



Non-equilibrium zinc uptake onto compost particles from synthetic stormwater

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HIGHLIGHTS

- ▶ Zinc uptake from synthetic stormwater on various compost particle sizes was studied.
- ▶ Uptake on smaller particles conformed to equilibrium assumptions.
- ▶ Intra-particle diffusion caused rate limited metal uptake on larger particles.
- ▶ Non-equilibrium modelling adequately modelled larger particles.
- ▶ Design of bioretention systems should consider filtration media particle size.

ARTICLE INFO

Article history:

Received 25 May 2012

Received in revised form 10 July 2012

Accepted 11 July 2012

Available online 22 July 2012

Keywords:

Compost

Lignocellulosic sorbents

Zinc

Adsorption

Hydrus 1-D

ABSTRACT

Zinc uptake onto different particle size compost was evaluated in batch and column studies using a synthetic stormwater to quantify sorption capacity and kinetics. The results showed that the pseudo equilibrium time for uptake increased from 2 h to greater than 120 h as the particle size of compost increased from 75 μm to 6.75 mm. This was due to intra-particle diffusion becoming a rate limiting process as the particle size increased. Column effluent data with 1.18 mm particles could be fitted by Freundlich isotherm while that from the 4.75 mm particles and a mixed particle size columns showed rate limited sorption with tailing and could not be adequately fitted using an equilibrium based isotherm. The results have established rate-limited sorption in amended filtration media due to larger particles under these flow conditions. This needs to be accounted for in the design of these filtration media and during performance modelling.

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1. Introduction

Traditionally, stormwater infiltration systems have been designed around being hydraulically effective and have used relatively inert media such as coarse sand/fine aggregate as a filtration media. Stormwater treatment within subsurface filtration media has occurred primarily through a physical process of filtering out contaminants. Whilst these inert media have proven to be effective in removing particulate-bound stormwater contaminants they have not been as effective removing dissolved metal constituents. Enhanced performance for dissolved metal removal can be achieved by incorporating reactive materials (amendments) such as agriculture waste (Sciban et al., 2007; Sud et al., 2008) which can provide removal through physical filtration as well as sorption and precipitation.

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Sorption is a general term to describe overall processes resulting in the transfer of dissolved solutes to solids. The prediction of dissolved metal sorption in filtration systems often relies on the assumption of local equilibrium between stormwater solutes and filtration media. Linear and non-linear isotherms are then used to quantify metal uptake. Factors such as flow, particle size and sorbent composition can affect the interaction between the solute and sorbent and may shift sorption from equilibrium to a non-equilibrium state. When non-equilibrium occurs, the breakthrough curve shows a diffuse front and tailing phenomena which results in rate-limited sorption. The mechanistic basis of these non-equilibrium phenomena may be physical and/or chemical. Physical non-equilibrium may occur due to two widely documented processes; film diffusion and intra-particle diffusion. Chemical non-equilibrium at the sorbent–solute interface may also control uptake kinetics through sorption onto or desorption from sites with relatively large activation energies, and the slow formation of surface precipitates (Sparks, 2003). Treatment effectiveness of filtration media under non-equilibrium conditions may differ significantly from that under equilibrium conditions due to rate-limited sorption.

While the process of non-equilibrium or rate-limited sorption has been recognised in structured soils (Kohne et al., 2009) and engineered treatment systems, there has been few studies about of its relevance and potential impact on stormwater filtration systems (Huang et al., 2006). There is a need for modelling tools to adequately predict the performance of bioretention systems and verify the suitability of current guideline (Roy-Poirier et al., 2010).

