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Zinc sorption onto different particle sizes of compost from aqueous solution

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ABSTRACT

The zinc adsorption capacity and kinetics of different compost particle sizes were investigated using batch and column experiments. The results indicated that the particle size influenced the sorption process. The surface area per unit weight of the sorbent increased as the particle size decreased. The adsorption equilibrium data fitted very well both the Langmuir and Freundlich isotherms. The estimated sorption capacities of different compost particle size in the column experiment were 22.9 mg/g (0.60 mm), 17.3 mg/g (1.18 mm) and 12.7 mg/g (4.75 mm) compared with Langumir isotherm predictions of 26.6 mg/g (0.60 mm), 18.7 mg/g (1.18 mm) and 15.6 mg/g (4.75 mm). It is evident that compost has a high affinity for zinc which reflects the physicochemical properties of the compost particles. These properties indicate that weak physical sorption and strong chemical sorption is likely to occur between zinc and the compost particles.

Keywords: Compost; Particle size; Sorption capacity; Zinc; Sorption kinetics; Equilibrium isotherms

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1. Introduction

Water pollutants discharged from municipal, industrial, commercial, residential and agricultural activities have negative effects on both human and environmental health. Many studies have shown that compost can reduce many water pollutants such as suspended solids, heavy metals, nitrogen, phosphorus, hydrocarbons, pesticides, petroleum products and other potentially hazardous substances [1–3]. Compost has been applied successfully as a best management practice in stormwater treatment systems such as compost blankets, compost filter berms and compost filter socks [4].

Some advantages for using compost as an adsorbent material is its availability from multiple sources (garden, forests, timber industry etc.) and that it is often considered as waste. This means that the compost has environmental benefits both as a sustainable resource and can be cost-effective compared with other adsorbents.

Compost is a general term and consists of humic substances, which perform like a polyelectrolyte and has a strong affinity to complex metal ions by either adsorption or ion exchange [5]. Compost results from the controlled biological decomposition of organic material such as yard trimmings, wood chips, vegetable scraps, paper products, sorted municipal solid waste, raw or treated sewage sludge, animal

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manure, paunch manure, plant or food residue or their mixtures [6]. The origin of compost as well as other factors (i.e. composting method) help create its physiochemical properties. Physiochemical properties such as surface area, particle and pore size, surface charge, cation exchange capacity and functional groups are considered the main controlling factors involved in the physical and chemical adsorption [7]. Moreover, these properties of the adsorbent will affect the heavy metal adsorption rate, capacity and uptake mechanisms.

Many studies have shown the potential for heavy metals sorption by compost from different sources. One gram of compost sourced from household and garden waste can remove 97.9% of lead, 97.7% of cadmium, 95.9% of zinc and 92.4% of copper from a 100 mg/L metal solution [8] while 6 g of mulch can remove more than 80% of copper and zinc [9]. It was also shown that the sorption capacity of compost sourced from kerbside (garden) waste was 11.2 mg/g at pH 5 [1]. Using municipal compost in combination with calcite to remediate acid mine drainage, the maximum sorption capacity of compost in a column was 3.9 mg/g at pH 6.5 [10]. However, in most of the published work, the physiochemical properties of compost are not well specified and there is no attempt to relate the adsorption process to these characteristics. Moreover, the effect of compost particles on the metal adsorption process using batch and column experiments is still not well demonstrated.

This paper aims to evaluate the adsorption capacity, mechanism and kinetics of different particle size of compost in removing zinc from single metal solution using batch and column experiments. Langmuir and Freundlich adsorption isotherm models were used to fit the data. The physiochemical characteristics of compost were investigated and compared with the adsorption mechanisms.

2. Experimental methodology

2.1. Materials

The compost (Australian Native Landscapes) was compliant with AS4454 and consisted of a screened composted leaf mulch (10–35 mm) sourced from garden organics. Garden organics includes putrescible grass clippings; non-woody garden organics; woody garden organics; trees and limbs; stumps and root balls. The compost was dried at 45℃ for 48 h and then ground using a hammer mill (Model No. ADEB80N2, John Morris Pty Ltd) until the required particle size range (0.6, 1.18 and 4.75 mm) was obtained. Three graded particle size ranges for the compost were used in the batch and column experiments (Table 1). Glass beads with a median particle size of 0.6 mm (Burwell Abrasive Blasting Equipment) were mixed with the compost particles. Distilled water was used as the background solution for the experiments. The pH of the zinc solution was adjusted using dilute HCl and NaOH solutions. The 25 L container holding the zinc solution was made of polyethylene and the tubing was 6 mm PVC.

