Zn(II) adsorption from synthetic solution and kaolin wastewater onto vermicompost

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A B S T R A C T

The adsorption of Zn(II) from both synthetic solution and kaolin industry wastewater by cattle manure vermicompost was studied. The adsorption process was dependent on the various operating variables, viz., solution pH, particle size of the vermicompost, mass of vermicompost/volume of the Zn(II) solution ratio, contact time and temperature. The optimum conditions for Zn adsorption were pH 6.0, particle size of $\leq 250\,\mu m$, 1 g per 10 mL adsorbent dose, contact time of 4 h and temperature of 25 °C. Langmuir and Freundlich adsorption isotherms fit well in the experimental data and their constants were evaluated, with R^2 values from 0.95 to 0.99. In synthetic solution, the maximum adsorption capacity of the vermicompost for Zn^{2+} ions was 20.48 mg g^{-1} at 25 °C when the vermicompost dose was 1 g 10 mL^{-1} and the initial adjusted pH was 2. The batch adsorption studies of Zn(II) on vermicompost using kaolin wastewater have shown the maximum adsorption capacity was 2.49 mg g^{-1} at pH 2 (natural pH of the wastewater). The small values of the constant related to the energy of adsorption (from 0.07 to 0.163 L mg^{-1}) indicated that Zn^{2+} ions were binded strongly to vermicompost. The values of the separation factor, R_L, which has been used to predict affinity between adsorbate and adsorbent were between 0 and 1, indicating that sorption was very favorable for Zn(II) in synthetic solution and kaolin wastewater. The thermodynamic parameter, the Gibbs free energy, was calculated for each system and the negative values obtained confirm that the adsorption processes are spontaneous. The $\Delta G°$ values were -19.656 kJ mol^{-1} and -16.849 kJ mol^{-1} for Zn(II) adsorption on vermicompost in synthetic solution at pH 6 and 2, respectively, and -13.275 kJ mol^{-1} in kaolin wastewater at pH 2.

1. Introduction

One important source of heavy metal pollution in surface waters is the direct or indirect discharge of wastewater from kaolin industry. Brazil is the second largest kaolin producer in the word (reserves of 14%). The mineral, $Al_4(OH_8)[SiO_{10}]$, is found in natural deposits of varied composition and among the uses of kaolin, stands out the utilisation as filler and coating in paper manufacturing, enhancing its density, brightness and smoothness [1].

Some contaminants of kaolin reduce its industrial application [2]. In order to improve kaolin quality it is necessary to remove contaminants such as iron oxides. The reduction of Fe(III) to Fe(II) is accomplished by using metallic Zn. Thus, Zn, Fe and Al are contaminants usually found in effluents from kaolin processing plants.

Vermicompost from different sources such as municipal solid waste [3], pig manure [4] and decomposed pods of green gram [5] promote plant growth. Vermicompost can also be obtained when cattle manure, together with soil, are used for earthworm diet. Earthworm species such as *Eisenia foetida* (Red of California), *Lumbricus terrestris* and *Lumbricus rubellus* have been successfully used in composting processes [6].

Substitution of conventional systems of effluent treatment is of particular importance. Recovered minerals or raw materials which have been processed into materials do not necessarily have to go to waste. Apart from critical environmental arguments, economic aspects speak for the reduction of metal wastes. In this context precipitation with lime (hydrous CaO), which is traditionally used for the removal of heavy metals from liquid effluents, can lead to an even more serious impact on heavy metal remobilization. The waste obtained is stored in large trenches and is not commonly reused. The stockpiling of such kind of residues on land may result in insidious leaching of metal by local acidic soils In addition, the high price of lime compared to vermicompost (1 ton of lime costs about 4.3 times that of vermicompost) in Brazil, is other limiting factor.

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The processing of wastewater should avoid the metal enrichment of river water, leading to a better environmental condition. The kaolin processing plants contribute to water contamination by heavy metals. Thus, it is necessary to develop low cost processes of effluent treatment.

At present there are only a few studies regarding the treatment of wastewaters containing heavy metals by vermicompost. The efficiency of this substrate for removing Cu, Cr, Ni, Zn and Cd from synthetic solutions and electroplating wastes under laboratory conditions were studied by Jordão et al. [7]. The authors found that metal concentrations in the purified effluents were below the maximum values established for waste discharges into rivers by the Brazilian Environmental Standards. They also reported that the vermicompost residues obtained from the metal retention process could be applied as a fertilizer to agricultural lands.

In a similar work, Jordão et al. [7] reported that Cu, Zn and Ni retention by cattle manure vermicompost from electroplating wastes were close to 100%. They also reported that it was not necessary to correct the effluent pH during the treatment process to reach the levels recommended by Brazilian legislation for discharge into water courses. The potential application of vermicompost to adsorb Cd from both synthetic solution and mineral water was evaluated by Pereira and Arruda [8]. They found that vermicompost presented an expressive Cd adsorption capacity ($38.6 \, mg \, g^{-1}$) when compared with other adsorbents.

Adsorption processes are found to be highly effective, cheap and easy to adapt. Langmuir and Freundlich isotherms have been commonly used to model data obtained in wastewater adsorption treatment systems [9,10]. Thus, with the purpose of establishing a preliminary report for the removal of Zn(II) from synthetic solution and kaolin wastewaters, experimental equilibrium data obtained for Zn adsorption on cattle manure vermicompost has been analyzed by the Langmuir and Freundlich isotherm equations. Experiments including the effects of particle size, mass of vermicompost/volume of the synthetic Zn(II) solution ratio, contact time, pH and temperature have also been conducted before the experiment to optimize the maximum adsorption capacity.