Although adding amendments to filter sand can potentially be a cost effective stormwater treatment strategy, quantitative relationships between filtration design parameters (e.g. residence time, media longevity) and woody filtration media characteristics (e.g. particle size, composition) need to be known to predict treatment performance. Whilst some of these relationships are well established for specialised sorbents such as activated carbon and zeolite there is less known about low-cost media such as woody materials. In particular, compost as a filtration media is still relatively novel. A limited number of studies on its dissolved metal uptake capacity (Seelsaen et al., 2006; Jang et al., 2005) have shown adequate performance under laboratory conditions. Many laboratory studies have determined the dissolved metals removal performance for woody materials (including compost) using particle sizes less than 1–2 mm and residence times which often result in pseudo-equilibrium data that can be fitted by linear or non-linear isotherms. However field application guidelines often allow larger particle sizes. For e.g. Wisconsin specifies only that 98% of compost should be less than 19 mm (DNR, 2006) while City of Portland (2008) is more restrictive and specifies greater than 50% of the compost must be greater than 0.4 mm, up to 60% greater than 2 mm, and 100% less than 12 mm. Therefore a significant fraction of compost particles can be larger than those used in most laboratory studies to evaluate contaminant removal. The link between laboratory performance and field application for these materials is important since the cost-effectiveness of these materials is impacted if they require extensive pre-processing (i.e. grinding, sieving, sorting) prior to application. This mismatch creates a knowledge gap about the relationship between treatment performance and the functional characteristics of the compost (e.g. particle size, composition) under conditions relevant to stormwater filtration treatment. In particular, how sorption is impacted by sorbent particle size needs to be understood.

The goal of this paper is to evaluate the sorption capacity and kinetics of variously sized compost particles in removing zinc from synthetic stormwater under hydraulic conditions relevant to stormwater filtration systems. This study specifically investigates the occurrence and prediction of rate limited sorption caused by compost of different particle sizes rather than the exact nature of the non-equilibrium processes. Batch experiments were used to explore relationships between particle size and rate-limited sorption under static conditions. These relationships and sorption parameters were further investigated under dynamic conditions using columns studies and numerical modelling. It is expected this study will be useful to other researchers and engineers wanting to use woody materials as a filtration amendment in stormwater treatment devices.

2. Methods

2.1. Materials

The compost used was provided by Australian Native Landscapes and was sourced from garden organics. Garden organics includes putrescible garden organics (grass clippings); non-woody garden organics; woody garden organics; trees and limbs; stumps and root balls. All woody filtration materials were then dried at 45 °C for 48 h. A sample as received prior to processing was desig-

nated Mix A. Other samples were then ground using a hammer mill (Model No. ADEB80N2, John Morris Pty Ltd.) and sieved until the required particle size range was obtained. Six graded particle size ranges for the compost were used in the batch and three particle sizes in the column studies (Table 1). It should be noted that all the compost particles were very elongate rather than spherical. Glass beads with a median particle size of 0.6 mm (Burwell Abrasive Blasting Equipment) were mixed with the compost particles. All weights reported in the paper are as dry matter.

The chemicals and nutrient concentrations used to create the synthetic stormwater (SSW) were adapted from Davis et al. (2001) (Table 2). Distilled water was used as the background solution for the SSW. The pH of the synthetic stormwater was adjusted using dilute HCl and NaOH solutions. The 25 Litre container holding the synthetic stormwater was made of polyethylene and the tubing was 6 mm PVC. All glassware in contact with samples was acid washed for 24 h with 0.1 M HNO₃ and rinsed with Milli-Q water.

2.2. Analytical methods

Samples from batch and column studies were analysed for pH and electrical conductivity (TPS, Model 90-FL). Samples were filtered with a 0.45 µm cellulose membrane filter and preserved by acidifying to pH < 2 using 1 N HNO₃ (APHA, 1998). The preserved samples were analysed for zinc concentrations using AAS or ICP-OES. The Cation Exchange Capacity (CEC) was analysed using saturated ammonium extractants at pH 7 method (Rayment and Higginson, 1992).

Total carbon and nitrogen for all solid materials were determined in duplicate using a Truspec Carbon Nitrogen determinator. Ash content was measured using the method for Total Volatile Solids (APHA, 1998) at 550 °C. Solid phase media used for the digestion studies were obtained in duplicate from the column experiments and then dried prior to acid digestion. The method used has been developed based primarily on that of Krishnamurthy et al. (1976). This method involves sand-bath heating/refluxing duplicated samples in nitric acid followed by hydrogen peroxide addition and filtration. The specific surface areas and pore characteristics of solid phase media were measured using BET/N₂ (Micromeritics Tristar) (Table 1).