2.2. Analytical methods

All water samples were measured for electrical conductivity (EC) and pH (TPS WP-81). Samples were filtered with a 0.45 μm cellulose membrane filter and preserved by acidifying to $pH < 2$ using 1 N HNO_3 [11]. The preserved samples were analysed for zinc concentrations using Atomic Absorption Spectrometry (GBC AAS932). All plastic and glass ware in contact with samples were acid washed for 24 h with 0.1 M HNO_3 and rinsed with Milli-Q water, unless otherwise noted. Cation exchange capacity (CEC) of different adsorbents was measured using saturated ammonium extractants (ammonium acetate) at pH 7 method [12]. Particle structure characteristics of various particle sizes of the compost were measured by Particle Analysis Service, CSIRO Minerals Commonwealth Scientific and Industrial Research Organisation T/A CSIRO using an adsorption analyser (Micromeritics Tristar BET/N2). Lignin, cellulose and hemicellulose were determined by the Wagga Wagga Feed Quality Testing Laboratory (Department of Primary Industries, NSW). Total carbon and nitrogen for all solid materials were determined in duplicate using a Truspec Carbon Nitrogen Determinator. Ash content

Table 1
Characteristics of compost

	Compost size (mm)		
Item	0.6–1.18	1.18–2.36	4.75–6.3
CEC (cmol/kg)	–	85.6	68
Lignin (%)	–	22	–
Cellulose (%)	–	27	–
Hemicellulose (%)	–	6	–
Residue (%)	–	45	–
Surface area (BET) (m^2/g)	1.07	0.98	0.66
Pore volume (cm^3/g)	0.0048	0.0036	0.0026
Pore width (nm)	18.0	14.8	15.3
C/N ratio	37	50	128
Ash (%)	17	10.9	4.7

Note: CEC: Cation Exchange Capacity.

was measured using the method for total volatile solids [11] at 550˚C.

2.3. Kinetics sorption batch experiments

One gram of the specified size of compost was added to 2 L PVC bottles filled with a solution of zinc (5 mg/L). The vessels were shaken on an orbital shaker at 200 rpm for 120 h. Samples (10 mL) were withdrawn at predetermined time intervals for zinc analyses. The total volume of all withdrawn samples was 60 mL, which had minimal effect on L/S ratio (decreased from 2000:1 to 1940:1). The initial pH for each vessel was initially set to 5.5 and was not adjusted during the sorption period and was measured immediately to each sampling event. Blank bottles with zinc solution without sorbent were used to check possible losses of the examined metal. All the sorption experiments were carried out in duplicate at the laboratory temperature 20 ± 1˚C. Metal sorption at different times, q_t (mg/g) was calculated using the mass balance between the solid and the solution.

2.4. Equilibrium sorption batch experiments

One gram of the specified size of compost was added to 2 L PVC bottles filled with a zinc solution. Zinc solutions varied from 1 to 100 mg/L. The vessels were shaken on an orbital shaker at 200 rpm for 48 h.

2.5. Column sorption experiments

The column was constructed in PVC class 18 with an inner diameter of 5.3 cm and a length of 58 cm, giving a cross-sectional area for filtration of 22 cm^2. The column was 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 were placed upon the end cap at the influent end of the column. A plastic mesh was placed over the glass beads to support the filtration media. The columns had a mix of the specified size of compost with 1,663 g of 0.6 mm glass beads (≈20–25% v/v compost). The mix was wetted and then added in increments using continuous column vibration without any compaction over the filtration media surface [13]. The final depth of filtration media in the column was approximately 55 cm with a total bulk density of 1.5 g/cm^3. The sorption column was initially saturated with distilled water for 2 h, then a zinc solution (~5 mg/L) was pumped using a peristaltic pump (Masterflex Model 7553-85) from a 45 L PVC container into the column in upflow mode. The average flow rate was approximately ~12 mL/min. The zinc solution used as the column influent had a pH of between pH 5 and 5.5. Metal salt and other reagents used were all of analytical grade. Experiments were stopped when the zinc effluent concentration approached the respective zinc influent concentration (~5 mg/L), then a desorption cycle started using distilled water (pH of 5.5, EC < 3.5) at similar flow rate ~12 mL/min. Influent and effluent samples were taken at different time intervals and analysed for electrical conductivity and pH in sorption/desoption experiment. Samples (40 mL) were filtered with a 0.45 μm cellulose membrane filter and preserved by acidifying to pH < 2 using 1 N HNO_3 [11].

2.6. Surface charge of compost

The surface charge characteristic of the compost was examined by zeta potential measurements (Malvern Zetasizer) under different values of pH (1.8–11.8). The distilled water without compost was used as the blank sample.

2.7. Fourier transform infrared analysis (FTIR)

The FTIR spectra of the compost was recorded using KBr disk in conjunction with a Perkin-Elmer infrared spectrophotometer having resolution of 4 cm^{-1} and range between 4,000 and 400 cm^{-1}. Duplicate KBr disks were prepared by mixing 0.003 g of compost-dried sample with 0.25 g KBr crystals, the resulting mixture being ground to a fine powder. Finally, the mixture was pressed into a KBr disk and used as such for FTIR studies.

2.8. Modelling of kinetic batch test data

Three kinetic models were used for correlation of the sorption data. These were the pseudo-first-order, pseudo-second-order and the Elovitch model.

The pseudo-first-order rate expression can be expressed as follows [14]:

$$\frac{\mathrm{dq_t}}{\mathrm{d}t} = k_1(q_\mathrm{e} - q_t) \tag{1}$$

where q_e and q_t are the mass of zinc ions adsorbed onto the sorbent (mg/g), at equilibrium and at time t, respectively, and k_1 is the rate constant of first-order (1/h).

The pseudo-second-order equation is based on the assumption that adsorption follows second-order chemisorption and is expressed as [15]:

$$\frac{\mathrm{dq_t}}{\mathrm{d}t} = k_2(q_\mathrm{e} - q_t)^2 \tag{2}$$

where k_2 is the rate constant of second-order sorption (g/(mg h)) and other terms as previously described.

