

Enhanced removal of nutrients, heavy metals, and PAH from synthetic stormwater by incorporating different adsorbents into a filter media

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Abstract:

Stormwater harvesting and reuse is an attractive option to lower the demand placed on other sources of water supply. However, it contains a wide range of pollutants that need to be removed before it can be reused or even discharged to the waterways and receiving waters. An experimental protocol to estimate the efficiency of a soil-based-filter medium for the treatment of stormwater pollutants from 1-3 years rainfall experienced in the field was developed using a laboratory column-set-up over short-term duration. The filter removed substantial amounts of PO₄-P and NH₄-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 PO₄-P and NH₄-N were satisfactorily described by the Thomas model. The majority of the nine heavy metals tested were removed by more than 50% for up to 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 polycyclic aromatic hydrocarbons (PAHs) (30-50%), while Soil-based filter + 10% zeolite + 0.3% granular activated carbon removed 65 to > 99% of the PAHs at 24 h operation.

Keywords: stormwater, granular activated carbon, zeolite, biofiltration, polycyclic aromatic hydrocarbon

1. Introduction

Water scarcity due to increasing human population, industries, and intensive agriculture, and persistent drought

is driving many countries around the world to explore alternative freshwater resources. This has encouraged the harvesting and reusing of stormwater to lower the demand placed on municipal water supplies. **If the stormwater is not harvested for reuse, it can freely runoff and increase pollution of natural waterways.** However, stormwater contains a wide range of pollutants (e.g. suspended solids, nutrients, heavy metals, polycyclic aromatic hydrocarbons (PAHs) that need to be removed before the water can be reused or discharged to the waterways.

Biofiltration is a comparatively recent technique to treat stormwater and remove a wide range of pollutants. It is popular in field applications due to its simplicity and cost effectiveness (Hatt et al. 2009a,b; Henderson et al. 2007; Hsieh and Davis 2005). Biofiltration systems are configured as vegetated filtration trenches or basins with an underlying porous collection pipe and are designed to remove fine suspended solids and dissolved pollutants. Many studies have been carried out on vegetated biofiltration systems for removal of nutrients (Chen et al. 2013; Kim et al. 2003), and heavy metals (Li and Davis 2008). **However, pollutant removal capacities of the filter medium below the vegetation level is poorly understood.** Treatment reliability is an important issue highlighted by the number of studies that report significant variations in pollutant removal rates. Pollution retention through bio-filter systems occurs mainly by evaporation, filtration, adsorption to the medium, precipitation and biological intakes by plants and microbes. However, the short contact time between pollutants and vegetation may reduce the biological uptake of nutrients and heavy metals from the stormwater (Denman et al. 2006). Hence it is important to improve the filter medium of the biofiltration system to enhance pollutant removal by adsorption or precipitation when stormwater percolates through the medium.

The present study evaluated the performance of a soil medium (R165) proposed for use as a filter below the vegetation in biofiltration basins in Blacktown, New South Wales, Australia to remove targeted pollutants. Apart from the performance of R165, other filter media such as zeolite and granular activated carbon (GAC) were mixed in with R165 to evaluate if pollutant removal could be further improved. Zeolite is well known for removing specific types of heavy metals (Nguyen et al. 2015) and ammonium (Cooney et al. 1999a,b) by cation exchange mechanism (Wang and Peng 2010). GAC is one of the most abundant adsorbents commonly used in water treatment and very effective in removing a wide range of organic pollutants including polycyclic aromatic hydrocarbons (PAH) and heavy metals through hydrophobic and electrostatic interactions, hydrogen bonding and chelation mechanisms (Eshwarasinghe et al. 2018, 2019; Sountharajah et al. 2016; Valderrama et al. 2008). The results of this study provide an in-depth knowledge on the application of zeolite and GAC as **filter media** for stormwater harvesting and reuse. **The originality of this study is the development of a novel experimental protocol to estimate the efficiency of a filter medium for the treatment of stormwater pollutants from 1-3 years rainfall experienced in the field using a laboratory column-set-up over short-term duration. The pollutants removals by the filter medium were estimated by incorporating three adsorbents of contrasting properties which is another**

novelty of the study.

2. Materials and methods

The laboratory testing mimics the 1-3 years rainfall conditions experienced in Blacktown, Sydney, Australia using a high flow rate of water continuously through a column containing a soil medium so that the total water input to the column for 8 hours is equivalent to 1 year of rainfall falling over the field site (calculations shown in Methods section). Column studies were carried out to assess the performance of the R165 soil media, which is proposed for use in Blacktown's biofiltration basins. The improvements in pollutant removal by incorporating small amounts of GAC (0.1-1%) and Zeolite (1-20%) with R165 were also evaluated.

2.1. Adsorbents

Zeolite: The zeolite used in the study is a locally available material which exhibits good adsorption capacity towards heavy metals (Nguyen et al. 2015). The zeolite was sourced from a natural deposit at Werris Creek, New South Wales and supplied by Zeolite Australia Pty Ltd., Australia. The Brunauer–Emmett–Teller (BET) surface area of zeolite was 15.4 g/m² (Nguyen et al. 2015). The zero point of charge (ZPC, the pH at which the net surface charge is zero) of zeolite was 2.2 (Nguyen et al. 2015), suggesting that at the pH of most stormwaters (which is 6-7) the net surface charge on this material is negative and favourable for the adsorption of positively charged metals and ammonium. The zeta potential value of zeolite is -17 mv at pH 6.5 (Nguyen et al. 2015).

GAC: GAC (particle sizes of between 0.3 and 2.4 mm) was purchased from James Cummins P/L, Australia. A particle size range of 0.4 -2 mm was collected by sieving the original material and used in the experiments. The BET surface area, pore volume and average pore diameter of the GAC were 1000 m²/g, 0.69 cm³/g and 2.7 nm, respectively. The scanning electron micrographs of the GAC revealed the presence of large numbers of micropores and mesopores, which results in GAC having a high surface area (Eeshwarasinghe et al. 2018).

R165: The characteristics of this biofiltration media are presented in Table 1. It shows that the media is loamy sand containing 95% sand.

Table 1. Characteristics of the bio retention media (R165)

Characteristics	Result	Unit
Electrical Conductivity @ 25°C	15	µS/cm
pH Value	6.8	pH Unit
Total Phosphorus as P	101	mg/kg
Total Nitrogen as N	220	mg/kg
Total Kjeldahl Nitrogen as N	220	mg/kg
Nitrite + Nitrate as N (Sol.)	1.5	mg/kg
Organic Matter	0.5	%
Total Organic Carbon	0.5	%
Clay (<2 µm)	5	%
Gravel (>4750 µm)	1	%
Silt (2-60 µm)	1	%
Sand (60-150 µm)	2	%
Sand (150-300 µm)	31	%
Sand (300-425 µm)	36	%
Sand (425-600 µm)	20	%
Sand (600-1180 µm)	4	%
Sand (1180-2360 µm)	1	%
Gravel (2360-4750 µm)	1	%
Moisture Content	5.3	%
Copper	<5	mg/kg
Lead	5	mg/kg
Nickel	<2	mg/kg
Zinc	9	mg/kg
Arsenic	<5	mg/kg
Cadmium	<1	mg/kg
Chromium	3	mg/kg
Mercury	<0.1	mg/kg

2.2. Synthetic stormwater

The characteristics of stormwater were determined from field samplings of stormwater during several rainfall events that occurred in Blacktown. This information was used here to prepare a synthetic stormwater solution containing the pollutants at concentrations that closely match field conditions in Blacktown.