2.3. Batch studies

Batch experiments utilised a 1.0 g sample of compost added to 2 Litres of SSW in a glass bottle and placed on an orbital shaker (Model PO1412, Paton Industries) at 200 rpm for 120 h. Samples were withdrawn using a syringe at predetermined time intervals and then analysed. The pH of the SSW solution was measured prior to sorbent addition and sample extraction. All batch experiments were conducted in duplicate with sorption results reported as averages. The relative standard error between duplicates is less than 5% for particles sizes less than 4.75 mm. A greater standard error for the 6.75 mm particles reflects their heterogeneity and the relatively small sample mass. All the sorption experiments were carried out at 20 ± 1 °C. The pH during the batch tests increased from approximately 4.9 to 5.4.

Metal uptake at different times, q_t (mg/g) was calculated using the mass balance between the solid and the solution as follows:

$$q_t = (C_o - C_t)V/M \quad (1)$$

where q_t the amount of metal ion sorbed at time t (mg/g), C_o the initial liquid phase metal ion concentration (mg/L), C_t is the liquid phase metal ion concentration at time t (mg L⁻¹), V the initial solution volume (L) and M is the mass of mixed sorbent (g).

Table 1
Characteristics of sorbents.

Size (mm)	Particle size range (mm)	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore width (nm)	C/N	Ash (%)	CEC (cmol kg ⁻¹)
0.075	0.075–0.6	1.31	0.0080	24.6	–	–	–
0.3	0.3–0.6	–	–	–	–	–	–
0.6	0.6–1.18	1.07	0.0048	18.0	37	17	–
1.18	1.18–2.36	0.98	0.0036	14.8	41	11	86
4.75	4.75–6.3	0.66	0.0026	15.3	128	4.7	68
6.3	6.3–9.5	–	–	–	–	–	–
Mix A	^a	–	–	–	–	–	–

CEC –Cation Exchange Capacity.

^a <1.18 mm (28%), 1.18–2.36 mm (3%), 2.36–4.75 mm (12%), 4.75–9.5 mm (50%), 9.5–19 mm (28%).**Table 2**
synthetic stormwater (SSW) characteristics.

Pollutants	Chemical	Range
Total Phosphorous (mg L ⁻¹)	Dibasic sodium phosphate (Na ₂ HPO ₄)	0.6
Organic Nitrogen (mg L ⁻¹)	Glycine (NH ₂ CH ₂ COOH)	4
Nitrate-Nitrogen (mg L ⁻¹)	Potassium nitrate (KNO ₃)	2
Copper (mg L ⁻¹)	Cupric sulfate (CuSO ₄)	1.0
Lead (mg L ⁻¹)	Lead chloride (Pb Cl ₂)	1.0
Zinc (mg L ⁻¹)	Zinc chloride (Zn Cl ₂)	5.0 ± 0.1
PH	–	4.8 ± 0.9
EC (μS cm ⁻¹)	–	53 ± 5
Temperature, (°C)	–	20 ± 1

EC –electrical conductivity.

2.4. Column studies

The columns were constructed in PVC class 18 with an inner diameter of 5.3 cm and length of 58 cm, giving a cross-sectional area for filtration of 22 cm². Since the ratio of column diameter to median particle diameter is high, the effects of channelling are expected to have negligible effect (Reynolds and Richards, 1996). Columns were constructed by sealing a PVC cap at the end of the column using Silastic. A layer of plastic mesh and then a 2–3 cm depth of 3 mm diameter glass beads followed by a further plastic mesh were placed upon the end cap at the influent end of the column. All columns had a mix of 68 g of compost and 1663 g of 0.6 mm glass beads (≈20–25% v v⁻¹ compost). The mix was wetted and then added in increments using continuous column vibration without any compaction over the filtration media surface. The final depth of filtration media in the columns was approximately 55 cm with a total bulk density of 1.5 g/cm³. Two columns were constructed for each size of compost (one for sorption and the other for bromide tracer experiment). The sorption columns were initially saturated with distilled water for 5 days, then SSW was pumped using peristaltic pump (Masterflex Model 7553-85) into the column in up flow mode. The average flow rate was 12 mL/min. Copper breakthrough (C/C₀) was only between 0.2 and 0.6 for the Mix A and 4.75 mm columns and approximately 0.1 for the 1.18 mm column after 1200 pore volumes (PV)(~620 h). It was therefore not reported in this paper. The effluent was not sampled for lead since the focus was on zinc and copper removal. The pH of the column influent comprised synthetic stormwater and varied between pH 5.4 and 5.5 up to 550 PV then 4.6–5.4 until 980 PV and then pH 5.1–5.7. In all columns, after an initial period (<100 PV) the effluent maintained a pH of 5.3–6.