The Elovich equation has been used to describe the kinetics of heterogeneous chemisorption of gases on solid surfaces [16]. The Elovich equation is generally expressed as:

$$\frac{\mathrm{dq_t}}{\mathrm{d}t} = \alpha \exp(-\beta q) \tag{3}$$

where q_t is the amount adsorbed at time t, α (mg/g) and β (mg/(g h)) are fitted parameters.

The fitted parameters for the first- and second-order equations were calculated using non-linear fitting (Microsoft Solver). This approach was used rather than linearization of the equations since linearization may result in improperly weighted data points during the analysis [17]. The mathematical models were tested for best fit using regression co-efficient (R^2), standard error (SE) as well as visually plotting the data.

In addition, the intraparticle diffusion model (Weber Morris plot) was used to give insight into the sorption process. The intraparticle diffusion rate equation expressed as [3]:

$$q_t = k_{\mathrm{ID}}t^{0.5} + c \tag{4}$$

where t is time, k_{ID} is a diffusion rate parameter and c gives information about the boundary layer.

2.9. Modelling of column experiments data

The Thomas model assumes Langmuir kinetics of sorption–desorption, that axial dispersion is negligible and that the sorption follows pseudo-second-order rate reversible reaction kinetics. It can be expressed as [18]:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left[\frac{k_{\mathrm{TH}}(q_0M - C_0V)}{Q}\right]} \tag{5}$$

where C = zinc concentration in the effluent (mg/L), C_0 = zinc concentration in the influent (mg/L), k_{TH} = Thomas rate constant (mL/(min mg)), q_0 = maximum amount of zinc that can be sorbed on compost (mg/g) under the specified condition, M = mass of the adsorbent (compost) (g), V = effluent volume (L), Q = flow rate (mL/min).

The linearised form of the Thomas model (Eq. (5)) is expressed as:

$$\mathrm{In}\left(\frac{C_0}{C} - 1\right) = \frac{k_{\mathrm{TH}}q_0M}{Q} - \frac{K_{\mathrm{T}}C_0}{Q}V \tag{6}$$

The kinetic coefficient k_{TH} and the adsorption capacity of the column (q_0) can be determined from a plot of ln (C_0/C −1) against V at a given flow rate.

3. Results and discussion

It has been recognized that the sorption of heavy metals occurs with different mechanisms such as ion exchange, precipitation and chemisorption on the adsorbent surface. The physiochemical properties of the adsorbent are the main factors responsible for these mechanisms.

3.1. Cation exchange capacity (CEC)

CEC is a good indicator for metal sorption by ion exchange. The values of CEC for 1.18 mm and 4.75 mm compost were 85.6 and 68 cmol/kg (Table 1).

These CEC values are consistent with reported values for three kinds of compost produced from city refuse, rice straw and bark wood which were 44.7, 91.1 and 123.1 cmol/kg, respectively [19]. This suggests that possible ion exchange type reactions between the zinc ions and the compost adsorbing surface can occur.

3.2. Lignin, cellulose and hemicellulose analyses

The values of cellulose, hemicellulose and lignin for the 1.18 mm compost are shown in Table 1. It has been reported that lignin is the main component responsible for adsorption by wood and that lignocellulose materials with a larger lignin content have a greater ability to uptake cadmium [20].

3.3. Particle structure characteristics

The specific surface areas, pore volume and size of various particle sizes of compost were shown in Table 1. The BET-specific surface of the different particle sizes of compost range between 0.66 and 1.07 m^2/g. The surface area increased as the compost particle size decreased. The pore volume of different compost particle size ranged between 0.0026 and 0.0048 cm^3/g with an increase in pore volume corresponding to a decrease in particle size.

3.4. Surface charge (PZC)

The surface charge and isoelectric points were measured using a zetasizer for compost as a function of pH (Fig. 1). The results show that the compost surface was negatively charged throughout the entire pH range investigated, and there is no isoelectric point in this studied pH range of 2–11.5. A similar trend was reported in the literature for agricultural adsorbents [21]. The surface charge characteristics of compost favour cation removal even under highly acidic conditions. This suggests that physical sorption processes between the metal ions and the solid adsorbing surface can occur.

3.5. FTIR analysis

Sorption of heavy metal ions is believed to occur by binding the metal ion with the hydroxylic, carboxylic and phenolic groups on the adsorbent. FTIR spectrum of compost is shown in Fig. 2. The image of spectra of compost is similar to other FTIR images of different compost and woody fibre materials in the literature [22–24].

FTIR spectrum for the compost showed a number of different peaks, indicating the complex nature of the sorbent. The major functional groups are: C–O (1,050 cm^{-1}) alcohols and carboxylic acids, –OH (3,426 cm^{-1}), C=C (1,660 cm^{-1}), C–N (1,230 cm^{-1}), N–H (1,548 cm^{-1}) and C–H (2,940 cm^{-1}) [22–25]. It has been documented that some functional groups such as the O–H, C=O and C–N which are found in compost, play a major role in heavy metal adsorption [24]. The FTIR suggests that chemisorption between the metal ions and the solid adsorbing surface can occur. Therefore, the data acquired from the compost characterization study suggest that both weak physical sorption and strong chemical sorption can occur with heavy metals in solution. The FTIR of the compost after zinc sorption did not show any significant alteration compared with the untreated compost.