Synthetic stormwater was used for all experiments. The use of synthetic stormwater circumvents the need to collect large quantities of stormwater in the field in Blacktown, store, and transport to the laboratory for testing. The concentrations of the constituents of interest in the synthetic stormwater were adjusted to the expected range that occurs in Blacktown. The concentrations remain the same throughout all tests providing an easy comparison of performance of different media used in the various column studies. This would not be possible if actual stormwater that was collected in the field were used. The composition of synthetic stormwater is shown in Table 2.

Analytical grade nitrate salts of heavy metals were used. Polycyclic aromatic hydrocarbons (PAHs) employed in the adsorption experiments were acenaphthene, phenanthrene and pyrene. All chemicals were obtained from Sigma-Aldrich (USA).

2.3. Methods

2.3.1. Column experiment

Column with dimensions 18.5 cm (diameter) x 18.5 cm (height) was used in the experiments. The R165 media was packed to a depth of 50 mm in the column. Coarse sand layers and gravels were placed above and below R165 as shown in Fig. 1. A layer of glass beads was placed on the top surface of the column for the added water to flow evenly through the column. The stormwater was passed through the column at a flow velocity of 100 mm/h for most experiments and at 300 mm/h for a few experiments. Downflow mode of operation was employed and effluent was collected at the bottom of the column at various times during the experiment. Pollutant concentrations in the influent solution (C_0) and in the effluent solution at various times (t) (C) were measured and the breakthrough curves (C_0/C vs time) were plotted. The breakthrough curves show the time-wise progress in pollutants removal by the column. The experimental set-up is illustrated in Fig. 1.

The breakthrough data for NH_4^+ and PO_4^{3-} were simulated using Thomas model (Thomas 1944; Nur et al. 2015; Eeshwarasinghe et al. 2018). Thomas model equation is given below.

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_T q_0 m_c}{Q} - k_T C_0 t$$

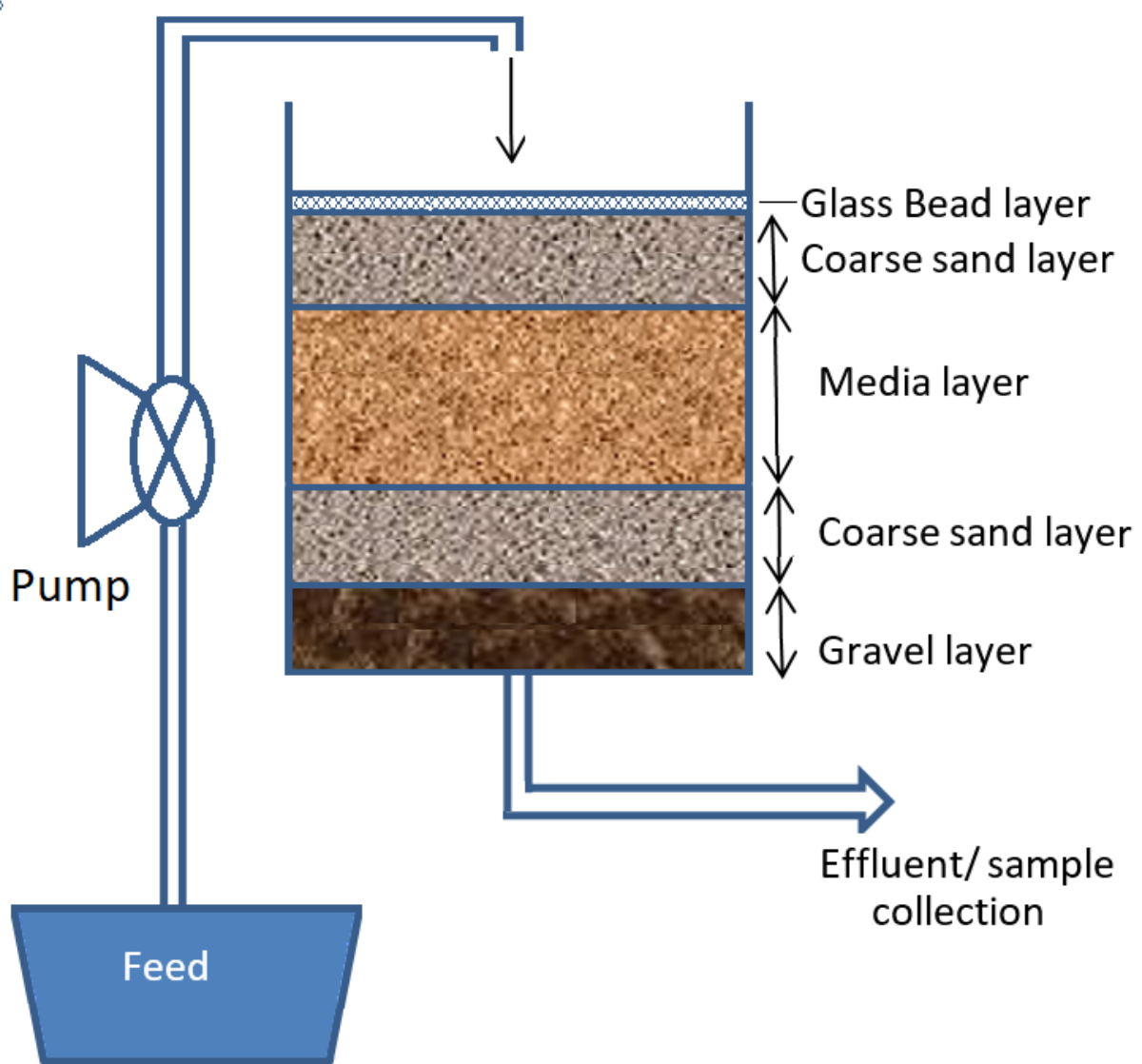
where, k_T is the Thomas rate constant (mL/min.mg), q_0 is the maximum solid-phase concentration of the solute

(mg/g), m_c is the mass of adsorbent in the column (g), Q is the volumetric flow rate (mL/min), C_o (mg P/L) is the inlet phosphate concentration; C (mg P/L) is the outlet phosphate concentration at time t (min). The values for k_T and q_0 were determined from the slope and intercept of a linear plot of $\ln(C_o/C - 1)$ vs t .