A bromide tracer was used to determine the hydrodynamic parameters and pore volume of the column. The bromide tracer columns were initially flushed with tap water through the influent end of the column at a rate of approximately 12 mL/min until a consistent effluent had developed (24 h), and then followed by

Milli-Q water for 10 min. A 100 mg/L bromide solution was prepared from KBr salt using Milli-Q water as the solution matrix and pumped at a rate of approximately 12 mL/min through the column. All effluent water passed through a flow cell containing a bromide ion selective electrode (Model BR43, ASI). A 7 point calibration curve was prepared using Milli-Q water to estimate the bromide concentration of the effluent.

2.5. Numerical modelling

Hydrus 1-D (Simunek et al., 1998) is a numerical model which solves the Richards' equation for variably saturated water flow and convection–dispersion type equations for solute transport. The governing flow and transport equations are solved using Galerkin-type linear finite element schemes. It also includes a Marquardt–Levenberg type parameter optimization algorithm for inverse estimation of soil hydraulic and/or solute transport and reaction parameters from measured transient or steady-state flow and/or transport data.

Within the model, sorption is expressed as Eq. (2) (Simunek et al., 1998):

$$S = \frac{K * C^\beta}{1 + \eta * C^\beta} \quad (2)$$

where S: Sorbed concentration (mg/g); C: Inflow concentration (mg L⁻¹); K: First adsorption coefficient (cm³ g⁻¹), also known as Freundlich constant; η: Second adsorption coefficient (dimensionless); β: Third adsorption coefficient (dimensionless), also known as 1/n where n is the sorption intensity.

For two site non-equilibrium sorption model, Hydrus 1-D assumed that sorption sites can be separated into two fractions; fraction f (type-1 sorption sites) is assumed to be instantaneous sorption (equilibrium sorption), whereas the remaining fraction 1–f (type-2 sorption sites) is assumed to be time-dependent (non-equilibrium sorption), and α: is a mass transfer coefficient (h⁻¹).

3. Results and discussion

3.1. Sorption capacity and batch kinetics

Zinc uptake for different compost particle sizes was measured at sequential times (Fig. 1). The error bars are plotted for all samples but it is only the largest compost size which shows a higher standard error.

The results show that the rate of zinc uptake decreased with time. The smaller particles (≤1.18 mm) reached a pseudo-equilibrium with similar zinc uptakes (7.7–8 mg/g) after 120 h. This suggests that all sorption sites were accessible at equilibrium regardless of particle size. This finding was unexpected and differs from other studies such as Sciban and Klasnja (2004). In a single

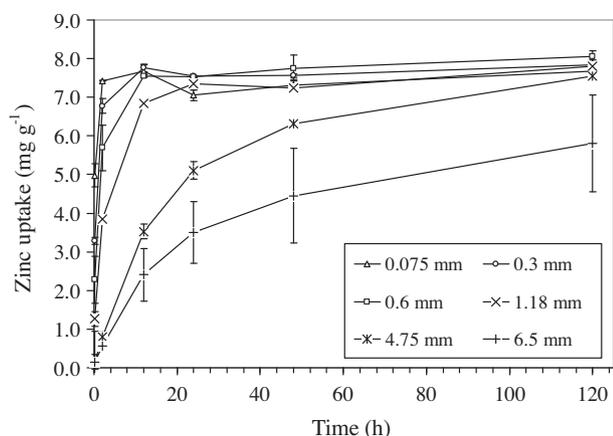


Fig. 1. Effect of different particle sizes upon zinc uptake kinetics with error bars.

solute study they found a 25% increase in dissolved copper uptake onto sawdust over this particle size range. This magnitude the increased uptake is consistent with the increase (25%) in the measured surface area over this particle size range (Table 1). These surface area and pore volume data are similar to other reported values for wood (Seelsaen et al., 2007; Papadopoulos et al., 2003). The reason for the observed lack of relationship between particle size and zinc uptake is not clear. A distinguishing characteristic of our batch tests were that we had a long equilibrium time which is typically two orders of magnitude greater than many metal uptake studies. Of interest is that studies of organic partitioning onto lignin in wood particles have found sorption to be independent of particle size (Mackay and Gschwend, 2000; Severtson and Banerjee, 1996). The nature of the sorption sites active in metal uptake and their accessibility in multi-solute solutions needs to be better understood for these woody media. Moreover, the presence and concentrations of electrolytes such as Ca and Mg ions in multi-solute solution will affect the efficiency of metals biosorption (Ofomaja et al., 2010).