2. Materials and methods

2.1. Sample collection and handling

Commercial samples of vermicompost of cattle manure (Super Húmus), which was produced in the Vista Alegre farm at the city of Ubá (State of Minas Gerais) was used as the adsorptive material. The raw vermicompost was air-dried for 72 h and used in the characterization experiments. For the adsorption experiments, the raw vermicompost was dried at 70 °C for 4 h.

Kaolin wastewater was obtained from a factory located in Mar de Espanha at the Minas Gerais State, where this mineral is mined and kaolin processing is conducted. The sample was collected in a plastic bottle that it was previously soaked in diluted HNO_3, rinsed with deionized water and wastewater before filling and refrigerated at 4 °C.

Two additional samples of treated kaolin wastes from the factory were also collected in plastic bottles and included a limed waste sample and a decanted limed waste sample. However, these samples were not used in this work for Zn adsorption studies, since their Zn concentrations (0.44 and $0.55 \, mg \, L^{-1}$, respectively) were below the maximum limit allowed by the Brazilian Environmental Standards [11] for industrial effluent discharges into water systems (<$5 \, mg \, L^{-1}$). These samples had the pH values of 11.24 and 12.24.

2.2. Vermicompost and kaolin wastewater characterization

The vermicompost pH was measured in deionizer water (solid/solution ratio of 1:2.5) using a pH meter. Moisture content of the vermicompost was determined by the percentage loss in weight after drying the sample at 60 °C and at 110 °C for 24 h; organic matter content was measured by ignition in a furnace at 550 °C for 24 h and ash content after heating at 800 °C for 2 h [12]. The C and H contents were measured with an infrared detector and the N content was measured with a thermal conductivity detector.

The carboxylic group content was determined in approximately 0.1 g of vermicompost. This amount was added to 10 mL of $0.5 \, mol \, L^{-1}$ $Ca(OAc)_2$ solution. After agitation of the mixture for 24 h, the carboxylic groups were determined by titration with a $0.1 \, mol \, L^{-1}$ NaOH solution to pH 9.8 [13].

A non-linear regression equation was adjusted to the titration data to differentiate the acid groups. For this purpose, 1 g of the vermicompost, previously sieved to a particle size of less than 0.177 mm, was titrated potentiometrically with NaOH solution and the pK_a values determined.

The particle size distribution was evaluated by a pipette method, using $1 \, mol \, L^{-1}$ NaOH solution as a dispersant agent [14].

The total concentrations of Cu, Ni, Zn, Mn, Fe, Pb, Cd, Ca, Mg, Na and K were determined in vermicompost using 0.5 g portions of air-dried samples. They were digested individually at 200 °C with 5 mL of 65% (w/v) HNO_3. A 5 mL aliquot of concentrated $HClO_4$ (70% w/v) as well as a 5 mL aliquot of HF (40% w/v) were added and the mixtures re-evaporated to near dryness. Finally, a 5 mL aliquot of 65% (w/v) HNO_3 was added. The mixture was re-evaporated to near dryness and diluted with deionized water to 25 mL [7]. The total metal concentrations in the resultant solutions were then measured by atomic absorption spectrophotometry (AAS).

The kaolin wastewater pH was measured by immersing a volume of 50 mL of the sample into the instrument cell. The values of the pH of limed waste sample and decanted limed waste sample were obtained in the resultant solutions after filtration. The concentrations of Fe, Mn, Cd, Cu, Cr, Ni, Zn, Al, Ca, Mg and Pb were determined in the wastewater after filtration by inductively coupled plasma optical emission spectrometer (ICP-OPS).

2.3. Metal adsorption studies

2.3.1. Preliminary experiments for Zn(II) adsorption optimization

All the parameters such as particle size range, mass of vermicompost/volume of the synthetic Zn(II) solution ratio, contact time, adsorption pH and temperature were optimized for the maximum adsorption capacity of the vermicompost. Batch adsorption experiments were carried out in 50 mL centrifuge tubes containing vermicompost sample in which it was added 10 mL of $150 \, mg \, L^{-1}$ $ZnCl_2$ (in $0.1 \, mol \, L^{-1}$ KCl in order to equalize ionic strength). The suspensions were mechanically stirred at 120 rpm, centrifuged and the Zn concentrations determined in the solutions. For optimization, particle size was varied between ≤ 105 and $\leq 2000 \, \mu m$ and mass of vermicompost/volume of the Zn(II) solution ratio varied between 0.25 g and 1 g 10 mL. The shaken time was examined in the range 1–28 h and solution pH in the range of 3.0–7.0. Temperature was evaluated in the range of 10 ± 2–40 ± 2 °C.

Each preliminary experiment was replicated three times and the Zn concentrations were determined by AAS. The adsorption of Zn(II) was calculated as the difference between that added and that in the supernatant.

2.3.2. Langmuir and Freundlich adsorption isotherms for the vermicompost using synthetic Zn solution and kaolin wastewater

The Zn(II) adsorption isotherms for the vermicompost using synthetic Zn solution were obtained at constant pH values and ionic strength. The experiment was conducted in 50 mL centrifuge tubes in which were added 1 g of the vermicompost (particle size $\leq 250\,\mu m$) and 10 mL of a synthetic Zn solution containing 0, 60, 120, 240, 300, 400, 500, 600, 700, 800, 1000, 1250, 1500, 1750 or 2000 mg L^{-1} Zn as ZnCl$_2$ (in 0.1 mol L^{-1} KCl). The pH of suspensions was adjusted to 6.0 ± 0.2 or 2.07 ± 0.2 with 10% NaOH and the suspensions were diluted with deionized water to 30 mL. The suspensions were shaken for 4 h at $25 \pm 2\,°C$, centrifuged and Zn concentrations determined in the solutions.