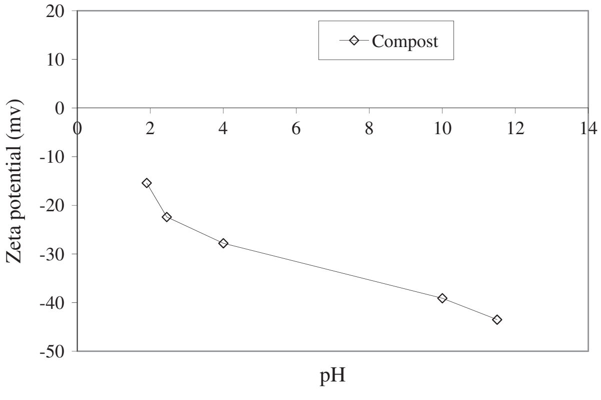

Fig. 1. Zeta potential values of compost.

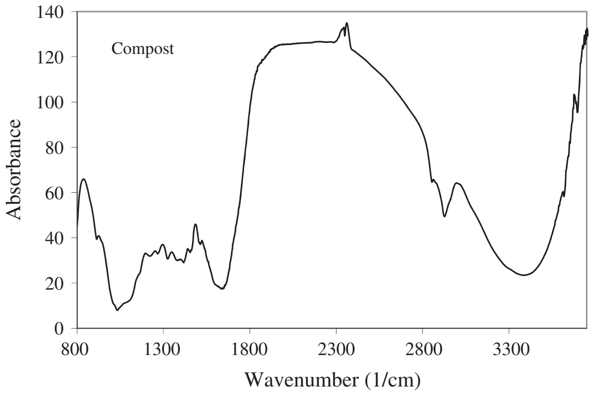

Fig. 2. Fourier transform infrared spectra spectrum of compost.

3.6. Influence of particle size on zinc sorption

The sorption uptakes are broadly similar for the compost across the different particle size ranges (Fig. 3).

The final sorption capacities of different particle sizes 0.6, 1.18 and 4.75 mm for compost are 7.4, 7.1 and 6.8 mg/g, respectively. It is likely the lowest value (compost 4.75 mm) may have increased slightly towards the value obtained for the 1.18 mm compost particles if the experiment had a longer residence time. It is evident from Fig. 3 that equilibrium sorption was reached earlier (<12 h) in the smallest particle

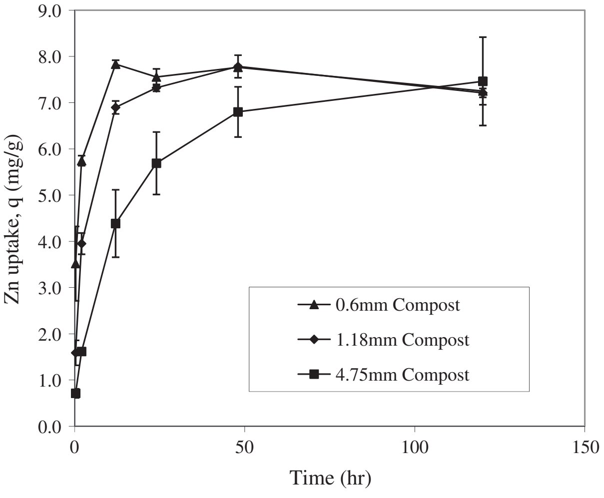

Fig. 3. Effect of particle size on the zinc sorption kinetics.

0.6 mm compared with the larger particles 1.18 mm (24 h) and 4.75 mm (48+h).

3.7. Sorption kinetics

The general trend evident in the kinetics data is similar to other studies with a faster initial sorption rate and then a slower rate as the system trends towards equilibrium. These slower rates can be due to: (1) diffusion to internal sites, (2) surface precipitation or (3) adsorption to sites that have a slower rate due to low affinity [25,26].

The kinetic data for zinc sorption onto the various compost particle size ranges were fitted to the various kinetic models (Figs. 4–6; Table 2).

Both the pseudo-first-order and pseudo-second-order kinetic model had a reasonable fit to the data; however, the higher R^2 and lower SE for the pseudo-second-order kinetic model suggests a better overall fit for the data. This is consistent with a review study [15] which showed that in most sorbent–sorbate published kinetic data, the pseudo-second-order model is more suitable than a pseudo-first-order model using linear regression method. Importantly, the rate constants in both models decreased as the particle size increased. The Elovitch model had a poor fit since it failed to capture the asymptotic nature of the sorption process as it trended to equilibrium.

The adsorption of zinc onto compost follows four main steps (i) migration of the zinc from the bulk solution to the surface of boundary layer surrounding the sorbent (ii) diffusion of the zinc across the boundary layer surrounding the sorbent particle (film diffusion), (iii) diffusion of zinc within the pores of the sorbent particle (intraparticle diffusion) and (iv) adsorption of the zinc on the sorbent surface (internal pores) [27].