The larger particles (≥ 4.75 mm) had lower uptake values (5.8–7.5 mg/g) after 120 h, presumably because they had not conclusively reached equilibrium at this stage. The impact of rate limited uptake upon particle size can be seen from the relative fraction of the zinc that was taken up after 2 h compared with the uptake at 120 h. It decreased from 0.96 to 0.09 as the particle size increased from 0.075 to 6.5 mm. The results for compost show that mass transfer limitations clearly have a significant affect upon the rate of zinc uptake, particularly for particle sizes larger than 1.18 mm.

In the column studies, zinc sorption uptakes were calculated from a mass balance on the influent and effluent concentrations as well as digestion of sorbents after the column tests had terminated. The uptake from the mass balance was 9.1 mg/g (1.18 mm), 7.8 mg/g (4.75 mm) and 9.7 mg/g (Mix A) while the digestion studies showed 9.3 mg/g (1.18 mm) and 8.5 mg/g (4.75 mm). There was negligible sorption onto the glass beads. These results show a decreased uptake as the particle size increased. This change was either 9% (digestion results) or 20% (mass balance calculations) depending on the measurement method. These results are also consistent with a measured decrease of 33% in particle surface area and 21% in CEC (Table 1). They are similar to the batch tests (~ 8 mg/g) and are within the reported values of 3–14 mg/g for woody materials in multi-solute solutions (Gibert et al., 2005; Seelsaen et al., 2007, 2006; Jang et al., 2005; Nwachukwu and Pulford, 2008).

Further analysis on the kinetics data was undertaken to better understand the rate limiting mechanisms which occurred in the

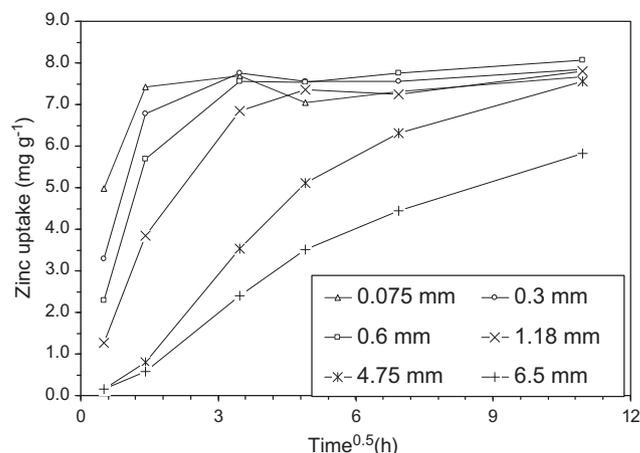


Fig. 2. Intra-particle diffusion plot of zinc uptake upon different particle sizes.

various compost particle sizes. An intra-particle diffusion model is often used to demonstrate that diffusion controlled phenomena are rate limiting (Sparks, 2003). The intra-particle diffusion rate equation is expressed as:

$$q_t = k_{ID}t^{0.5} + c \quad (3)$$

Where q_t is the sorption capacity at time t , k_{ID} is a diffusion rate parameter, t is time and c is a constant. A linear relation between q_t vs. $t^{0.5}$ is obtained if sorption is controlled by intra-particle diffusion. The intra-particle diffusion plot may have various slopes (Wu et al., 2001; Sun and Yang, 2003). A first steeper slope is attributed to external surface adsorption while a second, more gradual slope can occur due to intra-particle diffusion processes. A third portion is the final equilibrium stage, where the intra-particle diffusion starts to slow down due to the extremely low solute concentrations.