In the case of Langmuir and Freundlich adsorption isotherms for the vermicompost using kaolin wastewater from Mar de Espanha, the experiment was carried out at the natural wastewater pH (2.07) as described above. For this purpose, a 10 mL aliquot of wastewater containing Zn at the concentration of 0, 10, 20, 30, 40, 50, 60, 90, 120, 150, 210, or 232 mg L^{-1} was used.

2.4. Instrumentation and some relevant information

For pH determination, a DIGIMED pHmeter, model DM 21 was used. The titration was accomplished with a Mettler Toledo pHmeter, model DL-15.

The effect of temperature on Zn adsorption was evaluated in a model 116/2 Fanem water bath. When necessary, the suspensions were mechanically shaken in a model B4iV1 Jouan centrifuge.

Total metal concentrations in vermicompost sample as well as in the solutions from the Zn(II) adsorption experiments were determined with a Varian atomic absorption spectrophotometer (model SpectrAA-200), by direct aspiration of the solutions into an air–acetylene flame or nitrous oxide–acetylene flame. Background correction was used for Fe, Ca, Mg, Pb, Cd, Ni and Zn determinations. The metal concentrations in kaolin wastewater sample were measured with a Perkin Elmer inductively coupled plasma optical emission spectrometer (ICP-OES), model Optima 3300 DV. The instrumental parameters were adjusted according to the manufacturer recommendations.

All glassware and materials were cleaned for metal analysis. Certified analytical-grade reagents were used throughout. Blanks were run through all experiments. The calibration blank was checked at the beginning and at the end of the analysis for each group of samples to certify that the instrument calibration had not drifted.

The concurrent analyses of samples of Standard Sediments (National Institute of Standard & Technology no. 2704) gave the following values which are within the range of certified values: Zn = 447; Ni = 44.2; and Cu = 94.5 (in mg kg^{-1}); Al = 6.10 and Mg = 1.22 (in %).

3. Results and discussion

3.1. Vermicompost and kaolin wastewater characterization

The vermicompost characteristics are summarized in Table 1. The pH value of the vermicompost (7.1) was within the range commonly reported for this material, i.e., from 5.7 to 7.8 [8,15,16]. The moisture content of the vermicompost reached $47.4 \pm 0.41\%$, above the maximum limit (44%) allowed by Brazilian legislation for composted solid wastes used as fertilizer [17]. The vermicompost had a high organic matter content ($42.0 \pm 0.34\%$), a value above the minimum limit established by Brazilian legislation, i.e., 40% of total organic matter [17]. The ash content was above the values reported by other workers [7,15] for cattle manure vermicompost, 45.0% and

Table 1
Vermicompost characteristics[a]

Characteristic[a]	Mean ± standard deviation[b]
pH in H$_2$O	7.1 ± 0.03
Moisture	
60 °C (%, w/w)	42.8 ± 0.61
110 °C (%, w/w)	4.6 ± 0.20
Total °C (%, w/w)	47.4 ± 0.41
Organic matter (%, w/w)	42.0 ± 0.34
Ash (%, w/w)	57.9 ± 0.31
Carbon (%, w/w)	19.61
Hydrogen (%, w/w)	3.13
Nitrogen (%, w/w)	1.93
C/N ratio	11.85
Carboxylic groups (cmol$_c$ kg^{-1})	19.60 ± 0.18
Clay (%, w/w)	52
Silt (%, w/w)	15
Sand (%, w/w)	33
Total metal (mg kg^{-1})	
Al	16300 ± 490
Fe	20100 ± 35
Ca	6330 ± 1100
Mg	2670 ± 230
Pb	2.6 ± 0.7
Cd	1.7 ± 0.1
Cu	31.0 ± 3.7
Ni	21.7 ± 2.1
Zn	108 ± 4.4
Na	475 ± 46
K	6110 ± 460

[a] All data are expressed on a air-dry basis.
[b] Mean of three replicates, except C, H, N, clay, silt and sand contents (only one determination).

47.3%, respectively. However, the value found in the present work, $57.9 \pm 0.31\%$, is within the range (41.2–68.8%) reported by Pereira and Arruda [8]. Different values reported in the literature can be attributed to the presence of contaminants in the raw material as well those of contaminants produced during composting process.

The contents (%) of carbon (19.61), hydrogen (3.13) and nitrogen (1.93) were in good agreement with the values reported by Pereira and Arruda [8] for vermicomposts from different regions. They reported the following range values: carbon (10.4–33.2), hydrogen (1.8–3.0) and N (0.7–2.3). Compost application to soil is only beneficial when completely matured. The C/N ratio of compost in this condition should vary from 10:1 to 14:1 [12] and value found in this research study (11.85) was within this range (Table 1).

The total metal concentrations in the vermicompost were according to the results reported by other workers [7,15] for cattle manure vermicompost (Table 1). In general, metal concentrations found in the vermicompost were not very high. However, the high Al concentration (16,300 mg kg^{-1}) of the vermicompost was due to kaolinite present in the vermicompost sample, since composting process using earthworms are commonly conducted on soil [18].