Table 2. Characteristics of synthetic stormwater

Compound	Pollutant	Concentration (mg/L)	Compound	Pollutant	Concentration (mg/L)
KNO ₃	NO ₃ ⁻ - N	3	Ni(NO ₃) ₂	Ni ²⁺	0.002
KH ₂ PO ₄	PO ₄ ³⁻ - P	1.5	Cd(NO ₃) ₂	Cd ²⁺	0.01
NH ₄ Cl	NH ₄ ⁺ - N	0.65	Pb(NO ₃) ₂	Pb ²⁺	0.04
NaCl	Na ⁺	75-80	Cu(NO ₃) ₂	Cu ²⁺	0.08
CaCl ₂	Ca ²⁺	25	Zn(NO ₃) ₂	Zn ²⁺	0.1
MgCl ₂ .6H ₂ O	Mg ²⁺	13.5	AlCl ₃ .6H ₂ O	Al ³⁺	0.1
Humic acid	DOC	5-10	FeCl ₃	Fe ³⁺	0.15
pyrene	pyrene	0.03	Na ₃ AsO ₄	AsO ₄ ³⁺	0.05
Phenanthrene	Phenanthrene	0.03	Mn(NO ₃) ₂	Mn ²⁺	0.03
Acenaphthene	Acenaphthene	0.03		pH	6.8
Kaolin clay	Turbidity (NTU)	40		Conductivity (µS/cm)	650-700

Fig. 1. Schematic diagram of the column experiments



Rainfall intensity: Laboratory testing was conducted to mimic rainfall that occurs in Blacktown. The annual rainfall in Blacktown is 800 mm. The water flow through the column in experiments where the flow velocity is 100 mm/h (0.1 m/h) over an 8-hour duration is equivalent to 1 year of rainfall (800 mm/year). The rate of stormwater inflow to column at the rainfall intensity of 0.1 m/h (superficial velocity 100 mm/h, interstitial velocity 100 mm/h/porosity (0.3) = 333 mm/h) and 0.3 m/h (superficial velocity 300 mm/h, interstitial velocity 1000 mm/h) used in the study were 45 ml/min and 135 ml/min, respectively as shown below. These interstitial velocities are much higher than those reported for field soils (0-100 cm/day or 0-42 mm/h, Schneider et al. 2019). The higher velocities used in this study is to mimic 1-3 years of rainfall in the field equivalent to 8-24 h of continuous water flow in the laboratory column set-up.

$$\text{The surface area of the column is } 22/7 \times 0.185/2 \times 0.185/2 \text{ m}^2 = 0.0269 \text{ m}^2$$

For the rainfall intensity of 0.1 m/h, the rate of stormwater inflow to the column is $0.1 \text{ m/h} \times 0.0269 \text{ m}^2$
 $= 0.00269 \times 10^6 \text{ cm}^3/\text{h} = 2690 \text{ mL/h} = 2690/60 \text{ mL/min}$ or 45 mL/min

Similarly, for a rainfall intensity of 0.3 m/h, the rate would be 135 mL/min

The experiments were conducted until the media was exhausted for up to 25-30 h (run intermittently for 8 h/day) representing intermittent rainfall.

GAC, zeolite additives to enhance biofilter performances: Experiments were initially conducted using two separate columns, one with a mix of zeolite and R165 (1% Zeolite+R165) and the other with GAC and R165 (1% GAC+R165) at a flow velocity of 100 mm/h to evaluate any improvement to the performance of the bio-retention R165 media. Based on the outcome of these two experiments, further column experiments were carried out to test the improvement with varying amounts of zeolite (5%, 10%, 20%) and 0.3% GAC mixed with R165. Experiments conducted are summarized in Table 3. The percentage of GAC was reduced from that used in the initial experiments to reduce the cost of a filter that would be installed in the field.

Table 3. Summary of all experiments to simulate one-year rainfall (800 mm/year)

No	Filter media	Flow velocity
1	R165	100 mm/h (45 mL/min)
2	1% GAC mixed with R165	100 mm/h (45 mL/min)
3	1% zeolite mixed with R165	100 mm/h (45 mL/min)
4	5% zeolite mixed with R165	100 mm/h (45 mL/min)
5	10% zeolite mixed with R165	100 mm/h (45 mL/min)
6	20% zeolite mixed with R165	100 mm/h (45 mL/min)
7	0.3% GAC+10% Zeolite mixed with R165	100 mm/h (45 mL/min)
8	0.3% GAC+10% Zeolite mixed with R165	300 mm/h (135 mL/min)

Table 4. Analytical methods used for measuring stormwater parameters

Parameter	Measurement method
Heavy metals	APHA 3120 using 4100 MP-AES (microwave plasma - atomic emission spectrometry)
PAHs	Gas chromatography–mass spectrometry (GC-MS)
Total nitrogen, NH ₄ ⁺ , TKN, NO ₃ ⁻	EN ISO 11905-1 and DIN 38405-9 (Photometric method)
DOC	APHA 5310B-High temperature combustion method (using a Multi N/C 3100 analyser (Analytik Jena AG))
PO ₄ -P	Photometric method using HACH DR3900
Na ⁺ , Ca ²⁺ , Mg ²⁺	APHA 3120 using 4100 MP-AES (microwave plasma - atomic emission spectrometry)
Electrical conductivity	HACH HQ40d meter and CDC40101 probe
Turbidity	Turbidity meter
pH	HACH HQ40d meter and CDC40101 probe

2.3.2. Measured chemical parameters

Concentrations of dissolved nutrients (total N (TN), NH_4^+ , total Kjeldahl N (TKN), PO_4^{3-} , total P (TP)), and metals (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , AsO_4^{3-} , Fe^{3+} , Mn^{2+} , Al^{3+} , Ni^{2+}) in the influent and effluent were measured. Polycyclic aromatic hydrocarbons (acenaphthene, phenanthrene and pyrene) were measured only 2 times per experiment, once at the start of the experiment and secondly at the end, to avoid the expensive analytical costs. Other parameters (pH, turbidity, DO, EC, and DOC) were measured on an hourly basis. Analytical methods used in this study are presented in Table 4. The variation of flow rate over time and the degree of clogging of the filter medium were monitored continuously.

3. Results and discussion

3.1. Nutrients removal

PO₄-P removal: The removal rates of $\text{PO}_4\text{-P}$ during four columns test run at 100 mm/h are shown in Fig. 2a. The results show that the proportion of $\text{PO}_4\text{-P}$ removed decreased with time. The R165 media was exhausted within 15 h (equivalent to less than 2 years rainfall) in terms of removing $\text{PO}_4\text{-P}$. The addition of zeolite in larger amounts (or higher percentages) improved $\text{PO}_4\text{-P}$ removal rates extending the life of the R165 media up to more than 40 h (equivalent to 5 years rainfall) depending on the amount of zeolite used. More than 50% of the PO_4 was removed by R165 + 10 % zeolite media for up to 20 h (equivalent to 2.5 years rainfall).

NH₄-N: The removal of $\text{NH}_4\text{-N}$ during four columns test runs at 100 mm/h is shown in Fig. 2b. As in the case of $\text{PO}_4\text{-P}$ removal, the tests show that the R165 media was exhausted within 15 h. The addition of zeolite at increasing percentages improved $\text{NH}_4\text{-N}$ removal rates. The life of the media in the case of a 20% zeolite addition to R165 was extended to over 40 h (equivalent to 5 years rainfall).