The intra-particle diffusion plot (Fig. 2) shows the smallest particle size with two phases; a steep slope which can be attributed to film diffusion which then transitions into a flat pseudo-equilibrium phase. As the particle size increases a transitional phase between these, representing intra-particle diffusion increasingly dominates the rate of zinc uptake. It is particularly evident in the particle sizes greater than 1.18 mm. These findings of rate limited sorption are consistent with larger particles having a longer diffusion pathway for solutes to access internal sorption sites. There is insufficient early time data to quantify the significance of external adsorption compared with intra-particle diffusion controlled sorption.

Within these static or batch conditions other factors such as initial metal ion concentration, wood composition, pH and solution temperature which were not investigated as part of this study will have an impact upon metal uptake. For e.g. Gupta et al., (2010) found zinc uptake onto a hybrid precursor derived from rice in batch studies was temperature dependent with a rate limiting step potentially being chemisorption rather than diffusion. Our study which used larger particles was clearly diffusion limited at particle sizes greater than 1.18 mm. They also found that at pH above 6 zinc hydroxide precipitation occurred. Therefore metal uptake onto wood under these conditions may differ. Further research is needed with well-structured batch studies to better understand these processes and their impact on non-equilibrium metal uptake.

3.2. Column isotherm studies

The sustained performance of a filtration based treatment system for removing dissolved contaminants is often evaluated through the use of column tests and breakthrough curves. To

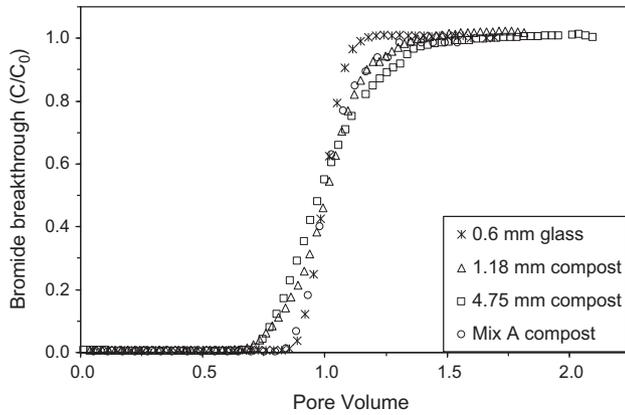


Fig. 3. Effluent data for bromide tracer .

Table 3

Column parameters.

Compost sample	Effective porosity	Pore volume (cm ³)	Longitudinal dispersivity (cm)
0.6 mm	0.36	410	0.11
1.18 mm	0.41	510	0.56
4.75 mm	0.37	470	0.96
Mix A	0.33	407	0.72

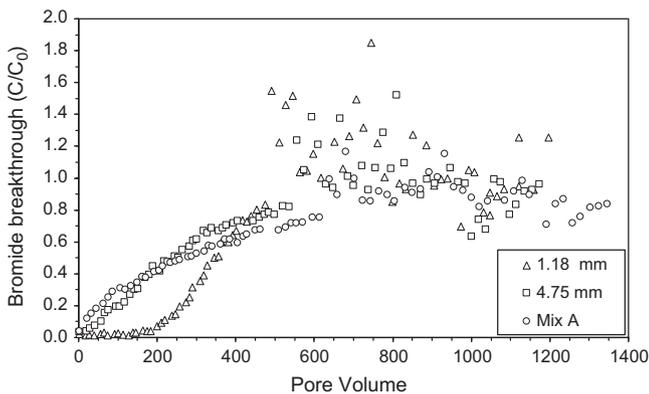


Fig. 4. Zinc effluent data.

examine hydraulic processes within the columns a tracer test was undertaken (Fig. 3).

The column containing only the 0.6 mm glass beads showed a sigmoid shaped breakthrough curve with the sharpest front. Fronting and tailing became more pronounced as the size of the compost particles added to the glass beads increased from 1.18 to 4.75 mm. Fronting is evident by the diffuse front in the breakthrough curve for the 4.75 mm column which causes early breakthrough of the bromide tracer, while tailing is delayed breakthrough. Interestingly, the column containing Mix A exhibited less asymmetry although it had a more diverse particle distribution than the other columns.