The use of non-linear regression obtained with the titration data allowed the determination of five classes of titrated groups. The first three pK_a values are in the region of typical pH for carboxylic groups, while the last two values are typical of phenols and amines [19,20]. The results found in the determination of the five titrated groups of humic acid in the vermicompost were close to those reported for humic substances (Table 2). From the volume of base consumed during titration (3.37 mL), it was possible to evaluate the charge of the material (32.7 cmol kg^{-1}) at the original pH of the vermicompost (7.1).

The kaolin wastewater pH from Mar de Espanha was 2.07. This result is far from those set by the Brazilian Environmental Standards [11] for effluent discharge into water-courses (from 5 to 9). The

Table 2
Values of pK_a obtained from the non-linear regression adjustment of the poten-tiometric titration curve of the vermicompost, compared with the mean values of humic acids described in the literature

	Titrated group				
	HA$_1$	HA$_2$	HA$_3$	HA$_4$	HA$_5$
pK_a[a]	3.50	5.31	6.88	8.97	10.88
pK_a[b]	4.28	4.96	6.07	7.48	9.31
pK_a[c]	3.54	5.29	6.90	8.30	9.56

[a] Values obtained in this work.

[b] Values from Guimarães [19] for humic acids extracted from cattle manure ver-micompost.

[c] Values from Masini et al. [20].

concentrations of Fe, Mn, Pb, Cu and Zn in the kaolin wastewater were also far from the Brazilian regulations (Table 3), indicating the enrichment of the effluent as well as the necessity of metal removal.

3.2. Metal adsorption studies

3.2.1. Preliminary experiments for Zn(II) adsorption optimization
3.2.1.1. Effect of particle size on Zn(II) adsorption. The adsorption is a surface phenomenon and is largely dependent on the superficial area of the adsorbent. The pulverization process of vermicompost

Table 3
Total metal concentrations in kaolin wastewater and the maximum values estab-lished by the Brazilian Environmental Standards (BES) for effluent discharge into water-courses[a]

Metal	Mean ± S.D. (mg L^{-1})[b]	BES maximum value (mg L^{-1})
Al	585 ± 5	–
Fe	710 ± 1	Dissolved 15.0
Ca	241 ± 3	–
Mg	48.1 ± 0.3	–
Mn	42.4 ± 0.6	Dissolved 1.0
Pb	3.0 ± 0.1	Total 0.5
Cd	<0.1[c]	Total 0.2
Cr	0.3 ± 0.01	Total 0.5
Cu	2.2 ± 0.02	Dissolved 1.0
Ni	0.06 ± 0.001	Total 2.0
Zn	232 ± 0.6	Total 5.0

[a] Brazil, 2005 [9].

[b] Mean of three replicates ± standard deviation.

[c] Value preceded by (<) symbol indicate detection limit.

results in greater superficial area and exposition of active sites to react. There was a decrease in Zn(II) adsorption when particle size was varied from ≤250 to ≤2000 μm (Fig. 1a), i.e., there was a decrease in the percentage of adsorption with the increase of the particle size. The smaller Zn(II) retention in the ≤105 fraction as compared with the ≤250 fraction was due to very fine particles
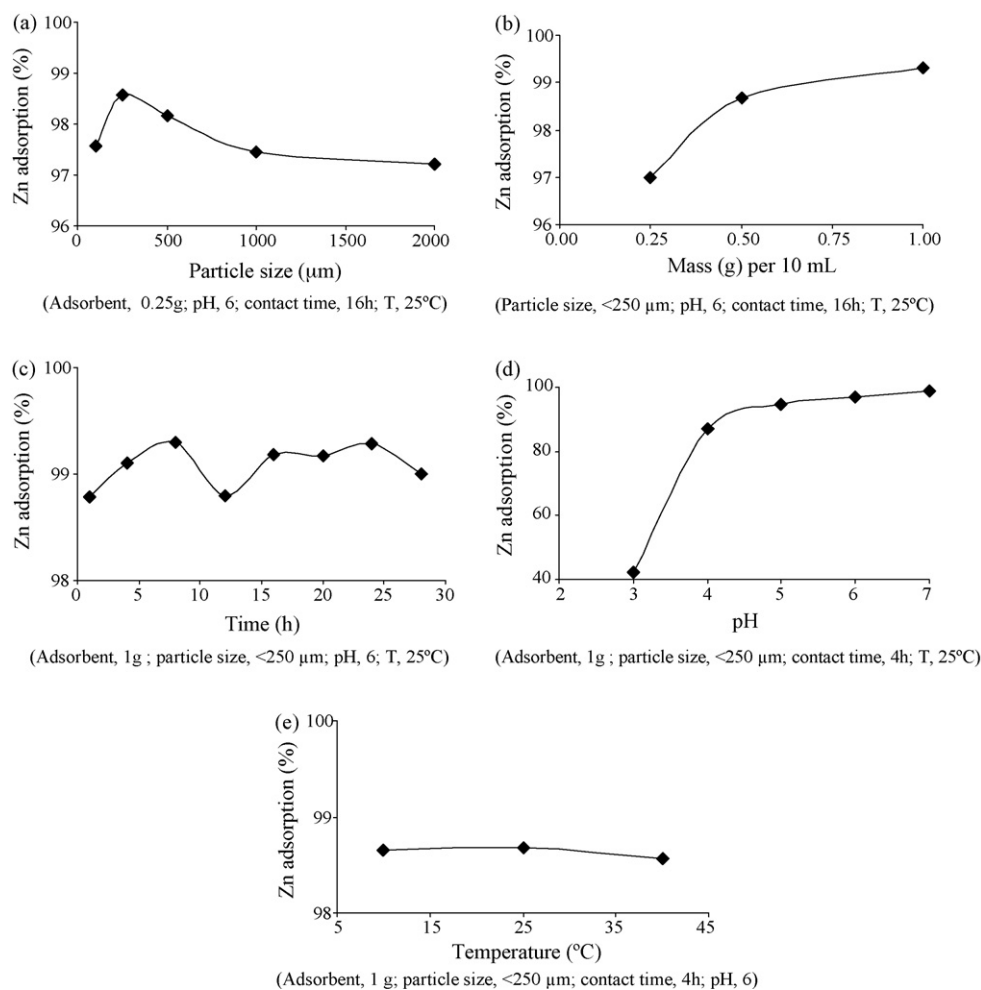