Previous research concluded that NH_4^+ and PO_4^{3-} were simultaneously removed from an aqueous solution using zeolites (Sun et al. 2011; Wild et al. 1996). NH_4^+ was removed by a cation exchange reaction on the zeolite, whereas the Ca^{2+} in zeolite contributed to the removal of PO_4^{3-} due to the formation of the surface precipitate of $\text{Ca}_3(\text{PO}_4)_2$. Another explanation for the enhanced adsorption of PO_4^{3-} is bridge provided by the positively charged Ca (Ca^{2+}) between the negatively charged zeolite and PO_4^{3-} (Zhan et al. 2017). Coorney et al. (1999a,b) investigated the capability of using Australian natural zeolite to remove NH_4^+ employing a fixed-bed ion-exchange process and achieved high removal efficiencies from wastewater. Furthermore, they observed a reduction of adsorption capacity of NH_4^+ in the presence of Ca^{2+} , Mg^{2+} and K^+ because these cations competed with NH_4^+ for adsorption.

Nutrients ($\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$) removal by the 10% Zeolite+R165 media at a flow velocity of 300 mm/h

was also investigated (Fig. 3). According to the breakthrough curve, the removal capacity decreased over the time and the column became saturated within 5 h. This means that the media would only be sufficient to remove a 1-2 years equivalent pollution load under this flow velocity. This is because at higher flow rate, a larger amount of nutrients enters the column per unit time and the media's capacity to adsorb nutrients becomes more quickly exhausted.

The results of the nutrients adsorption study showed that the column with R165 alone is not satisfactorily for removing both NH_4^+ and PO_4^{3-} for water discharge into a freshwater body to comply with the recommended Australian guidelines (ANZEC 2000). In contrast, the R165 column mixed with at least 10% zeolite is capable of sufficiently removing the nutrients for safe water discharge into a freshwater body (Supplementary Data I).

The Thomas model satisfactorily described the NH_4^+ and PO_4^{3-} breakthrough at the two flow velocities tested (Fig. 2 and 3) as shown by the high coefficient of determinations (R^2) (0.72-0.99, Tables 5 and 6). Increased percentage of zeolite in the filter medium increased the Thomas adsorption capacity for both NH_4^+ and PO_4^{3-} at the flow velocity of 100 mm/h (Table 5). When the flow velocity was increased, the adsorption capacity decreased for the 10% zeolite column (Table 5 and 6). This is probably because at higher flow velocity the nutrients had less time to interact with zeolite and get adsorbed (Nur et al. 2015).

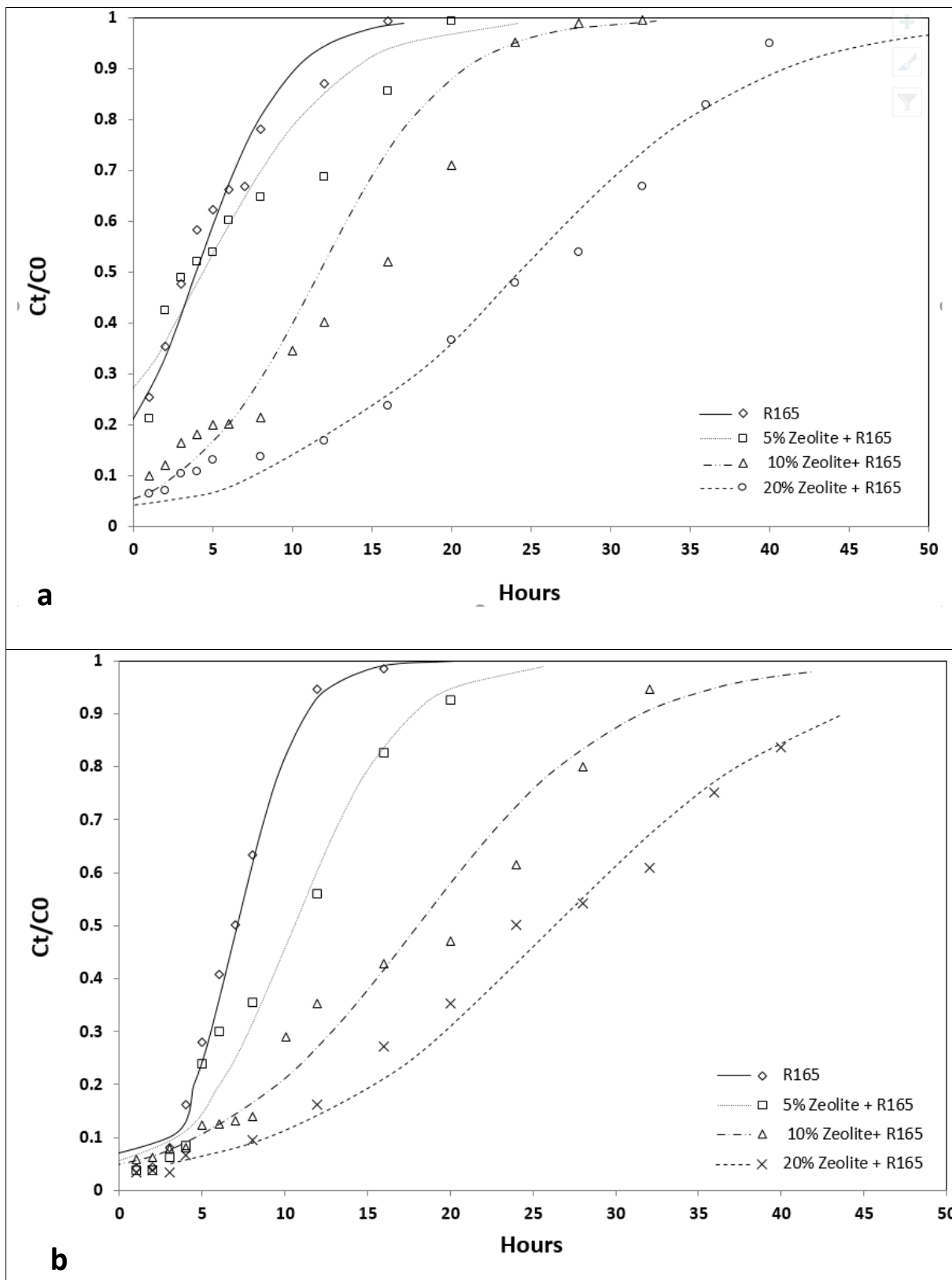


Fig. 2. The breakthrough curve for (a) $\text{PO}_4\text{-P}$ and (b) $\text{NH}_4\text{-N}$ removal by four columns at a flow velocity of 100 mm/h. Lines show the Thomas model simulation.