Inverse parameter fitting (Hydrus-ID) was used to determine the longitudinal dispersivity within the columns (Table 3). All of these values have a high coefficient of determination ($R^2 > 0.99$) and are within the published range (0.1–2 cm) for flows through disturbed and undisturbed, unconsolidated soils (Freeze and Cher-

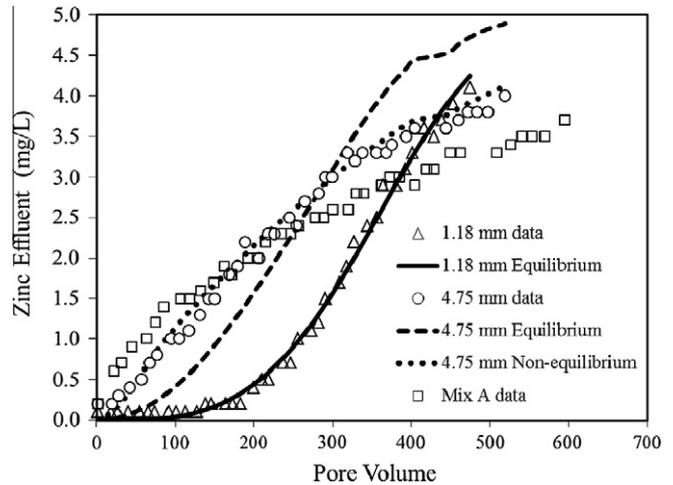


Fig. 5. Zinc effluent data for different particle sizes modelled with Freundlich isotherms using non-equilibrium and equilibrium parameters.

Table 4

Parameter estimates obtained during the application of the Freundlich non-equilibrium models to zinc BTC at input concentration of 5 mg/L zinc.

Column	f	k_f (cm ³ /mg)	β (1/n)	α (h ⁻¹)	R^2
<i>1.18 mm compost</i>					
Equilibrium model	1.0	0.43	1.29		0.994
Non-equilibrium model	0.87	0.31	1.22	0.015	0.997
<i>4.75 mm compost</i>					
Equilibrium model	1.0	0.90	1.49		0.958
Non-equilibrium model	0.32	0.90	1.48	0.024	0.992

ry, 1979). It was not possible in this study to distinguish whether these apparent dispersivity values can solely be attributed to mechanical dispersion rather than physical non-equilibrium processes.

The breakthrough curves for zinc in a multi-solute synthetic stormwater (SSW) onto three different particle sizes are shown in Fig. 4. Zinc concentrations in the effluent are continuously increasing until the compost is nearing its sorption capacity (zinc $C/C_0 > 0.83$). After this point all columns show erratic zinc effluent concentrations at times greater than the influent zinc concentrations. During this period the influent pH dropped less than one unit while the effluent remained the same. So while this may have exacerbated other effects we believe this zinc desorption was primarily due to displacement competition between zinc and the other solutes (copper, lead) which have a higher affinity. It is widely reported that sorption preference is $Pb > Cu > Zn$. Copper concentrations in the effluent (unpubl.) also show erratic behaviour with increased uptake as the zinc concentrations in the effluent increases due to zinc desorption. Desorption behaviour from multi-solute solutions have been reported in other studies (Juang and Lee, 1996; Deorkar and Tavlarides, 1997; Han et al., 2006; Al-Faqih et al., 2008; Kocasoy and Güvener, 2009; Ofomaja et al., 2010).

Analysis of zinc uptake for the various media has excluded late time data (zinc $C/C_0 > 0.83$) (Fig. 5). The zinc breakthrough curve for the 1.18 mm column showed a relatively sharp front with a sigmoid (*S*-shaped) breakthrough curve. In contrast, fronting is evident by the diffuse front in the breakthrough curve for both the 4.75 mm and Mix A columns. It causes early breakthrough of dissolved zinc. The Mix A, column which contained larger particles (78% > 4.75 mm) had the greatest fronting and tailing. The fronting

is seen from the breakpoint ($C/C_0 = 0.1$) for 4.75 mm column which occurs at 20 PV, less than 2 PV for the Mix A column and 200 PV for the 1.18 mm. This demonstrates the improved performance of the 1.18 mm column in terms of time till the breakpoint is reached.