Fig. 1. Adsorption of Zn(II) as a function of vermicompost particle size (a), mass of vermicompost/volume of the synthetic Zn solution ratio (b), contact time (c), pH (d) and temperature (e).

of soil present in the vermicompost sample. Composting process using earthworms are commonly conducted on soil and these very fine particles of soil reduced the adsorption capacity of the organic matter of the vemicompost.

3.2.1.2. Effect of mass of vermicompost/volume of the synthetic Zn(II) solution ratio on Zn adsorption.
The results showed that adsorption percentage increases with increasing adsorbent/adsorbate ratio (Fig. 1b). Maximum Zn(II) adsorption was reached at the 1/10 ratio (1 g per 10 mL) and it is due to the increase of the mass of the adsorbent (more surface area available for adsorption) that results in greater availability of reactive groups (increase in the number of active sites).

3.2.1.3. Effect of contact time on Zn(II) adsorption.
The speed of heavy metal adsorption depends on several parameters, including particle size and porosity of the adsorbent as well as molecular structure of the adsorbed compound [6]. In this work, the adsorption of Zn(II) by vermicompost was little influenced by contact time, ranging from 98.78% to 99.32% (Fig. 1c). Thus, the plot indicates that the remaining concentration of Zn^{2+} ions in solution was not appreciably changed from 1 to 28 h and revealed that a contact time of 4 h was sufficient for equilibrium to be established.

3.2.1.4. Effect of pH on Zn(II) adsorption.
The Zn(II) adsorption depended greatly on pH (Fig. 1d) and increased sharply with the increase in pH from 3.0 to 4.0, an interval when 42–87% Zn adsorption occurred. The influence of pH can be related with the fact that in an acid environment competition between metals and H^+ ions occurs and the metal retention in such condition is not significant. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption [21]. Taking into account that the final Zn concentration of 2.29×10^{-3} mol L^{-1} was used in this experiment, calculations based on the Kps of the Zn(OH)$_2$, 2.0×10^{-17} [22], point to precipitation of Zn as hydroxide at pH 6.98. This suggests that metal retention by vermicompost could occur by formation of complexes, electrostatic interaction and precipitation as hydroxide. Based on these results, the pH 6 was chosen for Zn(II) removal from synthetic solution. The adsorption experiment was also conducted at pH 2 in synthetic solution because it is the pH value of the natural wastewater sample. The experiment of Zn(II) adsorption onto vermicompost using kaolin wastewater was conducted only at pH 2 since at pH 6 contaminants such as Fe and Al present in wastewater could affect Zn retention.

3.2.1.5. Effect of temperature on Zn(II) adsorption.
As seen in Fig. 1e, the results demonstrated slight variations of Zn(II) retention and in this case, the procedure accomplished to supply or remove energy of the system is not suitable.

In most studies, adsorption is modeled in function of temperature to obtain the enthalpy of the reaction [23]. However, according to Angove et al. [24] some studies with heavy metals have shown that the adsorption mechanism, along with the process intensity (measured by the Langmuir Ads$_{max}$ parameter) was little altered with temperature and generally any conclusion about the phenomenon at 25 °C applies equally to other temperatures.

3.2.2. Langmuir and Freundlich adsorption isotherms for vermicompost and kaolin wastewater
The equilibrium sorption isotherm is important in the design of sorption systems. Equilibrium relationships between adsorbent and adsorbate are described by sorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium.

Table 4
Summary of the isotherm constants and the correlation coefficients for Langmuir and Freundlich isotherms

Parameter	Synthetic solution		Kaolin wastewater
	pH 6	pH 2	pH 2
Langmuir			
q_{max} (mg g^{-1})	20.30	20.48	2.49
b (L mg^{-1})	0.163	0.07	0.103
R^2	0.98	0.96	0.95
Freundlich			
K_f (mg g^{-1})	4.54	2.81	0.49
$1/n$	0.376	0.429	0.370
n	2.66	2.33	2.70
R^2	0.99	0.97	0.95

The surface adsorbent properties determine the sorption mechanisms. The most commonly reported mechanisms for metal ion sorption are ion exchange, electrostatic interaction, chelation, precipitation and complexation [25]. Langmuir [26] proposed the first isotherm model which assumed monolayer coverage of the adsorbent surface and finite number of identical sites. The model assumes not only a homogeneous surface of the adsorbent but also equivalent sorption energies for each sorption site, and no mutual interaction between the sorbed molecules [27].