Table 5. Thomas model parameters for the simulation of breakthrough curves in Fig. 2

		Co mg/L	M g	Q mL/min	q _o mg/g	K _T mL/min.mg	R ²
NH ₄ -N	R165	0.6	1800	45	3.6	0.0098	0.93
	R165+5% Zeolite	0.6	1890	45	3.8	0.0064	0.79
	R165+10% Zeolite	0.6	1980	45	9.6	0.0067	0.95
	R165+20% Zeolite	0.6	2160	45	18.2	0.0037	0.72
PO ₄ -P	R165	1.5	1800	45	16.1	0.0058	0.99
	R165+5% Zeolite	1.5	1890	45	22.7	0.0034	0.92
	R165+10% Zeolite	1.5	1980	45	36.9	0.0018	0.97
	R165+20% Zeolite	1.5	2160	45	49.4	0.0014	0.98

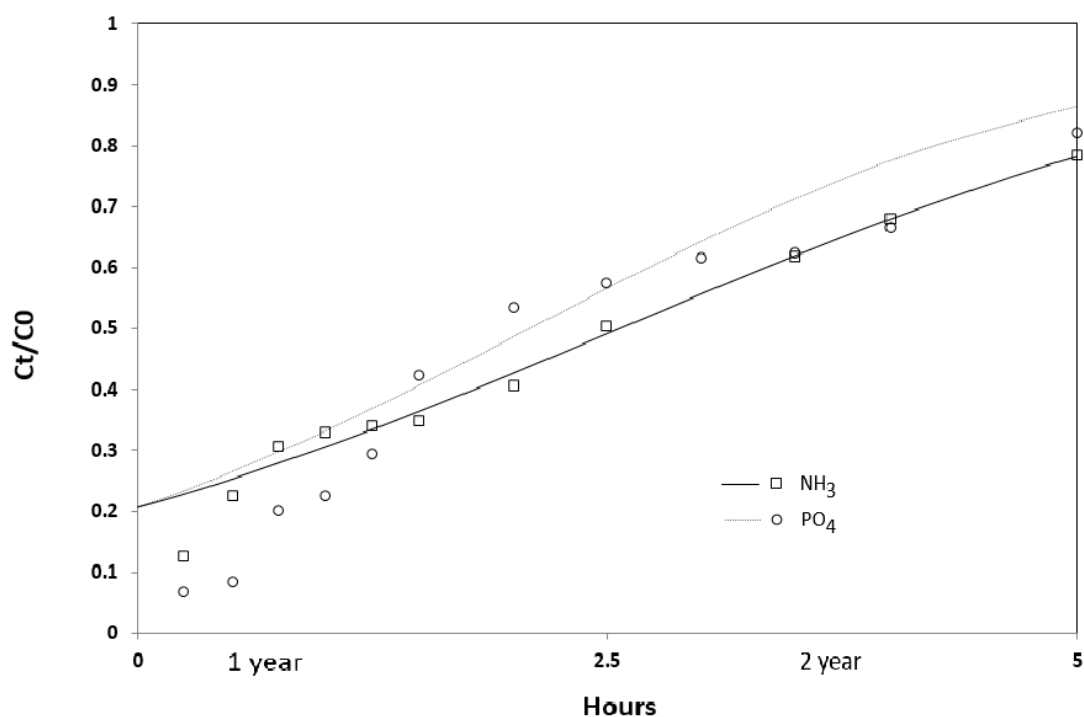


Fig. 3. The breakthrough curves for NH₄-N and PO₄-P removals by the 10% Zeolite + R165 column test at a flow velocity of 300 mm/h. Lines show the Thomas model simulation.

Table 6. Thomas model parameters for the simulation of breakthrough curves in Fig. 3

	Co mg/L	M g	Q mL/min	q _o mg/g	K _T mL/min.mg	R ²
NH ₄ -N	0.56	1980	135	5.8	0.0156	0.98
PO ₄ -P	1.2	1980	135	12.1	0.0089	0.87

Previous researchers have observed effective removal of total P (TP) by bio-filter media in laboratory scale experiments (Davis et al. 2003; Fletcher et al. 2007; Henderson et al. 2007). However, they reported high variability in total N (TN) removal from the media. Hatt et al. (2009b) conducted a field scale experiment on bio-filtration filter media (soil based) and while observing effective removal of TP, reported significant variability of TN concentrations in the effluent. Furthermore, they emphasized the need to use media containing low concentrations of P to prevent possible leaching of P from the medium. In the present study, R165 contained considerable amount of P (101 mg/kg) (Table 1), however TP was not detected in the leachate when R165 was leached with distilled water. TN and NO₃-N removals by R165 were not significant and highly variable. This remained so even with the addition of zeolite to R165 (Supplementary Data II).

Sonstrom et al. (2002) reported that a bio-filtration system retained 49% total suspended solids, 74% total P, 44% total Kjeldahl-N (TKN), 45% total Zn, 29% total Cu, 2% total Pb on a mass basis, and 99% faecal coliform on a concentration basis in a field study conducted at a commercial parking lot in Connecticut, USA. In Victoria, Australia, Hatt et al. (2009a) conducted a field scale study on the removal of pollutants using bio-filters from urban run-off and stated that nutrient retention was variable, and ranged from consistent leaching to effective and reliable removal, depending on the bio-filter design. Of the pollutants, nitrogen was found to be more difficult to remove because it is highly soluble and strongly influenced by the variable wetting and drying regime that is inherent in bio-filter operation. However, they reported that average removal efficiencies of total TKN and TP were 9% and 12%, respectively. They suggested that soil-based bio-filters especially those which were low in P content were suitable in removing TP.

3.2. DOC removal

The concentration of DOC in the feed was 8-9 mg/L. There was only a slight reduction in the concentration of DOC in the effluent and no significant removal was observed for DOC by R165. This remained so even with the addition of zeolite (Supplementary Data III). Even though GAC is known to remove DOC (Sountharajah et al. 2016), there was hardly any improvement in DOC removal in the column with the addition of GAC to the media and likely because of the low GAC dosage (0.3%) used in the experiment.

3.3. Heavy metals removal

Heavy metals removal by R165 was good for up to 3 h (40-90% for all heavy metals) (Fig. 4a). After 16 h the percentages of removal reduced to 45% for Zn, 30% for Cu, 20% for Pb and less than 10% for the remainder

of the heavy metals. The addition of 10% zeolite to R165 significantly increased the removal rates of most heavy metals and the life of the R165 media (Fig. 4b). The removal percentages of Ni, Fe, and Mn remained the lowest even after the addition of zeolite.