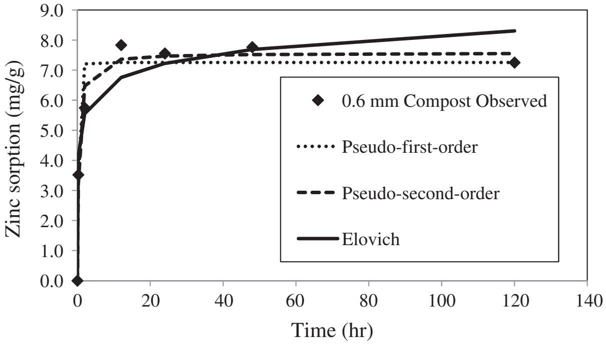

Fig. 4. Zinc sorption onto 0.6 mm compost with observed and predicted data.

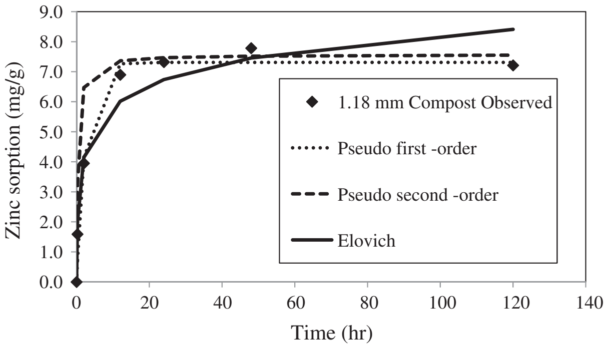

Fig. 5. Zinc sorption onto 1.18 mm compost with observed and predicted data.

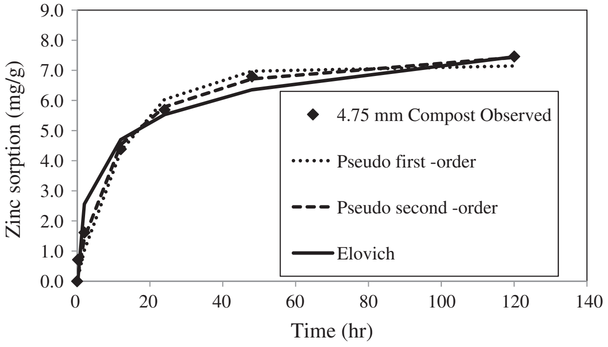

Fig. 6. Zinc sorption onto 4.75 mm compost with observed and predicted data.

A linear relation of q_t vs. $t^{0.5}$ is obtained if the sorption process is considered to be influenced by diffusion in the spherical particles and convective diffusion in the solution [28]. These linear relations may have different slopes due to separate stages of diffusion occurring in the adsorption processes [29–31]. These studies indicate that the first sharper line is the external surface adsorption or instantaneous adsorption, where external diffusion is rate-controlled. The second line is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage, where intraparticle diffusion starts to slow down due to the extremely low solute concentration in solution.

The first stage, film diffusion, doesn't appear because the initial sorption happened very quickly (within 30 min) (Fig. 7). The second stage is apparent and the calculated intraparticle diffusion rates (k_{ID}) and the intercept values (Table 2) decreased as the particle size increased. This suggests that as the particle size increases, the relative importance of film diffusion deceases and intraparticle diffusion dominates. The tendency for the plotted line to pass close to the

Table 2
Fitted and estimated parameters for the various kinetic models

Parameters	0.6 mm compost	1.18 mm compost	4.75 mm compost
Pseudo-first-order model			
k_1 (1/h)	2.5	0.42	0.08
q_e (mg/g)	7.26	7.31	7.15
R^2	0.95	0.99	0.99
SE	0.75	0.43	0.33
Pseudo-second-order model			
k_2 (g/(mg h))	0.39	0.08	0.01
q_e (mg/g)	7.57	7.7	8.0
R^2	0.98	0.99	0.99
SE	0.45	0.35	0.20
Elovich equation model			
α (mg/g)	1226.9	11.3	1.53
β (mg/g)	1.55	2.4	2.75
R^2 (g/(mg.hr))	0.95	0.95	0.97
SE	0.75	0.76	0.57
Intraparticle diffusion equation			
k_{ID} (mg/(g $h^{(0.5)}$))	3.0	1.7	1.2
Intercept	3.8	1.0	0.1
R^2	0.97	0.98	0.99

origin shows that intraparticle diffusion is the rate-controlling mechanism for the 4.75 mm particles, but that both film diffusion and intraparticle diffusion control the sorption rate in the smaller particles (see Fig. 7).

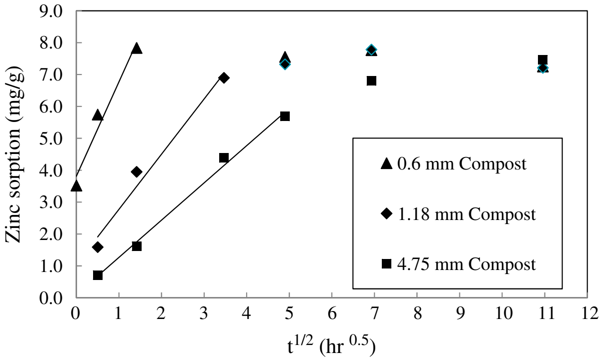

Fig. 7. Intraparticle diffusion model kinetics of compost and aged compost.

3.8. Sorption isotherms

Equilibrium sorption batch studies were conducted to determine the sorption isotherm for different particle sizes of compost using a range of zinc solution concentrations. The kinetic data show that equilibrium was effectively achieved after 48 h and so equilibrium tests were conducted over this time interval. A sorption isotherm is a plot of the equilibrium metal concentration (q_e) in the solid sorbent vs. the equilibrium metal concentration (C_{eq}) in the liquid phase (Fig. 8).