The Langmuir sorption isotherm has been successfully applied to many pollutants sorption processes and has been the most widely used sorption isotherm for sorption of a solute from a liquid solution. The test of data fit to the Langmuir equation by linearity of the "Langmuir plot", viz. C_{eq}/q plotted as a function of C_{eq}, is a poor test of fit because the plotting of C_{eq} against itself substantially decreases the data variability and always results in a statistically significant correlation coefficient [28]. In the present work, data were fitted to the non-linear Langmuir and Freundlich adsorption isotherms using the software STATISTIC® (StatSoft Inc.) to estimate adsorption constants that indicate the adsorption capacity and affinity of the vermicompost.

The non-linear Langmuir isotherm is mathematically represented by the following equation:

$$q_e = \frac{(q_{max} b C_e)}{[1 + (q_{max} C_e)]}$$

where q_e is the amount of metal ion adsorbed per g of vermicompost (mg g^{-1}), b is a constant related to adsorption energy (L mg^{-1}), q_{max} is the maximum metal adsorption capacity on vermicompost (mg g^{-1}) and C_e is the metal ion concentration at the equilibrium (mg L^{-1}). The q_e value quantitatively means the monolayer adsorption capacity of an adsorbent, while b is obtained from a reciprocal value of the concentration at which a half saturation of the adsorbent was attained.

The Langmuir constants, along with the correlation coefficients have been calculated from the corresponding plots (Fig. 2) for adsorption of Zn(II) on vermicompost and the results are presented in Table 4. While Fig. 2 shows the non-linear plot of C_e versus q_e, the q_{max} and b values are shown in Table 4. The parameter q_e reflects the metal affinity for the vermicompost binding sites. In synthetic solution, Zn(II) adsorption maximum calculated by the Langmuir equation using the non-linear form at 25 °C was 20.30 mg g^{-1} at pH 6 and 20.48 at pH 2, while the value for kaolin wastewater it was 2.49 mg g^{-1} at pH 2.

Small b values indicated that Zn^{2+} ions were binded strongly to vermicompost. According to the Langmuir model, adsorption occurs uniformly on active sites of the adsorbent and once an adsorbate occupies a site, no further adsorption can take place at this site [29].
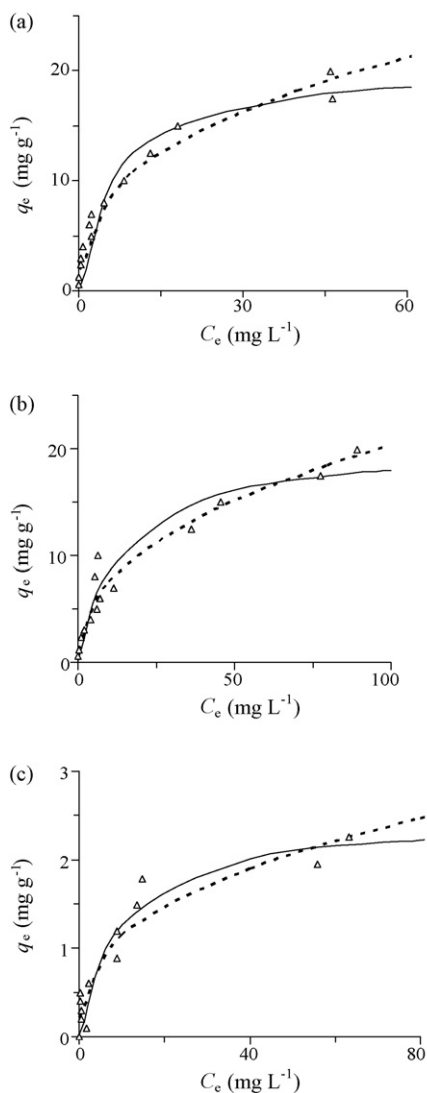
Fig. 2. Langmuir (—) and Freundlich (– – –) isotherms for Zn(II) sorption by vermicompost: (a) synthetic solution, pH 6; (b) synthetic solution, pH 2; (c) kaolin wastewater, pH 2; (△) experimental data.

Based on the correlation coefficients (R^2) obtained (Table 4), the adsorption of Zn(II) conformed to Langmuir isotherms (Fig. 2). The shape of the curves here presented showed that there was a great affinity among Zn(II) and the adsorption sites of vermicompost, despite the relatively high ash content (57.9%). The maximum adsorption capacity should be mainly correlated with the organic carbon content, although contaminants in the raw material and those contaminants produced during the composting process also can contribute to adsorption as well.

The shape of Zn(II) isotherm was of "L2" type, according to Giles classification for isotherms [30], indicating that the data have reached a maximum value, resulting in the presence of the plateau. L-isotherm type (or Langmuir isotherm type) is usually associated with ionic substrates (e.g., metal cations) sorption with weak competition from the solvent molecules [30].

The Zn(II) maximum adsorption capacities obtained in synthetic solution at pH 6 and 2 were almost the same, being the influence of H⁺ ions competition insignificant. Thus, the shape of the Langmuir isotherm at pH 6 was very similar to that of pH 2. The Langmuir isotherm obtained at pH 2 for the kaolin wastewater had a maximum adsorption capacity much smaller than that in synthetic

solution at pH 6 and 2. This was attributed to the smaller amounts of Zn present in kaolin wastewater than in synthetic solution.

