by adsorption onto granular activated carbon (GAC). The pseudo-first order (PFO) model satisfactorily described the kinetics of adsorption of the PAHs. Batch equilibrium adsorption data fitted well to Langmuir, Freundlich and Dubinin-Radushkevich models with the Freundlich model having the best fit. The Langmuir adsorption capacities for naphthalene, acenaphthylene, acenaphthene, fluorene and phenanthrene were 33.7, 76.6, 40.8,45.7 and 47 (mg/g), respectively. The adsorption affinities were related to the hydrophobicity of the PAHs as determined by the log k_{ow} values. Overall the results showed that GAC can be effectively used to remove PAHs from stormwater.

Polycyclic aromatic hydrocarbons and heavy metals are dangerous pollutants that commonly co-occur in water. Therefore, it is important to determine their adsorption capacities when they are present together, because there could be competition for adsorption between the two groups of pollutants and this would reduce their removal efficiency. Most previous adsorption studies were conducted either on PAHs or heavy metals separately and not when they occur together. An adsorption study conducted on the simultaneous removal of PAHs (acenaphthylene, phenanthrene) and heavy metals (Cd, Cu, Zn) by GAC showed that, when these pollutants are present together, their adsorption capacities were less than when they were present individually due to competition for adsorption. Between the two classes of pollutants, PAHs had higher adsorption capacities than heavy metals. The reduction in adsorption of PAHs by heavy metals followed the orders of heavy metals' adsorption capacity and reduction in the negative zeta potential of GAC (Cu > Zn > Cd).

Bio-retention beds constitute a widespread treatment measure used in sustainable stormwater management particularly by the local councils in Sydney, Australia. However, most of the bio-retention treatment systems are not efficient in removing pollutants from stormwater. Final part of the research was on evaluating the efficiency in removing pollutants using a bio-retention medium (R165, natural

soil with a texture sandy loam) and enhancing the pollutant removal capacity by mixing with GAC (0.3%) and zeolite (10%). Column experiments were carried out at the flow velocity of 100 mm/hr and 300 mm/hr in down-flow mode. The soil-based filter without additions removed substantial amounts of PO_4-P and NH_4-N for up to 8 h at a flow velocity of 100 mm/h which is a one-year time-equivalent of rainfall at a locality in Sydney, Australia. An addition of 10% zeolite to the soil-based filter extended the column saturation period to 24 h. The breakthrough data for PO_4-P and NH_4-N were satisfactorily described by the Thomas model. The majority of the nine heavy metals tested were removed by more than 50% for upto 4 h in the soil-based filter. This level of removal increased to 16 h when 10% zeolite was added to the filter. The column with the soil-based filter + 10% zeolite had higher affinity for Pb, Cu, Zn and As than Ni, with Pb having the highest percentage removal. Soil-based filter + 10% zeolite removed considerable amounts of 3 PAHs (30-50%), while Soil-based filter + 10% zeolite + 0.3% GAC removed 65 to > 99% of the PAHs at 24 h operation. Phenanthrene and pyrene were almost 100% removed. This application will greatly facilitate the reduction of pollutant concentration in biofilter-treated stormwater in many stormwater harvesting projects which are currently experiencing difficulties in achieving clean reusable water.