Brusseau et al. (1997) concluded that both rate limited sorption and nonlinear sorption can cause breakthrough curves to exhibit fronting and tailing. Rate limited sorption can be due to intrasorbent diffusion as well as physical and chemical non-equilibrium processes (Brusseau and Rao, 1989). The existence of non-equilibrium sorption in the columns was also examined through the use of inverse parameter estimation for equilibrium isotherm fitting using Hydrus1D. The zinc breakthrough curve for the column containing the 1.18 mm particle size fraction was fitted relatively well ($R^2 = 0.99$) by a nonlinear equilibrium-based Freundlich sorption isotherm (Fig. 5) but a poor fit for both the linear and Langmuir isotherms was observed. Jang et al. (2005) found that while both Langmuir and Freundlich isotherms fitted batch sorption tests data of dissolved metals on mulch, Langmuir had a better fit.

The breakthrough curve for the column containing the 4.75 mm particle size and Mix A fraction however could not be adequately fitted using a linear, Langmuir or Freundlich equilibrium-based isotherms. This suggests that increasing the compost particle size from 1.18 to 4.75 mm under these flow conditions caused a shift from equilibrium sorption to non-equilibrium (rate-limited) sorption. The residence time in the column was therefore not enough for the 4.75 mm or Mix A particles to attain equilibrium sorption with the zinc influent. This is consistent with the batch results which showed that the bigger particles (e.g. 4.75 mm) needed more time than the 1.18 mm particles to reach equilibrium sorption. It should be noted that the calculated solute residence time in the columns ranged from 0.5 to 0.7 h dependent on the compost particle size. Based on the batch test data, the 1.18 mm compost had an uptake of around 30% of its equilibrium value while the 4.75 mm particles had an uptake of around 5% of its equilibrium value. This could suggest that within the 1.18 mm column some degree of non-equilibrium sorption processes is occurring even though a nonlinear equilibrium isotherm can be adequately fitted. This phenomenon has also been reported by Chang et al. (2001). However the relatively small uptake for the 4.75 mm particles within the given residence time precludes fitting with an equilibrium isotherm.

The zinc breakthrough curve for the 4.75 mm compost column (Fig. 5) was fitted relatively well by the two site non-equilibrium model using the Freundlich sorption isotherm (Table 4). The optimised curve fitting results showed that 0.32 fractions of the sites were in equilibrium, and with sorption on the remaining (type-2) sites were in non-equilibrium.

Moreover the zinc BTC for the 1.18 mm compost column (Fig. 5) was fitted relatively well by the two site non-equilibrium model using the Freundlich sorption isotherm (Table 4). The results show that 0.87 fractions of the sites were in equilibrium, and with sorption on the remaining (type-2) sites in non-equilibrium. This suggests that the 1.18 mm compost column had 13% of non-equilibrium sorption sites compared with 68% for 4.75 mm.

However, the extent to which either physical or chemical processes contributed to the observed non-equilibrium flow and solute transport in the columns could not be established in this study. The presence of tailing in the tracer tests and the intra-particle diffusion plot (Fig. 2) show that physical non-equilibrium was significant at least for the 4.75 mm particles. It is important to recognise that other factors beside the adsorbent particle size can create non-equilibrium conditions due to the dynamic flow conditions. Quek and Al-Duri (2007) found column breakthrough curves were affected by initial metal concentration, flow rate and bed height for lead and copper uptake on coir. At lower flow rates the breakthrough curves were flatter due to a thicker boundary

layer around the particle leading to a greater film resistance. At lower influent solute concentrations there also a flatter curve due to lower adsorption driving forces. Therefore the intra-particle diffusivity changed under these operating conditions. They also suggested that film mass transfer would have a greater effect in column studies than in batch studies. Further studies using a flow interruption technique (Brusseau et al. (1997)) could be used to more definitively establish the nature and significance of non-equilibrium processes.

4. Conclusion

The results show that under static and dynamic conditions representative of stormwater filtration, particles greater than 1.18 mm exhibited rate limited uptake of dissolved zinc attributable to intra-particle diffusion which was successfully demonstrated using intra-particle diffusion and Hydrus-1D models. It was found that when the compost was near metal saturation that metal desorption occurred. This clearly shows that late-time breakthrough performance data was less predictable than early time data. These results have established that the particle size of compost is an important design parameter and can cause rate-limited sorption in filtration-based treatment of stormwater. However further research is needed to identify the type of non-equilibrium processes operating.

Acknowledgement

The CRC for Contamination Assessment and Remediation of the Environment (CARE) provided partial support for this research.

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