The isotherm represents the equilibrium relationship between the metal uptake by the adsorbent and the final metal concentration in synthetic phase, showing the sorption capacity of the adsorbent [31]. Sorption is a physical and/or chemical process in which a substance is accumulated at an interface between phases. The overall rate of sorption of metals on a solid waste matrix depends on composition (density, surface area) of the solid waste, concentration of adsorbate (metal ion) in solution, solid waste to solution ratio, contact time history of the solute concentration with the solid waste, solution sampling procedure, pH, temperature and biodegradable characteristics of the solid waste [32].

In order to justify the validity of cattle manure vermicompost as an adsorbent for adsorption, its adsorption potential ($\sim$20 mg g⁻¹) must be compared with other various adsorbents used for this purpose. The adsorption capacity of vermicompost for the removal of Zn(II) was within the range reported for other adsorbents, such as clarified sludge (15.53 mg g⁻¹), carrot residues (29.61 mg g⁻¹), calcined phosphate (20.60 mg g⁻¹), activated carbon (31.11 mg g⁻¹) [21] and bone charcoal (24 mg g⁻¹) [33]. In addition, vermicompost presents a low-cost (US$ 100 per ton), it is easy to acquire and the vermicompost residue obtained from wastewater purification might be used in cultivated lands.

The Langmuir parameters can also be used to predict affinity between adsorbate and adsorbent using the dimensionless separation factor R_L, which has been defined by Hall et al. [34] as

$$R_L = \frac{1}{1 + bC_0}$$

where R_L is the dimensionless separation factor, C_0 the initial concentration (mg L⁻¹) and b is the Langmuir constant (L mg⁻¹). The value of R_L can be used to predict whether a sorption system is "favorable" or "unfavorable" in accordance with the following criteria:

Separation factor, R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The R_L values of Zn(II) adsorption on vermicompost are shown in Figs. 3 and 4. The R_L values were between 0 and 1 and indicated that sorption was very favorable for Zn(II) in synthetic solution as well as in kaolin wastewater. Figs. 3 and 4 also show that sorption was more favorable for the higher initial metal ion concentration than for the lower one.

Adsorption of Zn to particles is presented in the form of a conditional particle–water distribution coefficient, K_d, mL g⁻¹:

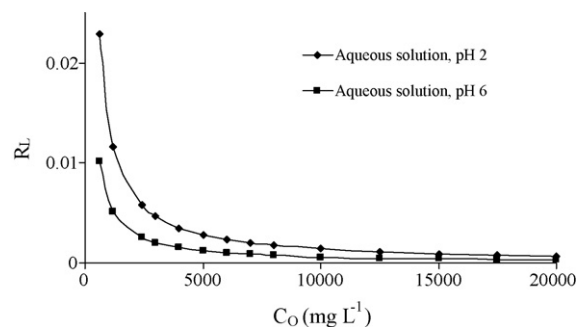$$K_d = \frac{[\text{Zn}]_{\text{ads}}}{[\text{Zn}]_w}$$

Fig. 3. Values of separation factor, R_L, for the adsorption of Zn(II) by vermicompost in synthetic solution at pH 6 and 2.
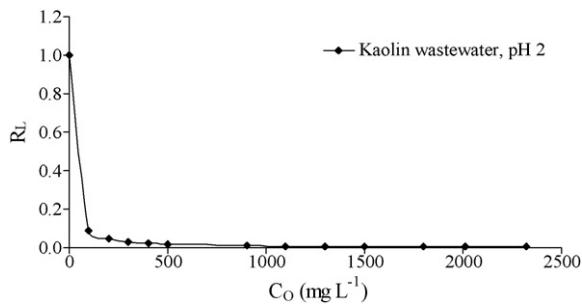
Fig. 4. Values of separation factor, R_L, for the adsorption of Zn(II) by vermicompost in kaolin wastewater at pH 2.

where ads and w refer to adsorbed and aqueous metal, respectively. A high value of distribution coefficient is the characteristic of a good adsorbent [35].

Table 5 shows the K_d values found in this study. In the experiments conducted in synthetic solution at pH 6, the vermicompost exhibited a K_d value of 39,129 L g^{-1} dry matter at C_e of 0.031 mg Zn(II) L^{-1}, while in synthetic solution at pH 2 the K_d value was 3899 L g^{-1} dry matter at C_e of 0.154 mg Zn(II) L^{-1}. In kaolin wastewater at pH 2, the K_d value was 3483 L g^{-1} dry matter at a C_e of 0.144 mg Zn(II) L^{-1}. Iqbal and Saeed [35] reported that the biosorbent developed by entrapping fungal hyphae in structural fibrous network of papaya wood (SFNPW) was successfully used for the removal of Zn(II) from synthetic solution. The SFNPW-immobilized fungal biomass exhibited a K_d value of 4134 L g^{-1} dry matter at C_e of 11.977 mg Zn(II) L^{-1}, while the distribution coefficient with free fungal biomass was 1558 L g^{-1} dry matter at C_e of 4.12 mg Zn(II) L^{-1}.

The Freundlich isotherm assumes the exponential distribution of sorption sites and energies and the interaction between adsorbed molecules on the surface. In 1906, Freundlich studied the sorption of a material onto animal charcoal [36]. He found that if the concentration of solute in the solution at equilibrium, C_e (mg L^{-1}), was raised to the power $1/n$ (constant indicative of the intensity of the adsorption), the amount of solute sorbed per unit weight of adsorbent (mg g^{-1}) being q_e, then C_e $1/n/q_e$ was a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non-ideal sorption and is expressed by the following equation:

$$q_e = K_f C_e^{1/n}$$

where K_f is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}).