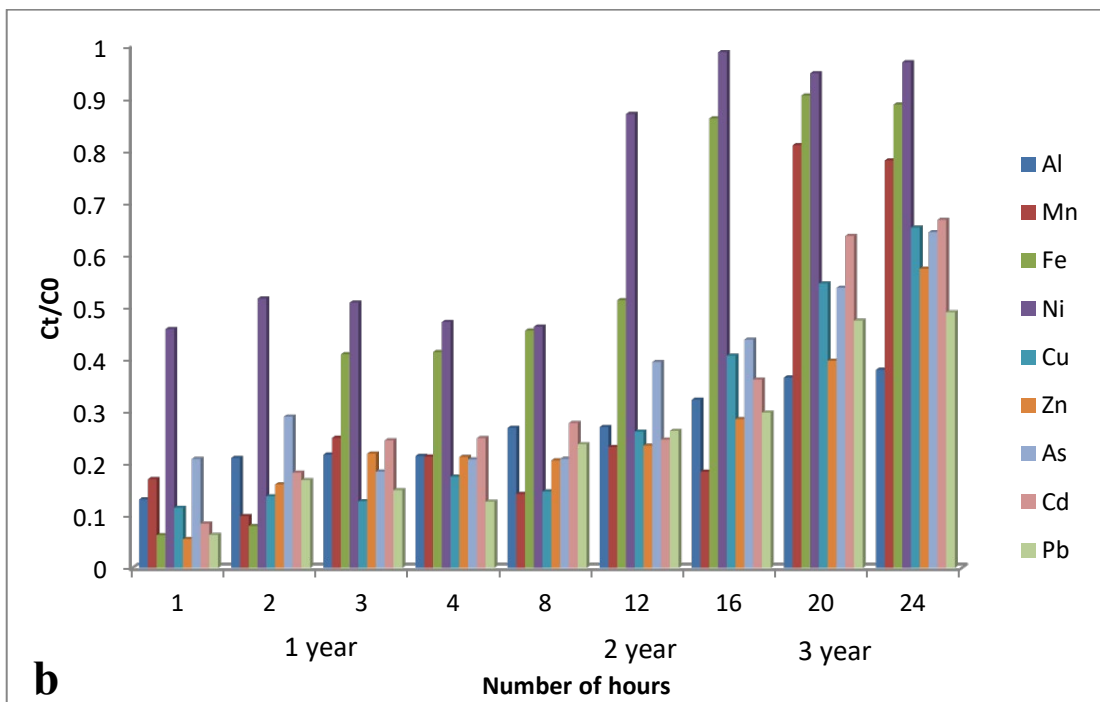
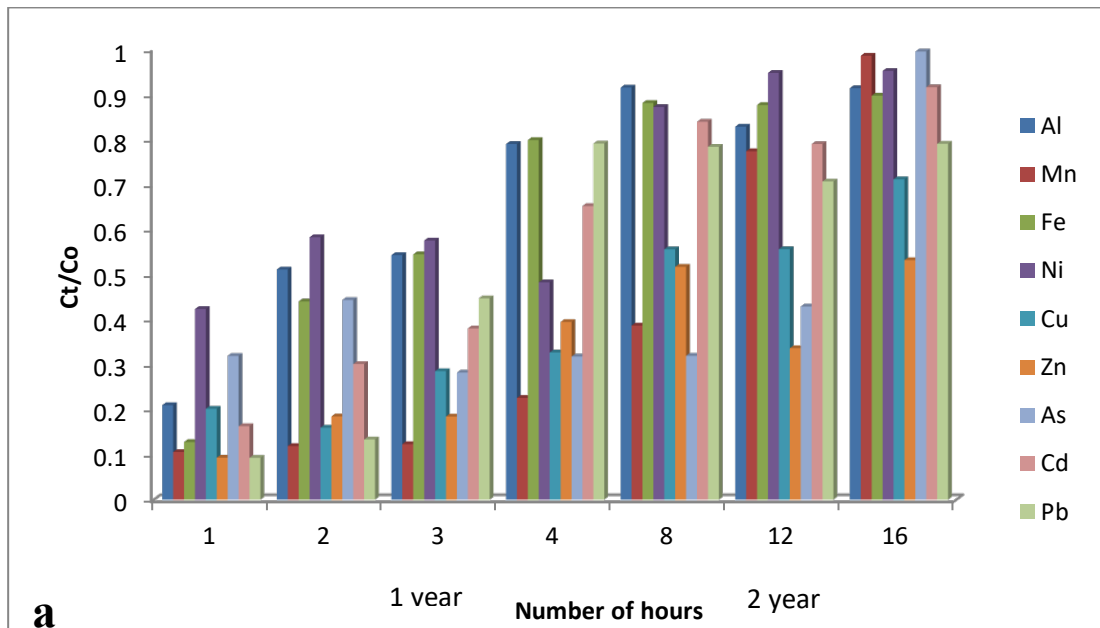


Fig. 4. Metals removal by (a) R165 (b) R165+10% zeolite at a flow velocity of 100 mm/h.

Of the heavy metals, R165+10% zeolite had the highest removal percentages for Pb, Cu, Zn, Cd and As and the lowest for Ni, Mn and Fe (Fig. 4b). Pitcher et al. (2004) conducted batch experiments using two zeolites, a synthetic zeolite and a natural mordenite to test their ability to remove dissolved heavy metals from simulated and spiked motorway stormwaters. They reported up to 42-89% reduction of heavy metals from the stormwater by mordenite and, also stated the percentage reduction order was Pb > Cu > Zn and Cd. Removal of heavy

metals mainly took place by ion exchange mechanism on the zeolite and through the impurities present in natural zeolites (Ćurković et al. 1997). The difference in the removal of heavy metals in percent terms depend on the concentrations of the heavy metals in the stormwater and the chemical characteristics of the heavy metals. The first hydrolysis constant of the metals (M) (MOH^+ formation) and solubility product of the metal hydroxides control the adsorption affinity of the metals (Nguyen et al. 2015). The lower the first hydrolysis constant, the greater the proportion of MOH^+ which has stronger adsorption than M^{2+} among the various metal species in solution. High solubility product favours precipitation of metals, especially on the surface of the adsorbent. Of the heavy metals tested, Pb has the lowest hydrolysis constant and the highest solubility product and therefore the highest removal percentage at 24 h (Fig. 4b), the longest filtration time that was tested. This agrees with the results of heavy metals adsorption on other adsorption media (Nguyen et al. 2015; Sountharajah et al. 2015).

The results of the heavy metals removal study show that use of R165 without additives as **filter** medium can remove only a one-year heavy equivalent metal load from stormwater to comply with the water quality required for safe disposal to natural waters. An addition of 10% zeolite to the medium increased the capacity of the **filter** to remove heavy metals and produce safe water for a period longer than two years.

3.4. Turbidity and conductivity removals

Fig. 5 shows the turbidity removal by the column experiments at 100 mm/h flow velocity. R165 reduced the turbidity by 68-78 % whereas the column of R165 mixed with 10% zeolite removed turbidity by 83-86%. When the flow rate increased (300 mm/h) in the latter column, the removal percentage decreased to 65-75%. This is due to the entry of a larger quantity of turbidity into the column per unit time.

The column containing R165 without additives and that containing R165 mixed with 10% zeolite decreased conductivity only during the first 4 h at the infiltration rate of 100 mm/h, and thereafter the turbidity remained the same as the influent solution (Supplementary Data IV). However, the reduction in conductivity was much higher in the latter column.