Fig. 8 shows sorption isotherm plots for zinc in a single metal solution with various compost particle sizes under a solution–solid ratio of 2,000:1 mL/g. The results show similar sorption trends for the different particle sizes. In general, sorption isotherms can exhibit different characteristics in shape, depending on the sorption mechanisms. The type of isotherm curve for the three particles can be classified as a Type I sorption curve [32] or a Type L [33]. This indicates that zinc sorption from the aqueous solution is strong. The isotherm curves show two different slopes: a relatively steep slope followed by a gradual slope. The first slope is for low zinc concentrations (1–10 mg/L) and the second at higher concentrations (10–100 mg/L). This implies that as the zinc concentration increases, the sorption mechanism seems to change from one sorption mechanism to another type resulting in a mixed-mode mechanism. The data also show that the zinc sorption capacity (in mg/g) is increased as the particle size of the compost decreases. Similar trends are recognised for heavy metal sorption in the literature [34,35].

Freundlich and Langmuir isotherms are commonly used to describe sorption data. The Freundlich isotherm is the earliest known relationship-describing adsorption equation and is often expressed as [36]:

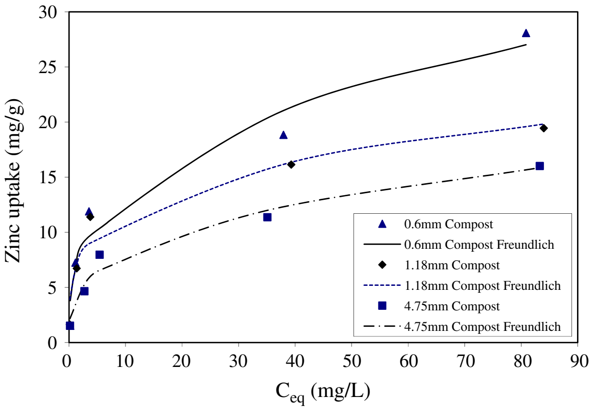

Fig. 8. Zinc sorption measured data and predicted Freundlich isotherm for different particle sizes of compost.

$$q_e = k_f\, C_{eq}^{1/n} \tag{7}$$

where q_e is the adsorption density (mg adsorbate/g adsorbent); C_{eq} is the concentration of adsorbate in solution; k_f and n are the empirical constants dependent on several environmental factors. The Langmuir isotherm is often used for adsorption of a solute from a liquid solution and is expressed as [37]:

$$q_e = \frac{q_m k_l C_{eq}}{1 + k_l C_{eq}} \tag{8}$$

where q_e is the adsorption density at the equilibrium solute concentration; C_{eq} is the concentration of adsorbate in solution; q_m is the maximum adsorption capacity corresponding to complete monolayer coverage; k_l is Langmuir isotherm constant related to the equilibrium constant or binding energy.

In order to convert the sorption isotherm experimental data into mathematical equations, simple Freundlich and Langmuir isotherm equations (Eqs. (7) and (8)) have been used to fit the zinc sorption data. Regression methods are usually employed to determine the parameters of isotherm equations. The fitted parameters for these equations were calculated using least squares regression (microsoft solver). The mathematical models were tested for best fit using regression coefficients (R^2) (Table 3).

Fig. 8 shows the predicted Freundlich isotherm plots for the experimental isotherm data of three particle sizes of compost. Examination of the plot suggests that the Freundlich isotherm has a good fit for the sorption of zinc on three particle sizes of compost; however, the goodness of the fit coefficient (R^2) was higher for the 0.6 mm size than the 1.18 and 4.75 mm compost size (Table 3).

The results indicate that the particle size influences the sorption efficiency as there is generally an increase of the surface area per unit weight of the sorbent with a decrease of its particle size. The surface area (BET) for 0.6, 1.18 and 4.75 mm compost is 0.92, 0.88 and 0.56 m^2/g, respectively. The results indicate a slight increase in the $1/n$ values with the decrease of the particle size, which indicates a decrease of sorption intensity. This is consistent with other findings that found the sorption intensity of Cd by chitosan increased with a decrease in the particle size [38]. The value of R^2 for all three particle sizes was very close to 1. The Freundlich K_f and $1/n$ values are similar for the different particle size of compost. Thus, the results indicate the mechanism of adsorption of compost is similar and is independent of particle size.

Fig. 9 shows the predicted Langmuir isotherm plots and experimental data. Examination of the plot suggests that the Langmuir isotherm also had a good fit for the sorption of zinc on all three particle sizes of compost. The goodness of the fit coefficient (R^2) for 0.6, 1.18 and 4.75 mm was 0.93, 0.98 and 0.95, respectively. The Langmuir parameters, q_m and k_l for each of the three isotherms have been estimated and are shown in Table 2. It is clear that q_m, the monolayer coverage for each particle size, increased from 13.2 to 25.4 mg/g as the particle size decreased from 4.75 to 0.6 mm. This may be attributed to the larger external surface available from smaller particles at a constant

Table 3
Langmuir and Freundlich isotherms model constants for the sorption of Zn by different particle size of compost

	Langmuir model			Freundlich model*		
	q_m (mg/g)	K_L (1/mg)	R^2	k_f (L/g)	$1/n$	R^2
0.6 mm	25.4	0.26	0.92	6.3	0.33	0.96
1.18 mm	18.7	0.42	0.98	6.5	0.25	0.95
4.75 mm	13.2	02.8	0.94	3.8	0.32	0.98

*Units for k_f are $mg^{1-1/n}\ kg^{-1}\ L^{1/n}$ and n is dimensionless.