Results obtained when Freundlich isotherm was used to model experimental data are presented in Table 4. The applicability of the Freundlich sorption isotherm is also analyzed by plotting C_e versus q_e and data were in good agreement as that the case of the Langmuir. Freundlich isotherm also represented the equilibrium data reasonably well (Fig. 2), with R^2 values from 0.95 to 0.99.

In the case of the Freundlich isotherm the affinity of the adsorbent for a metal can be measured by the parameter K_f. The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption. Values of K_f (in mg g^{-1}) reported in the literature [21] for different adsorbents include 0.687 (neem bark), 1.34 (activated alumina), 2.44 (rice husk ash) and 3.16 (clarified sludge). In this study, the values of K_f ranged from 0.49 to 4.54 mg g^{-1}. Values of n between 1 and 10 (i.e., $1/n$ less than 1) represent a favorable adsorption [37].

Vermicompost exhibited good adsorption capacity and the acquired adsorption data were better fitted to the Freundlich model than the Langmuir model. While Langmuir isotherms presume to reach an adsorption plateau where no further adsorption can occur, Freundlich isotherms presume that adsorption do not reach a maximum, but remain increasing slightly. The smaller R^2 value (0.95) for kaolin wastewater (Table 4) as compared with that of synthetic solution could be due the more complex matrix of the former.

Isotherms have been used to determine thermodynamic parameters of the process, for instance, free energy change [9]. The Gibbs free energy (ΔG°) for the adsorption process was obtained at 25 °C using the following equation:

$$\Delta G^\circ = -RT \ln K$$

where, R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and K is the equilibrium constant at temperature T in K obtained from the Langmuir isotherms. The equilibrium constant can be represented as follows:

$$K = \frac{C_s}{C_e}$$

where C_s is the concentration of the Zn(II) on the adsorbent at the equilibrium in mg L^{-1} and C_e is the equilibrium concentration of Zn(II) in solution in mg L^{-1} [23]. In this work, the $\ln K$ values obtained were 7.93 ± 1.40 and 6.80 ± 0.93 for Zn(II) adsorption in synthetic solution at pH 6 and 2, respectively, while in kaolin wastewater at pH 2 it was 5.36 ± 1.54.

The ΔG° values were -19.675 kJ mol^{-1} and -16.849 kJ mol^{-1} for Zn(II) adsorption on vermicompost in synthetic solution at pH 6 and 2, respectively, and -13.276 kJ mol^{-1} in kaolin wastewater at

Table 5
Values of distribution coefficient (K_d) for the adsorption of Zn(II) by vermicompost in synthetic solution and kaolin wastewater

Zn concentration at equilibrium (mg L^{-1})	K_d	Zn concentration at equilibrium (mg L^{-1})	K_d	Zn concentration at equilibrium (mg L^{-1})	K_d
Synthetic solution				Kaolin wastewater	
pH 6		pH 2		pH 2	
0.022	27272	0.154	3899	0.000	0.00
0.031	39129	0.386	3104	1.707	57.6
0.313	7659	1.108	2164	0.613	325
0.424	7074	2.178	1377	0.372	806
0.791	5056	3.932	1016	0.150	2666
2.212	2259	5.891	848	0.144	3483
1.950	3076	7.144	839	2.285	262
2.346	2983	11.321	617	8.925	99.8
4.637	1724	5.357	1492	8.835	139
8.350	1197	6.364	1570	13.540	110
13.053	957	36.377	347	14.830	120
17.996	832	45.747	327	55.883	35.0
46.275	377	77.393	225	63.317	35.6
46.000	434	89.104	223	–	–

pH 2. The Gibbs free energy indicates the degree of spontaneity of the adsorption process, where more negative values reflect a more energetically favorable adsorption process. It is noted that ΔG° up to $-20\,\mathrm{kJ\,mol^{-1}}$ are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while ΔG° values more negative than $-40\,\mathrm{kJ\,mol^{-1}}$ involve charge sharing or transfer from the adsorbent surface to the metal ion to form a coordinate bond (chemical adsorption) [38]. The ΔG° values obtained in this study for vermicompost confirm the feasibility of this adsorbent and spontaneity of the adsorption as well as that physical adsorption is the predominant mechanism in the sorption process. Referring to the ΔG° values obtained in this work and in view of favorable characteristics of vermicompost to adsorb heavy metals [39], it is obvious that vermicompost was a good adsorbent for removing Zn(II) from effluents.

4. Conclusions

The ability of cattle manure vermicompost to adsorb Zn(II) from synthetic solution and kaolin industry wastewater was investigated. Slight variations of Zn(II) retention were due to the increase of temperature while there was a small decrease in Zn adsorption (from 98.56% to 97.22%) when particle size of adsorbent increased (from <250 to $\leq$2000 μm). The values of the correlation coefficients (from 0.95 to 0.99) indicated that there was a strong positive relationship for the data and that the Zn(II)/vermicompost sorption data follows the Langmuir and Freundlich adsorption isotherms. The equilibrium isotherms were used for assess the maximum adsorption capacity of Zn(II) onto vermicompost and the values obtained were around 20 mg g^{-1} in synthetic solution and 2.49 in kaolin wastewater. The ΔG° values obtained in this study for vermicompost confirm the feasibility of this adsorbent and spontaneity of the adsorption. The physical adsorption was the predominant mechanism in the sorption process. Therefore, it pointed to the facts that vermicompost is a potentially important adsorbent for removing Zn(II) from industrial wastewaters.

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