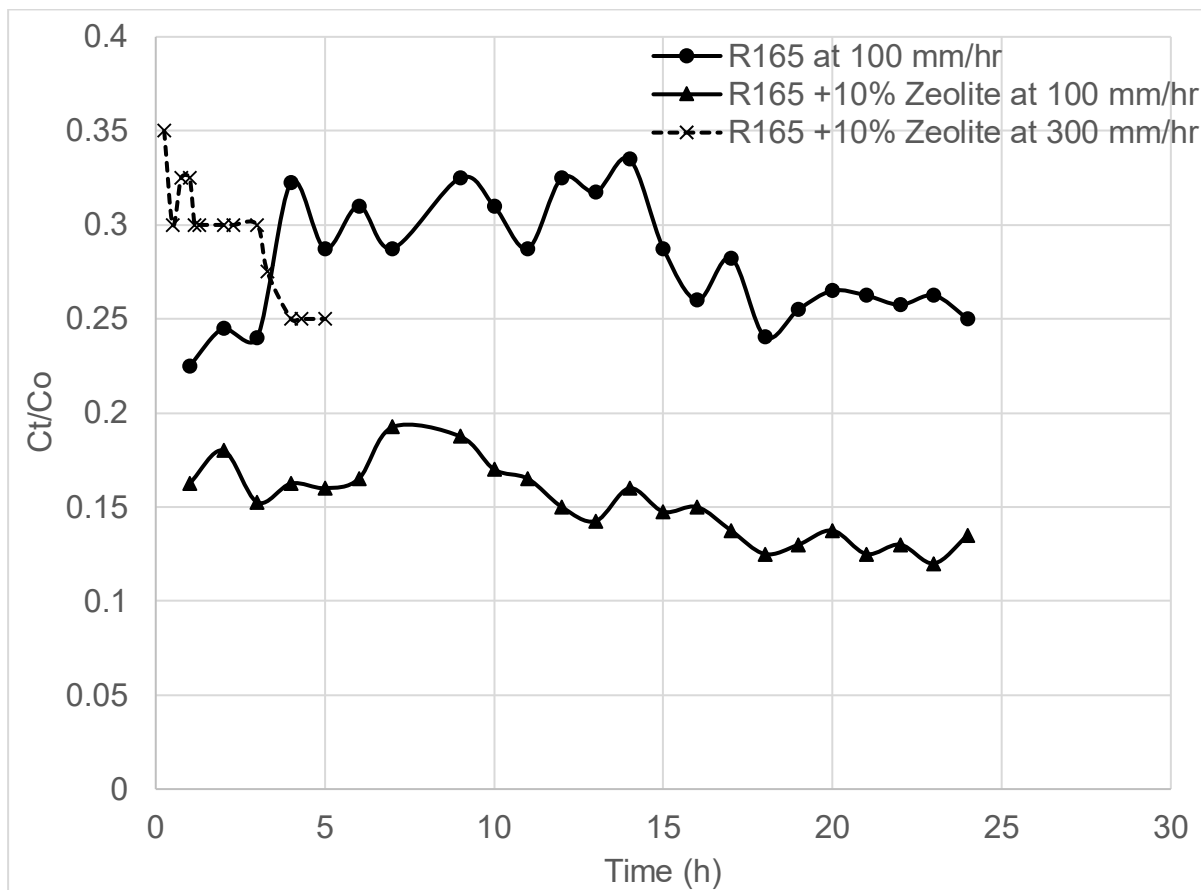


Fig. 5. Turbidity removal by two filter columns at flow velocities of 100 and 300 mm/h

3.5. Polycyclic aromatic hydrocarbons (PAH) removal

PAH removal by R165 at a flow velocity of 100 mm/h was 30-99% for acenaphthene, 50-99% for phenanthrene and 50-92% for pyrene (Fig. 6 a). The lowest removal for each PAH was, as expected, at the highest time of testing (20 h) at between 30 and 50% removal. The adsorbent medium was increasingly saturated with PAH as time progressed resulting in decrease in the available sites for further adsorption.

However, when 0.3% GAC and 10 % zeolite were mixed with R165, higher percentages of the PAHs were removed at both 100 and 300 mm/h flow velocities (Figs 6. b, c). The percentage removals at 20 h for the flow velocity of 100 mm/h ranged 65 to > 99% (Fig. 6 b) compared to 30-50% in the column with only R165. Phenanthrene and pyrene were almost completely removed. The higher percentage removals at the lower flow rate compared to the higher velocity is due to a lower amount of PAH entering the filter per unit time. The higher removals of PAHs even with the addition of a very small amount of GAC to the filter media was due to the high affinity of PAHs to GAC (Eeshwarasinghe et al. 2018) and not likely to be due to adsorption onto zeolite in the filter. Preliminary batch experiments on adsorption of phenanthrene on R165, zeolite and GAC at an equilibrium phenanthrene concentration of 0.5 mg/L showed that their adsorption capacities were 0.05, 0.05 and 20 mg/g,

respectively. This indicates that the adsorption capacity of GAC is nearly 400 times that of zeolite. Therefore, zeolite even with 33 times the weight of GAC (10% vs 0.3% GAC) in the filter media would not have made any significant contribution towards the removal of the PAHs. Huttenloch et al. (2001) also reported that the adsorption capacity of a natural zeolite, clinoptilolite for the PAH, naphthalene was almost zero. The inability of zeolite to adsorb PAHs is due to its low degree of hydrophobicity. To overcome this problem others have modified the surface of zeolite by grafting hydrophobic organic groups such as quaternary ammonium groups and surfactants which made the modified zeolite an attractive adsorbent for removing PAHs (Lemić et al. 2007; Wolowiec et al. 2017).

The removal percentage of acenaphthene was lower than that of phenanthrene and pyrene because the hydrophobicity of acenaphthene (log Kow 3.92) was lower than the other two PAHs (phenanthrene log Kow 4.46, pyrene log Kow 5.18) (Eeshwarasinghe et al. 2018). Acenaphthene appears to progress towards saturation of the three columns faster at both flow velocities than phenanthrene and pyrene, because of its lower adsorption capacity. Media containing 0.3 % GAC +10% Zeolite+ R165 at 100 mm/h resulted in nearly 100% removal of both phenanthrene and pyrene for an estimated period of three years equivalent rainfall.