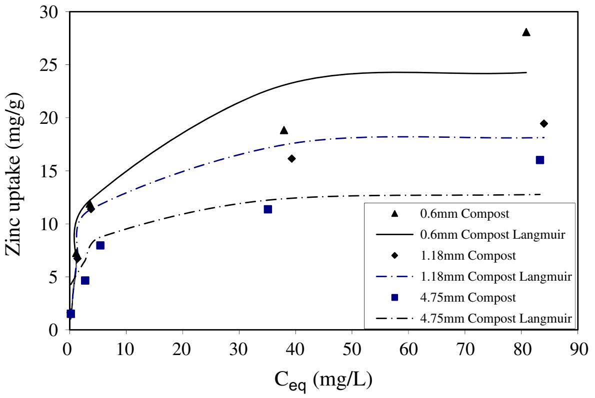

Fig. 9. Zinc sorption measured data and predicted Langmuir isotherm for different particle sizes of compost.

total mass of compost in the solution BET data, Table 1). The sorption capacity of copper has been found to increase from 9.7 to 13.7 mg/g as the particle size of tree fern sorbent decreased from 104–124 μm to 38–43 μm [39].

As can be seen in Table 3, the high correlation coefficient values ($R^2 > 0.92$) indicate that the Freundlich and Langmuir isotherms appear to produce a reasonable model for zinc sorption in all three particle sizes.

These adsorption isotherm equations are often found to provide a good fit of isotherm data. However, they must be considered simply as a curve fitting procedure using numerical relationships to provide the best fit to experimental data. Therefore, the isotherm parameters estimated by curve fitting are not valid if any operational conditions differ from those of the original experiment [40,41]. Moreover, Sparks [7] emphasised that adsorption isotherms are purely descriptions of macroscopic data and do not definitively prove a reaction mechanism. Mechanisms must be determined from molecular investigations, e.g. the use of spectroscopic techniques.

3.9. Sorption column experiments

Column experiments were conducted to give the accurate scale-up data necessary for the continuous flow columns used in field applications. To ensure conditions and capacities are comparable with those found in field applications, the experiments used a longer time scale with lower concentrations of influent. The column sorption experiments were continuously carried out for three weeks with an influent of 5 mg/L zinc solution at pH ~5.0 to prevent zinc hydroxide precipitation.

The breakthrough curves (BTCs) for zinc solution onto three different particle sizes are shown in Fig. 10. Zinc concentrations in the effluent were continuously monitored until the zinc C/C_o reached higher than 0.83 for each particle size.

The zinc BTC for the 0.6 mm and 1.18 mm columns showed a relatively sharp front with a sigmoid (S-shaped) BTC. In contrast, fronting is evident by the diffuse front in the breakthrough for the 4.75 mm column. It causes early breakthrough of dissolved zinc.

The breakpoint ($C/C_o = 0.1$) for the 4.75 mm column occurred very early at ~10 PV, at ~100 PV for the 1.18 mm and at 196 PV for the 0.6 mm column. This suggests that the removal of dissolved zinc by the small size (0.6 mm) compost was most effective during the first 196 PV, by the 1.18 mm size at 100 PV, and by the large size (4.75 mm) at 10 PV. The high rate of removal effectiveness within these mentioned PVs can be explained by rapid surface sorption of the zinc ion onto the compost surface. After these PV, the rate of zinc sorption was slow because the easily accessible surface sites were filled up. This slow rate of sorption can be explained by the effect of particle diffusion of zinc ions into the compost particle. These results suggested that the small particle size of the sorbent will improve removal efficiency. It is interesting to note that after 470 PV of pumping zinc influent through the columns, the zinc C/C_o values for 0.6, 1.18 and 4.75 mm column were ~0.95, 0.90 and 0.81, respectively. This suggests that the larger particle size still has greater ability to sorb the zinc than the smaller particles.

The calculated sorption capacity was 22.9 mg/g (0.60 mm), 17.3 mg/g (1.18 mm) and 12.7 mg/g

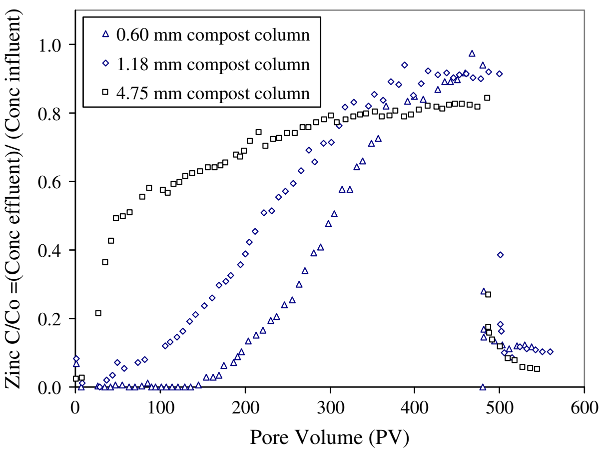

Fig. 10. Zinc sorption and desorption BTCs at different particle size of compost.

(4.75 mm). The results indicate that the zinc sorption capacity is significantly different for different particle sizes over the same time period.

These results show a similar trend to the batch results where zinc sorption increased as the particle size decreased. However, the zinc sorption capacity of the compost is higher in the case of the column experiment than the kinetic batch data and very close to the equilibrium batch data (Langumir parameters q_m) at each particle size. This may be due to the rate of adsorption in the column being higher than the kinetic batch experiment. It is well known that the adsorption rate depends on the concentration of solute in the solution. In the column experiment, the concentration in the solution in contact with a given layer of adsorbent in a column is relatively constant due to the flow through the column. However, in the kinetic batch experiment, the concentration of solute in contact with adsorbent gradually decreases as adsorption proceeds, so decreasing the rate of adsorption. A similar trend has been reported for mercury, lead and chromium uptakes by carbonaceous material. The uptakes from the waste slurry was higher in the column experiment than in the kinetic batch experiment [42].

Desorption of sorbed metal may be an important factor in using any sorbent as a filtration amendment. The desorption curves of zinc from compost at different particle sizes showed a very similar unsymmetrical shape (Fig. 10), with a rapid metal concentration decrease, followed by a flatter diminution. The result suggests that zinc sorption is generally irreversible, owing to strong interaction between zinc and the surface active sites of the compost at each particle size. The total amount of zinc desorbed during water flushing was calculated using the mass balance. The mass of zinc desorbed for 0.6, 1.18 and 4.75 mm compost was 0.57, 0.48 and 0.39 mg/g, respectively. The loss in all desorption experiments did not exceed more than 5% of the sorbed amount. Losses of the sorbed heavy metals on washing are probably due to the different types of sorption of the metals to the compost functional groups (sorption sites). This suggests that the strong chemosorption is more dominant than physical sorption on the compost particles.

3.10. Modelling of sorption column experiments

The Thomas model was applied to these data obtained from the column experimental studies to predict the BTC and to determine kinetic parameters within the column. The zinc sorption data at C/C_o ratios higher than 0.05 and lower than 0.85 were only used in Thomas fitting. Using Eq. (6), a plot of $\ln(C_0/C{-}1)$ vs. V gives a straight line with a slope of $(-k_T C_0/Q)$ and an intercept of $(k_T q_0 M/Q)$. The Thomas model parameters k_T and q_0 calculated from the slope and the intercept are shown in Table 4.

The results in Table 4 show that the Thomas model fitted the BTCs very well for the two small particle sizes 0.6 and 1.18 mm while it was a poor fit for the larger particle size 4.75 mm. The results showed that the Thomas model rate constant (k_{Th}) decreased from 0.1 to 0.03 L/(min mg) as the particle size increased from 0.6 to 4.75 mm. This trend is consistent with the trend for pseudo-second-order rate constant k_2 described in Section 3.7.

The results show the sorption capacity (q_o) of zinc onto compost values as predicted by the Thomas model was 22.4, 16.5 and 6.6 mg/g for the particle size 0.6 mm, 1.18 mm and 4.75 mm, respectively. This suggests that as the particle size increased, the metal uptake capacity decreased in the column. The zinc uptake was estimated from the mass balance in Section 3.7 for these columns and the values were 22.9 mg/g (0.6 mm), 17.3 mg/g (1.18 mm) and 12.7 mg/g (4.75 mm). This suggests that the Thomas model predicted very well the zinc uptake for 0.6 and 1.18 mm size and underestimated that for the large particle size (4.75 mm). This may be due to the shape of the BTC of zinc sorption of different particle sizes. Fig. 10 showed that the zinc breakthrough curve for the 0.6 and 1.18 mm columns showed a relatively sharp front with a sigmoid (S-shaped) BTC, which is the equilibrium transport. In contrast, the BTC curve of the 4.75 mm column exhibits a sharp front which then transitions to tailing and incomplete breakthrough. This is suggestive of non-equilibrium behaviour in the column. The Thomas model adequately predicts zinc transport under equilibrium conditions (0.6, 1.18 mm) in this column.

Table 4
Thomas model parameters at different particle size of compost

Particle size (mm)	Slope	Intercept	R^2	k_{Th} (L/(min mg))	q_0 (mg/g)
0.6	0.04	6.3	0.99	0.10	22.4
1.18	0.03	3.5	0.99	0.08	16.5
4.75	0.01	0.5	0.67	0.03	6.6

4. Conclusions

Compost characterization results show that weak physical sorption and strong chemical sorption can occur between the compost particles and dissolved zinc. The batch and column results indicated that the particle size influenced the sorption process, because of an increase of the surface area per unit weight of the sorbent with a decrease of its particle size. The equilibrium data were fitted very well by Freundlich and Langmuir isotherms. The estimated sorption capacities of different compost particle size by the Langmuir isotherm were varied from 15.6 mg/g (4.75 mm) to 26.6 mg/g (0.60 mm). The sorption capacities of different compost particle size in column experiment were 22.9 mg/g (0.60 mm), 17.3 mg/g (1.18 mm) and 12.7 mg/g (4.75 mm). From batch and column results, it is evident that compost media have high affinity for zinc which reflects the physicochemical properties of the compost particles.

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