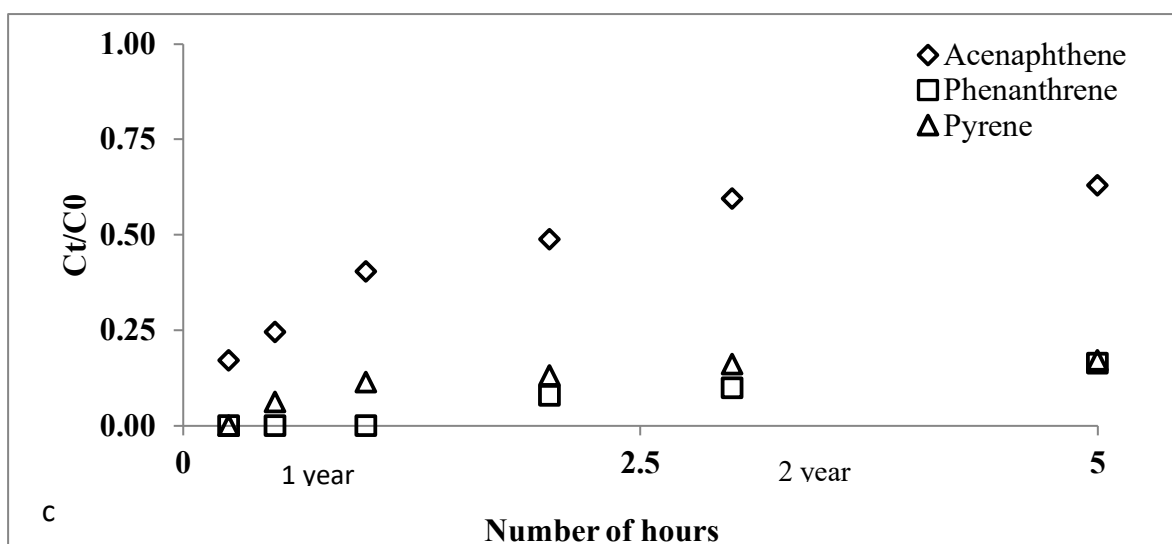
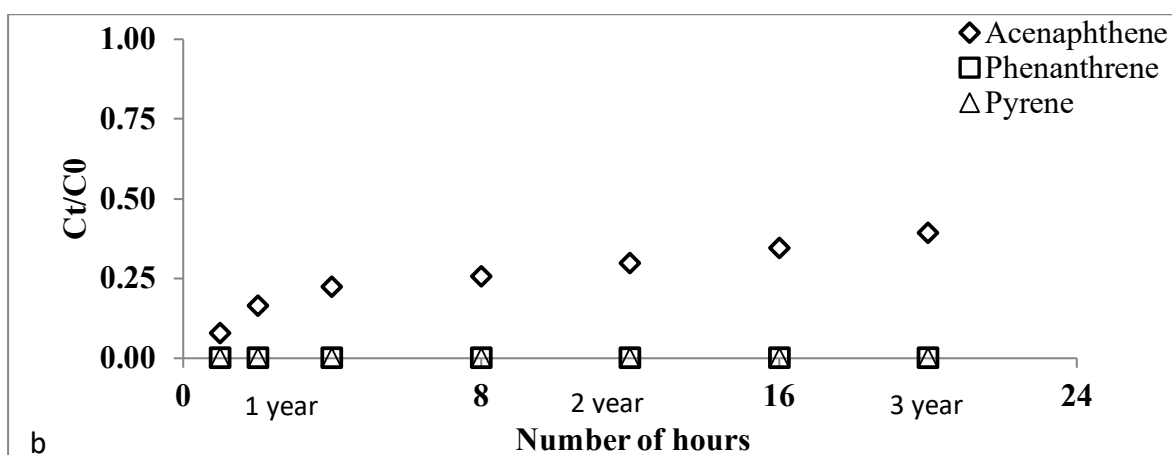
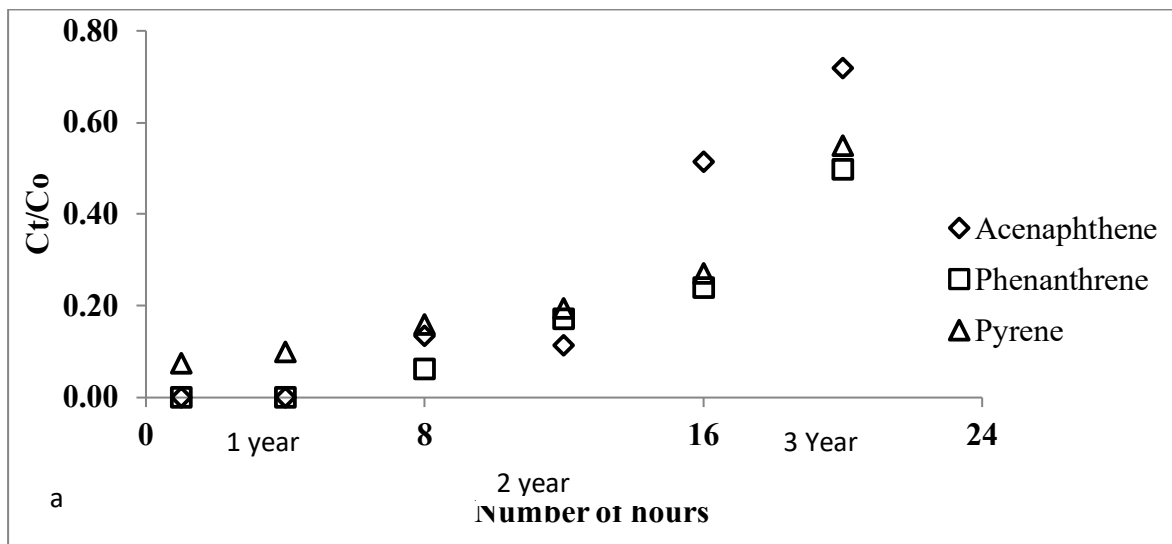


Fig. 6 (a) The breakthrough curve for PAH removal by the column with (a) R165 at flow velocity 100 mm/h; (b) 0.3% GAC + 10% Zeolite + R165 at flow velocity 100 mm/h; (c) 0.3% GAC + 10% Zeolite + R165 at flow velocity 300 mm/h.

4. Conclusions

A novel experimental protocol to estimate the efficiency of a filter medium for the treatment of stormwater pollutants from 1-3 years rainfall experienced in the field was developed using a laboratory column-set-up over short-term duration. The column with a soil-based filter medium (R165) is capable of removing PO₄-P and NH₄-N for up to 8 h at a flow velocity of 100 mm/h which is a time-equivalent of one year of rainfall at Blacktown, New South Wales, Australia. An addition of 10% of zeolite to R165 extended the column saturation period to 24 h. The breakthrough data for PO₄-P and NH₄-N were satisfactorily described by the Thomas model. However, the tested media were unable to remove TN and NO₃-N even with the addition of 10% zeolite, with higher variability of these pollutants in effluent concentrations.

The majority of the nine heavy metals tested were removed by more than 50% for up to 4 h in the soil-based filter. This level of removal increased to 16 h (rainfall equivalent to 2 years) when 10% zeolite was added to the filter. The column with R165 + 10% zeolite showed higher affinity towards Pb, Cu, Zn and As regardless of their initial concentrations and less affinity towards Ni.

Column with R165+10% zeolite removed considerable amounts of PAHs (30-50%) while a column with R165+10% zeolite+0.3% GAC removed 65- > 99% of PAHs from the influent at 20 h operation - phenanthrene and pyrene were almost completely removed. The removal percentage of acenaphthene was lower than phenanthrene and pyrene because the hydrophobicity of acenaphthene (log Kow 3.92) was lower than that of the other two PAHs (phenanthrene log Kow 4.46, pyrene log Kow 5.18).

Overall, the results indicated that modification of the soil-based filter medium with zeolite and GAC can increase the removal of nutrients (PO₄-P, NH₄⁺), heavy metals and PAHs from stormwater. 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.

Acknowledgement

We thank Craig Bush of Blacktown City Council, Blacktown, NSW, Australia for providing the biofilter media and offering suggestions for the study.

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